

Solid State Physics

Proceedings of the DAE Solid State Physics Symposium Volume 55 (2021)





Arup Biswas, Ajay K. Mishra and D. V. Udupa

Organized by Bhabha Atomic Research Centre Mumbai



Sponsored by Board of Research in Nuclear Sciences Department of Atomic Energy Government of India

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Bhabha Atomic Research Centre, Mumbai

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Editors

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Foreword

The 65th DAE SSPS was organized at the DAE Convention Centre, Anushaktinagar Mumbai during December 15-19, 2021. The prestigious DAE SSPS event, as we know, is held annually at different reputed universities and research institutions in the country and is one of the popular gatherings of scientists and researchers in the field of condensed matter physics. Due to the unprecedented circumstances arising out of the Covid pandemic, the event could not be held in 2020, which was a rare break in the consistency of SSPS series. The organizing committee decided to hold the event this year in the "Hybrid" mode, which appeared to be the best possible way, considering that the threat of resurgence of the pandemic still loomed large. The traditional way of full physical attendance with direct interaction is altered in the hybrid mode, where only the local participants attend in person at the venue, whereas all others participate by video conferencing using an online platform. While this mode has some obvious limitations and inconveniences, it has advantages of doing away with the need to travel for attendance and thus saving time and effort.

In spite of this changed format, we have tried to maintain the traditional style of the symposium, both in terms of the scale and in terms of the session layouts. This year the themes include Quantum Phenomena, Magnetism, Superconductivity, Strongly correlated Materials, Nano-photonics, Surfaces & Thin Films, Energy Materials, Matter under extreme conditions, Condensed Matter Theory, Chemical Physics and Experimental Techniques. There were nearly 834 contributory paper submissions, out of which 32 papers were accepted for oral presentation and 661 papers were accepted for poster presentation. A large proportion of nearly 60% contributory paper submissions are from students. The Young achiever award category attracted overwhelming response of 24 nominations whereas the best thesis awards category received 56 nominations. Three Young achiever awards and five best thesis awards including the "IPA Anil K & Bharathi Bhatnagar" best thesis award were presented in the symposium.

Organizing a symposium of this scale and size starting from the announcement, receipts of large number of abstracts and award nominations, their screening, planning the technical sessions especially in this totally new format, implementing the sessions and bringing out the proceedings is really an arduous task. A large number of colleagues have contributed to the success of this symposium and it is my proud privilege to thank them all. My special heartfelt gratitude to the scientific secretaries, the late Dr. C L Prajapat, Dr. Arup Biswas and Dr. Ajay Mishra, whose dedicated efforts and hard work have been instrumental to the success of this event.

(Dinesh V. Udupa) Convener, DAE-SSPS-2021

Preface: 65th DAE Solid State Physics Symposium

DAE Solid State Physics Symposium (DAE-SSPS) is one of the largest scientific events in India and held annually at different venues across the country with a broader objective to bring together researchers working in various branches of Condensed Matter Physics. In this series, the 65th DAE-SSPS was held at DAE Convention Centre, Anushaktinagar, Mumbai during December 15-19, 2021. Considering the COVID pandemic situation this year the symposium was held in hybrid mode viz. local participants from Mumbai participated physically while all others participated in virtual mode. The Symposium was attended by around 750 research students and scientists working in different universities and institutes in the country. A few distinguished scientists from abroad also attended the symposium virtually. Like every year, the symposium was organized by Bhabha Atomic Research Centre, Mumbai under the auspices of the Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Government of India. We had received nearly 920 contributory papers, out of which 741 papers were chosen for presentations after a peer review process by experts of the respective subjects categories. The technical sessions were categorized into plenary talks, invited talks, contributory papers in the form of oral and poster presentations, Ph. D. theses presentations, and Young achiever award nominees' presentations.

The topics covered in the symposium were: (a) Phase transitions and dynamics, (b) Soft condensed matter including biological systems, (c) Nanomaterials, (d) Experimental techniques and devices, (e) Glasses and amorphous systems, (f) Surfaces, interfaces and thin films, (g) Computational methods, and Electronic structures, (h) Single crystals growth and characterization, (i) properties, (j) Semiconductor physics, (k) Transport Magnetism, superconductivity and spintronics, (1) Energy materials, and (m) 1-D and 2-D materials. There were 8 thematic seminars: (i) Quantum Phenomenon, (ii) Condensed Matter Theory, (iii) Magnetism, (iv) Chemical Physics, (v) Strongly Correlated Materials, (vi) Glass, Alloy and composite Systems, (vii) Nano-Photonics, and (viii) Surface, Thin Films and Interfaces. Three outstanding plenary talks were delivered: Bandgap of Disordered Semiconductors in relation to Optoelectronic Devices by Prof. Amlan J. Pal (UGC-DAE CSR, Indore), Advanced magnetic x-ray spectro-microscopies of novel topological spin *textures* by Prof. Peter Fischer, Lawrence Berkeley National Laboratory, Berkeley CA, USA and *Multi-scale Modeling of Nanomaterials: From Nanotubes to Ants* by Prof. Douglas S. Galvao,State University of Campinas and Brazilian Academy of Sciences, Brasil, Besides 3 plenary talks, 43 invited talks, 30 oral presentations and more than 700 posters were presented in the symposium. In the concluding session, 26 best poster awards, 6 best Ph. D. thesis awards, and 4 young achiever awards (YAA) were presented this year.

We are grateful to Director BARC for gracing the symposium with his presence during inauguration. We are thankful to Director, Physics Group, BARC for his support and guidance towards organizing this symposium. We thank the members of the Advisory Committee and the Organizing Committee of the DAE SSPS 2021 for their valuable suggestions and guidance in the organization of the symposium. The symposium organization owes its success to the untiring efforts of many staff members of various divisions of BARC. We are thankful to all of them. We also express our gratitude to all the participants for their contributions. We also thank the manuscript reviewers, poster reviewers, members of the YAA, Ph. D. thesis and poster evaluation committees for giving their valuable time and efforts in selection of the manuscripts and award winners under various categories.

> **Editors** Arup Biswas, Ajay K Mishra and D. V. Udupa Bhabha Atomic Research Centre, Mumbai, India

प्रस्तावनाः ६५वीं प.ऊ.वि. ठोस अवस्था भौतिकी संगोष्ठी

प. ऊ. वि. ठोस अवस्था भौतिकी संगोष्ठी (डी ए ई-एस एस पी एस) भारत में सबसे बड़े वैज्ञानिक कार्यक्रमों में से एक है और यह संगोष्ठी संघनित पदार्थ भौतिकी की विभिन्न शाखाओं में काम करने वाले शोधकर्ताओं को एक साथ लाने के व्यापक उद्देश्य के साथ देश भर में विभिन्न स्थानों पर प्रति वर्ष आयोजित की जाती है। इस श्रृंखला में, 65 वीं डी ए ई-एस एस पी एस दिसंबर 15-19, 2021 के दौरान डीएई कन्वेंशन सेंटर, अणुशक्तिनगर, मुंबई में आयोजित की गई थी। इस वर्ष कोविड महामारी की स्थिति को ध्यान में रखते हुए यह संगोष्ठी मिश्रित तरीके से आयोजित की गई थी। मुंबई के स्थानीय प्रतिभागियों ने व्यक्तिगत रूप से भाग लिया, जबकि अन्य सभी ने परोक्ष तरीके से भाग लिया। इस संगोष्ठी में देश के विभिन्न विश्वविद्यालयों और संस्थानों में कार्यरत लगभग ७५० शोध छात्र, छात्राएं और वैज्ञानिकों ने भाग लिया। इस संगोष्ठी में विदेशों से कुछ प्रतिष्ठित वैज्ञानिक भी वस्तुतः परोक्ष रूप से शामिल हुए। हर साल की तरह, भाभा परमाणु अनुसंधान केंद्र, मुंबई द्वारा परमाणु विज्ञान में अनुसंधान बोर्ड (बीआरएनएस), परमाणु ऊर्जा विभाग, भारत सरकार के तत्वावधान में संगोष्ठी का आयोजन किया गया था। हमें लगभग 920 अभिदायी पत्र प्राप्त हुए थे, जिनमें से 741 पत्रों को संबंधित विषयों की श्रेणियों के विशेषज्ञों द्वारा एक सहकर्मी समीक्षा प्रक्रिया के बाद प्रस्तुतीकरण के लिए चुना गया था। तकनीकी सत्रों को परिपूर्ण वार्ता, आमंत्रित वार्ता, मौखिक और पोस्टर प्रस्तुतियों के रूप में अभिदायी लेख, पीएचडी थीसिस प्रस्तुतियों, और युवा विजेता पुरस्कार नामांकित की प्रस्तुतियों में वर्गीकृत किया गया था।

संगोष्ठी में शामिल विषय थे: (1) प्रवस्था संक्रमण और गतिशीलता, (2) जैविक प्रणालियों सहित नरम संघनित पदार्थ, (3) नैनो-पदार्थ, (4) प्रायोगिक तकनीक और उपकरण, (5) कांच एवम अभणिभ पदार्थ (6) सतह, इंटरफेस और तन् फिल्में, (7) कम्प्यूटेशनल विधियां, और इलेक्ट्रॉनिक संरचनाएं, (8) एकल क्रिस्टल वृद्धि और लक्षण वर्णन, (9) अपवाहन गुण-धर्म, (10) सेमीकंडक्टर भौतिकी, (11) चुंबकत्व, अतिचालकता और स्पिंट्रोनिक्स, (12) ऊर्जा पदार्थ, और (13) 1-डी और 2-डी पदार्थ। 8 विषयगत सेमिनार थे: (i) कांटम फेनोमेनन, (ii) कंडेंस्ड मैटर थ्योरी, (iii) चंबकत्व, (iv) रासायनिक भौतिकी, (v) अत्यधिक सहसंबद्ध सामग्री, (vi) ग्लास, मिश्र धातु और मिश्रित सिस्टम, (vii) नैनो-फोटोनिक्स, और (viii) सतह, पतली फिल्म और इंटरफेस। इस संगोष्ठी में तीन उत्कृष्ट व्याख्यान भी प्रस्तुत किए गए। प्रो. अमलान जे. पाल (यूजीसी-डीएई सीएसआर, इंदौर) द्वारा ऑप्टोइलेक्ट्रॉनिक उपकरणों के संबंध में अव्यवस्थित अर्धचालकों का बैंडगैप, प्रो. पीटर फिशर, लॉरेंस बर्कले नेशनल लेबोरेटरी, बर्कले सीए, युएसए त्द्वारा नवीनतम टोपोलॉजिकल स्पिन बनावट की उन्नत चुंबकीय एक्स-रे स्पेक्ट्रो-माइक्रोस्कोपी, और प्रो. डगलस एस. गाल्वाओ, स्टेट यूनिवर्सिटी ऑफ कैंपिनास और ब्राजीलियन एकेडमी ऑफ साइंसेज, ब्रासिल, मल्टी-स्केल मॉडलिंग ऑफ नैनोमैटेरियल्स: फ्रॉम नैनोट्यूब टू एंट्स ा 3 पूर्ण वार्ता के अलावा, इस संगोष्ठी में 43 आमंत्रित वार्ता, 30 मौखिक प्रस्तुतियाँ और 700 से अधिक पोस्टर प्रस्तुत किए गए। समापन सत्र में इस वर्ष 26 सर्वश्रेष्ठ पोस्टर पुरस्कार, 6 सर्वश्रेष्ठ पीएचडी थीसिस पुरस्कार और 4 युवा उपलब्धि पुरस्कार (वाईएए) प्रदान किए गए।

उद्घाटन के दौरान निदेशक, बी ए आर सी की उपस्थिति के साथ संगोष्ठी की शोभा बढ़ाने के लिए हम उनके के आभारी हैं। हम इस संगोष्ठी के आयोजन में समर्थन और मार्गदर्शन के लिए निदेशक, भौतिकी वर्ग, बीएआरसी के आभारी हैं। हम सलाहकार समिति और डीएई एसएसपीएस 2021 की आयोजन समिति के सदस्यों को संगोष्ठी के आयोजन में उनके बहुमूल्य सुझावों और मार्गदर्शन के लिए धन्यवाद देते हैं। संगोष्ठी संगठन की सफलता का श्रेय भापअ केंद्र के विभिन्न प्रभागों के कई स्टाफ सदस्यों के अथक प्रयासों को जाता है। हम उन सभी के आभारी हैं। हम सभी प्रतिभागियों के योगदान के लिए उनका आभार भी व्यक्त करते हैं। हम लेख समीक्षकों, पोस्टर समीक्षकों, वाईएए समिति के सदस्यों, पीएचडी थीसिस और पोस्टर मूल्यांकन समितियों के सदस्यों को धन्यवाद देते हैं, जिन्होंने विभिन्न श्रेणियों के तहत लेख एवं पुरस्कार विजेताओं के चयन में अपना प्रयास एवं बहुमूल्य समय दिया।

> संपादक अरूप बिस्वास, अजय कुमार मिश्रा, डी. व्ही. उडुप्पा भाभा परमाणु अनुसंधान केंद्र, मुंबई

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Bandgap of Disordered Semiconductors in relation to Optoelectronic Devices

Amlan J. Pal^{1,2}

¹UGC-DAE Consortium for Scientific ResearchUniversity Campus, Khandwa Road, Indore ²School of Physical SciencesIndian Association for the Cultivation of ScienceJadavpur, Kolkata

Email: <u>director@csr.res.in</u>

Abstract

Disordered semiconductors have attracted significant attention for basic studies in physics as well as in a range of optoelectronic applications. Device physics in such applications, in principle, depended on light-matter interactions in which the optical bandgap and transport gap of the semiconductors play a primary role. Hence, appropriate tuning of the bandgap in disordered semiconductors remained important in optimizing the device performance.

In many disordered semiconductors, the relationship between composition and functional properties, such as optical bandgap, often exhibits a quadratic behavior giving rise to a phenomenon, called "bandgap bowing". The underlying mechanism of this 'bow-like' evolution of bandgap in some oxides, chalcogenides, and of late halide perovskites is yet to be understood. To know the origin of bandgap bowing, we have probed the conduction and valence band-edges (CB and VB) of some alloyed semiconductors to inquire about the band responsible for yielding the bowing.

In such semiconductors, the presence of a significant density of defect states within the bandgap results in sub-bandgap absorbance in the absorption spectrum (Urbach tailing). While optical absorption spectroscopy provides a 'macroscopic' insight into the phenomenon, the contribution of individual band-edges is needed to be identified on a 'microscopic' scale. We have obtained accurate information on the band-edges leading to a precise quantification of Urbach energy in disordered semiconductors.

To optimize the performance of optoelectronic devices, it is a prerequisite to visualize the band-diagram of the active layers with respect to the electrodes as 'seen' by charge carriers. In this regard, we have employed scanning tunneling spectroscopy (STS) to probe the energy levels of a range of semiconductors upon varied formation conditions. STS probed the density of states (DOS) of the semiconductors and thereby CB and VB, separately, with respect to the Fermi energy (E_F). Such information when combined with the E_F obtained from Kelvin probe force microscopy (KPFM) studies can provide the complete energy landscape of a semiconductor and also of heterojunction devices.

Advanced magnetic x-ray spectro-microscopies of novel topological spin textures

Peter Fischer^{1,2}

¹Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA, USA ²Physics Department, University of California, Santa Cruz, CA, USA

Email: <u>pjfischer@lbl.gov</u>

Abstract

Spin textures and their dynamics hold the key to understand and control the properties, behavior and functionalities of novel magnetic materials, which can impact the speed, size and energy efficiency of spin driven technologies. Topology, frustration, and bespoke geometries that impact spin textures have recently attracted significant scientific interest and led to intense research addressing a broad spectrum of challenging scientific and technological questions, including stability, dynamics, nucleation, and transport in novel spin textures, such as chiral bobbers, magnetic hopfions and torons, skyrmion tubes, and curvilinear magnetism [1].

Advanced characterization tools that provide magnetic sensitivity to spin textures, disentangling the role of individual components in heterogeneous material at high spatial resolution, ultimately at buried interfaces and in all three dimensions [2], and at high temporal resolution to capture the spin dynamics across scales, are required to address those questions, and are therefore of large scientific interest.

Various magnetic soft X-ray spectro-microscopies [3] using polarized soft x-rays provide unique characterization opportunities to study the statics and dynamics of spin textures in magnetic materials combining X-ray magnetic circular dichroism (X-MCD) as element specific, quantifiable magnetic contrast mechanism with spatial and temporal resolutions down to fundamental magnetic length, time, and energy scales.

Current developments of x-ray sources aim to increase dramatically the coherence of x-rays opening the path to new techniques, such as ptychography [4] or x-ray photo-correlation spectroscopy (XPCS) [5] that allow unprecedented studies of nanoscale heterogeneity, complexity, and fluctuations.

I will review recent achievements and future opportunities with magnetic x-ray spectro-microscopies. Examples will address static properties and dynamic behavior of various magnetic skyrmion [6,7] and Hopfion [8] textures with potential application to novel magnetic logic and storage devices, and will include results from an XPCS study at LCLS with a novel 2-pulse scheme that allowed to discover an unexpected and drastic change of the correlation times in nanoscale spin fluctuations near phase boundaries, i.e., in the skyrmion phase, and near the boundary with the stripe phase of a multilayered Fe/Gd system [5].

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Multi-scale Modeling of Nanomaterials: From Nanotubes to Ants

Douglas S. Galvao

State University of Campinas and Brazilian Academy of Sciences

Email: galvao@ifi.unicamp.br

Abstract

The sp, sp2, sp3 carbon hybridizations allow an almost infinite number of different structures with tunable mechanical and electronic properties. These structures can exhibit different topologies with different electronic dimensions (0-fullerenes,1-nanotubes, 2-graphene, 3-diamond). These topologies can be exploited to create a large class of different materials, such as buckypapers [1], carbon nanotube-based artificial muscles [2,3], foams [4], auxetic crystals [5], etc. These materials present extremely complex morphologies, which results in a difficult challenge to realistically model their mechanical and structural properties. In this talk, we will present and discuss multi-scale (from nano to macro scale) approaches to model these materials, including the use of bioinspired artificial intelligence methods (such as the bioinspired ANT algorithms). Of particular interest are the new molecular dynamics simulations techniques based on reactive potentials that allow handling multi-million atom systems. These techniques can be also used for non-carbon materials, such as chalcogenides [6] and non-van der Waals solids [7].

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The Langevin approach to nonequilibrium correlated electron systems

Pinaki Majumdar HRI, Prayagraj, UP, India

Email: pinaki@hri.res.in

Abstract

The Langevin equation has been a major tool for studying dynamicsin classical stochastic systems. It can probe equilibrium fluctuations, the approach to equilibrium, and even driven systems. While itsorigin lies in probing "single particle" motion it is frequently used in extended, or many particle, systems. Can this approach be of help inunderstanding the thermal physics of correlated quantum systems? Iwill outline the approach, and discuss examples from electron-electronand electron-phonon systems, both in and out of equilibrium.

Topological quantum magnets: From concept to materials realizations

Bahadur Singh

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, India

Email: <u>bahadur.singh@tifr.res.in</u>

Abstract

The realization of topological materials which exhibit exotic, disorder-resistant states has opened a new realm ofmaterials research not only for their potential for exploring fundamental physics questions but also for the opportunities they offer for sparking the next technological revolution. I will discuss how the interplay of wavefunction topology, crystalline symmetries, and quantum interactions generate exotic topological phases that can be manipulated through external controls of electric/magnetic fields, strains, pressure, and photo- or chemical doping. I will highlight some of our recent breakthroughs aimed at the prediction of topological quantum magnets that can support unconventional topological states at the charge neutrality point with anomalous transport properties.

Experimental Realization of Quantum Phenomenain 1D Antiferromagnets

Anup Kumar Bera

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

Email:akbera@barc.gov.in

Abstract

The field of low-dimensional quantum magnetism started a century ago during the early development of quantum mechanics. ErnstIsing, in 1925, derived an exact solution of the one dimensional (1D) spin-chain (having a preferred direction) with nearest neighbor interaction only [1]. Followed by, Bethe introduced his famous "ansatz" method in 1931 to find the exact quantum ground state of the antiferromagnetic Heisenberg model in 1D [2]. The ground states of 1D uniform S = 1/2 chains are different in theIsing and Heisenberg models. While the chain becomes ordered at zero temperature in the Ising limit, it remains disordered even at zero-temperature in the Heisenberg limit. Further, Haldane in 1983 shown that the integer and half-integeruniform Heisenberg spin-chains are fundamentally different [3]. The spin-1/2 chain has gapless excitations— spinonscarrying fractionalizedspin S = 1/2. On the other hand, the uniform spin-1 chain has gapped excitations where nonmagnetic spin singlet ground state is well separated in energy from the first excited states of spin-triplets (magnons carrying spin S = 1).

However, the experimental realization/verification of the basic theory of low-dimensional (low-D) magnetism, as advanced by Ising,Heisenberg and Bethe,begins much laterin the last decade of the 20th century. Over last two decades, the advancement of solid state chemistry to synthesis model low dimensional spin-systems, as well as the advancement of experimental facilities, especially neutron scatterings, with dedicated sample environments allow to explore and realize various quantum phenomena in low dimensional spin systems mainly based oncomplex transition metal oxides.

In this talk, I will present our experimental results (especially by using neutron scatterings technique) of the naturally grown quasi-1D spin-chain antiferromagnets SrM2V2O8 (M = Ni and Co) [4-13]. The results provide experimental realization of several quantum phenomena of the 1D antiferromagnets, including—topologically protected Haldane state, field-induced quantum phase transition, condensed matter analogue of the quark-confinement, quantum criticality, and the Bethe-string states.

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Topological Weyl Fermions Measured on the Surfaces

Rajib Batabyal

UGC-DAE Consortium for Scientific Research, Indore, Indore

Email:rajibbatabyal@gmail.com

Abstract

Existence of topological "Fermi-arc" surface states is guaranteed by the bulk Weyl nodes and appears as a consequence of bulk-boundary correspondence in Weyl semimetals. Bulk Weyl nodes are formed when non-degenerate band touches each other under broken inversion or time reversal symmetry. We carried out scanning tunneling spectroscopy (STS) experiments to visualize the topological surface Fermi arcs in both the inversion and time reversal symmetry broken Weyl semimetals e.g. TaAs and Co3Sn2S2 respectively and verify their classifications. In inversion symmetry broken TaAs, we find high level of topological protection of the surface Fermi arcs against the surface potential through its structure of the plane-wave like Bloch wave function in the Brillouin zone (BZ). On the other hand, in time reversal symmetry broken Co3Sn2S2, we find the topological Fermi arcs are highly susceptible to the surface potential that changes its connectivity in the BZ on different surface terminations and the dispersion of the arcs. This allows to manipulate these topological arcs through the surface potential.

Diffusion and Sintering of Ultrasmall Nanoparticles: Mechanisms & Scaling Relations

Shobhana Narasimhan

Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bangalore 560064

Email: shobhana@jncasr.ac.in

Abstract

Small nanoparticles supported on substrates are of technological interest because they can be excellent catalysts for many industrially and environmentally important reactions. They can also possess interesting physical properties, e.g., small particles of some elements can be nanomagnets, even if the corresponding bulk material is non-magnetic. Properties of interest, such as chemical reactivity and magnetic moments, are highly size-sensitive -- typically, the catalytic activity of metal nanoparticles increases sharply as the size is decreased. However, nanoparticles are intrinsically unstable with respect to sintering: it is always energetically favorable for two or more nanoparticles to coalesce to form a larger-sized particle. This process is one of the important causes of nanocatalyst degradation. It is therefore of interest to study the processes by which nanoparticles diffuse on substrates, and fuse together.

I will present work in our group on the diffusion and sintering of ultrasmall small noble metal particles on a MgO support. We find that these clusters diffuse by unexpectedly complex motions that do not correspond to simple translations. The diffusion mechanism depends upon both the atomic species and the number of atoms in the nanoparticle. We find unexpected scaling relations between diffusion barriers and other quantities (such as the melting temperature of the bulk metal), we will discuss the origin and implications of such scaling relations.

Inversion and Quantum Oscillations in Kondo insulators

Brijesh Kumar

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067

Email:bkumar@jnu.ac.in

Abstract

The quantum oscillations observed in Kondo insulators pose a challenge to the commonknowledge that the de Haas-van Alphen effect occurs only in metals. In this talk, we will presentour understanding of this problem in terms of an original theory of Kondo insulators [1,2],formulated using a novel representation of electrons [3]. Through this theory, we have discovered the inversion exhibited by the gapped charged quasiparticles in Kondo insulators, and found this inversion to determine whether or not the quantum oscillations would occur in the insulating bulk.

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Theoretical modeling of charge-disproportionation in BaBiO3

Rajamani Raghunathan

UGC-DAE Consortium for Scientific Research, DAVV Campus, Khandwa Road, Indore.

Email: rajamani@csr.res.in

Abstract

Nature and mechanism of charge ordering (CO) in BaBiO₃ (BBO) has been debated for past several yearsbetween complete CO ($Bi^{3+}-Bi^{5+}$), oxygen 2p - 2p fluctuation in the negative delta regime and incomplete CO *a.k.a.* charge-disproportionation (CD) ($Bi^{4+\delta} - Bi^{4+\delta}$) (0< δ <1) [1-3]. Here, we present a new mechanism for CD using a molecular orbital (MO) approach [4]. We show that CD in BBO is governed by the dynamic fluctuation between Bi 6sp – O 2p hybridization that favours Bi⁵⁺charge state and Bi 6p – O 2p hybridization that favours Bi³⁺ charge state, driven by the octahedral breathing mode. The model is further validated with results from density functional theory calculations using hybrid functional, HSE06. We also employ strain as an external perturbation to tune the CD and further show that CD can also be asymmetric ($Bi^{4+\delta} - Bi^{4+\delta}$) (0< $|\delta 1|$ and $|\delta 2|<1$). Results from x-ray spectroscopic studies also demonstrate the dynamic nature of CD that becomes quasi-static at room temperature in strained thin films and thus endorses our proposed model.

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Electronic and Phononic Features for High Thermoelectric Performance

David J. Singh

Department of Physics & Astronomy, University of Missouri, Columbia MO 65211-7010, USA

Email: singhdj@missouri.edu

Abstract

The thermoelectric figure of merit, ZT, is a combination of thermal and electrical transport quantities that is strongly contraindicated in the sense that the particular combination of high electrical conductivity, high thermopower and low thermal conductivity does not naturally occur in textbook models. This talk discusses electronic and lattice dynamical features that resolve these contradictions in half-Heuslers and other materials thus providing ways of designing and discovering new themoelectrics.

Signatures of Topological Superconductivity in Sr intercalated Bi2Se3

S. Patnaik

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067

E-mail: spatnaik@mail.jnu.ac.in

Abstract

The discovery of Dirac and Weyl semimetals has brought forth the condensed matter realization of Dirac/Weyl fermions, which were previously theorized as low energy excitations in high energy particle physics. In the recent past we have witnessed some exceptional developments in chalcogenide and pnictide materials that have been identified with such properties. Superconductivity derived from such exotic systems promises to usher-in new understanding of correlated electronic systems. In this talk we shall review electromagnetic properties of topological superconductor Sr-intercalated Bi₂Se₃ and study its pairing mechanism by muon spin rotation measurements. Furthermore, several transition metal mono-pnictides are under intense investigation for understanding properties of inversion-symmetry broken Weyl semimetals. Non-trivial Berry phase and chirality are important markers for characterizing topological measures of Weyl semimetals. We shall also discuss aspects of exceptional magneto-resistance seen in the normal state of these topological semimetals.

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Superconductivity and metallic state transport in magic angle twisted bilayer graphenes

Girish Sharma

School of Basic Sciences Section, Indian Institute of Technology, Mandi ,H. P.-175005 India

Email: girish@iitmandi.ac.in

Abstract

We discuss our proposal of a purely electronic mechanism for unconventional superconductivity recently observed in twisted bilayer graphene (tBG) close to the magic angle. Using the Migdal-Eliashberg framework on a one-parameter effective lattice model for tBG, we show that a superconducting state can be achieved by means of collective electronic modes in tBG. We posit robust features of the theory, including an asymmetrical superconducting dome and the magnitude of the critical temperature that agree with experiments. The second half of my talk is devoted to discussing a rigorous theory for phonon-dominated transport in twisted bilayer grapheme describing its unusual signatures in the resistivity (including the variation with electron density, temperature, and twist angle) showing good quantitative agreement with recent experiments. We go well beyond the usual treatment of electron-phonon theory, including both interband and intraband processes, considering the finite-temperature dynamical screening of the electron-phonon matrix element, and going beyond the linear Dirac dispersion. Comparison of experimental data with Planckian dissipation is also shown to be inconsistent.

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Elucidating the integrity during crisis in colloidal & emulsion droplets by SANS and SAXS

Debasis Sen

¹Solid State Physics Division,Bhabha Atomic Research centre, Mumbai-400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, India

Email: debasis@barc.gov.in

Abstract

Colloids and emulsions are ubiquitous and they form an interesting branch in science owing to the various intriguing interactions among the constituent phases. Such interactions are amalgamation of various effects, namely, electro-static, van der Waals, excluded volume, etc. As soon as the continuous medium of a colloidal dispersion i.e., the solvent, starts disappearing throughrapid evaporation, the interaction among the particles gets significantly altered. The extent of the modification depends on competitive dominance of the aforementioned factors. The attractive capillary force tries to setup a strong integrity among the constituent particles which are under a crisis-like situation owing to the sudden disappearance of the solvent. In fact, the process of drying of liquid droplets is widely used in various industries including food and pharmaceutical industries and this process is known as spray-drying. Since last decade, the above-mentioned industrial process has re-embellished itself in nano-science and nano-technology. Contact-free evaporatingcolloidal droplets exhibit spectacular behaviors due to sudden transition from dispersion to powder state associated with assembly of the nanostructures. With the help of such evaporative assembly process, a wide variety of hierarchically structured micro/meso/macro-porous granules have been realized. Such highly correlated nanostructured micro-granules also act as hosts for investigating various nanoconfinement based Physics problems owing to existence of the nanometric interstitial pores. Further, understanding of thebuckling-induced shape transformation duringsuch evaporative-assembly processremains another important aspect. Quantification of the (i) structure of these granules, extending over nanometer to micrometer length scale, and (ii) understanding of the confinement-driven time-dependent processes are crucial and challenging. Owing to their complex structure, over hierarchical length scales, it demands the use of scattering techniques accessing wide range of wave-vector transfer along with complementary imaging methods. In this regard, small-angle neutron scattering (SANS), X-ray scattering (SAXS) and scanning electron microscopy (SEM) have been found to be effective in probing such nano-structured granular materials. SANS facilities at Dhruva reactor, laboratory-based SAXS and recently commissioned SAXS beamline (BL-18) at Indus-2, RRCAT have been utilized to unravel the structural correlations in these fairly high-surface area porous granules and dendritic nanosphers. In this presentation, we will discuss some of our recent results on such hierarchically-structured granular materials and will also touch upon a few time-dependent processes in these materials.

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A Versatile X-ray Scattering and Diffraction Beamline forEngineering Applications at Indus-2 Synchrotron Source

Pooja Gupta, P.N. Rao, M.K. Swami, A. Bhakar, and S.K. Rai*

Synchrotrons utilisation section, Raja Ramanna centre for advanced technology, PO RRCAT, Indore, Madhya Pradesh,

452013, India

*Email: sanjayrai@rrcat.gov.in

Abstract

A hard X-ray engineering applications beamline (BL-02) was commissioned recently and started operation in March 2019 at Indian synchrotron source, Indus-2. This bending magnet-based beamline is capable to operate in various beam modes viz; white, pink and monochromatic beam. The beamline utilizes X-ray diffraction technique in energy dispersive and angle dispersive modes to carry out experiments mainly focused on engineering problems viz; stress measurement, texture measurement and determination of elastic constants in variety of bulk as well as thin film samples. The talk will give details of the physics design, optics, experimental stations and recent results of the beamline. Experiments executed to validate the beamline design parameters and to demonstrate the capabilities of beamline willbe described. The future facilities to be incorporated to enhance the capabilities of the beamline shall be discussed.

Creating tunable finite temperature half-metal out of an antiferromagnetic Mott insulator.

Gour Jana, Abhishek Joshi, Subhajyoti Pal, and Anamitra Mukherjee*

School of Physical Sciences, National Institute of Science Education and Research, HBNI, Jatni 752050, India

Email:anamitra@niser.ac.in

Abstract

Sustaining exotic quantum mechanical phases at high temperatures is a long-standing goal of condensed matter physics. Among them, half-metals are spin-polarized conductors that are essential for realizing room-temperature spin current sources. However, typical half-metals are low-temperature phases whose spin polarization rapidly deteriorates with temperature increase. In this talk, we will first show that a low-temperature insulator with an unequal charge gap for the two spin channels can arise from competing Mott and band insulating tendencies. We will demonstrate that thermal fluctuations can drive this insulator to a half-metal through a first-order phase transition by closing the charge gap for one spin channel. We will show within a Kubo-Greenwood transport formalism that this half-metal has 100% spin polarization at the onset temperature of metallization, and tuning the strength of electron repulsion can enhance the onset temperature while preserving spin polarization. We will end with a discussion of experimental scenarios for realizing this novel finite-temperature half-metal.
Multiferroic properties of Pb based perovskites

Basavaraj Angadi

Department of Physics, Bangalore University, Bangalore

Email: <u>brangadi@bub.ernet.in</u>

Abstract

The complex Pb(B' B")O3 structured perovskites exhibiting multiferroic properties have gained much attention in recent years due to their potential for technological applications. For example, the Pb based complex perovskites, PbFe0.67W0.33O3 (PFW) and PbFe0.5Nb0.5O3 (PFN) shows multiferroic behaviour below certain temperatures. At room temperature, PFW and PFN exhibit cubic (Pm-3m) and monoclinic (Cm) structure, respectively. Both are antiferromagnetic with Neel temperature around 380 K for PFW and 143 K for PFN. In this talk, I will discuss the synthesis and multiferroic properties of PFN, PFW and their solid solution with another room temperature multiferroic BiFeO3 through temperature dependent Neutron diffraction, magnetization, dielectric, Mossbauer measurements. The polycrystalline PFN-PFW (PFWN), PFN- BiFeO3, PFW- BiFeO3 solid solutions were prepared through the Columbite method (solid state reaction method) with low temperature sintering technique. The nuclear and magnetic structures of solid solutions were determined by the Rietveld refinement of neutron diffraction data measured at different temperatures from 2.8 to 295 K. A possible model for antiferromagnetic order is proposed with a propagation vector k = ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) and the G type antiferromagnetic structure. The magnetic moment of antiferromagnetically ordered Fe3+ ions is determined and found to be μ Fe = 3.826 μ B. The dielectric constant exhibits an anomaly around TN, which indicates magnetoelectric coupling. These features are attributed to the inherent coupling between the ferroelectric and antiferromagnetic orders in the multiferroic system.

Anchoring Cu(II)-Based S=1/2 Kagome Lattices on Functionalized Graphene

Nirmalya Ballav

Department of Chemistry, Indian Institute of Science Education and Research, Dr. Homi Bhabha Road, Pune - 411 008,

India

Email: <u>nballav@iiserpune.ac.in</u>

Abstract

Cu(II)-based atacamite family of minerals have emerged as promising candidates for the investigation of quantum spin liquid (QSL) states. Herein, starting from Cu(I) precursors, we have synthesised phase-pure Cu(II)-based S=1/2 kagome spin lattices at near-ambient conditions. When graphene oxide (GO) was taken along with other reactants, the oxidation of Cu(I) to Cu(II) was accompanied by the reduction of GO to rGO which not only led to the anchoring of various S=1/2 spin lattices onto rGO but also the magnetic exchange interactions were notably modulated by the diamagnetic rGO matrix. Overall, a series of S=1/2 kagome spin lattices are explored, all belonging to the atacamite family of minerals and are known to be antiferromagnetic insulators. Specifically, strongly coupled kagome planes (clinoatacamite), weakly coupled kagome planes (barlowite), and weakly coupled and magnetically isolated kagome planes (paratacamite and herbertsmithite) – were successfully anchored to rGO matrix. The resultant atacamite-rGO nanocomposites were assigned as magnetic semiconductors and electron doping of the kagome spin lattices by rGO is proposed.

Phase Transitions and Disorder: A Tale of Two Scheelites

Brendan J. Kennedy

School of Chemistry, The University of Sydney, Sydney NSW Australia

Email: <u>brendan.kennedy@sydney.edu.au</u>

Abstract

It is the best of hettotypes. It is the worst of aristotypes. An aristotype represents the highest symmetry crystal structure that can be attained for a given system. Many inorganic systems exhibitlower symmetry phases, orhettotypes, that are crystallographically related to the aristotype as isotropy subgroups. The hettotypestructure can, therefore, be described by a symmetry-breaking distortion of the aristotype structure. The distortion contains contributions from the different modes; The correlated atomic displacements or modes that contribute to the lower symmetry aredescribed by the irreducible representations of the aristotype space group.

High resolution powder diffraction methods, especially neutron diffraction, are well established tools for the study of phase transitions and combining such studies with group theory is a powerful approach to gain deep insight symmetry lowering in complex oxides. This talk will illustrate this using scheelite as an example. The scheelite structure is named for the Swedish chemist CarlScheele after the tetragonal structure displayed by CaWO₄ that is described in space group $I4_1/a$. As occurs for perovskite (CaTiO₃) this structure is not the aristotype, rather the WO₄ tetrahedra are rotated about the *c*-axis and the aristotype is described by space group $I4_1/amdas$ seen in RbReO₄ at high temperatures. The irrep of the mode is Γ_3^+ . Replacing the Rb with Tl in TlReO4lowers the symmetry to a unique monoclinic structure and TlReO4 displays phase transitions to the $I4_1/a$ structure upon both heating and cooling. Such re-enterent phase transitions are unusual. PDF analysis of total neutron scattering data reveals evidence for hidden order in both the high and low temperature tetragonal forms that is associated with the stereochemical activity of the Bi $6s^2$ lone pair electrons. The difference between the average and local structures in this and related systems will be presented.

Jammed micelles in water-free supercooled matrix: Evidence from small angle scattering

P. A. Hassan

Chemistry Division, Bhabha Atomic Research Centre, Mumbai- 400 085, India.

Email: hassan@barc.gov.in

Abstract

Amphiphilic molecules self assemble in water to form dynamic equilibrium structures such as micelles. Mostly, micelle formation is reported in liquids and undergo random Brownian motion in the solvent due to its colloidal size. However, dynamically arrested micelles can be formed by common amphiphiles in room temperature supercooled solvents. Small angle x-ray/neutron scattering provides unequivocal evidence for the formation of micelles in supercooled matrix. The micelles can be formed by dissolving an amphiphile in a molten mixture of sugar (e.g., sucrose, fructose or glucose) and urea or urea derivatives at elevated temperatures (~70-90°C). These micelles get trapped in a supercooled state upon cooling the mixture to 15°C, forming a sugar glass. This opens a new area of research using room temperature supercooled solvents as the matrix for micelle formation. Unlike normal micelles in water, which form only above the Kraft temperature, these micelles in sugar glass can sustain subzero degree Celsius temperatures (-25°C) without phase separation. The present study shows an example of solid-like assemblies of soft materials, dispersed in another amorphous matrix. Since all components used in this formulation are solid at room temperature, the supercooled micelles can be considered as a micro-heterogeneous amorphous solid, akin to alloy formation in metals.

Exploring the Role of Crystal Chemistry in Materials Science

Deepak Chopraa*,

Crystallography and Crystal Chemistry Laboratory, Department of Chemistry, Indian Institute of Science Education and Research Bhopal, Bhopal 462066, Madhya Pradesh,

Email: dchopra@iiserb.ac.in

Abstract

The importance of the crystal chemistry of organic solids has been well-established in the literature and the role of intermolecular interactions in this regard is of extreme relevance.1The prevalence of polymorphism is also well known in the literature2. Extensive screening for polymorphism, including solvatomorphism, in a library of small molecules containing halogen substituted ethynyl phenyl benamidesresulted in the formation of crystalline anhydrous polymorphs3, solvates of hexafluorobenzene4, and the observation of SCSC phase transitions5 in the solid state. This has relevance in associated applications as photoluminescent solids6 and dielectrics.7The current talk shall address the relevance of intermolecular interactions and the associated crystal chemistry to understand the formation of crystalline solids with diverse properties.

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Nanostructured calcium cobalt oxide with enhanced properties for thermoelectric generation

Ajit K. Mahapatro*, Nidhi Puri, and Ram P. Tandon

Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India

*Email: amahapatro@physics.du.ac.in, ajit.physics.du@gmail.com

Abstract

New materials and nanostructures are the key factors to engineer efficient devices necessary for advancement of next generation technologies. Energy harvesting and conversion of waste heat to useful form of energies could reduce the greenhouse effect resulting due to excess heat generation from various natural and artificial sources. Thermoelectric generation acknowledges a tool for converting waste heat into electrical energy by adopting sustainable, environmental friendly, and cost effective technique. Calcium cobalt oxide (Ca₃Co₄O₉), a misfit-layered oxide structure consisting of Ca₂CoO₃ and CoO₂ subsystems stacked alternatively along the c-axis, has been exhibiting favorable properties for considering as efficient thermoelectric material [1].

Highly pure and perfectly composed micro/nano-structures of Ca₃Co₄O₉ with high thermal and chemical stabilities are synthesized, consolidated them to achieve fully dense pellets using hot-press(HP) technique, and the electronic and thermoelectric behaviors are recorded using temperature dependent current-voltage, conductivity, and Seebeck coefficient measurements. Mott's 3D variable range hopping conduction at low bias region through closely packed and partially oriented textured grains formed during the HP process [2], space charge limited current at high bias region, and observation of anisotropic behaviour in the electronic resistivity are the inherent properties identified in Ca₃Co₄O₉ ceramics prepared using the as-synthesized microstructures. At high temperatures of 700 K, the enhancement of around 11 times in the power factor in Ca₃Co₄O₉ ceramics prepared using nanostructurescompared to that of as-synthesized micro-plates due to simultaneous increment of Seebeck coefficient and negligible increment in resistivity, is attributed to the raise in scattering due to introduction of more number of grain boundaries in bulk nanostructured ceramics [3]. The currently prepared nanostructured Ca₃Co₄O₉demonstrates favorable properties for exhibiting enhanced thermoelectric behavior by following low cost processing techniques and could be considered for future mass-scale production for real world application.

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Time Differential Perturbed Angular Correlation Spectroscopy: A Potential Tool to probe Materials Structure in Atomic Scale

D. Banerjee

Radiochemistry Division (BARC), Variable Energy Cyclotron Centre, Kolkata-700064, India

Email: dbanerjee@vecc.gov.in

Abstract

At Radiochemistry Laboratory (BARC), VECC, Kolkata, we have developed the Time Differential γ - γ Perturbed Angular Correlation (TDPAC) Spectroscopy consisting of CeBr3 scintillator detectors. The TDPAC is a nuclear probe technique based on hyperfine interaction where suitable radionuclide (called as "PAC Probe or Spy") is incorporated in host compound in high dilution to get the information inside the host system at the nearest neighbour of the PAC probe atom. TDPAC is an effective spectroscopic tool to determine the local structure around the probe atom and to understand the different atomic scale physico-chemical phenomena (in situ/ex situ) occurring in the host compound. Due to the sensitivity of Electric Field Gradient (EFG), TDPAC is a potential tool to identify the different intermediate phases [1] and phases with very similar lattice parameters [2] which are otherwise very difficult to be distinguished by conventional spectroscopic techniques. Different PAC probes used in the PAC studies have been produced either in Reactor at BARC or Cyclotron at VECC. The hyperfine interaction of the transition moment of nuclei with the EFG produced due to surrounding charges is utilized to obtain the atomic scale information. In the present talk, the potential application of the TDPAC in the identification of the different intermediate phases in oxide semiconductors will be discussed.

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Microcantilevers for Ultrafast Humidity and Ultrasensitive Temperature Sensing Applications

K. Prabakar*, S. Balasubramanian and M. Raghu Ramaiah

Surface and Nanoscience Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil

Nadu, India - 603102

Homi Bhabha National Institute, Kalpakkam, Tamil Nadu, India - 603102

*Email:kpr@igcar.gov.in

Abstract

Microcantilevers (MC)are the simplest MEMS structures and have emerged as a promising technology for various sensing applications such as ultrasensitive mass measurements, environmental monitoring, bio-molecular sensing and detection of chemical analytes such as explosives. In this talk, our recent work on the development of ultrafast relative humidity (RH) and ultrasensitive temperature sensors using MCs will be presented. For RH sensing, micropatterned SiO₂ MCs of various dimensions were fabricated using direct laser writer and wet chemical etching methods and were tested for RH sensitivity in the range of 20% to 90% RH. It is shown that introduction of controlled micropatterns on MC surface provides aneffective way toenhance the RH sensitivity (10.45 Hz/% RH)without compromising other sensor characteristicssuch as response and recovery time(~ 1 s). These superior characteristics of micropatterned MCs allowedthe realtime monitoring of RH variation during human breathing cycles. Similarly, for temperature sensing applications, photo-induced deflection studies were carried out on Bimaterial MCs (BMC). Laser beam induced deflection in uncoated, Au, and Al coated Si MCs ofvarious dimensions was studied, using an AFM head. MC flipping experiments revealed that stress contribution in BMCscan originate either from photostriction or photothermal effects and it dependscritically on the MC dimensions and direction of laser exposure. Effect of laser parameters such as wavelength, modulating frequency and MC physical dimensions on the deflection sensitivity, response time and noise characteristics of BMCs was carried out. It is shown that a maximum temperaturesensitivity of ~62 mK/nmand an optimum noise equivalent power of 566 pW/√Hzcan be achieved by tuning the laser parameters and BMC dimensions.

Emergent non-Fermi liquid behaviour in disordered, strongly interacting systems

N S Vidhydhiraja

Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur, Bengaluru, Karnataka 560064, India

Email: raja@jncasr.ac.in

Abstract

Abstract: We provide strong evidence for a quantum critical point (QCP) associated with the destruction of Kondo screeningin the Anderson-Hubbard model for interacting electrons with quenched disorder. The evidence comprises three elements: (a) the identification of an energy scale, ω *, that delineates infrared Fermi-liquid damping from higherfrequency non-Fermi liquid (nFL) dynamics; (b) the finding that this crossover scale ω * appears to vanish withincreasing disorder; and (c) the concomitant appearance of a finite intercept in a broad distribution of Kondo scales. Our findings indicate a Kondo destruction scenario, albeit distinct from the local QCP picture. The nFL behavior isshown to stem from an interplay of strong electron-electron interactions and the systematic inclusion of short-rangedynamical fluctuations induced by the underlying random potential. The results have been obtained through a computational framework based on the typical medium dynamical cluster approximation.

Spin-orbit coupled Dirac Fermions

Subhro Bhattacharjee

International centre for theoretical sciences, Tata Institute of Fundamental Research Bengaluru, Karnataka, 560 08, India

Email: <u>subhro@icts.res.in</u>

Abstract

One of the central quests of present condensed matter research is to find new phases of quantum matter. In this regard, a crucial ingredient is the emergence of novel implementation of symmetries. In this talk, I shall discuss how new and enhanced symmetries may arise at low energies in a two dimensional honeycomb system due to spin-orbit coupling in certain heavier transition metal compounds. The resultant Dirac semimetal phases, as I shall discuss, act as parent phases for several unconventional topological phases and associated phase transitions.

Strong Electronic Correlations Observed in Colossal Thermoelectric Material K0.65RhO2 Using Angle-Resolved Photoelectron Spectroscopy (ARPES)

S. Thirupathaiah

S. N. Bose National Centre for Basic Sciences, Kolkata

Email: <u>setti@bose.res.in</u>

Abstract

Using angle-resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) calculations we studied the low-energy electronic band structure of K0.65RhO2. We identify a highly correlated hole pocket on the Fermi surface of K0.65RhO2. Most importantly, two kinks at the binding energies of 75 and 195 meV have been observed below the Fermi level. While the low-energy kink at 75 meV can be understood as a result of the electron-phonon interaction, the high-energy kink at 195 meV is a new finding of this system, leading to anomalous band renormalization, possibly originated from the bosonic excitations at higher frequencies. We further notice that the high-energy anomaly has important implications on the colossal thermoelectric power of K0.65RhO2.

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Spin-orbitronics: Interconversion between charge and spin currents

Chandrasekhar Murapaka

Department of Materials Science and Metallurgical Engineering Indian Institute of Technology Hyderabad

Email:mchandrasekhar@msme.iith.ac.in

Abstract

Interconversion between charge and spin currents has attracted great research interest in the past decade1,2. Spin-orbit interaction at the interface between ferromagnet/non-magnetic materials is at the basis of the recent advances in pure spin current based spintronics devices such as spin-orbit torque magnetic random access memory (SOT-MRAM). In-plane current through a non-magnetic materials can generate transverse spin current via spin Hall effect that leads the switching of adjacent ferromagnetic layer. The efficiency of charge to spin conversion strongly depends on the spin-orbit coupling (SOC) of the non-magnetic layers which can be quantified from spin Hall angle, ratio of spin current to charge current. In this talk, I will demonstrate the spin-orbit torque induced switching in (Co/Ni) ferromagnetic layers adjacent to a heavy metal Ta. The effect of Ta layer thickness on the efficiency of the switching will be presented. Later, I will discuss about the possibility of using rare-earth metals to harvest spin currents due to relatively large SOC. The SOT switching between (Co/Ni)/Ta and (Co/Ni)/Tb are systematically compared in our study3. The spin Hall angle of Tb is found to be 3 times higher as compared to the conventional heavy metals. I will discuss about the spin-orbit torque based reconfigurable logic we have proposed and demonstrated4. The second part of my talk I will discuss about our recent studies on the spin to charge conversion via spin-pumping experiments in ferromagnetic/heavy metal interfaces. The detailed study of systematic investigation of the effect of seed layer on the crystalline phase and spin Hall angle of the heavy metal will be presented5.

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Defect induced Non-ergodic Ground States in Martensites

K. R. Priolkar

School of Physical and Applied Sciences, Goa University, Taleigao Plateau, Goa 403206 India

Email: <u>krp@unigoa.ac.in</u>

Abstract

Point defects above a critical concentration suppress the long-range order and realise in a non-ergodic state like glass. This is true for a crystal to glass, ferromagnet to spin glass, ferroelectric to a relaxer or martensite to strain glass. Though there are several studies on glass transition, very few studies focus on identifying the defect phase and understanding the structural distortions caused by the doped impurities. Using Extended X-ray Absorption Fine Structure (EXAFS) and other structural probes we elucidate the structure of the defect phases and the structural distortions responsible for strain glassstate in the martensitic alloys.

In Ni-rich NiTi, the body-centred cubic Ni defect phase embedded among the B19' martensitic NiTi grains is responsible for martensite to strain glass transition [1]. A similar defect phase, cubic \Box -FeNi, results in strain glass state in Ni₂Mn_{1.5-x}Fe_xIn_{0.5}[2]. We also discuss scenarios of martensite to ferromagnetic austenite transformation doped Heusler martensites [2,3].

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Tailoring the properties of composites with carbon nanomaterials as reinforcement

Kinshuk Dasgupta

Materials Group, Bhabha Atomic Research Centre

Email: <u>kdg@barc.gov.in</u>

Abstract

Carbon nanomaterials can have wide range of structures and properties namely, 'zero' dimensional carbon dot, 'one' dimensional carbon nanotube, 'two' dimensional graphene and 'three' dimensionalnanodiamond. These nanomaterials when incorporated into polymer matrix, metal matrix and ceramic matrix composites, alter the properties in these composites. The microstructure and the properties can be tailored by controlling the composition and the processing parameters. This talk will showcase several such applications carried out in our group, where tremendous improvement in specific properties could be achieved through reinforcement with carbon nanomaterials.

Positron beam studies on the Irradiation damage resistance in High entropy alloys

S. Abhaya

Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam- 603 102, Tamilnadu, India

Email: sab@igcar.gov.in

Abstract

High entropy alloys (HEAs) are a family of multi elemental alloy systems containing more than four elements in near/equiatomic proportions [1]. In HEA, all the elements are principal elements and the high configurational entropy which arises due to the presence of multiple elements, drives the alloy system to form a random solid solution having a simple FCC, BCC, or HCP structure rather than forming intermetallics [1]. The application of HEA as a nuclear structural material has driven a lot of research works into understanding the defect microstructures produced upon heavy ion implantation using Transmission electron microscopy technique, as the major workhorse [2]. Similarly, molecular dynamic simulation studies have also been carried out to support the experimental findings and provide insights into the defect evolution and the microstructural response of the system with elevated temperatures [3]. All these experimental findings show high phasestability, improved resistance to radiation-induced segregation, void swelling, and helium bubble growth [4].

Positron annihilation spectroscopy (PAS) is an excellent non destructive defect characterization tool which can detect vacancy defects starting from monovacancy to small vacancy clusters to voids [5]. Variable low energy positron beam setup at IGCAR, Kalpakkam enables non- destructive depth profiling of implantation induced defects such as vacancy defects, stacking fault tetrahedrons (SFT), voids, helium bubbles etc., up to a depth of few hundreds of nm of the material [6].

This talk will focus on the application of the HEA as a reactor structural material citing the recent research works and also quoting some of our experimental findings relating to the implantation induced defects in FeCrCoNi using the variable low energy positron beam setup [7].

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Doping site induced modification of the magnetic structure of MnNiGe alloys

S. Chatterjee

UGC-DAE Consortium for Scientific Research, Kolkata Centre, Sector-III, LB-8, Salt Lake, Kolkata:- 700106, India

Email:souvik@alpha.iuc.res.in;souvikchat@gmail.com

Abstract

The magnetic equiatomic alloys (MEAs) with general formula MM'X (M/M' = transition metals, and X = non-magnetic sp element) and their derivatives haverecently been identified as the new shape memory alloy class. Apart from the shape memory effect, various interesting magneto-functional properties are also associated with MEAs, including giant magnetocaloric effect, large magnetoresistance, exchange bias effect, magnetic memory, etc. Among MEAs, MnNiGe is the most studied one. The pristine MnNiGe alloy undergoesa martensitic phase transition (MPT) around 470 K and orders antiferromagnetically below 346 K. For enhanced magneto-functionality, the researchers have adopted several doping strategies. Some of such strategies are (i) doping of foreign elements in Mn/Ni/Ge sites, (ii) self doping, (iii) creation of vacancy in Mn/Ni/Ge sites, (iv) application of external pressure (P), etc. The main aim behind such strategies is to reduce the martensitic phase transition below or around the magnetic transition temperature for enhanced magneto-functionality. In the case of foreign element doping, dc magnetic investigation indicates that the magnetic nature of different phases depends strongly on the doping sites. For Ni/Mn site doping cases, the doped alloys undergo magnetic and structural transitions simultaneously. On the other hand, Ge-site doped alloys undergo a martensitic transition in the magnetically ordered austenite phase. Previous neutron powder diffraction (NPD) studies indicate the spiral antiferromagnetic structure of pure MnNiGe alloy. However, very few NPD studies have been performed to explore the magnetic structure of doped MnNiGe alloys. This work aims to probe the effect of foreign element doping at Mn, Ni, and Ge siteson the magnetic structure through NPD study in ambient and high-pressure conditions. In the case of Ge-site doping, we observed a commensurate to incommensurate antiferromagnetic transition around MPT. Interestingly, both Ni and Ge site doped alloys show helically modulated incommensurate antiferromagnetic structure, whilst, a cycloidal modulation has been observed for the incommensurate antiferromagnetic structure of the Mn site doped alloy. A significant change in magnetic structure has also been noticed in the presence of external pressure.

Pressure tuning of material properties: selected examples from the joint Indo-Italian beamline "Xpress" at Elettra–Synchrotron Trieste.

Boby Joseph

Elettra Sincrotrone-Trieste S.C.p.A., Area Science Park, Basovizza, Trieste 34149, Italy

Email: <u>boby.joseph@elettra.eu</u>

Abstract

Pressure is a thermodynamic variable extremely useful in altering the material properties. For condensed matter physicist tuning of the electronic properties are of utmost important; for chemist, it is the bonding properties and for the material scientist, the functional properties. In all such cases, high-pressure from few to few tens of giga-Pascal (GPa) are found to be of great use. We elaborate this by discussing three different systems: First, we discuss the pressure effects on the suppression of a charge density wave transition in LaAuSb2 and its connection to the structural degrees of freedom [1]. We then present inputs from the high-pressure diffraction on the occurrence of meta-valent bonding state in doped GeSe [2]. In the third example, we demonstrate the realization of a novel hybrid nanocomposite with interesting gas sensing properties using combined pressure-temperature treatment of a porous system [3]. Excellent high-pressure diffraction data were essential in all the above cited examples which were available thanks to the Indo-Italian high-pressure diffraction beamline facility – Xpress, at the Elettra synchrotron radiation center at Trieste. The salient features of this facility will be presented. In particular, citing few recent scientific out-puts from the Indian research groups [1,2,4,5], the broader appeal of the facility, also to non-specialists of the high-pressure field, will be high-lighted.

This presentation will also provide a brief introduction to the Elettra synchrotron radiation facility, the Indo-Italian collaboration existing there and the opportunities for the Indian user community in availing this facility.

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Thermodynamic Behaviour of Graphite Under Extreme Conditions of Nuclear Radiation, Pressure and Temperature

Ranjan Mittal

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

Email: <u>rmittal@barc.gov.in</u>

Abstract

Graphite is used as a moderator and reflector material in nuclear fission reactors. Graphite also serves as a non-replaceable structural component in reactor cores, which must remain stable over the lifetime of the reactor while operating at elevated temperatures. In a reactor, neutron irradiation damage in graphite results in the formation of structural defects, such as displaced atoms, vacancies, and higher order aggregates that raise the internal energy. Relaxation of the defects leads to spontaneous release of energy at around 473 K, which is referred as Wigner energy. This stored energy associated with defects can surprisingly reach large energy densities with values as high as 2.7 MJ/kg. The bursts of released energies may be intense enough to cause fires in reactor and lead to nuclear accident. Recently we have thoroughly investigated thermodynamic behaviour of graphite under extreme conditions of nuclear radiation, pressure and temperature by numerous experiments and ab-initio simulations.

We have investigated graphite samples that had been irradiated with neutrons at various levels of fluence in the CIRUS research reactor at Trombay, India over a period of almost 50 years. We have performed neutron diffraction, X-ray diffraction, small-angle X-ray scattering, Raman scattering, differential scanning calorimetry and specific heat measurements, which have been complemented by state-of-the-art ab-initio simulations of the defect structure and dynamics. We have identified various 2-, 3- and 4-coodinated topological structures at atomic level in defected graphite, and provided microscopic mechanism of defect annihilation on heating and release of the Wigner energy. Our studies showed that the annihilation process involves cascading cooperative movement of atoms in multiple steps involving an intermediate structure [1]. Neutron diffraction studies revealed [2] persistence of some of the defects in graphite at high temperatures much greater than 653 K, where the Wigner energy is completely released. We infer that the remnant defects may be intralayer Frenkel defects, which do not store large energy, unlike the interlayer Frenkel defects that store the Wigner energy. The experimental observations are complemented by abinitio calculations [2].

We have also investigated the anisotropic thermal expansion of graphite using ab-initio calculations [3] of phonons. We find that the negative thermal expansion (NTE) in the a-b plane below 600 K and very large positive thermal expansion along the c-axis up to high temperatures arise due to various phonons polarized along the c-axis. While the NTE arises from the anharmonicity of transverse phonons over a broad energy range up to 60 meV, the large positive expansion along the c-axis occurs largely due to the longitudinal optic phonon modes around 16 meV.

Static compression of hexagonal graphite (HG) results in transformation to hexagonal diamond (HD) or cubic diamond (CD) over wide range of pressure and temperature. Recent shock studies of the transition from HG to HD or CD have created much interest in understanding the mechanism of these transitions. The nucleation and growth mechanism of these phase transitions, as found in static experiments, has been investigated in literature. However, the transition in shock experiments occurs at a fast time scale of ~ps, and may involve a different mechanism. We have used ab-initio molecular dynamics simulations [4] to elucidate the mechanism of the phase transition in shock experiments from hexagonal graphite (HG) to hexagonal diamond (HD) or to cubic diamond (CD). The transition from HG to HD is found to occur swiftly in very small time of 0.2 ps, with large cooperative displacements of all the atoms. We have also performed calculations of the phonon spectrum in HG at high pressure, which reveal soft phonon modes that may facilitate the phase transition involving the sliding and puckering of the HG layers. We have further calculated the Gibbs free energy, including the vibrational energy and entropy, and derived the phase diagram between HG and CD phases.

The detailed results will be discussed.

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Recent advances in the study of plastic strain induced phase transitions under high pressures

K. K. Pandey

High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

Email: <u>kkpandey@barc.gov.in</u>

Abstract

In conventional hydrostatic or quasi-hydrostatic high-pressure studies, phase transitions (PT) are mostly pressure or stress induced. These PTs initiate at pre-existing defects or nucleation sites below the yield. Whereas, under high-pressure torsion (HPT) new defects are permanently generated during plastic flow. This leads to much more dislocations in a pileup and may drastically reduce PT pressure, sometimes even by two orders of magnitude. These plastic strain induced PTs require completely different thermodynamic treatment and experimental characterization [1-3]. Rotational diamond anvil cell (RDAC) [4] which are similar to conventional diamond anvil cell (DAC), but with additional degree of freedom of rotation of one anvil with respect to another, are best suited for these studies. I will present some of the recent developments for quantitative experimental characterization along with a few representative studies on metallic [5] and non-metallic systems.



Fig. Schematics of rotational diamond anvil cell.

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Experimental evidence of a novel anomalous transport regime in hybrid, non-Hermitian disordered systems.

Sushil Mujumdar*, HimadriSahoo, M Balasubrahmaniyam, SandipMondal and R Vijayaraghavan.

Tata Institute of Fundamental Research, Mumbai, 400005, India.

*Email:mujumdar@tifr.res.in

Abstract

Non-Hermiticity modifies the transport properties of complex systems in various intriguing ways. In this work, we report an anomalous transport regime wherein an unexpected rise in transmission of hybrid quasiparticles is observed under localizing disorder. The behavior can be traced to the confluence of hybridization and non-Hermiticity, in which the former results into the formation of a miniband of eigenvalues under disorder, while the latter allows hopping of the quasiparticles between the eigenmodes. The enhanced transmission is facilitated by the formation of necklace states in the Anderson localizing system. We demonstrate experimental results confirming the anomalous regime at microwave frequencies in a one-dimensional spoof surface plasmonic system.

Graphene drum resonators coupled over long distances: towards controlled phononic time crystals

Saikat Ghosh

IIT Kanpur, UP, India

Email: gsaikat@iitk.ac.in

Abstract

Suspended graphene membranes provided a powerful NEMS platform for envisioning new technologies and in exploring science at the interface of strong mechanical nonlinearity and quantum dynamics. Here we will argue with three examples from our laboratory on the versatility of graphene resonators for such platforms. Firstly, we will demonstrate graphene as a motion sensor that can be used to detect femto-meters of displacement induced on a Silicon Nitride(SiN) substrate, which is also a resonator (1). In the second example, we will discuss how one can induce a large nonlinear response on SiN resonator mode, along with a novel frequency comb signature, by coupling it to graphene modes (2). Finally, we will discuss a novel mechanism of coupling two distant graphene resonators, separated by 40 microns, via the intermediate SiN resonator modes. We found a new dynamical phase, where persistent beats or frequency combs in the spectra coexist with synchronization of the two distant drum resonators (3). Such coupling between two drums can be readily extended, towards realizing large area phononic time crystals, with controllable dispersion and response.

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Organic Photodetector As Next Generation Light Detection: Challenges And Opportunities

Jitendra Nath Roy^{1,2}

¹Department of Physics, Kazi Nazrul University, Kalla (CH), Nazrul Road, Asansol, Paschim Bardhaman. 713340, West

Bengal, India.

²Centre of Organic Spintronics and Optoelectronics Device, Kazi Nazrul University, Kalla (CH), Nazrul Road, Asansol, Paschim Bardhaman. 713340, West Bengal, India.

Email: jn.roy@knu.ac.in and jnroys@yahoo.co.in

Abstract

One of the important optoelectronic components is photodetector whose performance significantly influences the performance of the whole optoelectronic integrated components. The photodetector provides a great solution to global challenges in energy, health care, communication, information processing., remote control, industrial automation, night surveillance, environmental monitoring, biological detection and so forth [1-3]. A high-performance photo-detector should satisfy the **5S** requirements of Sensitivity, Signal-to-noise ratio, spectral Selectivity, Speed, and Stability. Those **5S** requirements have been reasonably optimized in traditional inorganic photodetectors and has led them to form the base of present-day light-detection technology. However, their *rigid structure* and *limited area scalingat low cost* have hindered their application in several emerging fields, such as context-aware optical sensing, touch less interactive computing, wearable biometric monitoring, biomedical imaging, distributed ionizing-radiation detection etc. Furthermore, *complicated manufacturing process* and *less effectiveness in cost-saving* have also restricted their applications. In this direction, 'Sensors' based on organic photodiodes have become one of the most innovative technologies [2-7].

There are several advantages of organic photodetector (OPD) over inorganic photodetector:

- Light weight, mechanical flexibility and compatibility with large and rigid substrate.
- Ease of production, chemical modification and easy to fabricate at low temperature.
- ✤ Large optical absorption coefficients (10⁵/cm).
- *Organic optoelectronic devices are more <u>Energy Efficient</u> and <u>Eco friendly</u>.*

Such devices can be easily integrated into various systems, such as flexible, wearable or portable electronics. Recent research has demonstrated reasonably well figures of merit of organic photodetectors, compared to common inorganic photodetectors in the area of \blacklozenge wider dynamic range; \blacklozenge broader spectral range; \blacklozenge better responsivity.

Organic Photodectors also bear a potential market worldwide. According to the report of *Research Reports World*, Organic Photodetectors can have widespread implications for many markets for consumers and enterprises [8]. Manufacturers across industries are constantly researching for ways to develop newer functionalities in their products. Moreover, a change in the base material itself would be at the base of a range of further innovations. An attitude of developing ground breaking innovations is therefore fueling the research happening towards Organic Photodetectors. The major players in Organic Photodetector market include ISORG, Silvaco, Inc, NikkoIA SAS, OSRAM GmbH, & Albis Optoelectronics AG.

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Defect mediated multicolored emission from pristine ZnO nanostructure: A voyage towards single source white LED

Mrinal Pal

CSIR-Central Glass and Ceramic Research Institute, Kolkata - 700032

E-mail: palm@cgcri.res.in

Abstract

Recently, UV/NUV excitable RGB phosphors with precisely tuneable PL emission properties have been in highdemand for their suitability in the fabrication of white LEDs. We have tried with success to generate for the first-time multiple emission havingtuneable PL intensity, shade, and color temperature in pristine zinc oxide. The ZnO nanopowder was prepared by a facile and cost-effective aqueous solution-precipitation method. The as-synthesized nanopowder was annealed at different temperatures ranging from 150 _C to 850 _C and all these samples were characterized by XRD, FESEM, EDX, BET, Raman spectroscopy, and UV-Vis spectroscopy to have insight into their microstructural, compositional, and band-structure details. Optical studies of the samples were conducted using PL and s-PL spectroscopy. Color coordinates of the samples were obtained from the CIE plots derived from the PL spectra. The CIE coordinates were further used to calculate the CCT values of the samples and they are found to be suitable in cold light applications. These nanostructured zinc oxide particles being sufficiently large in size are extremely stable and expected to show photoluminescence for a longer period of time than nanorods and quantum dots. PL studies of the samples revealed that various emission is originating from crystalline point defects, viz. zinc interstitial (Zni), and oxygen interstitial (Oi). Annealing at different temperatures triggered changes in the defect concentrations leading to the corresponding changes in the intensity, shade, and color temperature of the blue phosphorescence.

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Surface Micro Engineering of Silicon for Efficient and Cost Effective PEDOT:PSS/Silicon Hybrid Solar Cells

Sanjay K. Srivastava^{1,2*}

¹Photovoltaic Metrology Section, Advanced Material and Devices Metrology Division, CSIR-National Physical Laboratory,

New Delhi-110012 (India)

²Academy of Scientific and Innovation Research (AcSIR), CSIR-NPL campus, New Delhi-110012, (India)

*Email:srivassk@nplindia.org; sksrivastava78@gmail.com

Abstract

Solar photovoltaic (SPV), which is dominated by silicon (Si) based homojunction solar cells, is one of the most reliable technologies for harvesting solar energy. However, these PV cells are based on high thermal budget dopant-diffusion and annealing processes (\geq 850°C), in atmosphere of phosphorus or boron, depending upon type of impurity in Si wafer) [1, 2, 3]. Naturally, these processes are time consuming, complex and in turn increase per unit power cost of the SPV devices. This has driven significant research interests towards combining the best of both organic and inorganic systems. Organic carrier selective layer with Si is a promising approach for the next generation of cost-effective solar cells owing to their unique properties like light weight, cost effectiveness and environment friendly [4, 5]. The organic/Si hybrid solar cells (HSCs), in principle, can achieve comparable efficiency to that of a conventional Si homojunction solar cell as light absorption and photocarriers generation take place in the Si wafer only in suchHSCs architecture [4].



Figure 1:(a) Schematic of process flow of making of micro-structured Si surface from the as-cut solar grade Si wafers and PEDOT:PSS/n-Si interface(junction), (b) Schematic of hybrid solar cell device structure (Ag/PEDOT:PSS/-n-Si/In:Ga), (c) schematic of the operation principle of such HSCs, and (d) solar cell performance characteristics of the champion HSC.

Most commonly, an inexpensive, highly conducting and transparent polymer namely, poly(3,4-ethylenedioxythiophene)poly(styrene sulfonate) (PEDOT:PSS), which acts as a p-layer (carrier selective hole transport) is coated over n-type crystalline Si surfaces resulting into a Schottky junction at the PEDOT:PSS/Si interface [4, 5]. The PEDOT:PSS is suggested to play four vital roles in such HSCs, namely; (i) it induces an inversion layer in n-Si (i.e., a p-dopant-free, Si p–n junction is formed) to block electrons and extract holes, (ii) it transports holes to the metal anode, (iii) it acts as a surface passivation layer to reduce interfacial recombination, and (iv) it increases light harvesting by reducing reflection losses. The HSCs based on PEDOT:PSS/n-Si, have attracted a lot of attention toward the development of low-cost and efficient photovoltaic devices.

However, it requires extensive control and optimization of the photoelectric property of the PEDOT:PSS thin films, Si surface properties, PEDOT:PSS/n-Si hetero-interface, n-Si/rear electrode contact, and so on. An appropriate PEDOT:PSS/Si interface

formation and its properties are key to achieve high-performance solar cells. Effective surface nano/micro-engineering of the Si wafers, can play important role in achieving not only effective light harvesting but also a quality PEDOT:PSS/n-Si heterointerface leading to high efficiency HSCs [6]. For example, recently highly efficient PEDOT:PSS/Si HSCs (with photoconversion efficiency >12.25%) could be achieved via an effective surface micro-engineering of the as-cut, low-cost solargrade thin Si wafers, by a simple one-step aqueous KOH process (see Fig. 1). The process reduces the weighted surface reflectivity from >35% to <9% in broad spectral range in addition to removing the surface saw-damages of the wafers completely. The combined effect in turn improves the PEDOT:PSS/Si interface (junction) property leading to a highly efficient PEDOT:PSS/Si HSCs even in its simplest possible device structure.

Thus, a simple yet efficient HSCs on such economic solar-grade Si wafers, commonly used for the conventional Si solar cells, could be demonstrated.Further, it is shown that effective micro-engineering of the commercial as-cut Si wafers removes the surface-damages on both sides which if not addressed properly, cause very high surface recombination losses and has detrimental effect on the polymer/Si junction and hence the PV performances. The talk will discussfew such examples of efficient hybrid solar cellarchitectures employing different simple and cost effective micro-and nano-structuring schemes of Si wafers, carried out at CSIR-NPL during past 5 years.

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Probing Magnetic Properties of Oxides Thin Films Using XMCD Studies at Indus-2 Synchrotron Source

R. J. Choudhary

UGC DAE Consortium for Scientific Research, Indore

Email:ram@csr.res.in

Abstract

The wide range of exotic structural, electronic, dielectric and magnetic properties exhibited by the transition metal oxides (TMOs) emanate from the competing forces encountered by transition metal (TM)-3d electrons, such as electron-electron Coulombic interaction which favors localization of electrons, and TM 3d-O 2p hybridization which facilitates the electrons delocalization. Strain engineering in thin films of these materials provides a window to tune these parameters and hence control over their electronic and magnetic ground states. It is of huge importance and fundamental in nature to ascertain an unequivocal origin of modifications in the electrical, electronic and magnetic properties of these films or their hetero-structures, in order to tune their properties. A comprehensive study using resonant photoemission spectroscopy (RPES), X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) experiments, which are feasible at Indus synchrotron sources at RRCAT, Indore, allows us to unravel the coupling among structural, electronic and magnetic properties. We take an example of orthorhombic brownmillerite (BM) SrCoO_{2.5} (SCO), which is an antiferromagnetic insulator in bulk form. The RPES studies reveal that the electronic ground state of the system transforms from $3d^n$ in bulk to $3d^{n+1}L$ (L: O-2p hole) in the strained thin film due to enhanced hybridization strength. XAS and XMCD experiments performed at Indus-2 synchrotron source reveal that the strained SCO thin films possess negative charge transfer energy (Δ) value and it transforms from antiferromagnetic in bulk to ferromagnetic in the strained thin film. The induced ferromagnetism is described in terms of the negative Δ , O-2p hole density, and charge & spin-state disproportionation in the system. Interestingly, when this ferromagnetic strained SCO film is integrated with another ferromagnetic La_{0.7}Sr_{0.3}MnO₃ film, the heterostructure reveals unusual exchange biasing. The electronic, orbital, and spin reconstruction taking place at the interface between these two ferromagnetic oxides materials lead to an antiferromagnetic interaction between the moments at Mn site and Co site across the interface, as divulged from theXMCD studies.

Unique Magnetotransport in KTaO3 based conducting interfaces: Planar Hall effect, Anomalus Hall effect, Shubnikov-de Haas oscillations, Berry's phase, Chiral Anomaly(?)

Suvankar Chakraverty *

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Mohali, India

*Email:suvankar.chakraverty@inst.ac.in

Abstract

Abstract: In recent times, momentum dependent splitting of spin-bands in an electronic system, the "Rashba effect", has gained a lot of interest because of its applications in future generation spintronic devices. [1,2] The Rashba effect is important not only because it has tremendous potential for technical applications, but also it is a hunting ground of emergent physical properties owing to the linear dispersion relation at the crossing point of the two spin bands.[3] In this work, we present observation of emergent phenomena arising at the interface of two insulating perovskite oxides due to Rashba spinband splitting. In our first work, we improvise a novel conducting interface by juxtaposing KTaO3 (KTO) with another insulator, namely LaVO3 (LVO).[4] This heterointerface exhibits strong spin-orbit coupling which is the highest among perovskite oxide heterostructures reported so far. The system is also found to show signature of topological chiral anomaly via observation planar Hall effect (PHE) and anomalous inplane magnetoresistance (AMR) similar to that observed for topological systems. [5] In our next work, we show the realization of conducting interface between ferromagnetic EuO and non-magnetic KTO. [6] This heterostructure is found to exhibit Shubnikov-de Haas oscillations. The observed oscillations suggest the presence of two Fermi surfaces. For both the Fermi surfaces, we have seen the presence of a non-trivial "Berry phase" suggesting that the surfaces enclose a "Dirac point" and the Berry phase originates from the inner and outer Fermi surfaces of the Rashba spinsplit bands. Analysing the SdH, Hall and magnetoresistance data, we have drawn a possible band diagram near the Fermi surface for EuO-KTO heterointerface. Our observations suggest that perovskite oxides with strong spin orbit coupling and relativistic conduction electrons could be a hunting ground not only for spintronic materials but also for emergent physics.

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Engineering van der Waals solids for tunable optical and electronic properties

Satyaprakash Sahoo

Laboratory for Low Dimensional Materials, Institute of Physics, Bhubaneswar

Email:sahoo@iopb.res.in

Abstract

Atomically thin two dimensional (2D) van der Waals (vdW) solids, especially transition metal dichalcogenides (TMDCs) have attracted prodigious attention to the versatile research in semiconductor technologies, nearly outclassing conventional semiconductors owing to their excellent physical properties. The layer dependent variable bandgap, strong spin orbit coupling, interlayer twist-angle in vdW heterostructures provide multiple degrees of freedom to probe various electronic, optical and thermal properties. In this talk, I will discuss about growth of large scale, high quality monolayer MoS₂ towards the realization of high-performance hysteresis free field-effect transistor. Minimization of the charge trapping under pulsed I~V measurements, provides the intrinsic transistor behavior with record high mobility.¹Moreover, the generated moiré patterns in twisted bilayer MoS₂ modify the lattice dynamics through periodic potential, which enable pathways to control the phonon-phonon interactions and quantum behaviors in vdW heterostructures. Electric field modulated carrier transfer in MoX₂/WX₂ heterostructures with varying stacking geometries can be achieved for efficient performances in optoelectronic devices.²

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Lithium based Battery: Fundamentals and Challenges Ahead

Balaji P Mandal

Chemistry Division, Bhabha Atomic Research Centre, Mumbai - 400094

Email : <u>bpmandal@barc.gov.in</u>

Abstract

Lithium-ion battery is the latest addition to the family of rechargeable battery type. These batteries use intercalated lithium compounds as the electrode materials. Different cathode materials like LiCoO₂, LiMn₂O₄, LiCo_{1/3}Mn_{1/3}Ni_{1/3}O₂, LiFePO₄ have been tried in recent past. Among these cathodes, LiFePO₄ has become most attractive cathode material due to safety, low cost, low toxicity, stable voltage platform and long cycle life. However, due to poor electronic conductivity and slow diffusion of lithium ion in pure LiFePO₄, restrict its use for wide applications. The use of nanosize LiFePO₄ allows for fast lithium diffusion and to improve the electronic conductivity, few important approaches have been proposed like coating the particles with a conductive film of carbon or wrapping the particles with graphene, and doping with aliovalent or isovalent ions. In the anode side, molybdenum-based electrodes like MoS₂ and Mo₂C are found to be suitable candidates for lithium ion battery. The intercalation and deintercalation mechanism have also been derived using different techniques. The futuristic lithium-based battery will be of Li-S battery due to higher energy density. In those batteries the issues are low cycle life due to dissolution of sulphur in the electrolyte. However, by suitable modification in the electrode and electrolyte the dissolution can be minimized.

Surface modification by metal-oxide nanoparticle coatings for improving the cycling characteristics of the cathode material

Madhu Chennabasappa^{1, 2} *, Joshua R. Buettner-Garrett², Venkatesan Manivannan², Brandon Kelly²

¹Department of Physics, Siddaganga Institute of Technology, B H Road, Tumkur – 572103, Karnataka, India ²Department of Mechanical Engineering, Colorado State University, Fort Collins, USA.

*Email: madhuc@sit.ac.in

Abstract

The cathode materials in the ternary system (1-x-y) LiNiO₂ · xLi₂MnO₃ · yLiCoO₂ shown in the diagram are obtained through scalable, co-precipitation followed by solid state reaction at 975 °C. The compositions on the ternary diagram {a combination of LiNiO₂, Li₂MnO₃, and LiCoO₂ layered structures} are chosen through an arrangement conducive to mathematical modelling. The X-ray diffraction studies on the synthesised materials confirm the α -NaFeO₂ structure, except in compositions close to LiNiO₂ on the ternary. Through electrochemical testing revealed the specific capacity from 150 to 250 mAh/g for different samples based on their compositions. The samples with high manganese concentration delivered higher capacity in excess of 225 mAh/g in the first cycle, however, the subsequent cycles resulted capacity fading. We have tried to modify the surface of these cathode materials in order to increase the capacity retention. Metal oxide (Al₂O₃, ZnO, AlPO₄) nanoparticles are separately coated and the capacity retention is compared. Differential scanning calorimetry (DSC) testing on this material was promising as it showed an exothermic reaction of 0.2 W/g at 200° C when tested up to 400° C. Cost for laboratory quantities of material yielded \$1.49/Ah, which is significantly lower than the cost of LiCoO₂ due to the low cobalt content, and the straightforward synthesis.



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Designing of Carbon Based Energy Material

Utpal Sarkar

Department of Physics, Assam University, Silchar-788011, India

Email: <u>utpalchemiitkgp@yahoo.com</u>

Abstract

This talk aims to explore the promising applications of several carbon allotropies and its structural derivatives in the field of energy[1,2]. The intrinsic band gap of these allotropies are occasionally tuned to suits for technological applications. Using density functional theory methodology, structural and electronic properties of these materials will be discussed with special emphasis on nanoscale capacitor and anode-material designing. How doping affects these properties will also be analysed. A novel two-dimensional carbon material, namely pentagraphyne[1] is proposed which is energetically favourable than other graphyne members.Remarkable carrier mobility along with its superior optical performance renders it to be a potential candidate for future electronics, photovoltaic solar cells, and optoelectronic devices. Graphyne, twin-graphene and pentagraphyne immerged as an excellent candidates for nanocapacitor[3-5] Na-ion battery[6,7] and thermoelectricity[8].

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Dielectric Relaxation Investigations In A Ferroelectric Liquid Crystal

T Hemalatha, P Indhumathi, A H Shijin, V S Vimal, R K Yokesh, N Pongali Sathya Prabu, M L N Madhu Mohan*

Liquid Crystal Research Laboratory Bannari Amman Institute of Technology, Sathyamangalam – 638 401.

*Corresponding author: mln.madhu@gmail.com

Abstract

Dielectric relaxations in a ferroelectric liquid crystal namely Camphoric acid (CA) reacted with alkyloxy benzoic acid (BAO) and the resultant homologous series of HBFLC is discussed. The mesogen exhibits smectic C^* and smectic G^* phases. Arrhenius plots are constructed in smectic C^* phase elucidating data from eighteen temperatures which covers the entire thermal span of smectic C^* . A molecular modelling of the mesogen is given which gives the explanation for various relaxation frequencies.

Introduction

Hydrogen bond liquid crystals (HBLC) are classified under soft condensed matter. HBLC form a separate branch of liquid crystals. These supra molecular HBLC can be isolated by various techniques among them most prominent is converting a dimeric carboxylic acid in to a monomeric form by dissolving the same in a non-polar solvent like Dimethyl formamide (DMF). The advantage of this technique is no loss of ingredients during the reaction hence highest yield is expected. The HBLC synthesized by this technique are reported to be chemically stable, thermally sustainable against degradation of the sample. HBLC were investigated by many researchers, prominent among them is Kato group. If ferroelectricity is induced through optically active ingredient in a HBLC then the resultant is referred as Hydrogen bond ferroelectric liquid crystals (HBFLC).

To form a HBFLC, it is adequate if complimentary bonds namely proton donor and electron acceptor pairs are available naturally in the chemical ingredients. Furthermore, multiple H-bonds can be envisaged through abundant availability of multiple proton donor and electron acceptor pairs. The influence of multiple H-bonds in a HBFLC is an interesting research problem. Usually, the origin of various phases in a hydrogen bond complex is attributed to the l/d ratio of the HBFLC mesogen where 1 is the length of the molecule while d is the chemical dimensions (width) of the molecule. However, new smectic phases like smectic X*, smectic R* have their origins from the inter-digitation of the smectic layers. Prominently reentrant smectic phases owes their explanation to the molecular level orientation / inter-digitation within smectic layers. In the present work, a ferroelectric liquid crystal namely camphoric acid with benzoic acid is experimented in smectic C* phase at eighteen different temperatures for elicitation of dielectric relaxations.

Results and Discussion

Ferroelectric ingredient Camphoric acid (CA) is reacted with alkyloxy benzoic acid (BAO) and the resultant homologous series of HBFLC comprises of eight mesogens with varying alkyloxy benzoic acid from pentyloxy to dodecyloxy. Standard synthetic route is adopted for the synthesis of these HBFLC.

The synthesized HBFLC are filled in to a ten micron polyamide buffed cell through capillary action in isotropic phase. Silver wires are connected to the liquid crystal cells which act as leads. Before filling the cell, the leads capacitance is calculated.

The HBFLC filled cell is mounted in INSTEC hot and cold stage HCS-402 whose temperature is programmed by INSTEC standalone temperature controller mk2000 to an accuracy of 0.1 °C. This setup is placed between the crossed polarizers of Nikon Polarizing Microscope (E600 POL) equipped with Nikon CCD system (DS-U1). The image storage, retrieval and analysis is done by Nikon Image Software system (NIS).

The calibration of the empty liquid crystal cell is done with temperature from 25° C to 200° C and frequency derived from Wayne Kerr (6500B) from 5 Hz to 13 MHz. Simultaneous textural observations are done through the microscope to ensure the phase identification. The HBFLC is heated to its isotropic temperature and cooled at a rate of 0.1° C to Smectic C* phase. This slow cooling helps in proper alignment of the sample and eliminates the crystal defects.

The sample chosen for the study is Camphoric acid with heptyloxy benzoic acid abbreviated as CA+7BAO. This sample exhibits two smectic phases namely smectic C* followed by smectic G*. The onset of smectic C* from isotropic is at 129.1°C while the onset of smectic G* is at 84.6°C. The liquid crystal from smectic G* turns to crystal at 59.3°C. These transition temperatures obtained by Polarizing microscopic study are in concurrence with the data elucidated from DSC. The thermal span of smectic C* is ~ 45° C.

Figure 1 illustrates the dielectric dispersion curves for eighteen temperatures in smectic C* phase. A meticulous observation of figure 1 gives the following points.



Fig. 1. Dielectric dispersion curves in Sm.C*

1. As the temperature is decreased from 113^{0} C to 86^{0} C, the magnitude of the dielectric dispersion curve also suppresses. It may be recalled that this phenomenon is reported to be associated with the helical pitch present in the HBFLC. The unwinding of the helical pitch can be accomplished either by application of attenuated external field to the sample or by variation of temperature gradient.

2. As expected, the length of ε_0 to ε_{∞} progressively diminishes with alteration of temperature. A proof of such behavior is seen in the magnitude of the dispersion curve.

3. A subtle change of relaxation frequency with temperature is also noticed from figure 1.

4. In the entire span of smectic C^* , the variation of relaxation frequency is proportional to the temperature. It may be noticed that at phase transition from Sm. C^* to Sm. G^* this proportional variation is severely affected.

An Arrhenius plot is constructed with logarithm of frequency on Y axis and absolute temperature inverse on X axis. Such a plot for CA+7BAO in smectic C* is shown in figure 2. A linear fit is performed to the data points to elucidate the activation energy from the slope of the fit obtained. It may be noticed from figure 2, the standard deviation from each of the points to the linear fit is within the experimental limits. Thus the activation energy in the phase smectic C^* is calculated from the dielectric spectroscopic data.



Fig. 2. Arrhenius plot for CA+7BAO



Fig. 3. Molecular modelling

A molecular modelling for the observed dielectric relaxation process is appended in figure 3. The molecule is supposed to comprise of flexible and rigid cores. The rigid core is the aromatic benzene moiety while the rest of the molecular structure is attributed to flexible part. This relaxation observed in smectic C* phase is attributed to the flexible part of the mesogen.

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Effect Of Electron-Hole Concentration On The Self-Trapping Transition Of Polaron In the Presence Of Strong Coulomb Correlation

Debika Debnath^{*}, and Ashok Chatterjee

School of Physics, University of Hyderabad, Hyderabad, India, 500046

*Corresponding author: debika.physics@gmail.com

Abstract

The two-dimensional Holstein-Hubbard model has been studied for the strongly correlated electrons. A series of canonical transformations have been performed followed by an averaging with the generalized all phonon state to eliminate the phonon degrees of freedom. In order to study the system in the strongly correlated regime, the electronic Hamiltonian is transformed to an effective t-J model and using the Hartree-Fock approximation, the ground state energy of the system is solved with variational technique by the use of Zuberev's Green function method. It has been found that the polaronic mobility ceases as the electronic concentration in the system increases and with the strengthening of the on-site electron-phonon interaction, the polaron gets trapped in its own potential at lower electronic density.

INTRODUCTION

The polaron physics has potential application in studying the electronic and transport properties of various materials, such as high temperature superconductor (HTSC), colossal magneto-resistance materials, cuprates etc. The electron-phonon (e-p) coupling coefficient has a pivotal role to the polaronic mobility. For the weak e-p interaction coefficient, the polaron can move through the lattice. For the stronger e-p interaction (int.) strength, the mobile polaron may get trapped in its own potential and become localized. The transition from this mobile large polaron to the localized small polaron is called as the self-trapping transition (STT). It has observed that the electron-hole been also concentration and the e-p int. strength both have a competitive effect towards the polaronic STT.

Sankar and Chatterjee (SC) [1, 2] have studied the STT for the strongly correlated electronic system using a variational technique followed by the zero phonon average to the Hamiltonian. In our present work, we have modified the SC's work and the effects of electron density towards the STT have been studied. We have considered the two-dimensional Holstein-Hubbard model followed by a series of canonical transformations and a general many phonon averaging to eliminate the phonon degrees of freedom from the system. The electronic Hamiltonian is then transformed to the t-J model and it is solved using the Hartree-Fock approximation. Gutzwiller approximation and Zuberev's Green function method have been the tools to solve the system. Next we have finally calculated the ground state energy of the system using numerical variational method and the

effective hopping parameter for the polaron have been studied with respect to the e-p int. coefficient and electron-hole concentration in the system.

THE MODEL

The Hamiltonian for the system is described as:

$$H = -t \sum_{\langle ij \rangle \sigma} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + \omega_0 \sum_{i} b_i^{\dagger} b_i + V \sum_{\langle ij \rangle \sigma\sigma'} n_{i\sigma} n_{j\sigma'} + g_1 \sum_{i\sigma} n_{i\sigma} (b_i^{\dagger} + b_i) + g_2 \sum_{\langle ij \rangle \sigma} n_{i\sigma} (b_j^{\dagger} + b_j)$$
(1)

where the parameter *t* refers to the nearest-neighbour hopping integral and *U* is the onsite Coulomb correlation energy. $c_{i\sigma}^{\dagger}(c_{i\sigma})$ is the creation (annihilation) operator for an electron with spin σ at site *i* and $b_i^{\dagger}(b_i)$ is the creation (annihilation) operator for a phonon at the site *i* with frequency ω_0 . The number of an electron at site *i* with spin σ is $n_{i\sigma} = c_{i\sigma}^{\dagger}c_{i\sigma}$. *V* measure the strength of the NN electron correlation. The on-site e-p interaction coefficient is g_1 and NN e-p interaction constant is g_2 .

FORMULATION

A series of canonical transformations are performed on the Hamiltonian *H*, using the generators (i) $G_1 = \frac{g'_1}{\omega_0} \sum_{i\sigma} n_{i\sigma} (b_i^{\dagger} - b_i) + \frac{g'_2}{\omega_0} \sum_{\langle ij \rangle \sigma} n_{i\sigma} (b_{i+\delta}^{\dagger} - b_{i+\delta})$, (ii) $G_2 = \alpha_s \sum_i (b_i b_i - b_i^{\dagger} b_i^{\dagger})$, (iii) $G_3 = \alpha_d \sum_{i\sigma} n_{i\sigma} (b_i b_i - b_i^{\dagger} b_i^{\dagger})$, (iv) $G_4 = \frac{1}{2} \sum_{i \neq j} \beta$ ($b_i b_j - b_i^{\dagger} b_j^{\dagger}$). To eliminate the phonon degrees of freedom from the system, the transformed Hamiltonian is averaged over the all phonon state, $|\Phi_{ph}\rangle = \sum_{n=0}^{M} c_n |\varphi_n(x)\rangle$.

The electronic Hamiltonian is then transformed to an effective t-J model and using the Gutzwiller approximation [3, 4] we write $(1 - n_{i\overline{\sigma}}) c_{i\sigma}^{\dagger} c_{j\sigma} (1 - n_{j\overline{\sigma}}) \cong \varphi_t c_{i\sigma}^{\dagger} c_{j\sigma}$, where $\varphi_t = 2x_h/(1 + x_h)$. Here the hole concentration in the system is denoted by, $x_h = (1 - n)$, with the electronic concentration *n*. Finally the Hartree-Fock approximation have been used to solve the Hamiltonian. The average occupation number per site (n), the Hartree correction to the kinetic energy term (p) are calculated using the Zuberev's Green function technique [5]. In our work we have considered the system at $T \rightarrow 0$.

Therefore the ground state (GS) energy per site is given by, $\varepsilon_0 = n\varepsilon_e - (\varphi_t t_{eff} + p\tilde{f}) zp + Nz \left[\frac{1}{4} (\tilde{f} - 4V_1^e)n^2 + \tilde{f}p^2\right] + K.$ (2)

Here $\tilde{J} = \varphi_J J = 4J/(1 + x_h^2)$. The GS energy is calculated by numerically minimising the equation (2) with respect to all the variational parameters g'_1 , g'_2 , α_s , α_d , β , and c_n 's. The parameters ε_e , t_{eff} , V_1^e and *K* are complicated equations (not written here).

RESULTS AND DISCUSSIONS

The GS energy with respect to the on-site e-p interaction strength has been plotted for different hole concentrations. The energy is found to be lower than the SC result.



Fig. 1. GS energy with respect to the e-p int. coefficient.



Fig. 2. Effective hopping parameter (t_{eff}) with respect to the electronic concentration (n) for different onsite e-p interaction strength (g_1) .

It has been found in Fig. 2. that the polaronic mobility started to decrease (for a specific g_1) from the bare Hubbard parameter t, as the electronic concentration increases. After a certain value of n, the polaron becomes trapped in its own potential, resulting the STT and t_{eff} becomes zero. As the e-p interaction increases, the effective polaronic mobility decreases and the STT occurs at lower electron density.

CONCLUSION

The change of the effective hopping parameter with respect to the electronic concentration shows the present result denotes higher effective hopping than the SC result which carries important information of the polaron mobility, band width and effective mass. Therefore this result has pivotal role in high temperature superconductors and cuprate meterials.

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Omnipresent instability criterion of birefringent Kundu-Eckhaus model with nonic nonlinearity

P.Mohanraj^{1*}, **R.Sivakumar**¹, and **K.Porsezian**¹

¹Department of Physics, Pondicherry University, Puducherry-605014, India.

*Corresponding author: mohanrajsphysics@gmail.com

Abstract

We investigate the modulational instability (MI) in a coupled birefringent Kundu-Eckhaus (KE) model with the help of pulse propagation technique. Using standard linear stability method, we detail study the effect of both self and cross phase modulation of KE fiber system without four wave mixing term. Also, we investigate the impact of nonic nonlinearity in a coupled birefringent media with the support of contour image through dispersion relation for small perturbation. Using omnipresent modulational instability criteria, the coss phase modulation and self phase modulation effects on optical wave propagation in birefringent fiber are discussed in the presence of both cubic and nonic nonlinear term.
Amorphous-Crystalline Phase Induced Properties Change Of In₁₅Sb₁₀S₁₅Se₆₀ Thin Films Upon Thermal Annealing

Abinash Parida^{1*}, D. Sahoo¹, Ramakanta Naik¹

¹Department of Engineering and Materials Physics, ICT-IOC, Bhubaneswar, 751013, India

*Corresponding author: abinashparidaiocb@gmail.com

Abstract

The present study reports the amorphous to crystalline phase transformation by thermal annealing at two different temperatures and related optical properties change in $In_{15}Sb_{10}S_{15}Se_{60}$ thin films. The different phases developed with annealing temperature as found from the XRD and the related surface morphology were noticed from the FESEM data. The bandgap reduced and the refractive index increased with annealing. The influence of temperature on the variation of different parameters were elaborately explained on the basis of defect states in localized region. The optical conductivity and electrical conductivity both increased with annealing.

INTRODUCTION

The amorphous to crystalline transition in amorphous materials form the basis of information encoding used for rewritable discs. The peculiar sensitive property of amorphous-crystalline and reversible phase transformation makes it suitable for optical recording medium [1]. The most disorder state to order state transition suits these materials for high resolution display and high-density information storage devices [2]. In this regard, quaternary chalcogenides have a direct bandgap and high optical absorption coefficient which make them a perfect candidate to be used in solar cell applications as a photo absorber. Moreover, quaternary chalcogenides also show large nonlinear optical properties, potentially used for optical switching and fiber optics [3]. Selenium is taken as the base material in the present composition because Se-based alloys have high transmittance, refractive index, high frequency weak absorbing tail and excellent nonlinearity [4]. Indium chalcogenides are photosensitive materials that are used in IR optics. Whereas, antimony chalcogenides are lowtemperature semiconductors widely used for electric to thermal energy conversion. The various reports on annealing-induced changes in quaternary chalcogenides thin film have shown notable changes in structural, morphological, and optical properties. The present study reports on annealing-induced amorphous to crystalline transition in the quaternary In15Sb10S15Se60 thin film and related changes in its optical parameters with annealing temperature.

EXPERIMENTAL PROCEDURES

The bulk $In_{15}Sb_{10}S_{15}Se_{60}$ samples were prepared by the conventional melt quenching method. Thin films of thickness ~800nm were prepared from the bulk by thermal evaporation method at a vacuum of 10^{-5} Torr. The thin films were annealed at $150^{\circ}C$ and $250^{\circ}C$ under vacuum condition. The structural study was done by X-ray diffractometer (XRD), surface morphology by field emission scanning electron microscopy (FESEM), compositional study by energy dispersive X-ray analysis (EDX) and the optical measurements by UV-VIS spectrophotometer over the range of 400-1100 nm.

RESULTS AND DISCUSSION

The XRD patterns as shown in Fig.1 infers the as-prepared film is of amorphous nature whereas the amorphouscrystalline conversion occurred at both 150°C and 250°C annealing temperature. The crystallinity increased at 250°C than 150°C annealing. Various phases developed with increase in annealing as indexed in Fig.1.



Fig. 1. XRD spectra, EDX and FESEM picture of the as-prepared and annealed thin films

The crystallite size (D_{hkl}) was estimated using the well-known Scherrer's equation [5]

Crystallite size (D) = $0.9\lambda/\beta cos\theta$ (β in radian) (1) where λ , β , θ are the wavelength of CuK_a, Full width half maxima (FWHM) and Bragg angle respectively. The average D was found to be 14.52 nm for 150°C annealed film which increased to 22.04 nm for 250°C film. The appearance of crystallites is clearly seen in the two annealed films as shown in FESEM images in Fig.1 (inset). The presence of the elements is well confirmed from the EDX spectra as shown in Fig.1 (inset). The chemical composition was found to be nearly same as that of the calculated one with an error of 3%.

The transmittance of the film reduced and the absorption edge shifted towards lower energy side as presented in the bandgap calculation plot Fig.2. The Tauc relation was used to evaluate the direct optical bandgap of the material by using the equation [6]

$$(\alpha h \nu)^2 = B^2 (h \nu - E_g) \tag{2}$$

Where α *h*, *v*, *E*_g and B are the absorption coefficient, Plank's constant, frequency, optical band gap, and Tauc parameter respectively. The straight-line fitting of dependence between $(\alpha hv)^2$ and photon energy (hv)provided the direct optical bandgap values such as $1.64\pm0.01eV$ (as-prepared), $1.59\pm0.01eV$ ($150^{\circ}C$), and $1.32\pm0.02eV$ ($250^{\circ}C$) for the thin films [Fig.2]. The amorphous-crystalline transformation induced reduction in bandgap is well explained by the Mott-Davis model [7]. The 0.27 eV decrease in E_g is for $250^{\circ}C$ film from the $150^{\circ}C$ film.



Fig. 2. Bandgap calculation and (inset)variation in refractive index for the films.

As the film structure was converted into a crystalline one, the ' α ' value increased than that of the amorphous one. This change in absorption coefficient and transmittance (not shown) changed the refractive index (n) significantly as shown in Fig.2 (inset). The value of 'n' of the films was obtained from the inverse synthesis method [8]. The increased 'n' value with annealing satisfied the Moss rule i.e. Egn⁴~constant [9]. The electronic state in the materials can be obtained from the optical conductivity (σ_{opt}) as well as electronic conductivity (σ_{elec}) which are expressed as [10]

$$\sigma_{opt} = \alpha nc/4\pi , \quad \sigma_{elec} = \lambda nc/2\pi \tag{3}$$

The increase in σ_{opt} with annealing is due to the increase in absorption coefficient and increase in refractive index by thermal annealing (Fig.3). However, the σ_{elec} was found to be decreased with wavelength and increased with annealing temperature (Fig.3-inset). The ability of absorbing the electromagnetic radiation is expressed in terms of optical density (OD= α .d). This is a useful parameter that shows the propagation of electromagnetic radiation through the material system used to manufacture several optoelectronic devices. The OD value was found to be increased with annealing (not shown here) due to the increase in α value. It would be also interesting to observe the changes in non-linear optical parameters by such changes in the linear parameters due to annealing.



Fig. 3. Variation of optical and electrical conductivity for asprepared and annealed films.

CONCLUSION

In summary, the structural transition from amorphous to crystalline changed the optical as well as the structural parameters. The crystallite size increased with annealing along with the formation of different phases. The change in absorption edge reduced the optical bandgap whereas the refractive index increased with annealing. The electronic as well as the optical conductivity increased with annealing. The OD value also increased which is suitable for various optoelectronic applications.

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Topological Phase Transition at Quantum Criticality

Ranjith R Kumar^{1,2} and **Sujit Sarkar**¹

¹Theoretical Sciences Division, Poornaprajna Institute of Scientific Research, Bidalur, Bengaluru-562164. ²Graduate studies, Manipal Academy of Higher Education, Madhava Nagar, Manipal-576104.

*Corresponding author: ranjith.btd6@gmail.com

Abstract

The physics of edge modes is an intriguing phenomenon observed in topological materials such as topological insulators and superconductors. Finite bulk gap facilitates the existence of theses edge states. Recently, the topological states of matter have witnessed a new physical phenomenon where gapless edge and bulk excitations coexist. This implies the presence of exponentially localized edge modes even at criticalities. The criticalities with topological and non-topological properties enable one to look into an unprecedented and interesting multicritical phenomenon: topological phase transition at criticality. We explore the existence of such topological transition and develop a suitable theoretical framework to characterize them based on the diverging nature of the curvature function.

Introduction

In the quest of classifying novel phases of quantum matter in the absence of local order parameter, topology of electrons wavefunction plays a prime role. It allows one to distinguish between gapped phases in terms of a quantized invariant number, which count the number of stable localized edge modes present. The transition between the distinct phases involves a bulk band gap closing at the topological phase transition point, across which the number of edge modes changes. The localization length of the edge modes at topological gapped phases diverge as the system drives towards the transition point or criticality.

Surprisingly, this conventional knowledge is revised recently, realizing even criticalities can host the stable localized edge modes despite vanishing bulk gap. The critical point between distinct topological gapped phases traps the edge modes during the topological transition between them. This results in the non-trivial criticalities with unique topological properties even in the presence of gapless bulk excitations. The localized edge modes at criticality are realized to be protected by novel phenomena such as finite high energy charge gap (in bosonic models) and kinetic inversion (in fermionic models). They also remain robust against interactions and disorders.

In this work, we find the topological properties of criticality causes an unconventional topological transition between criticalities which occurs without band gap opening and closing. This transition drives the system into the criticalities with distinct topological nature through multicritical points. We try to address this unusual transition at criticality and establish it as a generic property in an extended topological insulating and superconducting models.

Model

We consider one dimensional lattice chain of spinless fermions in momentum space. We define a generic extended two band Bloch Hamiltonian of the form

$$\mathcal{H}(k) = \chi(k). \sigma = \chi_{\chi}(k)\sigma_{\chi} + \chi_{\chi}(k)\sigma_{\chi}$$

where $\chi_x(k) = \Gamma_0 + \Gamma_1 \cos k + \Gamma_2 \cos 2k$ and $\chi_y(k) = \Gamma_1 \sin k + \Gamma_2 \sin 2k$ and $\sigma = (\sigma_x, \sigma_y)$ are the Pauli matrices. The model represents extended Su-Schrieffer-Heeger (SSH - topological insulator) and extended Kitaev (topological superconductor) models by uniquely defining the parameters. The parameters, Γ_0 describes onsite potential, Γ_1 describes nearest neighbor interactions and Γ_2 describes next nearest neighbor interactions.



Fig. 1. Topological phase diagram of model Hamiltonian. Number of edge modes at gapped phases (colored area) and criticalities (colored lines) are represented as 'w'. The points $MC_{1,2}$ are the multicritical points.

In general, the model with nearest and next nearest neighbor interactions, can support three distinct gapped phases, which are distinguished by the number of edge modes they possess. The criticalities at which the bulk gap closes i.e., with excitation spectra $E_k = \pm \sqrt{\chi_x^2(k) + \chi_y^2(k)} = 0$, occur for $\Gamma_1 = -(\Gamma_0 + \Gamma_2)$, $\Gamma_1 = (\Gamma_0 + \Gamma_2)$ and $\Gamma_0 = -\Gamma_2$, with three multi-critical points (two of them are identical), as shown in Fig.1.

Curvature Function Renormalization Group (RG) at Criticality

Topological phase transition at criticality can be induced by changing the underlying topology of the system upon tuning the parameters Γ_c appropriately. The information of the topological property of the system is embedded in the curvature function F(k, Γ_c) defined at momentum k. The curvature function of the generic model at criticality can be written using the critical line relations of the parameters as

$$F(k,\Gamma_{\Gamma_1=\pm(\Gamma_0+\Gamma_2)}) = \frac{\chi_x \,\partial_k \chi_y - \chi_y \,\partial_k \chi_x}{\chi_x^2 + \chi_y^2}$$

As one tunes the parameters at criticality Γ_c towards a multicritical point Γ_{mc} , the curvature function diverges at k_0 . Topological transition is signaled as the sign of the diverging peak flips if the parameters are tuned across the multicritical point. This is the characteristic feature of topological transition at criticality through the multicritical points MC_{1,2}.



Fig. 2. Curvature function renormalization group flow at criticality.

Based on the divergence of the curvature function at criticality, a scaling theory has been developed. This can be achieved by the deviation reduction mechanism where the deviation of the curvature function from its fixed-point configuration can be reduced gradually. In the curvature function at criticality F(k, M_c), for a given Γ_c in the parameter space, one can find a new Γ'_c which satisfies, F(k₀, Γ'_c) = F(k₀ + δ k, Γ_c), where δ k is small deviation away from k_0 , satisfying F(k₀ + δ k, Γ_c) = F(k₀ - δ k, Γ_c). As a consequence of the same topology of the system at Γ_c and at fixed point Γ_c^f , the curvature function can be written as F(k, Γ_c) = F^f(k, Γ_c^f) + F^d(k, Γ_c^d), where F^f(k, Γ_c^f) is curvature function at fixed point and F^d(k, Γ_c^d) is deviation from the fixed point. The fixed-point configuration is invariant under the scaling operation i.e., F^f(k₀, Γ_c^f) = F^f(k₀ + δ k, Γ_c^f).

Iteratively performing the scaling procedure drive $|F^{d}(k_{0},\Gamma_{c}^{d})| \rightarrow 0$. This yields the RG equation

$$\frac{d\Gamma_c}{dl} = \frac{1}{2} \frac{\partial_k^2 F(k, \Gamma_c)|_{k=k_0}}{\partial_{\Gamma_c} F(k_0, \Gamma_c)}$$

The distinct critical phases with different topological characters can be distinguished from the RG flow. The multicritical points and fixed points are then easily captured by analysing the RG flow lines. Performing this scheme to the model Hamiltonian, we obtain the RG equations at criticalities

$$\frac{\mathrm{d}\Gamma_0}{\mathrm{d}l} = \frac{\Gamma_0(\Gamma_0 + \Gamma_2)}{2(\Gamma_0 - \Gamma_2)} \text{ and } \frac{\mathrm{d}\Gamma_2}{\mathrm{d}l} = -\frac{\Gamma_2(\Gamma_0 + \Gamma_2)}{2(\Gamma_0 - \Gamma_2)}$$

Both the criticalities $\Gamma_1 = \pm(\Gamma_0 + \Gamma_2)$ yield the same RG equations. The RG flow lines are showed in Fig.2, where the multicritical point MC_1 is manifested as a line $\Gamma_0 = \Gamma_2$ with all flow lines flowing away. Therefore, the condition for a critical point is satisfied by MC_1 , which indicate that it's a critical point through which topological phase transition at criticality occurs. The multicritical point MC_2 is at $\Gamma_0 = -\Gamma_2$ which is an unstable fixed point with all the flow lines are flowing away.

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Quantitative Phase Fraction Analysis of Ball Milled FeSiB Powder Mixture using the Rietveld Method: Effect of Micro-absorption

Ashok Bhakar^{1,2}, Pooja Gupta^{1,2}, Archna Sagdeo^{1,2} and S. K. Rai¹

¹Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India, and ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India.

*Corresponding author: kashok@rrcat.gov.in

Abstract

X-ray diffraction (XRD) based Rietveld method is commonly used for quantitative determination of crystalline phase fractions in a powder mixture containing multi-phase components. The accuracy and reliability of this method is strongly dependent on the relative (X-ray) micro-absorption effects of particles of various phases present in the mixture. In multi-phase Rietveld refinement proper correction is required to account for this effect. This effect is known by the Brindley particle absorption contrast effect in literature. In this work a mixture of elemental Fe, Si and B powder is studied using Cu K_{α} radiation source and effect of microabsorption on quantitative phase fraction analysis is discussed.

Introduction

XRD data of polycrystalline materials is commonly used to perform the quantitative phase analysis (QPA) and use of Rietveld method provides good results¹. QPA methods are valuable in quality control in material science, pharmaceutical, forensics, phase identification of minerals in archaeological, naturally occurring geological samples (ores, rocks, fuels) and their grade for extraction of mineral deposits and many more^{2,3}. In general these samples are mixture of substances having vastly different micro-absorption effects and require Brindley correction for reliable QPA⁴.

Fe-based alloys are technologically important due to their good mechanical and magnetic properties and low cost⁵. Addition of Si and B to Fe-alloys is often required to enhance these properties and used in making tool steels, electrical steels and transformer cores etc. In this study a mixture of FeSiB powder is chosen for QPA using Cu K α radiation due to their largely different micro-absorption factors.

Experimental details

The stoichiometric ratios of high purity elemental powders of Fe (99.998%), Si (99.999%) and B (99.995%) were ball milled for short time (15 minutes) in Planetary Mill Pulverisette–5, FRITSCH, Germany, under argon atmosphere to homogenize the mixture of Fe₇₅Si₂₀B₅ powder (atomic %). The ball-to-powder weight ratio was kept 16:1 and rotation speed was kept 350 rpm. XRD measurement was carried out using Bruker D8 advance powder diffractometer equipped with Cu K α radiation source. The Rietveld refinement based QPA of XRD data of powder mixture was carried out using FullProf software⁶ and pseudo-Voigt peak profile function.

The instrumental zero corrections, unit cell parameters, full width at half maximum and asymmetry parameters were refined and background was modeled using Chebyshev polynomial.



Fig. 1. (a) Two phase Rietveld refinement of XRD data of $Fe_{75}Si_{20}B_5$ mixture powder. (b) & (c) show the fitting quality of the low angle and high Bragg peaks. Blue and black hkl values correspond to the Bragg positions of Fe & Si, respectively. The Rietveld R factors (not corrected to background) are Rp 2.76%, Rwp 3.65%, Rexp 3.32% and χ^2 :1.21.

Result & Discussion

The XRD pattern of ball milled Fe75Si20B5 powder (corresponding weight %=87.18:11.69:1.13) is shown in Fig. 1(a). Diffraction peaks corresponding to B phase were not observed probably due to its small wt.% and relatively low X-ray scattering power. Therefore QPA using two phases of Fe and Si was performed with expected renormalized wt.%: of Fe:Si ~ 88.2:11.8 and minimum detection limit of about 1 wt.% can be considered. The QPA overestimate wt.% of Si (14.5%) phase by more than 20% and underestimate Fe phase fraction. This effect arises due to strongly different absorption contrast factor of Fe & Si powder for Cu Ka radiations. The linear absorption coefficient of Fe (~2545 cm⁻¹) is ~ 18 times larger than Si (~140 cm⁻¹) and requires Brindley correction of particle absorption contrast for reliable QPA⁴. The Brindley particle absorption factor (τ) for 'ith' phase is given by:

$$\tau_i = \frac{1}{V_i} \int_0^{V_i} \exp[-(\mu_i - \mu_a)x] dV_i \qquad 1)$$

Here: $\frac{\mu_a}{\rho_a} = \sum_i \frac{\mu_i}{\rho_i} w_i \quad and \quad \frac{1}{\rho_a} = \sum_i \frac{1}{\rho_i} w_i$

with V_i: volume of particle of 'ith' phase, μ_i , ρ_i and w_i are the linear absorption coefficient, density and weight fraction of 'ith' phase and μ_a (~1745 cm⁻¹) and ρ_a are mean linear absorption coefficient and density of the FeSiB matrix. The μ value of B is ~ 4.5 cm⁻¹. As per this eq. (1) knowledge of two parameters ($\mu \&$ V) is sufficient for applying Brindley correction ' τ '.

The SEM micrographs of initial Fe powder (already reported in ref. 7) show broad particle size distribution varying from ~ $0.2 - 2 \mu m$. The shape of particles is also approximately spherical. In such broad particle size distribution defining mean value is difficult, therefore in this work three different mean particle size of radius 0.4, 0.5 and 0.6 μm are considered. The mean particle size of Si powder is also considered to be same as that of Fe powder. It is assumed that particle size distribution after ball milling for such short time of 15 minutes is nearly the same as initial powders. This is expected also because particles are already in micron range and require extensive milling for further reducing their size.

Brindley had calculated the τ values for spherical particles of radius R_i versus (μ_i - μ_a) R_i which are used in present work and given in Table 1 for different mean particle sizes. The eq.(1) is valid for medium powders⁴ i.e. $|\mu_i$ - $\mu_a|R_i$ values lying in the range of 0.01 to 0.1 and applicable in present case. After applying this correction weight % of both phases comes closer to nominal (expected) values. The quality of two phase Rietveld refinement of XRD pattern is shown in Fig 1(a, b & c) and their phase fractions are reported in Table 1. Refined unit cell parameters of bcc-Fe (Im-3m) and fcc-Si (Fd-3m) phase are 2.8668(5) and 5.4301(7) Å and matches well with the reported results for pure Fe & Si powder⁷. This also suggests that both Fe and Si powder are present in their unmixed states after milling for short time of 15 minutes.

 Table 1. Micro-absorption correction parameters used for the Rietveld refinement and corresponding weight %.

	R (µm)	(μ _i -μ _a)R	$\boldsymbol{\tau}_{\mathrm{i}}$	Wt. %
Fe	0.6	0.048	0.935	87.9±0.5
	0.5	0.04	0.945	87.5±0.5
	0.4	0.032	0.954	87.2±0.5
Si	0.6	-0.096	1.154	12.1±0.5
	0.5	-0.08	1.124	12.5±0.5
	0.4	-0.064	1.097	12.8±0.5
Fe	Withou	85.5±0.5		
Si				14.5±0.5

Conclusion

Quantitative phase analysis of ball milled $Fe_{75}Si_{20}B_5$ (at.%) mixture is carried out which contains phases with strongly different absorption contrast factors. In such mixtures the weight fraction of low absorbing phase (like Si here) is overestimated while high absorbing phase (like Fe here) will be underestimated. The weight % of Si phase was overestimated by ~ 23 ± 5 % which reduces to ~6 ± 5 % by applying Brindley correction factor assuming mean particle radius of 0.5 micron. The weight % of Fe phase was underestimated by ~ 3% which reduces to less than 1 % subsequent to applying correction.

This study infers that use of Brindley correction is very critical for estimating phase fraction in alloys/ samples having high absorption contrast phases.

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$\label{eq:constraint} Investigation of Piezoelectricity and Photo-luminescence in Eu Doped (Na_{0.41}K_{0.09}Bi_{0.5})TiO_3$

Pinki Yadav¹, Ankur Sharma¹, Gurvinderjit Singh^{1,2} and Indranil Bhaumik^{1,2}

¹Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400 094, India ²Laser and Functional Materials Division, Raja Ramanna Centre for Advanced Technology, Indore - 452 013, India.

*Corresponding author: pinkiyadav@rrcat.gov.in

Abstract

The piezoelectric and photoluminescence response has been investigated for europium doped NKBT $(Na_{0.41}K_{0.09}Bi_{0.5}TiO_3)$ ceramics. The optimum piezoelectric response was observed for 1.0 at.% europium doping, afterwards a gradual fall in the piezoelectric response was evident. On the contrary photoluminescence intensity increases with the increase in the europium content. No quenching effect was observed in the luminescence intensity till 3.0 at.%. The results are explained on the basis of amphoteric nature of europium and lack of direct correlation between photo-luminescence and piezoelectricity.

Effect of temperature on the phase formation of pure (BaFe₁₂O₁₉) and zinc-zirconium co-doped barium hexaferrite (BaZnZrFe₁₀O₁₉) samples using Rietveld analysis.

Swati Verma¹, Aanchal Chawla¹, Sachin Kumar Godara², Mandeep Singh^{1*}

¹Department of Physics, Guru Nanak Dev University, Amritsar-143005 ²Department of Chemistry, Guru Nanak Dev University, Amritsar-143005

*Corresponding author: jmskhalsa@gmail.com

Abstract

From a performance standpoint, structural changes in ferrites that occur as a result of doping and increased processing temperature are critical. A manual comparison of experimental X-ray diffraction (XRD) peak locations with reference data is usually used to determine phase evolution. The M-type (MFe₁₂O₁₉, where M is usually Barium (Ba), Strontium (Sr), or Lead (Pb)) phase evolution in undoped as well as Zinc (Zn) –Zirconium (Zr) co-doped barium hexaferrite samples synthesised using solid state reaction route is investigated in this study using a combination of Pawley and Rietveld analysis. The raw mixed a) undoped and b) Zn-Zr co-doped barium hexaferrite samples were calcined at temperatures ranging from 900 °C–1350 °C for various periods of time (6-12 hours) durations. The structural investigations show that between 1200 °C and 1350 °C, a single M-type phase forms (in both undoped and doped samples). Below 1200 °C, the Fe₂O₃ phase in undoped materials and the ZrO₂ and ZnFe₂O₄ phases in doped samples have been detected as impurities. In both cases, the structural data was successfully revised using the P63/mmc (number 194) space group.

Introduction

Hexaferrites have remained relevant both scientifically and technologically since their discovery (in the 1950s). Their designation as hexaferrites stems from their hexagonal crystal structure. Their most prominent application is in the field of magnetic data storage [1]. They are also used as components in high frequency electrical devices (such as phase shifters (in millimeter wavelength range) and isolators), as microwave absorbing materials and spintronic devices [2-4]. Among M, X, Y, W, Z and U –type categories, M-type hexaferrites (MFe₁₂O₁₉ a) are easy to synthesize and have better magnetic properties [5]. A number of studies report the impact of single diamagnetic substituent on the structural properties of M-type Barium hexaferrite. However, only a few studies have been reported in literature on the simultaneous Zn-Zr substitution into BaFe₁₂O_{19.} There are no publications that show the evolution of structural characteristics of Zn-Zr codoped BFO as a function of calcination temperature via chemical or solid-state reaction pathway. This presents the structural evolution of study BaZnZrFe₁₀O₁₉ (BZFO) samples as a function of calcination temperature from 900 °C - 1350 °C along with undoped (BFO) samples for comparison purpose.

Experimental

The $BaZnZrFe_{10}O_{19}$ (BZFO) and $BaFe_{12}O_{19}$ (BFO) polycrystalline ceramics samples were synthesized using conventional solid state reaction route. The raw

materials a) BaCO₃, Fe₂O₃, ZnO and ZrO₂ for BZFO samples and b) BaCO₃ and Fe₂O₃ for BFO samples were stoichiometrically weighed and were ball milled (using 20 calcia stabilized zirconia balls) in acetone medium for 48 hours. The obtained mixtures (both types) were air dried and calcined for 6 hours in the 900 °C – 1350 °C temperature range. To investigate the effect of calcination time on phase stability, both the samples were also calcined for 12 hours at 1200 °C and 1350 °C. The XRD data was collected over as calcined powder samples. The XRD data was recorded using SHIMADZU (MAXIMA XRD-7000) diffractometer equipped with CuK_a anode (λ =1.5405 Å). Fullprof software was used to carry out Rietveld refinement.

Results and Discussions

X-ray diffraction (XRD)

The phase evolution of BZFO samples synthesized using conventional solid state reaction technique (calcined between 900 °C – 1350 °C) was carried out using a combination of Pawley/Rietveld analysis. The Pawley fitted data of the 900 °C - 1350 °C calcined BZFO samples is shown in Figure 1a-f. It is clear from Figure 1a-c that a number of diffraction peaks remain unexplained (mismatch between black and red data) as long as the calcination temperature is below 1200 °C indicating that single hexagonal (BZFO) phase does not take place below 1200 °C. Monoclinic ZrO₂ and cubic ZnFe₂O₄ are present as intermediate phases in the 900 °C – 1150 °C calcination range. At 1200 °C, all the intermediate

phases disappear and only a single BZFO phase remains. The BZFO samples have been observed to remain phase pure in the investigated temperature range i.e., upto 1350 °C (Figure 1e, f).



Fig. 1. The XRD diffractograms of a) 900 $^{\circ}$ C, b) 1000 $^{\circ}$ C, c) 1100 $^{\circ}$ C, d) 1200 $^{\circ}$ C, e) 1300 $^{\circ}$ C and f) 1350 $^{\circ}$ C calcined (for 6 hours) BZFO samples.



Fig. 2. The Rietveld refined data of a) 1200 $^{\circ}$ C and b) 1350 $^{\circ}$ C calcined BFO samples, c) 1200 $^{\circ}$ C and d) 1350 $^{\circ}$ C calcined BZFO samples.

The phase evolution of BZFO samples was compared against undoped BFO samples (data not shown). The comparison with the reference database shows that all these additional peaks could be explained using a single hexagonal Fe_2O_3 phase (ICSD 98-002-2616) and the Fe_2O_3 phase begins to

decrease in concentration and disappears completely at 1200 °C. The Pawley fitting hence establishes that BZFO and BFO are phase pure between 1200 °C– 1350 °C. The Rietveld refined data of BFO and BZFO samples calcined for 6 hours at 1200 °C and 1350 °C is shown in Figure 2a-d (1300 °C data is not shown). The lattice parameters of the BFO and BZFO samples do not vary significantly with calcination temperature or duration. However, the lattice parameters of the BZFO samples are significantly larger as compared to the BFO samples due to higher atomic radii of Zn²⁺ and Zr⁴⁺ ions as compared to Fe³⁺ ion [5] as shown in Table 1.

Table 1. The comparative structural parameters of BFO and BZFO samples at different calcination temperatures and durations.

Calcination temperature	Sample	6 hour duration		12 hour duration	
	_	а	с	а	c
		(Å)	(Å)	(Å)	(Å)
1200 °C	BFO	5.89214	23.21487	5.89151	23.21532
	BZFO	5.92860	23.53445	5.92832	23.54094
1300 °C	BFO	5.89116	23.21065	-	-
	BZFO	5.92838	23.54956	-	-
1350 °C	BFO	5.89111	23.21656	5.89082	23.21593
	BZFO	5.92870	23.57391	5.92879	23.56785

Conclusion

The BFO and BZFO samples have been successfully synthesized using solid state reaction technique. Both types of samples are multiphase below 1200 °C and crystallise in a single M-type hexaferrite phase in the temperature range of 1200 °C to 1350 °C. The greater atomic radii of Zn and Zr dopants have been ascribed to the larger lattice parameters of the BZFO samples.

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Effect of Niobium(Nb⁵⁺) Substitution on Dielectric and Piezoelectric Properties in (Na_{0.41} K_{0.09} Bi_{0.5}) TiO₃ Ceramics

Ankur Sharma¹, Pinki Yadav², Indranil Bhaumik^{1,2}and Gurvinderjit Singh^{1,2}

¹Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400 094, India ²Laser and Functional Materials Division, Raja Ramanna Centre for Advanced Technology, Indore – 452 013, India

*Corresponding author: ankur@rrcat.gov.in

Abstract

In the present study, we focused on the dielectric andpiezoelectric properties of niobium modified($Na_{0.41} K_{0.09} Bi_{0.5}$) TiO₃ceramics which were prepared by conventional solid-state reaction method. The dielectric measurements reveal gradual lowering of depolarization temperature with the increase in niobium content which implies disruption of ferroelectric ordering. The piezoelectric coefficients were found to increase till 0.5 mol% of Nb and for higher doping concentration the coefficients decrease rapidly. The results have been explained on the basis of donor like behavior of Nb doping at lower concentration and for higher doping concentration based on lowering of depolarization temperature.

Ise/a Ratio The Driving FactorFor The ScalingOf Martensitic Transition Temperature In Heusler Alloys?

N.Maneaand K. R. Priolkar^{*}

Schoolof Physical and Applied Sciences, Goa University, Taleigao Plateau, Goa-403 206, India

*krp@unigoa.ac.in

Abstract

Martensitic transition temperature (T_M) generally scales with the average valence electron per atom (e/a) ratio in Ni-MnHeulser alloys. The e/a ratio can be increased either by increasing Ni content in lieu of Mn or Ga (Ni-rich) or by substituting Mn for Ga (Mn-rich). For the first time a difference between the behavior of Ni-rich and Mn-rich alloys is identified. While both, Ni-rich and Mn-rich Ni-Mn-Ga alloys exhibit martensitic transition, only Mn-rich Ni-Mn-Sn alloys display martensitic behaviour.

Continued functions and resummation methods

Venkat Abhignan and R. Sankaranarayanan

Department of Physics, National Institute of Technology, Tiruchirappalli- 620015, Tamil Nadu, India.

*Corresponding author: yvabhignan@gmail.com

Abstract

Fewresummation methods are discussed where convergence nature is optimized using continued functions to get precise measures for critical exponents. These simple tools are helpful in handling divergent solutions obtained from perturbative renormalization techniques used in field theories to study continuous phase transitions.

Quantum Oscillation Signatures in Nodal Line Semimetals under Steady and Oscillating Variation of Magnetic Field

Satyaki Kar¹

¹A.K.P.C. Mahavidyalaya, Bengai, Hooghly, West Bengal 712611, India

*Corresponding author: satyaki.phys@gmail.com

Abstract

Quantum oscillation in nodal line semimetals (NLSM) is probed on the basis of spectral calculations in a NLSM continuum model under strong magnetic field. From the Landau level spectra and its evolution with field, we quantify the Fermi level fluctuations. At the same time, the bifurcation of the spectral peaks due to Zeeman splitting and turning of the same due to changes in effective electronic masses are also reported. The direction of magnetic field is an important parameter to the problem and density of states show series of peaks in succession only if the field lies normal to the nodal plane. For magnetic field in the nodal plane, the density of state peaks do not repeat periodically with energy anymore. There one also gets topological oscillations at low energies. Thus properly chosen oscillating field variation can result in topological transitions to occur periodically in these systems.

Pressure Induced Structural Phase Transition in TetragonalBaCu₂(VO₄)₂: A Raman Spectroscopic and XRD Investigation

Swayam Kesari^{1, 2}, Alka B. Garg^{2, 3}, S. N. Achary^{2,4}, Rekha Rao^{1, 2, *}

¹Solid StatePhysics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India ³High pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

⁴Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India.

*Corresponding author: rekhar@barc.gov.in

Abstract

The high pressure structural stability of orthovanadate $BaCu_2(VO_4)_2$ is investigated using in-situ Raman spectroscopy and synchrotron X-ray diffractionup to 26 and 28 GPa respectively. The observations suggest onset of a pressure induced structural phase transition above 18 GPa. X-ray diffraction indicates that the new structure could be lower symmetry crystal structure than tetragonal while the Raman spectroscopic study indicates change in local symmetry around vanadium atom or V-O coordination.

High Pressure Raman Investigation on Thullium Doped Ceria

Nishant N Patel^{*1} and Meenakshi Sunder¹ ¹High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085

*Corresponding author: nnpatel@barc.gov.in

Abstract

High pressure room temperature Raman investigation on thulium doped ceria (Ce_{0.8}Tm_{0.2}O_{1.9}) was carried out up to 24.2 GPa. The ambient fluorite structure (SG: Fm3m) was observed to remain stable up to 18.8 GPa above which a phase transition was observed. The phase transition was found to be reversible.

Structural, Electrical and Optical Properties of Lead Free BFO Modified Sodium Potassium Niobate Ceramics

A. Rashid¹,N. V. Giridharan¹ and Narkavi Nandhini A¹

Advanced Functional Materials Laboratory, Department of Physics, National Institute of Technology,

Tiruchirappalli-620 015, India

*Corresponding author: giri@nitt.edu

Abstract

KNN ($[K_{0.5}Na_{0.5}]NbO_3$) based ceramics are considered to be a very good candidate to replace lead based materials. The system under investigation (1-x) ($K_{0.5}Na_{0.5}]NbO_3$)-xBiFeO3 ceramic were prepared using conventional solid state reaction method. The room temperature crystal structure of pure KNN is confirmed as orthorhombic. A well-defined phase boundary between orthorhombic and tetragonal phases is obtained at x=0.01 composition and on further addition of BFO it turns to a pseudocubic phase with slight distortions in tetragonal symmetry. Remnant polarisation P_r has shown an enhanced valueof 18.56 μ C/cm² for x=0.01. The optical bandgap shifts from 3.3 to 2.7eV with the addition of BFO in KNN.

Anomalous behaviour of CaHfO₃ at Low Temperatures

Sourabh Wajhal¹, S. K. Mishra^{1,2}, A. B. Shinde^{1*}, and P. S. R. Krishna¹ ¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai - 400085

²Homi Bhabha National Institute, Mumbai - 400085

*Corresponding author: abshinde@barc.gov.in

Abstract

Crystal structure and phase stability of CaHfO₃ ceramics prepared by solid state reaction method is investigated till 2K using neutron diffraction. It is found to be stabilized in orthorhombic distorted perovskite $(a^{-}b^{+}a^{-})$, space group *Pnma*) crystal structure from 2K to 300K. Temperature dependence of volume shows quantum (2 K \leq T \leq 75 K) and classical (100 K \leq T \leq 300 K) behaviours accompanied by anomalies in spontaneous strain, orthorhombicity and octahedral tilt angle. Temperature dependent lattice parameters along the crystallographic axes<100>, <010> and <001> are found to be anisotropic in nature.

Phase Formation Study in Residue During Incineration of Combustible Wastes

Keyur C. Pancholi^{1,2}, Param Jeet Singh^{3,*}, A. Ananthanarayanan⁴, V. Shrihavi⁵, Ajay K. Mishra^{1,5}, D. V. Udupa^{1,3}, C. P. Kaushik^{1,2}

¹Homi Bhabha National Institute, ²Waste Management Division, ³Atomic & Molecular Physics Division, ⁴Process Development Division, ⁵High Pressure & Synchrotron Radiation Physics Division, BARC, Mumbai, India

*Corresponding author: singhp@barc.gov.in

Abstract

Phase transformation study on residual ash samples is presented in this manuscript. Samples are collected from plasma incinerator commissioned at BARC, Mumbai for management of combustible and potentially contaminated radioactive solid wastes. Characterization of end residue is a very important aspect to understand phase changes and reactions happening inside the plasma chamber at high temperature environment. Residues, in the form of ash, rock and glass phases were collected and analysed using EDS and XRD techniques. Elemental composition observed are correlated with respective phases of compounds possible in the residual samples. Phase formation kinetics among ash, rock and glass phases is presented here.

Introduction

The management of active, secondary wastes generated from the nuclear industry is gaining increasing importance. In view of the volume of such wastes generated, various volume reduction processes including compaction, densification by melting or conventional incineration etc. have been carried out. To further aid efficiency, a plasma pyrolysis and incineration system has been developed at Bhabha Atomic Research Centre (BARC), Mumbai, India [1] for low level radioactive solid wastes. A detailed characterization of the incineration residues will be useful in optimizing further management strategies [2]. In this manuscript, we explore the nature of various residues recovered from the plasma pyrolysis chamber and attempt to correlate and understand the same with processing conditions.

Materials and method

Sample collection

Residue samples are collected from an engineering scale plasma pyrolysis based incinerator commissioned at BARC, Mumbai, India for combustible, potentially contaminated radioactive waste forms. Details of the plasma pyrolysis incinerator is described elsewhere [3]. Briefly, the waste is processed using a 30 KW non transferred DC air plasma, having a plume edge temperature >2000 K, in presence of very low amount of N₂. The samples were largely powdery material, referred to as Ash in further discussions, and small quantities of a rock like phase, called Rock in further discussions and a glassy region, known as Glass in the vicinity of

the plasma torch, often in close contact with the water cooled jacket of the torch.

Analysis techniques

Residue samples are analysed using Energy Dispersive Spectroscopy and (EDS) X-Ray Diffraction (XRD) techniques. The EDS measurements are collected using an environmental SEM (Model: Philips XL30ESEM) operating in conjunction with an Oxford Instruments XMAX80 EDS system. The samples were carefully spread on a graphite tape to allow adequate conductivity. The XRD experiments are carried out using monochormatised X-rays with wavelength λ =0.6343Å on powder samples, in transmission geometry at BL-11, Indus-2 synchrotron source at RRCAT, Indore, India.

Result and Discussions

Compositional Analysis (EDS)

The residue from waste incineration generally contains oxides of Al, Si, Ca, Fe *etc.* [4]. A comparison of the EDS spectra (*cf.* Fig.1) of Glass, Rock and Ash samples indicates that the Ash contains high concentration of CaO, while it is deficient in SiO₂ and Al₂O₃. The Glass sample has composition similar to calcium alumino-silicate glassy slag, containing high concentration of CaO and SiO₂. The Fe₂O₃ concentration in the glass and the ash are similar. The Rock sample has a low CaO percentage, but contains a larger concentration of SiO₂ and Al₂O₃, which preclude glass formation. Both the Rock and Glass show lower chlorine concentration than the Ash

indicating that these samples may have experienced higher temperatures during processing. Based on the compositions, it is most likely that the ash provides fluxing agents such as CaO, which then allows easy melting of the rocky regions if exposed to the plasma torch directly. When the source is put off, or the phase comes in contact with the water cooled jacket of the torch which into rapidly cools of this region leading of glass formation.



Fig. 1. EDS spectra of Glass (a), Rock (b) and Ash (c) phases of residue samples from plasma incinerator.

Structural Analysis

In confirmation of the visual inspection, XRD patterns of Rock and Ash samples (*cf.* Fig. 2) exhibit the sharp peaks characteristic of a crystalline material. In contrast, the Glass sample shows a broad peak indicating its amorphous nature.



Fig. 2. XRD pattern of residue samples after plasma incineration of waste.

XRD pattern of the Ash sample matches well with the tetragonal pyro silicates with space group P-421m, with varying concentration of Na, Mg, Ca, Al, etc. The diffraction pattern for the Rock phase primarily consists of contributions from SiO₂, CaO and hexagonal Al₂O₃. In order to further understand the Glass sample, we attempted to fit the broad diffraction peaks with two diffraction peaks centred at $2\theta \sim 10.6^{\circ}$ and 12.6° as shown in Fig. 3. These two diffraction peaks from the Rock and Ash phases respectively. These peaks correspond to the first sharp diffraction peaks (FSDP) of silica and other glasses. Their corresponding second sharp diffraction peaks (SPDP, pk3 and pk4) are observed at $2\theta \sim 17.6^{\circ}$ and 24.0° respectively. Thus, we can infer that the glass phase has molecular signatures from rock and ash phases manifested in its short range ordering. Indeed, this observation affirms that the Ash is acting as a fluxing agent allowing the Rock phase to melt when in contact with the high temperature plasma. When the torch is turned off, the molten region in contact with the torch is quenched as the torch is surrounded by a water cooled jacket, likely resulting in glass formation.



Fig. 3. Fit to XRD data of residue in Glass phase. The Pk1, Pk2 show FSDP while pk3 and pk4 show their corresponding SSDP, characteristic of glassy materials.

While further studies to understand the mechanism including ex-situ lab trials are underway, the formation of a glass phase may point out to a promising direction in direct vitrification.

Conclusion

EDS and XRD analysis of residues from plasma incineration of actual waste are presented. The studies presented indicate the formation of various types of residues after plasma pyrolysis. The Ash residue comprises mainly of CaO and SiO₂, while the Rock residue comprises Al₂O₃ and SiO₂. It is evident that regions exposed to the direct plume of the plasma torch with adequate residence time show melting of the Rock residue, fluxed by the CaO rich ash, followed by quenching when in direct contact with the water cooled jacket of the plasma torch. Indeed, this may open avenues for plasma aided vitrification, which requires further studies and optimization.

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Structurally Engineered Ferroelectric Phase in Sodium Niobate

S. K. Mishra^{1,2*}, Sourabh Wajhal¹, A. B. Shinde¹, P. S. R Krishna¹ and R. Mittal^{1,2}

¹Solid StatePhysics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India -400085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, India - 400 094

*Corresponding author: skmsspd@barc.gov.in

Abstract

We have structurally engineered ferroelectric phase in NaNbO₃ bythe application of chemical pressure. In order to explore phase stability of this ferroelectric phase with temperature, we analyzed the temperature dependent powder neutron diffraction datauptocryogenic temperatures. Temperature dependent neutron diffraction patterns do not show appreciable change either in intensity or appearance/disappearance of the observed peaks downto 6K, ruling out any structural transition in the entire temperature range of 300 K to 6 K. Structural parameters obtained by detailed Rietveld analyses of temperature dependent powder diffraction data show that pseudo cubic cell parameters a_p , b_p and c_p come closer with a monotonic increase in the cell parameters with increasing temperature. The electric polarization has been estimated using a simple ionic model and its value is found to decrease with increasing temperature. Total spontaneous polarization was estimated using refined structural data to be ~ $3.2 \,\mu$ C cm⁻² at 6K.

Low-Temperature Spin Relaxation Dynamics in Chiral Ferromagnet Co_{4.5}Fe_{3.5}Zn₈Mn₄

Arnab Bhattacharya*, I. Das

*Condensed Matter Physics Division, Saha Institute of Nuclear Physics, HBNI, 1/AF, Bidhannagar, Kolkata-700064

Corresponding author: arnababir7@gmail.com

Abstract

We report the spin relaxation dynamics of chiral ferromagnet $Co_{4.5}Fe_{3.5}Zn_8Mn_4$ compound. The compound forms in the cubic chiral space group of P4₁32. The system undergoes both ferromagnetic and spin-glass like transitions at the temperatures of $T_c = 210$ K and $T_g = 12$ K respectively. Study on spin relaxation behavior indicates towards the spin-glassy ground state at T<T_g.

Introduction

Non-collinear spin textures have recently attracted researchers as a source of many complex emergent phenomena. One of the space groups, which holds such a chiral structure is $P4_132$. These compounds show helical ordering of magnetic spins, which is resulting due to the competition between ferromagnetic (FM) and antisymmetric Dzyaloshinskii-Moriya (DM) interactions.

Recent discovery of magnetic skyrmionic phase in chiral magnets such as Co-Fe-Zn-Mn alloys has paved the way to understand this type of emergent behavior. This family of alloys shows FM and a magnetically frustrated phase transitions at much lower temperatures, caused by the β -Mn moments. These compounds have an antiferromagnetic (AFM) interaction between two layers of Mn moments in the hyper-kagome coordinate 12d sites. The doping of the parent Co₈Zn₈Mn₄ compound with Fe reduces the number of electrons per unit cell. With increasing Fe concentration in the parent system, the strength of the DM interaction decreases systematically.

Here, we have chosen the particular composition of $Co_{4.5}Fe_{3.5}Zn_8Mn_4$ to explore the spin frustration phenomenon present below a certain spin glass transition temperature, T_g .

Experimental Details

The sample was prepared using the standard solidstate reaction technique. The pure elements Co, Fe, Zn and Mn from Alfa Aesar (purity 99.97%) were taken in stoichiometric ratio, well-mixed, pelletized, and annealed at 1000°C for 10 days. The phase purity of the sample was checked using the Rigaku TTRX-III X-Ray Diffraction (XRD) setup. The samples were found to form in cubic P4₁32 space group with lattice parameter a = 6.387Å, that matches well with the previous reports as shown in Fig. 1. The SQUID- VSM from Quantum Design, USA was used to perform the dc magnetization measurement.



Fig. 1. Profile fitted XRD data recorded at room temperature.

Results and Discussions



Fig. 2. Temperature dependence of dc magnetization for the applied field of 100 Oe measured in ZFC and FC protocols.

Fig.2 shows the temperature variance of magnetization recorded at H = 100 Oe under zero-field-cooled (ZFC) and field-cooled (FC) protocols. It shows a FM transition at $T_c = 210$ K. The ZFC and FC curves don't merge right from T_c and the bifurcation further increases below T_g . This bifurcation exists upto the field of 3 kOe (not shown herewith), suggesting the presence spin glass-like nature at the low temperature region.

Different kinds of spin-glassy systems are identified by their magnetic relaxation behavior. Here, we have measured the relaxation in ZFC protocols. The sample was cooled from paramagnetic (PM) region to the desired temperatures. After allowing the system to reach thermal equilibrium, a small field is applied and the evolution of magnetization with time M(t) has been measured. The relaxation behavior has been recorded at various constant temperatures and magnetic fields (keeping the temperature constant). The M(t) curves for various temperatures and magnetic fields are shown in Fig. 3(a) and 3(b) respectively. The magnetization increases with time and follows the stretched exponential nature given by Kohlrausch-Williams-Watts (KWW) equation:

$$M(t) = M_0 \{ 1 + a \, e^{\left[-(t/\tau)^b \right]} \} \tag{1}$$

where τ is the characteristic relaxation time and *b* is the shape parameter.



Fig. 3. Spin relaxation dynamics, M(t) recorded (a) at various temperatures under 100 Oe magnetic field, and (b) under various applied magnetic fields at T = 5 K. The solid lines are fitting lines using KWW equation, Eq. 1.

On fitting the M(t) using Eq.1, we find the value of b lies in between 0.29 and 0.35. The value of τ ranges a few tens of minutes, quite a few order greater than the sweep rate such that all the data are unrelaxed.



Fig.4. Memory effect by FC protocol as discussed in text.

The memory effect has been measured here using the FC protocol. The sample has been cooled under 100 Oe applied field from PM region to the intermediate temperatures, $T_{stop} = 7$ K, 5 K, and 3 K and the field was subsequently stopped and the system was made to wait for $t_w = 1.5$ hr. After reaching the lowest temperature of 2 K, the sample was heated back to the PM region, while recording M(T). The M^{mem}_{FCW} curve tries to follow the M^{stop}_{FCW} curve. The referential field cooled warmed magnetization, M^{ref}_{FCW} curve has also been shown in Fig. 4.

Conclusion

The AFM-type of interaction that exists between the Mn atoms in the crystal lattice results in the frustrated spin-glass ground state for the $Co_{4.5}Fe_{3.5}Zn_8Mn_4$ compound. The chirality of the lattice plays an important role in **arisal** of the spin-glassy state of the system. Further experiments such as AC susceptibility and neutron diffraction are required to clearly the ground state of these systems.

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Influence of Fe doping in Structural and Electronic Properties of topological insulator PbBi₂Te₄: Experimental & Theoretical Insight from DFT Simulations

Sumita Sura^{1,2,*}, B. Chakraborty¹, Bharat Bhooshan Sharma¹, Konstantin Glazyrin³, and Nandini Garg^{1,2}

¹High Pressure and Synchrotron Radiation Physics Division, BARC, Mumbai, India ²Homi Bhabha National Institute, Mumbai, India ³DeutschesElektronenSynchrtron (DESY), Germany

*Corresponding author: sumitasura.05@gmail.com Abstract

 $PbBi_{1.95}Fe_{0.05}Te_4$ was investigated for electronic and structural properties. We have carried out high pressure x-ray diffraction experiments up to 18 GPa. Signatures of structural phase transitions were observed at 7 and 18 GPa. The second, high pressure phase at 18 GPa was determined to be a cubic substitutional alloy phase. Density functional theory predicts that $PbBi_2Te_4$ loses its topological character when doped with Fe and shows conducting bulk states.

Phase Transition In Selenium Doped Ge-Sb-Te Thin Film For Phase Change Memory

Shahin Parveen¹, Nidhi Bhatt¹, and Pumlianmunga^{1*}

¹Department of Physics, Jamia Millia Islamia, New Delhi (India), 110025

*Corresponding author: pumlianmunga@jmi.ac.in

Abstract

 $Ge_2Sb_2Te_5(GST)$ is extensively studied for phase change random access memory (PCRAM) applications due to its excellent reversible phase transition from amorphous to crystalline phases under high electrical pulses and high switching speed. However, one of the major problems with GST is the high current density required to melt the sample in the SET-RESET transformation. In the present work, GST has been doped with Se, and an increase in the optical band gaps in the amorphous (RESET) and crystalline (SET) states are observed. A significant increase in the SET resistance is also observed in the resistance versus temperature curve which will make it a better candidate for PCRAM.

High Pressure Raman Spectroscopic Investigation OnThe Magnetoelectric Material Co₄Ta₂O₉

Rajesh Jana¹, Alka B. Garg², and Rekha Rao¹

¹Solid State Physics Division, ²High Pressure &Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400085,India

*Corresponding author: rajeshjana8@gmail.com

Abstract

In recent times, the family of honeycomb antiferromagnets $A_4M_2O_9(A = Fe, Co, Mn \text{ and } B = Nb, Ta)$ has drawn special attention because of their rich magnetic properties, spin-flop transition and magnetoelectric effect. High pressure investigation on these materials with corundum-type trigonal structure assume significance as pressure-tuning of the crystal structure of these materials can modify magnetoelectric properties. We have synthesized and studied the magnetoelectric material $Co_4Ta_2O_9$ at ambient and high pressures using Raman scattering up to 23 GPa. At ambient pressure, 16 Raman modes have been detected, which are assigned according to the earlier Raman study on the isostructural system $Mn_4Nb_2O_9$. The appearance of two new prominent Raman modes and a few low intensity modes have been observed above 20 GPa, suggestingthe onset of a structural transition.Comparing structural transitions in similar structure materials, we speculate the high pressure phase above 20 GPa might be monoclinic.

Kuramoto model with additional nearest-neighbor interactions: Existence of a nonequilibrium tricritical point

Mrinal Sarkar¹, and Shamik Gupta^{2,3}

¹Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India ²Department of Physics, Ramakrishna Mission Vivekananda Educational and Research Institute, Belur Math, Howrah 711202, India

³Quantitative Life Sciences Section, ICTP, Strada Costiera 11, 34151 Trieste, Italy

*Corresponding author: mrinal@physics.iitm.ac.in

Abstract

The Kuramoto model serves as a paradigmatic framework to study the phenomenon of spontaneous collective synchronization. The usual Kuramoto model involves phase oscillators of distributed natural frequencies interacting via a mean-field interaction. In our present work, we study a variation of the model by including nearest-neighbor interactions on a one-dimensional periodic lattice. For unimodal and symmetric frequency distributions, we show that a competition between the two types of interactions brings in new features, and consequently, the resulting dynamics in the nonequilibrium stationary state exhibits a very rich phase diagram with both continuous and first-order transitions between synchronized and unsynchronized phases, with the transition lines meeting at a tricritical point. Our results are based on numerical integration of the dynamics as well as an approximate theory involving appropriate averaging of fluctuations in the stationary state.

INTRODUCTION

Competing interactions are known to result in interesting stationary and dynamical features in systems comprising many interacting degrees of freedom. Here we explore this theme within the ambit of a many-body system involving phase oscillators, namely Kuramoto oscillators, of distributed natural frequencies interacting via a mean-field and a nearest-neighbor interaction on a one-dimensional periodic lattice. The phase evolution equation of the i^{th} oscillator is given by

$$\frac{d\theta_i}{dt} = \sigma\omega_i + r\sin(\psi - \theta_i) + K\sum_{j \in nn_i}\sin(\theta_j - \theta_i),$$

where ω_i is the natural frequency of the *i*th oscillator sampled independently from a unimodal and symmetric distribution $g(\omega)$ with mean zero and width σ . The second term on the right hand side (rhs) may be interpreted as a torque (in suitable units) arising from a mean-field interaction and expressed in terms of the usual Kuramoto synchronization order parameter $re^{i\psi} \equiv \frac{1}{L} \sum_{j=1}^{L} e^{i\theta_j}$ (*L* being the linear dimension of the lattice). On the other hand, the third term on the rhs is the torque due to a nearest-neighbor interaction, with the sum over *j* restricted to the nearest neighbors of the of *i*, and *K* being the nearest –neighbor coupling strength which can take both positive (cooperative with the mean-field) and negative (competitive with the mean-field) values.

The dynamics of the model is strictly non-Hamiltonian, and it relaxes to a nonequilibrium stationary state at long times. In the absence of the

nearest-neighbor interaction (K = 0), the dynamics is that of the usual Kuramoto model [1], well known in the field of nonlinear dynamics as a paradigmatic framework to study the phenomenon of spontaneous synchronization abound in nature. The dynamics in the limit of infinite system-size exhibits a continuous transition as one tunes σ across the critical value $\sigma_c =$ $\pi q(0)/2$, with the system existing in the synchronized phase at low σ and in the incoherent phase at high σ . On the other hand, the model when considered with solely nearest-neighbor interaction has been shown to not exhibit any macroscopic phase locking and hence any synchronized phase on a one-dimensional periodic lattice [2]. In this backdrop, we ask the following: How does the inclusion of nearest-neighbor interaction modify the stationary-state phase diagram? Do new phases emerge? What is the order of transition between the different phases?

RESULTS AND DISCUSSION

In order to gain preliminary insights into possible dynamical behavior, we initiate the system with a synchronized phase, and numerically integrate the governing dynamics by employing RK4 method with integration time-step dt = 0.01 and for Gaussian $g(\omega)$ on a lattice of size L = 3200. The behavior of stationary-state order parameter r with σ for various values of K suggests the existence of both synchronized and incoherent phases and a phase transition between them. The latter appears to be continuous (continuous variation) for positive and low negative values of K, and to be first-order-like (sharp jump) for large negative K.

Further confirmation is done by studying the behavior of stationary-state r on tuning σ adiabatically from low to high values and back in a cycle. Such a study does not yield any hysteretic behavior for positive and low negative values of K, thereby implying the corresponding transition being a continuous one, while for large negative K it shows the existence of a hysteresis loop, thereby bearing a clear signature of a first-order transition.



Fig. 1. The complete phase diagram of the model in the $(\sigma - K)$ plane showing synchronized and incoherent phases separated by a line of transition that is either first-order (blue squares) or continuous (red circles). The two lines meet at a tricritical point, shown by a green star.

Our next task is to obtain numerically the phasetransition lines in the $(\sigma - K)$ plane, and to locate the tricritical point, defined as the point at which the firstorder and continuous transition lines meet. In the region of continuous transition, we analyze the finite-L data for stationary r by resorting to the finite-size scaling theory for equilibrium critical phenomena and obtain the transition point as well as the critical exponents in the thermodynamic limit. In the region of first-order transitions, for a large but finite L, the critical point is estimated as the point at which the probability distribution of stationary r shows bimodal behavior with two peaks of equal heights.

The stationary-state phase diagram of the model in the $(\sigma - K)$ plane is shown in Fig.1 for Gaussian $g(\omega)$, where the circles in red constitute the line of continuous transition, while the line of first-order transition is represented by squares in blue. The tricritical point is located at $(\sigma_{Tri} \approx 0.23, K_{Tri} \approx$ -0.19) and is denoted by a green star. From the phase diagram, we see that for K > 0, when both the meanfield and the nearest-neighbor interaction favor global synchrony, one has a continuous phase transition, as expected. For negative values of K, there is instead a competition between the two types of interaction. One has a continuous transition as long as $K > K_{Tri}$ and otherwise a first-order transition. We recover the results for the usual Kuramoto model for K = 0. Exact results for $\sigma = 0$ is obtained by minimizing the underlying potential, yielding the critical point ($K_c = -0.25, \sigma = 0$)[3].



Fig. 2. Shown is the behavior of stationary r with σ , obtained from theory and numerics, on a lattice of size L = 3200, for K = -0.04 (a), and K = -0.1 (b).

We apply an approximate time-averaged theory to obtain the behavior of stationary *r* in the region of continuous transition. We have defined a time-averaged local order parameter for the *i*th oscillator as $r_i^{(T)}e^{i\psi_i} \equiv \sum_{j=1}^L W_{ij} < e^{i\theta_j} >$, where W_{ij} is the weighted adjacency matrix defined as follows: $W_{ij} \equiv (1/L)(1 - \delta_{ij}) + K\delta_{i,j\pm 1}; i, j = 1, 2, ..., L$. We have obtained in the limit $L \rightarrow \infty$ a self-consistent equation determining $r_i^{(T)}$ and hence $r = \frac{1}{(1+2K)L-1} |\sum_{i=1}^L r_i^{(T)}|$. The behavior of stationary *r* obtained from the theory is in very good agreement with numerics deep in the region of continuous transition, but shows deviation as one approaches tricritical point, as shown in Fig.2.

CONCLUSION

It would be interesting to formulate a theory that would explain the behavior of stationary r in the parameter regime of first-order transition as well as for parameter values to the right of the tricritical point as the latter is approached from the side of continuous transition.

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Spall Fracture in OFHC Copper under Dynamic Loading

D. Mukherjee¹*, S. Gandhi¹, A. S. Rav¹ and K. D. Joshi^{1,2}

¹Applied Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India ²Homi Bhabha National Institute, Mumbai, India 400094

*Corresponding author:debojyoti@barc.gov.in

Abstract

Plate impact experiments were carried out in oxygen free high conductivity (OFHC) copper using single stage light gas gun facility to understand the behaviour of spall fracture strength and yield strength under dynamic loading condition. For each experiment, the rear free surface velocity history was monitored using in-house developed photon Doppler Velocimetry (PDV) and the same exploited to determine the spall strength and dynamic yield strength of this material. Planar shock loading experiments conducted in the velocity range of 260 m/s to 720 m/s evealed that the spall strength of copper varies from 1.06 GPa to 1.21 GPa with corresponding average strain rates ranging from $1.70 \times 10^4 \text{ s}^{-1}$ to $3.51 \times 10^4 \text{ s}^{-1}$. This value of spall strength is almost five times more than the quasi-static value of 0.233 GPa(ultimate tensile strength). Similarly, the dynamic yield strength of ~0.24GPa-0.40GPa, is also significantly higher than the static value of 0.218 GPa.

First Principles Study of Rutile Structure of ThO₂

Shilpa Singh^{1,4,*}, Sanjeev K. Gupta¹, Yogesh Sonvane², K. A. Nekrasov^{3,5}, A. Ya. Kupryazhkin³ and P. N. Gajjar⁴

¹Computational Materials and Nanoscience Group, Department of Physics, St. Xavier's College, Ahmedabad 380009, India

²Advanced Materials Lab, Department of Applied Physics, S.V. National Institute of Technology, Surat 395007, India

³Ural Federal University, Yekaterinburg 620002, Russia

⁴Department of Physics, University School of Sciences, Gujarat University, Ahmedabad 380009, India ⁵Institute of High-Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences, Yekaterinburg 620002, Russia

*Corresponding author: shilpa.singh@sxca.edu.in

Abstract

ThO₂ is found in fluorite (cubic) structure in nature and is used as nuclear fuel material. At higher pressure, fluorite structure transforms to cotunnite (orthorhombic) structure. These two structures of ThO₂ have been studied extensively. In present work, we have studied the stability and thermo-physical properties of rutile (tetragonal) structure of ThO₂ and compared it with properties of cubic structure. We have used density functional theory (DFT) with spin orbit coupling (SOC) to carry out our work. The optimized lattice parameters of rutile ThO₂ are found as a = c = 5.29 Å and b = 3.75 Å. The absence of negative phonon in phonon dispersion curve shows stability of these structures. Cubic ThO₂ shows higher value of vibrational specific heat and vibrational entropy than rutile ThO₂.

High Pressure Study of Thorium Dicarbide (ThC₂): An *Ab-initio* Investigation

B.D. Sahoo¹ and K.D. Joshi^{1,2}

¹ Applied Physics Division Bhabha Atomic Research Centre, Mumbai, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, India

*Corresponding author: bdsahoo@barc.gov.in

Abstract

Systematic first-principle calculations have been performed to understand the structural stability of thorium di-carbide (ThC₂) under hydrostatic compression using the evolutionary structure search algorithm as implemented in the universal structure predictor: evolutionary Xtallography (USPEX) code in conjunction with ab-initio electronic band structure calculation method. ThC₂ exists in monoclinic crystallographic phase with space group (SG) C2/c. Our calculations under GGA approximation predict the high pressure structural sequence of monoclinic I (SG no. 15, C2/c) \rightarrow monoclinic II (SG no. 12, C2/m) \rightarrow orthorhombic I (SG no. 71, Immm) \rightarrow hexagonal (SG no. 191, P6/mmm) for this material with transition pressures of ~ 3.3 GPa, 58.3 GPa, 191.6 GPa and 255.0 GPa, respectively.

Effect of doping Nb⁵⁺ in NBBT and study of electrical properties and energy storage performance

M William Carry^{1*}, S Vinoth Rathan¹, Muthu Senthil Pandian¹, P Ramasamy¹

¹SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam- 603110, Tamilnadu. *Corresponding author: <u>carrywilliam5234@gmail.com</u>

Abstract

The lead-free ferroelectric energy storage devices of (0.94) (Na_{0.5}Bi_{0.5}) TiO₃-(0.06) BaTiO₃+ x wt.% Nb⁵⁺ (x=0%-2.5%) was synthesised by the solid-state reaction technique. The phase has been confirmed by X-ray powder diffraction analysis. The electrical properties of the material were analysed and subsequent energy storage density (W), energy efficiency (η), and energy loss (W_{rec}) were investigated.

1. Introduction

Researchers have been continuously developing lead-free materials for the replacement of lead-based materials due to its toxicity^[1]. A great improvement has been established in the research field of processing and characterization of $(Na_0 5Bi_0 5)$ TiO₃-BaTiO₃ (NBBT) based ceramics and crystals were grown across the morphotropic phase boundary (MPB) with the coexistence of two phases (rhombohedral- tetragonal) with $x=0.06-0.07^{[3-4]}$. NBT-BT system belongs to Perovskite (ABO₃) structure, Bi, Na and Ba occupy A-sites in the structure. Ti acts as a central metal ion and occupy B-Nb⁵⁺ was doped in a series of NBT-BT sites. compositions across the morphotropic phase boundary (MPB) and electrical properties were investigated. By substituting of Nb⁵⁺ for Ti⁴⁺ diverse properties and microstructure have been discussed [4-^{6]}. Eventually, the good piezoelectric and dielectric properties for Nb⁵⁺ doped NBBT in B-site vacancies. Therefore, Nb doped NBBT ceramics can be improved by substituting Nb⁵⁺ for Ti⁵⁺ in a small amount. In this work structural, electrical properties and energy storage performance of pure and Nb⁵⁺ doped NBBT ceramics have been reported.

2. Experimental section

2.1 Materials and synthesis

The starting materials of Bi_2O_3 , Na_2CO_3 , Ba_2CO_3 , TiO_2 and Nb_2O_5 were weighed according to the equation (0.94) ($Na_{0.5}Bi_{0.5}$)TiO₃-(0.06)BaTiO₃. Dopant (x)Nb₂O₅ is incorporated according to (x/100) wt. % when x=0, 0.01, 0.015, 0.020, and 0.025. The synthesized powders were blended by binder of polyvinyl alcohol (PVA). The pellets were prepared with dimensions 13mm in diameter and 1mm in

thickness. The formation of the phase was identified using X-ray Powder diffraction analysis (XRPD). The piezoelectric coefficient d_{33} and g_{33} were also investigated. P-E hysteresis loop and energy storage density were also examined.

Result and Discussion

Structural investigation



Fig. 1 powder X-ray diffraction pattern of the NBBT(x=0-2.5%) ceramics

Figure 1 portrays the XRPD of Pure and Nb⁵⁺ doped NBT-BT for the phase confirmation. The diffraction peaks are sharp and this indicates the good crystallinity of the synthesised polycrystalline materials. Phase exists as pure perovskite structure when x = 1-1.5%. A secondary phase starts to appear at x>1.5%, the reason is the solubility limit of Nb⁵⁺ in the NBBT lattice has been reached [6]. With

increasing the doping content of Nb^{5+} , the amount of the second phase becomes more and more.

Electrical properties

Piezoelectric



Fig. 2. (a) d_{33} and g_{33} values of NBBT (x=0-2.5%) ceramics; (b) the energy storage density W and energy loss W_{rec} ; (c) energy storage efficiency η of NBBT (x=0-2.5%) ceramics.

Fig. 2(a) shows the piezoelectric constant d_{33} and piezoelectric voltage coefficient g_{33} . The piezoelectric constant d_{33} was measured using Berlincourt quasistatic meter. The sample was polled under DC field of about 1- 2.5 kV/mm at 60 °C for 30min, and electrodes were immersed in silicone oil to avoid electric shock and thermal explosion. Piezoelectric coefficient (d_{33}) was measured and it was found to be ~160 pC/N at x=1.5%. Nb5+ (1.5%) doped NBBT ceramics exhibits better piezoelectric properties across the MPB than other concentrations. The piezoelectric voltage coefficient (g_{33}) was also calculated.

Ferroelectric

P-E hysteresis loop of NBBT ceramics for all the ratios were measured. Remnant polarization (P_r), maximum polarization (P_m) and coercive field (E_c) NBBT ceramic were subjected to P-E measurement and it shows ferroelectric behaviour, as NBBT is non-centrosymmetric. This type of materials possesses Curie temperature (T_c), as they follow the Curie-Weiss behaviour. T_c denotes the 2nd order phase transition from Ferro-Paraelectric and this was confirmed from the temperature-dependence of dielectric measurement. When the alternating field is applied polarization will take place and it was seen in the P-E hysteresis loop, which is +P_r and +P_s, and

when the field is reversed polarization will occur that is $-P_r$ and $-P_s$.

Conclusion

Polycrystalline ceramic sample of pure $0.94(Na_{0.5}Bi_{0.5})-0.06BaTiO_3$ (NBBT) and Nb⁵⁺ doped (x=0-2.5%) respectively were prepared bv conventional solid-state reaction. All Nb5+ doped NBBT ceramics are composed of a perovskite phase as well as a small number of secondary phases were observed (x = 2-2.5 %). The perovskite structure was confirmed from the XRPD analysis. Eventually addition of Nb⁵⁺ results in improvement in piezoelectric property. The energy storage density was calculated from the P-E hysteresis loop. Enhancing the piezoelectric property by the addition of Nb⁵⁺ at x=1.5 wt. % and d_{33} was found to be ~160pC/N and this can be applicable for piezoelectric materials. Finally, the Nb⁵⁺ doping in B-site of ABO₃ structure of NBBT with coexistence of two phases changes the electrical property of the material.

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Interplay of Symmetry and Defects during the Topological Phase Transitions

Y R Kartik^{1,2} and Sujit Sarkar¹

¹ Theoretical Sciences Division, Poornaprajna Institute of Scientific Research, Bidalur, Bengaluru 562 164, India ² Graduate Studies, Manipal Academy of Higher Education, Madhava Nagar, Manipal 576 104, India **Corresponding author: yrkartik@gmail.com*

Abstract

To investigate the effect of defects on the properties of a topological material, we analyze Kitaev chain with the addition of engineered effective term, in a theoretical way. Here we analyze the momentum space characteristics like topological invariants, quasi-particle excitation energy, topological quantum critical lines, ground-state energy, and symmetry. We show the behavior of defects and its consequences on the momentum space characteristics of the Kitaev chain. With the appearance of fractional topological invariants, we observe a transformation of system from BDI symmetry class to AIII symmetry class.

Introduction

Phase transition is a fundamental phenomenon that distincts different phases of matter with the breaking of the order parameter. Landau theory of symmetry breaking explained this phenomenon very effectively, until the discovery of topological state of matter. With the absence of order parameters, topological invariant has been an efficient tool to characterize the different topological phases. With the help of localization of edge modes, topological materials became a new platform for the realization of new exotic particles, unlike bosons and fermions under different conditions. Electronic band structures topological insulators/superconductors/semilike metals have been enormously used for the realization of particles like Majorana edge modes, massive Dirac modes and chiral edge modes both theoretically and experimentally.

Defect formation is the typical situation during the experimental setup of a topological system. Defects arise because of the electronic band structure, lattice deformation of influence of external parameters. These defects are natural and can influence the properties of the system. Thus, it is always necessary to understand the nature and behaviour of the defects. In this work, we consider the defect in the form of a perturbation. Our study is more from a simulation perspective, which helps to understand the interplay between defects and topological phase transitions.

Model Hamiltonian

Here we consider Kitaev Hamiltonian with the presence of an engineered defect. Our Hamiltonian is expressed as $H_T = H_{BdG} + H_{eff}$, where H_{BdG} is the

initial Hamiltonian and H_{eff} is the effective term which is an engineered defect. Initial Hamiltonian is

$$H = -\mu \sum_{i=1}^{L} c_{i}^{\dagger} c_{i} + \sum_{i=1}^{L-1} (-tc_{i}^{\dagger} c_{i+1} - \Delta c_{i}^{\dagger} c_{i+1}^{\dagger} + H.c)$$

Where c_j and c_j^{\dagger} are the annihilation and creation operators with H.c. as Hermitian conjugate. After Fourier transformation, the model can be written in Bogoliubov–de Gennes (BdG) format as,

$$H_{BdG} = \chi^{(1)}\sigma_{\rm z} + \chi^{(2)}\sigma_{\rm y}$$

Where $\chi^{(1)} = -\mu - 2t \cos k$ and $\chi^{(2)} = \Delta \sin k$. Here σ_y and σ_z are the Pauli spin matrices. We add an engineered defect through an effective term $H_{eff} = \delta k. \sigma_1$, where the defect appears in the σ_z basis of the Hamiltonian. This defect is equivalent to the perturbation, which is linear in momentum. However, the addition of defect does not violate dimensionality and the Hermiticity properties of the system.

Momentum space characterization

Topological systems are known for symmetry protected edge states, and the phase transition occurs with the vanishing of the quasi-particle energy in the excitation spectrum ($E_k = \left(\chi^{(1)^2} + \chi^{(2)^2}\right)^{1/2}$). The phase boundaries are called critical lines, and they differentiate different topological phases. Each phase has a distinctive quantized topological invariant called winding number (W= (1/ 2π) $\int_{\pi}^{\pi} \frac{\partial}{\partial k} \tan^{-1} \left(\frac{\chi^{(2)}}{\chi^{(1)}}\right) dk$) which has a stable ground state energy ($E = \sum_i E_k$). The second-order derivative of the ground state energy shows a

discontinuity; thus topological phase transitions are known to be second-order phase transitions $(E''(t) = -1/2\pi \int_{-\pi}^{\pi} (\partial^2 E / \partial k^2) dk).$

The system with the absence of defect behaves as Kitaev chain, a toy model famous for its significance in realising the Majorana quasiparticles. Here the quantized winding number (W=1) represents the localized Majorana zero modes and the absence of edge mode (W=0) represents the insulating phase (Fig.1a, c). The transition from W=1 to W=0 occurs through a gap closing in the energy spectrum at k = 0 or $k = \pm \pi$ (Fig.1b). As the ground state of the energy signifies the system's stability, we can observe the topological transitions showing a second-order transition (Fig1 d). The system falls under BDI symmetry class as it preserves time-reversal symmetry, particle-hole, and chiral symmetry.



Fig. 1. Topological properties of the model without defect (a) Phase diagram (b) Quasi excitation energy showing gapless condition at k=0 and π . (c) Topological invariant number showing quantization at W= 1 (d) Ground state energy showing second-order phase transition at t=-0.5 and 0.5.

The system behaves quite differently with the introduction of the defect. Due to the introduction of defect, the quantized winding number remains unaltered, but a new region of fractional winding number (W=1/2) (Fig. 2 a, c). This region is a stable gapped phase which appears with the gap closing either at $k = -\pi$ or $k = \pi$ (Fig. 2b). The stable ground state energy shows the second-order phase transition, corresponding to the transitions among W=1/2 and W=1 (Fig. 2 d). The system now falls under AIII symmetry class as it breaks time-reversal symmetry but preserves chiral and particle-hole symmetry.



Fig. 2. Topological properties of model with defect (a) Phase diagram (b) Quasi excitation energy showing gapless condition at k=0, $-\pi$ and π . (c) Topological invariant number showing quantization at W= 0.5 and 1 (d) Ground state energy showing second-order phase transition at t=-0.5,0.25 and 0.75.

Conclusion

In this work, we try to understand the behaviour of topological model in the presence of the defects. The initial Hamiltonian represents a tight-binding model, and the effective term describes the defect in the form of linear momentum. Because of the nature of the effective term, there occurs a torsion in the lattice system, resulting in dislocations and disclinations. In our Hamiltonians the periodicity of the Bloch space breaks, and the system produces fractional winding number along with integer one. Even though the system transforms from BDI to AIII symmetry class, the topological properties are preserved.

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Improved Carrier Mobility of MAPbBr₃ Perovskite Crystal Prepared via Low- temperature In-situ Growth Method

Kunchanapalli Ramya^{1#}, Arindam Mondal^{2#}, Satyajit Gupta^{2*}, Sabyasachi Mukhopadhyay^{1*}

> ¹Department of Physics, SRM University, AP- Andhra Pradesh, 522240 ²Indian Institute of Technology Bhilai, Raipur, Chhattisgarh-492015, India

> > #Contributed equally

*Corresponding author: satyajit@iitbhilai.ac.in, Sabyasachi.m@srmap.edu.in

Abstract

In the current utilization of organic halide perovskites, single crystals show promising properties for optoelectronic applications. The requirement of low trap density and high carrier mobilities with the simple solution grown method is essential for application in semiconductor devices. For this, in-situ, room-temperature assisted synthesis of methylammonium lead bromide (CH₃NH₃PbBr₃) crystals using N-methyl formamide (NMF) as a solvent and source of methyl ions during the crystallization process was explored towards understanding the structural, optical, and electronic properties of as-grown crystals. With the approachability of this simple method and also with the improved structural stability, carrier mobility values, the as-grown crystals are useful in photovoltaic applications.

Introduction

Hybrid metal halide perovskite crystals (HaP) play a vital role in the next generation of optoelectronic devices such as lasing, photodetectors, light-emitting diodes, and photovoltaic cells. This is because of their tunable optical properties, long carrier lifetime, high mobility, and low cost. Compare to the polycrystalline films, single crystals of MAPbBr₃ possess long carrier diffusion lengths, low trap density, and better stabilities.[1] These properties give a better view and provide the potential applications of MAPbBr₃ single crystals. The growth process of single crystals has acquired a wide range of difficulties such as slow growth and poor quality for the required optoelectronic applications.[2] So, the requirement of both high-quality and large-scale perovskite single crystals attracts potential applications. On this front, HaP crystals grown from low-cost solution process methods produce broad attention, with great potential for future commercialization in optoelectronic devices. Various methods were reported to synthesize HaP single crystals with different compositions, sizes, including the traditional high-temperature Bridgman method, crystallization by anti-solvent vapor assisted method, inverse temperature crystallization method. A simpler, and cost-effective route of crystal deposition is required in growing scalable single crystals for optoelectronic devices. Thus, with the utilization of Nmethyl formamide (NMF) as a source of methylammonium ions, is used in this study to synthesize MAPbBr₃ (MA=CH₃NH₃⁺) crystals at room temperature. The wide applicability of this method lies in avoiding expensive precursor salts as well as eliminating the use of toxic solvents. Highquality, large-scale single crystals were fabricated. The structural, optical, and electrical characterization was carried out to investigate their optical and transport parameters. We also demonstrated the potential use of these synthesized crystals by examining the charge transport properties with various applied bias voltages.

Results and Discussion

The XRD patterns of MAPbBr₃ crystals (fig 1) depict indexed peaks of



Fig. 1. XRD pattern from a face of MAPbBr₃ single crystal.

(010), (021), (022), (122), (030), and (031), which correspond to the cubic phase of $MAPbBr_3$ single crystals. [3]

The thermal stability of the MAPbBr₃ crystals was examined as a function of temperature through thermo-gravimetric (TGA) analysis under the N₂ atmosphere. Two stage chemical degradation occurs, defragmentation of the organic cation (methyl ammonium bromide-MABr) occurs at ~ 310°C. At the final stage (at 510°C, complete degradation of the HaP structure with a sharp weight loss.[4]



Fig. 2. Transmission spectrum of MAPbBr₃ from UV-Vis spectroscopy which describes the decrease in transmittance at 571 nm

The optical activities of the MAPbBr₃ crystals were examined using UV-Vis spectroscopy. Figure 2 represents optical transmission spectra of the crystals; where the sharp decrease in the transmittance at the vicinity of 571 nm suggests a direct-band gap nature of the materials. The bandgap of the crystal was determined to be 2.17 eV utilizing Tauc plot analysis. The experimentally obtained bandgap of MAPbBr₃ crystals is comparable with the earlier reported bandgap of HaP crystals. [5]



Fig. 4. Dark I-V characteristics using the SCLC method

The carrier transport in dark was studied by the space charge limited current method.[2] The I-V curve of the crystals is divided into three parts as shown in fig.3. the trap density was calculated by trap-filled limit voltage (V_{TFL}) by the equation

$$n_t = \frac{2V_{TFL}\mathcal{E}_0\mathcal{E}_r}{\mathcal{E}L^2} \quad Eq \ (1)$$

Here, \mathcal{E}_0 is the vacuum permittivity, \mathcal{E}_r is the relative dielectric constant and L is the crystal thickness. The trap density of MAPbBr₃ single crystals was found to be 3.35×10^{10} /cm³ the carrier mobility of the crystal was found by fitting I-V of the crystal with Mott-Gurney law. The carrier mobility was found to be $27.51 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ using the equation

$$J_d = \frac{9\mathcal{E}_r \mathcal{E}_0 \mu V^2}{8L^3} \quad Eq \ (2)$$

The calculated electrical mobility for MAPbBr₃ single crystals synthesized using the low-temperature solution grown method is higher at room temperature as compared to the previously reported studies and the trap density is in good agreement with the limit of the required optoelectronic applications. [1,2]

In the conclusion, we have synthesized $MAPbBr_3$ crystals with a low temperature in-situ grown method. The improved structural stability and carrier mobilities of the crystal synthesized following the method could be useful to prepare crystals for optoelectronic applications.

Acknowledgment

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Influenceof Sintering Temperature on Structural and Dielectric Properties of BaZr_{0.15}Ti_{0.85}O₃

Yogesh Kumar^{a*},Vidushi Karol^aand Anshu Sharma^a

^aDepartment of Physics, Maharaja Agrasen University, Baddi, Solan, India (174103) **Email:* ysg.1992@gmail.com

Abstract

In this study, the influence of sintering temperature on the structural and dielectric properties of $Ba(Zr_{0.15}Ti_{0.85})O_3$ is examined. The samples prepared via solid state reaction route were sintered at 1100 ^{0}C and 1300 ^{0}C . Phase analysis was done by X-ray diffraction. The dielectric properties were analysed over a comprehensive range of frequency and temperature. The analysis of diffraction pattern shows an increase in crystallinity and shift of peaks towards lower diffraction angle. The dielectric constant increase with increase in sintering temperature and dielectric loss has value less than 1.

Modulational instability of spin-orbit coupled Bose-Einstein condensates with higher-order interaction

R. Sasireka¹, S. Sabari², and A. Uthayakumar¹

¹Department of Physics, Presidency College (Autonomous), Chennai - 600005, India ²Department of Physics, Government College for Women, Kumbakonam – 612001, India

*Corresponding author: sasirekasabari@gmail.com

Abstract

We study the effect of higher-order interactionon the modulational instability(MI) of spin-orbit coupledBose-Einstein condensates (BECs). The analysis performed for equal densities of the components. Different combinations of the signs of intraand inter-component interaction strengths are considered. Effects of the two-body interaction, higher-order interaction, Rabi coupling and spin-orbit coupling on the MI of the spin-orbit coupled(SOC) BECs are investigated, which is not discussed before.

High Temperature Structural Phase Transitions in Lead-free Piezoelectric Ba_{0.95}Ca_{0.05}Sn_{0.09}Ti_{0.91}O₃ Ceramic

Pravin Varade^{1,} *, Rachna Selvamani², Adityanarayan Pandey¹, V. B. Jayakrishnana², N. Venkataramani¹, P. U. Sastry^{2,3}, Ajit R. Kulkarni¹

¹Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai ²Solid State Physics Division, Bhabha Atomic Research Center, Mumbai ³Homi Bhabha National Institute, Mumbai, 400094

* Corresponding author: pravinvarade123@gmail.com

Abstract

High temperature structural investigations were carried on $Ba_{0.95}Ca_{0.05}Sn_{0.09}Ti_{0.91}O_3$ ceramic powdersynthesized by solid-state reaction method. The line-profile and Rietveld refinement analyses for temperatures ranging from 300K-500K revealed a co-existence of tetragonal, orthorhombic phases at 300K and tetragonal, cubic phases in the range 320-375K. Our results are in correlation with the observed anomalies in the dielectric response.

Introduction

Barium titanate (BaTiO₃) is one of the most widely studied lead-free piezoelectric material. It undergoes polymorphic phase transitions in the temperature range 200-405K; from the hightemperature paraelectric cubic (C) phase to tetragonal (T) phase at 405 K, to orthorhombic (O) phase at 273 K and then to rhombohedral (R) phase at 200 K [1]. The reported piezoelectric charge coefficient (d₃₃) of BaTiO₃ ceramics is 190 pC/N at room temperature and is as high as 420 and 300 pC/N in the vicinity of T-O and to O-R transition temperatures. This behaviour is exploited to achieve a high piezoelectric coefficient at room temperature by bringing the T-O transition temperature (T_{T-O}) to near room temperature by introducing dopants in BaTiO₃. With the addition of Ca, the C-T transition temperature remains nearly unchanged, whereas the temperatures of T-O and O-R transitions shift to much lower temperatures (T_{T-O}~193K and T_{O-} _R~123K) for 15 % of Ca [2]. Similarly, introducing Sn at Ti-site results in the shift of T_{T-O} and T_{O-R} towards room temperature. In the mixed system, Ba_{0.94}Ca_{0.06}Ti_{1-x}Sn_xO₃, C-T transition temperature decreases from \sim 358K for x = 0.05 to \sim 237K for x = 0.20 which also exhibits diffuse phase transition [3].

Recently, we have reported enhanced electromechanical properties in $Ba_{0.95}Ca_{0.05}Sn_{0.09}Ti_{0.91}O_3$ (BCST) ceramic at near room temperature which was attributed to the presence of phase coexistence [4]. In view of the importance of the polymorphic phase transitions, it is imperative to have a detailed understanding structure of BCST. In this paper we report the structural study of BCST at high temperatures using X-ray diffraction (XRD) technique.

Experimental

BCST ceramic was prepared by a conventional solid-state reaction route. Details are reported elsewhere [4]. XRD of the sintered powders was performed using rotating anode type x-ray source with CuK_{α} radiation. The samples were heated in a heater attached to the diffractometer. Data were collected in situ from RT to 500K in the angular range 2θ of 20° - 90° . The line profile analysis and full pattern refinements were carried out using FULLPROF Rietveld program. In all the refinements, the data of full angular range have been used, although in the figures only a limited range has been shown to highlight the changes clearly.Dielectric measurements were done using Impedance Analyzer (Alpha High Resolution: Novocontrol, Aachen, Germany) in the temperature and frequency range of 223K-473K and 1Hz to 1MHz, respectively.

Results and Discussion

Fig 1 shows a region of the XRD patterns consisting (200), (310) and (222) pseudo-cubic reflections at various temperatures. It is evident that, for T = 300K the (200) reflections are broad, but two distinct peaks having almost equal intensity are present. This suggests the orthorhombic phase with lattice parameters $a\neq b\neq c$. For T > 300K, the (200) peak splits into (002) and (200)/(020) peaks, indicating a tetragonal structure. This is more clearly visible in higher angle (310) peak. However,

the (222) peak is nearly a singlet with asymmetric broadening toward the high angle side.



Fig.1. Evolution of portion of powder XRD pattern of $Ba_{0.95}Ca_{0.05}Sn_{0.09}Ti_{0.91}O_3$ with temperature.

A broad hump for (200) and (310) reflections at 300K indicates presence of mixed crystallographic



Fig.2. Observed (dots), calculated (continuous line) and difference (bottom line) profiles obtained from the Rietveld refinement of BCST

phases. The X-ray line profile analysis revealed acrossover from O to T phase upon heating from 300K to 500K. To investigate these observations in detailed, full pattern Rietveld refinement was carried out in the temperature range (300-500K) (Fig 2). Results showed coexistence of T (P4mm) 300K. and O (Amm2) phases at For 320K<T<375K, refinements indicated mixed T and C (Pm3m) phases and single (C) phase above 400K. The volume fractions of these phases are estimated. Our results are in accordance with the observed anomalies in the dielectric response of BCST (Fig 3). Detailed results will be presented in the conference. Further studies by other techniques are under progress.



Fig.3. Variation of dielectric constant with temperature. Inset shows the temperature dependence of $tan\delta$

Conclusions

The high temperature structural investigations of $Ba_{0.95}Ca_{0.05}Sn_{0.09}Ti_{0.91}O_3$ ceramic carried out using X-ray diffraction (XRD). The line-profile and Rietveld refinement analysis for temperatures ranging from 300K-500K revealed a co-existence of mixed P4mm-Amm2 phase at room temperature and P4mm-Pm3m phase in a high temperature interval. The results are concurrence to dielectric properties.

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Non-Hermitian Topological Quantum Criticality

S Rahul^{1,2}, Sujit Sarkar¹

¹Division of Theoretical Sciences, Poornaprajna Institute of Scientific Research, Bidalur, Bengaluru -562164, India., ²Manipal Academy of Higher Education, Madhava Nagar, Manipal - 576104, India.

*Corresponding author: sujit.tifr@gmail.com

Abstract

Non-Hermitian topological systems are becoming increasingly important in the field of condensed matter because it opens a more realistic and practically possible area to understand the interaction between the system and the environment. We study and present the results of non-Hermitian effect on topological quantumcriticality. We use the zero mode solutions (ZMS) to present the topological quantum criticality phase diagram. We observe an interesting feature of multicritical point for the non-Hermitian system. We also present one to one correspondence between the Hermitian and non-Hermitian topological quantum criticality.

Photoinduced Phase Transitions in Azo doped Cholesteric Liquid Crystal

Ramadevi Suguru Pathinti¹, Buchaiah Gollapelli¹, Mohit Mittal¹ and Jayalakshmi Vallamkondu^{1,2,*}

¹Department of Physics, National Institute of Technology, Warangal, Telangana, India, 506004 ²Center for Advanced Materials (CAM), NIT-Warangal, Telangana, India, 506004 *Corresponding Author: jayalakshmiv@nitw.ac.in

Abstract

In this paper the quantitative comparison of the photo-induced phase transition activity photoresponsive azo dye doped cholesteric liquid crystal was investigated under UV light (365 nm) irradiation with two intensities 2 and 5 mW/cm². The conversion of *trans to cis* isomerization of azo molecules caused a shift ΔT upon incident UV irradiation. The dynamic response times are calculated by specifying response times for UV ON and OFF cases in the CLC–I shift region at different temperatures and intensities.

Introduction

Cholesteric liquid crystal (CLC) is regarded as a onedimensional photonic crystal because of its selforganized helical structurally arranged in layers in a periodic spiral structure, the layers are parallel, and the interlayer distance between adjacent layers that rotate 360° along the long axis is called a CLC pitch (P). The reflective bandwidth of a single-pitch CLC obeys the Bragg reflection law provided by $\lambda = n \times P$, $\Delta \lambda =$ $\Delta n \times P$, where λ represents the reflective wavelength, n represents the average refractive index, P represents the CLC pitch, $\Delta\lambda$ represents the reflective bandwidth, and Δn represents the birefringence. The CLC can be photoresponsive by doping made with а photosensitive molecule such as azobenzene shows photo response that can find prominent applications in smart windows¹, switchable gratings² and Storage devices³. Azobenzene molecules consist of azo (-N =N-) groups of appropriate photosensitive materials that can show photoisomerization and can lead to changes in the physical properties of the surrounding medium. Briefly, azo groups can change their molecular shape from a potentially more stable rod-shaped trans isomer to bent shaped cis isomers when irradiated with UV light (usually 365 nm) and visible light excitation can be returned to its trans isomer⁴. This subsequent reverse transformation is naturally possible when there is no light-stimulating conditions (i.e., in the dark) by the thermal back relaxation process over a period of minutes to several hours. Therefore, the azo compound stabilizes the LC in the trans isomer with the rodshaped molecules and destabilize the LC in the cis isomer with the bent shaped molecules⁵.

In this study, the photo-induced shift and dynamic behavior of flat azo-CLC samples were examined quantitatively to understand the optical properties and response time behavior. The transitions from CLC phase photo-induced isotropic (CLC–I) and thermal recovery of cholesteric liquid crystal (I–CLC) from isotropic (CLC-I).

Materials and methods

Initially CLC mixture was prepared by mixing 2.22 wt% of right-hand chiral dopant R5011(Merck) in nematic liquid crystal E7 (Merck) and photoresponsive CLC by adding 5 wt% 4, 4' -Azoxydianisole (TCI Chemicals) (azo dye) to CLC. The right-handed CLC and azo dye mixtures was stirred at 75°C were use DMF for proper mixing of these two mixtures. The commercial planar LC cells of 5µm thickness are filled with CLC doped azo dye mixture by capillary action at isotropic temperature. The photo-induced phase transition studies are conducted with the experimental setup consisting of an LC cell placed in a hostage (Linkam Scientific, LTS 420) to monitor temperature and was mounted between crossed polarizers and He-Ne laser. Photodetector (Thorlabs, DET10A2) that records transmission intensity with time. This setup is connected to a PC controlled digital multimeter (Keithley 2010). A UV Lightningcure (LC8, Hamamatsu, China) is illuminated on the cell at a certain angle to the cell normal with intensity 2 and 5 mW/cm². The Optical Polarizing Microscope (POM) is used for optical characterization.

Results and discussions

Figure 1 shows the textures of pure CLC and CLC/Azo dye doped composite systems under cross-polarized condition shows the homogeneous dispersion of azo dye in the CLC matrix.



Fig:1. Polarizing optical microscope textures of pure CLC and CLC/Azo dye under cross-polarized condition

Photoinduced phase diagram

Fig. 2 shows the phase transitions of sample in the presence and absence of UV irradiation. Initially, in the CLC phase the transmitted intensity is maximum and shows abrupt decrease at the I phase. At the 2 and 5 mW/cm² intensity, due to the conversion of *trans* to *cis* isomers of azo dye i.e., photoisomerization was triggered a downward change in the transition temperature.



Fig.2. Temperature dependence of the transmitted He– Ne laser intensity obtained without and with UV irradiation (2 and 5mW/cm²). Table shows the shift in transition temperatures

Dynamics in the $T_{\rm CLC\mathchar`-I}$ shift region

To compare the response behavior, we have conducted dynamic studies by irradiating UV light for 6 minutes and switched OFF. After switching ON UV light, there was a sharp fall in transmitted intensity, which leads to a photoinduced CLC-I transition forming bent-shaped *cis* isomers. As UV radiation is turned OFF, the thermal I-CLC transition is recovered by the increase in transmitted intensity. The reason behind this transition is the reconversion of the bent-shaped cis isomers into *trans* isomers preceding to return the CLC phase by thermal back relaxation with a noticeable delay.

We have defined three different response times τ_{on} , τ_{off} , and τ_{delay} . The time taken for the laser intensity to change from 10% to 90% of the total response with UV radiation ON due to photochemical process is defined as τ_{on} . The time taken for laser intensity to change from 90%–10% upon switching UV radiation OFF due to thermal back relaxation is defined as τ_{off} . and τ_{delay} is the time taken to effective change in the intensity after switching OFF. As the temperature increases, the response time τ_{on} increases where as τ_{off} and τ_{delay} decreases.



Fig. 3. Thermal variation of response times τ_{on} (a), τ_{off} (b) and τ_{delay} (c) at 2 and 5 mW/cm² UV intensities.

Conclusions

UV light irradiation changed the photo-induced phase to photo responsive azo-CLC. The observed change of ΔT (shift in the CLC–I transition due to UV radiation) concerning incident UV intensity is agreeable to the molecular mean-field model. The response dynamics as the UV light is turned ON and OFF demonstrate, the latter process includes a delay in time and an actual response time.

Acknowledgments

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Temperature-Dependent Raman studies of lead-free K_{0.5}Na_{0.5}NbO₃ piezoelectric ceramics

Subingya Pandey, Pamu Dobbidi*

Indian Institute of Technology, Guwahati Guwahati-781039

*Corresponding author: pamu@iitg.ac.in

Abstract

 $K_{0.5}Na_{0.5}NbO_3$ (KNN) is well studied due to its excellent electrical, dielectric, ferro, and piezoelectric properties. KNN ceramics have been synthesized by the solid-state reaction method. The X-ray diffraction pattern confirms the orthorhombic phase corresponding to the Amm2 space group. The effect of temperature variation on the Raman spectrum has been studied briefly. The prominent peaks corresponding to v_1 stretching mode and v_5 bending vibration modes are related to the internal vibrations of the NbO₆ octahedron. The Raman intensity is enhanced and shifts towards the higher wavenumber at low temperatures. Similarly, there is a Raman shift along the lower wavenumber with a temperature rise. An indication of phase transition has been observed around -80°C and 210°C because of spectral change and corresponding shifts.

Introduction

Lead-based ceramics are now replaced with leadfree ceramics to avoid the adverse harmful effects on human health [1]. The lead-free K_{0.5}Na_{0.5}NbO₃ (KNN) piezoelectric ceramic has become a potential candidate for its advantages in the biological and environmental fields to replace lead-based ceramics like PZT because of the comparable piezoelectric properties [2]. Since the properties of piezoelectric materials can be enhanced by applying external stimuli like electric or magnetic fields, light, temperature etc, they can be used in the manufacturing of electronic instruments such as sensors, actuators, electroactive polymers, etc. KNN exhibits an orthorhombic crystal symmetry at room temperature. Many studies were done on the KNN ceramics, and understanding the crystal structure is essential. However, the temperature-dependent Raman study is not available. To understand the transport, thermoelectric performance based on thermal conductivity, isotopic effects, lifetime of phonons, we need to have a brief knowledge on temperature variation Raman studies [3]. The Raman spectra at room temperature exhibits the orthorhombic Amm2 phase. In this present study, we have gone through the formation of phase pure KNN ceramic and studied the variation of Raman spectra with temperature.

Experiment Details

The conventional solid-state reaction technique was used to prepare the polycrystalline sample of KNN. The raw materials taken are potassium carbonate (K_2CO_3 , M/s Sigma Aldrich, purity 99.0%), sodium carbonate (Na_2CO_3 , M/s Sigma Aldrich, purity

99.5%), and niobium pentoxide (Nb₂O₅, M/s Sigma Aldrich, purity 99.9%). Since the alkali elements are volatile, an extra 5 wt.% of Na₂CO₃ was added to compensate for the loss. These ingredients taken in stoichiometry are mixed in a planetary ball mill (M/s Fritsch, Pelverisette 6) for 5 hours in acetone medium. The mixed powder was dried and calcined at 750°C for 5 hrs. The calcined powder was grounded again for 5 hrs, dried, and pressed uniaxially to form cylindrical discs of 10mm diameter and 1-2mm thickness in a KBr press under the pressure of 1500 kg/cm². The discs were then sintered at 1000°C for 5 hours for densification.

The crystalline phase of the ceramic sample at room temperature was checked by an X-ray diffraction pattern carried out by X-ray Cukα (1.5406 Å) diffractometer (M/s Rigaku TTRAX-III,18kW). A brief study of the temperature-dependent (-180°C to 400°C) Raman spectroscopy was carried out by Raman Spectrometer (M/s LabRam HR, Horiba Jobin Yvon).

Results and Discussions

The X-ray diffraction pattern of KNN-5 wt.% Na₂CO₃ calcined at 750°C, and sintered at 1000°C for 5 hours is shown in Fig. 1 (a), it confirms the formation of phase pure KNN that exhibits orthorhombic structure with Amm2 space group without the presence of any secondary phases that generally arises because of volatilization of alkali elements. Indexing is performed based on the ICDD file no. 01-085-7128. The average crystallite size was calculated using Debye-Scherrer equation

$$\tau = k\lambda/\beta \cos\theta \tag{1}$$

where τ denotes the crystallite size, k is the shape factor (0.89), λ is the wavelength (0.15406nm), β is the full width at half maxima (in radian), and θ being the Bragg's angle. The average crystallite size and unit cell volume was calculated to be 29nm and 125.219±1.11 Å³ respectively. The lattice parameters are found to be a=3.9455±0.0012 Å, b=5.6398±0.0027 Å, c=5.6274±0.0489 Å. Fig. 1 (b) shows the surface



Fig. 1. (a) XRD patterns of KNN-5 wt.% Na₂CO₃ ceramics calcined at 750°C, and sintered at 1000°C (b) FESEM image of KNN-5 wt.% Na₂CO₃ ceramic sintered at 1000 °C.

morphology of KNN ceramic indicating the uniform growth of grains arranged in cuboidal shape. The average grain size is found to be 7.3µm (inset). Raman spectroscopy allows understanding the structural deformations and compositional studies of KNN ceramics. As per the group theory, orthorhombic Amm2 symmetry consists of $4A_1 + 4B_1 + 3B_2$ + A2 Raman and infrared active modes except for A2 (silent mode). The Raman spectra of KNN corresponds to the internal vibrations of the NbO6 octahedron that consists of $1A_{1g}(v_1) + 1E_g(v_2) + 2F_{1u}(v_3, v_4) + 1F_{2g}(v_5) + 1F_{2u}(v_6)$. At room temperature, the $F_{2g}(v_5)$ and $A_{1g}(v_1)$ bands at 260cm⁻¹ and 615 cm⁻¹ are strong because of their perfect octahedral symmetry. υ_1 , υ_2 , and υ_3 are the stretching modes, and remaining are the bending modes [4]. Below 200cm⁻¹, the small bands correspond to Na⁺/K⁺ translational mode, and another weak band at 860 cm⁻¹ indicates the perovskite structure of KNN. Fig. 2 (a) shows the Raman spectra at low temperatures. The blue shift (along the high wavenumber side) for v_5 and v_1 is due to increased compressive strain and binding strength that shortens the chemical bond length between Nb⁵⁺ and its O₂ atoms (hardening). Fig. 2 (b) shows the intensity and spectral change at -80°C, indicating the transition from rhombohedral to orthorhombic phase.



Fig. 2. Low-Temperature variation Raman Spectra of KNN-5 wt.% Na₂CO₃ ceramic.



Fig. 3. High-Temperature variation Raman Spectra of KNN-5 wt.% Na₂CO₃ ceramics.

Fig. 3 (a) shows the redshift (less wavenumber side) Raman spectra with an increase in temperature up to 190° C because of the tensile strain and expansion of the material, leading to an increase in chemical bond length of molecules (softening). Fig. 3 (b) shows the spectral change around 210°C, indicating the transition from orthogonal to tetragonal phase. Fig. 3 (c) follows the same pattern as Fig. 3 (a) with rise in temperature from 210°C to 400°C.

Conclusion

Phase pure KNN has been successfully synthesized by the solid-state reaction method. The room temperature X-Ray pattern and Raman spectra confirms the orthogonal phase with the Amm2 space group. The crystallite size was found to be 29 nm. The temperature variation Raman spectra clearly indicate phase transition from rhombohedral to orthorhombic and orthogonal to tetragonal phase at -80°C and 210°C, respectively. A clear blue and redshift have been observed with the temperature variation. Above 400°C, there is a possibility of another phase transition from tetragonal to cubic phase structure.

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Synthesis of Nano-alpha Silicon Carbide by Reaction Conversion Method

Rohini Garg^{*}, Abhijit Ghosh and Ashok Arya

Glass and Advanced Materials Division, Bhabha Atomic Research Center, Mumbai, India, 400085

*Corresponding author: <u>rohini.iisc@gamil.com</u>, rohinig@barc.gov.in

Abstract

Carbon soot pellets were successfully converted into silicon carbide pellets by solid -vapour reaction with SiO vapour at 1500°C under Ar gas flowing at atmospheric pressure in tubular alumina reactor. The holding time for reaction as well as flow rate of Ar gas was varied ranging between 6h-20h and 50-250 ml/min respectively. The structural and microstructural property of synthesized SiC was characterized using X-ray diffraction (XRD), Raman spectroscopy and scanning electron microscopy (SEM). Carbon residues were removed by heating it over 750°C for 6h. It has been observed that final yield and phase structure of synthesized SiC is dependent on reaction holding time and Ar gas flow rate.

Fascinating phase evolution in the x Na_{0.5}Bi_{0.5}TiO₃- (1-x) NaNbO₃ lead free binary solid solutions

Jayakrishnan V B^{1,2}, S K Mishra^{1,2}, and P U Sastry^{1,2}

¹Solid StatePhysics Division,BARC,Mumbai 400085 ²Homi Bhabha National Institute, Mumbai 400094

*Corresponding author: psastry@barc.gov.in

Abstract

The structural studies of lead free solid solutions $xNa_{0.5}Bi_{0.5}TiO_3(NBT) - (1-x) NaNbO_3(NN) for <math>0 \le x \le 1$ is done using X-ray diffraction. The appearance/disappearance of the super lattice reflections along with the change in the intensities of the main cubic perovskite peaks in diffraction data provides clear evidence for structural phase transitions with composition. TheDetailed Rietveld refinements revealed that these solidsolutions systematically undergo structural phase transitions from the room temperature AFE (*Pbcm*) phase of pure NN to FE (*R3c*) phase of pure NBT through different phases. Initially the AFE orthorhombic (*Pbcm*) to ferroelectric (*Pmc2*₁) at x>0.05 then FE orthorhombic (*Pmc2*₁) to Paraelectric (PE) (*Pbnm*) at x> 0.20 after that PE Orthorhombic (*Pbnm*) to AFE (*P4bm*) at x>0.70 finally to AFE Tetragonal (*P4bm*) to FE Rhombohedral (*R3c*) at x> 0.80. The dielectric measurements at room temperature recorded also shows the anomalies with composition.

Temperature Dependent Crystal Structure Of CaCeTi₂O₇

Shrikant Padhy^{1,2}, Rakesh Shukla^{1,2}, P. S. R. Krishna³, S. Muhammed⁴, S. N. Achary^{1,2, *}, A. K. Tyagi^{1,2}

¹ Chemistry Division, Bhabha Atomic Research Centre, Mumbai, 400085, India
 ² Homi Bhabha National Institute, Anushakti Nagar, Mumbai, 400094, India
 ³ Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India.
 ⁴ Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India.

*Corresponding author: sachary@barc.gov.in

Abstract

Herein the evolution of crystal structure of pyrochlore type $CaCeTi_2O_7$ in between 50 to 1273K is reported from low temperature powder neutron diffraction and high temperature powder X-ray diffraction studies. The Ca and Ce is statistically occupied in the A site of pyrochlore lattice forming distorted eight coordinated polyhedra while the Ti atoms are occupied in the B sites forming regular octahedra. Besides, the powder neutron diffraction studies revealed no detectable oxygen vacancies, suggesting that all the Ce atoms are in 4+ oxidation state. The unit cell parameter shows a smooth variation with increasing temperature, and the coefficient of volume thermal expansion in between 50 to 1273 K is 32.6 x 10^{-6} K⁻¹.

Modulational instability of spin-orbit coupled Bose-Einstein condensates with two- and three-body interactions

R. Sasireka¹, S. Sabari², and A. Uthayakumar¹

¹Department of Physics, Presidency College (Autonomous), Chennai - 600005, India ²Centre for Nonlinear Science, Department of Physics, Government College for Women (A), Kumbakonam – 612001, India

*Corresponding author: sabari.cnls@gcwk.ac.in

Abstract

We study the modulational instability of spin-orbit coupledBose-Einstein condensates with two- and three-body interactions (TBIs). The analysis performed for equal densities of the components. Different combinations of the signs of intra- and intercomponent interaction strengths are considered. Effects of the two-body interaction, TBI, Rabi coupling and spin-orbit coupling on the modulational instability of the spin-orbit coupledBose-Einstein condensates are investigated, which is not studied before.

pH Dependent Structural Evolution of Plant NanoFibrillar-Network During Dehydration: Real time SAXS investigation

Debasis Sen^{1,3*}, Avik Das^{1,3}, Jitendra Bahadur^{1,3}, Himal Bhatt²

¹Solid State Physics Division, ²High Pressure and Synchrotron Radiation Physics Division,Bhabha Atomic Research Centre, Mumbai, 400085³Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094

*Corresponding author: debasis@barc.gov.in

Abstract

Dehydration driven structural shrinkage of fibrillar network is an important and ubiquitous phenomenon in nature. We have used time-resolved small-angle X-ray scattering (SAXS) to get the insight into such nano-structural modifications. Temporal evolution of shrinkage of inter-fibrillary voids is found to be strongly dependent on the nature of hydration medium. For neutral and acidic media, temporal shrinkage follows a logistic model but shrinkage in case of alkaline medium remains insignificant. For neutral and acidic media, the Porod level, an indicator of contrast weighted volume fraction, exhibits a maximum. However, a contrasting behaviour is observed for alkaline medium. Scanning electron microscopy and infrared spectroscopy reveal significant alteration of nano-fibrils under hydration in strong alkaline medium.

A Spectroscopic Ellipsometric Study of PVDF/PEG Polymer Blends

Shivangi Bidoliya^{1, 2}, and Maheswar Panda^{*1}

¹Department of Physics, Dr Harisingh Gour Vishwavidyalaya (A Central University), Sagar, India, 470003 ²Indian Institute of Technology (BHU), Varanasi, India, 221005

*Corresponding author: panda.maheswar@gmail.com

Abstract

Polymer blends (PB) comprised of polyvinylidene fluoride (PVDF)/ polyethylene glycol (PEG) were synthesized in the form of thin films through the two step solution casting method. The optical properties of the PB were studied through spectroscopic ellipsometric study in the visible region of wavelength (500 nm -800nm). The various optical constants (e.g. refractive index, extinction co-efficient, etc.) & their dispersion behavior over the visible range of wavelengths show large variation as a function of compositions due to the different extent of interaction of matrix/filler. The optimized parameters were obtained for the 20% PB sample suggesting the sample to be a better material, suitable for various optical applications.

Introduction

Polymer nanocomposites (PNC) have recently become a very important class of materials because they provide multifunctional properties, along with better performance which can be utilized in numerous applications in various fields like polymer dielectrics, polymer ferroelectrics, polymer piezoelectrics, polymer magneto-electrics, environmental as remediation materials, and also as optical/optoelectronics materials.¹⁻³ Polymer blends (PB) of two compatible polymers are interesting from the point of their optical/optoelectronics applications. Polyvinylidene Fluoride (PVDF) is a polymer, known to possess outstanding electrical characteristics including piezo-, pyro-, Ferro electric properties and mechanical properties. Also, it is known to have good thermal stability, high chemical corrosion resistance as well as heat resistance, making PVDF a popular choice for a variety of applications.¹ Polyethylene glycol (PEG) is also an optically active polymer to be used in blends.

In the present article, the optical properties of the PVDF/PEG blends in terms of various optical parameters in the visible range of wavelength are the point of interest.

Experimental Details

A series of PB based on PVDF with varying weight fractions of PEG from 0.0 to 0.4 were prepared. The amount of PVDF/PEG corresponding to different weight fraction were taken and mixed with sufficient amount of acetone and then stirred with a moderate speed using hotplate magnetic stirrer along with continuous heat supply up to 170°C for half an hour. In order to prepare the thin film of PB through spin coating, a small amount of a solution is poured to the glass substrate by a micro pipette, which is then

rotated at a high speed of 5000rpm for 20 seconds in order to spread it using centrifugal forces, making a dry thin film available on the substrate. The ellipsometric measurements were carried out with the help of J.A. Wollam M-2000 spectroscopic ellipsometer.

Results and Discussion

Ellipsometric studies measure the changes in the state of polarization of light upon reflection from the surface of the samples. Figure 1 shows the variation of ellipsometric parameters psi (Ψ) and delta (δ)



Fig. 1. Variation of real and imaginary parts of polarization parameter with wavelength for all PB(a) psi (Ψ) and (b) delta (δ) .

as a function of the wavelength in the visible region for all PB with varying weight % of PEG. The changes in these parameters with varying wt% clearly indicate significant changes in the amplitude and phase ratios of S and P polarized light. Further in this case the variation of Ψ and δ becomes more significant with increase in weight percentage. The parameters Ψ and δ are very sensitive for the PB with higher wt% of PEG in comparison to the PB with lower wt% of PEG. The PB with 20 wt % PEG shows the constancy of Ψ and δ over the whole visible wavelength region, is attributed to the higher extent of homogeneity of the sample.²



Fig. 2. Variation of real and imaginary parts of refractive index with wavelength for all PB (a) real part of refractive index (n), (b) imaginary part of refractive index i.e., extinction coefficient (k).

The figure 2 shows the variations in the real and imaginary parts of the complex refractive index (n = n + ik) for all the PB with wavelength in the range 500-800nm, where 'n' and 'k' represents the refractive index and extinction coefficient of the PB films. Significant changes can be observed in the parameter n and k for PB with both higher and lower concentrations of PEG. It can be observed for the PB with 20 wt % PEG, the value of n~1.1 and k~0.05, are found to be almost constant in the range of 500-800nm, attributed to the higher extent of homogeneity of the PB.² These changes become more prominent for other PB with varying wt% of PEG.



Fig. 3. Variation of real and imaginary parts of complex dielectric function with wavelength for all PB (a) real part of complex dielectric function (ε '), (b) imaginary part of complex dielectric function (ε '').

The variation of real and imaginary parts of the complex dielectric function ($\varepsilon = \varepsilon' + i\varepsilon'$) are shown in the Fig. 3 for all the PB with wavelength in the visible range of 500 nm -800nm, where ε' and ε'' represents the real and the imaginary parts of the PNC films. In Figure 3, similar types of observations were observed as in figure 1 & 2. The value of $\varepsilon' \sim 1.2$ and $\varepsilon'' \sim 0.1$ are almost constant for the PB with PEG wt% as 0.20,² while there are large variations for other PB, making the 20 wt% PB suitable for optical applications.

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Distribution of Non-ionic Micelles Adsorption on Different Sized Silica Nanoparticles

Himanshi Singh^{1,2*} and Vinod K. Aswal^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094

*Corresponding author: himanshi@barc.gov.in

Abstract

The adsorption of non-ionic surfactant C12E10 micelles on two different sizes of anionic silica nanoparticles (16 and 27 nm) has been studied by small-angle neutron scattering. The number of adsorbed micelles per nanoparticle strongly depends on nanoparticle curvature and increases with nanoparticle size, as a result, their surface density increases but the fraction of adsorbed micelles decreases with increase in nanoparticle size. In a bimodal system of these nanoparticles, three possibilities of micelles adsorption are examined (i) preference for larger sized nanoparticles, (iii) preference for smaller sized nanoparticles and (iii) no preference for any size. The results support to the non-preferential adsorption of micelles on different sized nanoparticles.

Resonator-based, Functionalized Biosensor for Diagnostics of Dengue NS1 Antigen

Vivek Kale¹, Sweta Rath², Chetan Chavan³, K.G. Girija⁴ S.N. Kale^{*}

^{1,2,3}Department of Applied Physics, Defence Institute of Advanced Technology, Girinagar, Pune 411025, INDIA ⁴Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, INDIA

*Corresponding author: sangeetakale2004@gmail.com

Abstract

A non-invasive microwave-based complementary split-ring resonator (CSRR) sensor is proposed to detect the dengue NS1 antigen. The CSRR antenna structure is etched out of copper, on the ground plane of a microstrip line using a printed circuit board (PCB) technology on the FR4 substrate. The micro-strip transmission line coupled with CSRR acts as a sensor whose sensing mechanism is based on the interception of the electromagnetic field around the resonator, which leads to a shift in the resonance frequency. To detect dengue NS1 antigen, the sensor is functionalized with the antibody of NS1 using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) as the linker molecule. Upon immobilizing NS1 antibody on the CSRR structure, the sensor offers high sensitivity in the form of a change in the power of the signal due to antigen-antibody interaction. The sensor shows a power shift of ~24dB for 10 μ l of dengue NS1 antigen. A highly sensitive sensor is hence demonstrated.

Host-parasite coevolution: Role of spatial topography of fitness landscape on evolvability of hosts

Saumya Suvarna, Madhu Priya*, and Nishi Srivastava

Department of Physics, Birla Institute of Technology Mesra, Ranchi, 835215

*Corresponding author: madhupriya@bitmesra.ac.in

Abstract

We study a mathematical model which describes the host-parasite coevolution in a fluctuating environment by incorporating mutation, selection, and asexual reproduction. The role of spatial topography of the fitness landscape on the evolutionary dynamics of a finite population of hosts is investigated. We report the dependence of time required by the host population to attain the global maximum of the fitness landscape on the ratio of the global and local fitness peak heights for different host mutation rates and different degrees of virulence. We find a faster optimization of hosts' fitness and a reduced dependence of optimization time on the degree of parasitic infection in case of a higher disparity between the global and the local fitness peaks.

Introduction

Biological evolution is a complex phenomenon and can be mathematically understood as an optimization problem in many variables. Biological species evolve towards increasing their fitness, which is a measure of the species' reproductive success. The primary factors driving and shaping the evolutionary dynamics are selection, mutation, and reproduction [1]. Many species interact with each other, thereby affecting each other's evolutionary pathways, and such interactions have been characterized under a broad field, namely coevolution. One such ubiquitous phenomenon in nature is host-parasite coevolution. In such interactions, the parasite species reduces hosts' evolutionary advantage under a given environment, thereby reducing its fitness. The hosts initially provide a supportive environment to parasites which may later become hostile if parasites trigger an immune response in the hosts. Thus, the interactions between hosts and parasites adds a fluctuating component to each other's environment which has been considered a critical factor in driving the spatial and temporal diversity in nature [2, 3].

Priya et al. developed a mathematical model to study the evolutionary dynamics of hosts in the presence of parasites [4]. The model considers a finite population of hosts evolving in an otherwise stationary environment that gets a dynamic component to its overall fitness landscape due to the parasite population constantly evolving to infect the host population. The authors report that the parasites speed up the evolution of the host population towards the global fitness peak, thus facilitating a swifter response of the host population in case of an environmental shift. In the present work, we explore the mathematical model discussed above to study the effect of the static part of the hosts' fitness landscape, particularly the height of the fitness peaks on the evolution of hosts. In the next section, we have provided a brief discussion of the mathematical model used, followed by the section on results where we report the outcomes and the conclusions drawn.

Mathematical Model

The model obtains the coevolutionary dynamics of hosts and parasites in terms of two coupled differential equations as shown below [4],

$$\frac{\partial}{\partial t}m_{s}(x,t) = \tilde{f}_{s}(x,t)m_{s}(x,t) + \mu_{s}\frac{\partial^{2}}{\partial x^{2}}m_{s}(x,t) - m_{s}(x,t)\int_{-\infty}^{\infty}dy\,\tilde{f}_{s}(y,t)\,m_{s}(y,t), \qquad (1)$$

where S = H for hosts and S = P for parasites. The variable $m_S(x, t)$ represents the frequency of host/parasite population with a genotype x at time t. The variables $\tilde{f}_H = f(x) - \alpha f_H(x, t)$ is the effective fitness landscape under which the hosts evolve, where the static part of fitness landscape is assumed to be double Gaussian with a local peak at x_1 and a global peak at x_2 with widths σ_1 and σ_2 , respectively, $f(x) = A \exp \left[-\frac{(x-x_1)^2}{2}\right] + A \exp \left[-\frac{(x-x_2)^2}{2}\right]$ (2)

$$f(x) = A_1 exp \left[-\frac{(x-x_1)^2}{2\sigma_1^2} \right] + A_2 exp \left[-\frac{(x-x_2)^2}{2\sigma_2^2} \right]. (2)$$

The variable α is called the degree of virulence and is a measure of the strength of the parasitic infection to hosts. The effective fitness landscape of parasites $\tilde{f}_P = f_P(x, t)$. The functions f_H and f_P are the dynamic component of the fitness landscapes of the hosts and parasites, respectively, and are given by the relation, $f_S = c_S \int_{-\infty}^{\infty} exp[-\beta_S(x-y)^2]m_{S'}(y,t)dy$, where it is to be noted that $S \neq S'$ and S, S' = H, P. The parameters c_s includes the dimensionality of the fitness function and β_s is related to the range of genotypic interaction between the hosts and the parasites. The parameters μ_H and μ_p correspond to the host and the parasite mutation rates, respectively.

Results and Discussion

At time t = 0, the host population starts evolving according to its effective fitness landscape and reaches the local peak at $x = x_1$ in time t_1 . It continues to evolve further till it attains the global peak at $x = x_2$ at $t = \tau$, which is referred to as the optimization time. It is to be noted that for all the results presented here, the unit of time is taken as $1/(2.5A_1)$. Priya et al., in their work, demonstrated that in the presence of parasites, the host population reaches the global fitness maximum faster [4]. In the current work, we study the time required by the host population to attain the global maximum, i.e., τ as a function of global to local fitness peak ratio $\delta = A_2/A_1$.



Fig. 1(a). The dependence of time taken by the host population to reach the global peak as a function of peak height ratio δ for different host mutation rates. (b) The variation of optimization time τ with δ for different values of degree of virulence α .

In Fig. 1(a), we plot τ as a function of δ for different host mutation rates as shown. For all the cases studied here, μ_p is taken as 0.9 while the parameters σ_1, σ_2, c_s and β_s are all taken to be unity. It is observed that for a fixed mutation rate μ_H , the optimization time decreases as the ratio of the peak heights δ is increased. This can be attributed to the increase in

strength of drift (see Eq. (1)) towards the global maximum as the δ value increases. As the host mutation rates are increased, the host population attains the global maximum faster for a given δ as is evident from a decrease in τ with increase in μ_{μ} . The time evolution of host population is governed by Eq. (1). It is to be noted that the second term in the righthand-side (R.H.S.) of Eq. (1) represents the diffusion of host population in genotypic space which is much slower than the drift governed by the first term in the R.H.S. The last term does not contribute to the dynamics, rather it keeps the population constant at a given time. Thus, if we ignore the last two terms, the dynamics of the host population will satisfy $m_H(x,t) \propto exp[-\tilde{f}_H(x,t)t]$. We thus roughly estimate \tilde{f}_H by fitting the curves obtained in Fig. 1(a) with an exponential function and find it to be ≈ -1.7 .

We also investigate the dependence of τ on δ for different degrees of virulence α in Fig. 1(b). For a fixed α , we observe that the optimization time decreases with increase in δ . This is in agreement with Fig. 1(a). We also note that if α is increased for a fixed value of δ , τ decreases confirming the observations made in the previous work [4]. Upon comparing the plots with an exponential function ($\propto exp(-\tilde{f}_H t)$), we obtain the value of $\tilde{f}_{H}(x, t)$ approximately in the range -1.8 to -0.8 for α ranging from 0.05 to 0.25. At higher δ values, we observe a weaker dependence of optimization time on the host mutation rates or the degree of parasitic infection as compared to the lower δ values. However, the dependence of optimization time on μ_H is more prominent than its dependence on the degree of the parasitic infection at higher disparity of local and global fitness peaks. From our findings, we conclude that higher peaks in a fitness landscape not only increase the average fitness of a species but they also facilitate a faster evolution of the species which is crucial for the survival of the host species in a dynamic environment.

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Effects of L-Phenylalanine on a Model Phospholipid Membrane

Prashant Hitaishi and Sajal K. Ghosh*

Department of Physics, School of Natural Sciences, Shiv Nadar University, Gautam Buddha Nagar, Uttar Pradesh 201314, India

*Corresponding author: sajal.ghosh@snu.edu.in

Abstract

Biological cell membranes play a crucial role in controlling the physiological activities of various chemical components in a living organism. Despite of various roles that include causing diseases in humans, the effect of phenylalanine (Phe) on cellular membrane is still not clear. In this work, the physical and structural changes in a model cellular membrane in the presence of L-Phe have been investigated using surface pressure-area isotherms and X-ray reflectivity technique.

Introduction

Phenylalanine (Phe) is an amino acid that acts as the building block of proteins. It is found in various food sources and also supplied additionally through derived supplements. The physiological concentration of Phe in blood is 25-100 μ M. Various diseases have been reported due to increased concentration of it such as phenylketonuria (PKU), hyperphenylalaninemia and amyloidogenic disorder.

The effects of two enantiomers, L-Phe and D-Phe on membrane has been reported recently using a phospholipid vesicle as a model membrane [1]. The fluidity of the membrane was reported to increase with L-Phe concentration while the addition of an enantiomeric mixture of D-Phe and L-Phe increased the membrane rigidity. The D-Phe showed the ability to inhibit the effects of L-Phe on membrane hence, acted as a stabilizing agent. Using various microscopic techniques, fibrillar morphologies are observed in the presence of L-Phe that ruptures with the addition of D-Phe.

The 1, 2-dipalmitoyl-sn-glycero-3-phosphocholine is one of the important saturated phospholipids that is in general, used to model mammalian cell membrane. This lipid has been utilized here to mimic a cell membrane by forming a lipid layer at air-water interface and multilayers on a solid substrate. Then, the interaction of Phe has been monitored to conclude the effects of the molecule on the membrane.

Materials

Zwitterionic phospholipid 1, 2-dipalmitoyl-snglycero-3-phosphocholine (DPPC) was purchased from Avanti Polar Lipids in powder form. Lphenylalanine (L-Phe) and spectroscopic grade chloroform were purchased from Sigma Aldrich (USA). De-ionized (DI) (Milli-Q, Millipore) water with resistivity ~ 18 M Ω -cm and pH ~ 7.5 was used throughout the experiment. The silicon (100) wafers with one side polished surface was purchased from Waferpro.

Methodology

Surface pressure-area isotherms:

A Langmuir trough of size $56 \times 15 \times 0.2$ cm³ (Apex, India) with two symmetric Teflon barriers and a Wilhelmy balance has been used for experiments on a lipid monolayer formed at air-water interface. To study the physical and thermodynamic properties of monolayers, surface pressure-area isotherms were recorded at temperature of 24°C. The powder DPPC lipid was dissolved in chloroform to get a concentration of 0.5 mg/ml. L-Phe was dissolved in DI water to attain 0.1 and 5 mM solutions which are used as sub-phase to measure isotherms.

X-ray reflectivity (XRR):

The supported lipid multilayer samples for XRR were prepared on Si substrate using well established dropcast method. Aqueous solution of L-Phe was mixed in chloroform solution of DPPC to get final sample with 0, 5, 10, 15 and 20 molar percent (mol%) of L-Phe in DPPC.

Results and Discussions

The surface pressure-area isotherms of monolayer of DPPC formed at the air-water interface is shown in Fig. 1. The high surface area per molecule describes the liquid extended (LE) phase with a week inter molecular interaction. On compressing the monolayer, the lipid molecules form a compact film of lipid condensed (LC) phase with a plateau region in between the LE and LC phases. In presence of 0.1 mM L-Phe, there is no significant change in lift-of-area, however, for 5 mM solution it increased from ~ 117 to 128 Å² causing an expansion of the lipid film.



Fig. 1. Surface pressure-area isotherm of DPPC lipid monolayer formed at air-water interface. Inset exhibits the in-plane elasticity of respective isotherms.

The in-plane elasticity of the lipid film as shown in inset of Fig.1 can be evaluated using the relation, $E = -A \left(\frac{\partial \pi}{\partial A}\right)_T$ where A is the mean molecular area and π is the lateral pressure at a given temperature (T) [2]. The plateau signifying the coexistence region shifts towards the higher pressure and becomes less prominent at high concentration of L-Phe. This effect can be clearly observed as broadening of dip in the elasticity curve corresponding to the coexistence region in the pressure range of 10 to 20 mN/m. The overall elasticity of the LC phase within the pressure range of ~20 to 40 mN/m decreases systematically. This results clearly explain a membrane with higher fluidity and flexibility. Such a fluid membrane in presence of Phe can increase the membrane permeability.



Fig. 2. X-ray reflectivity data of DPPC multilayers in presence of L-Phe at 85% relative humidity (RH). Inset exhibits the d-spacing of lamellar phase.

X-ray reflectivity experiments on a supported lipid multilayer system is a well-established technique to explore the structural information of a model cellular membrane. Because of amphiphilic nature of lipids, they form multiple bilayers on a hydrophilic surface where the bilayers are separated by a thin layer of water in between them. Such a one dimensional arrangement of lipid bilayers form a lamellar phase. The equidistant Bragg peaks from such a lamellar phase of DPPC lipids corresponding to a gel phase have been observed to shift to a lower q_z with the addition of L-Phe in the membrane. It is indicated by a line drawn for 3rd order Bragg peaks in Fig. 2. The inter bilayer repeat distance which is called the '*d-spacing*' increases from 61.83 ± 0.43 to $64.40 \pm$ 0.47 Å for a pure DPPC system to the system with 20 mol% of added L-Phe. Due to presence of Phe in lipid membrane, either the chain of lipids can be flexible due to random conformation or can be straightened due to decrease in tilt angle. However, a random chain leads to the reduction in d-spacing, ultimately providing lower *d-spacing* that is not the case here. Therefore, the second possibility prevails to increase the *d-spacing* by increasing the bilayer thickness. Such a structure would make the bilayer more flexible compared to the compact chain with a tilt in the chain. This result is in consistent with the isotherm measurements that indicated a membrane with higher flexibility and area per molecule.

Conclusions

The present study has established that the Phe molecule intercalates in the lipid membrane and increases the flexibility of the membrane. It ultimately expands the area per molecule which may lead to higher intermolecular separation to form a more permeable cellular membrane. This could be the causes of many diseases in humans.

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Experimental Investigation of Phases Of Different Lattice Structures Of Surfactants-DNA Complexes

Amit Kumar Majhi¹, VA Raghunathan²

¹Gour Mohan Sachin Mandal Mahavidyalaya, Bireshwarpur, West Bengal, India, 743345, ²Soft Condensed Matter Physics, Raman research Institute, Bangalore, India, 560080

*Corresponding author: kumaramitmajhi@gmail.com

Abstract

Small angle X-ray scattering (SAXS) technique reveals the structures of surfactants-DNA complexes, which acquires hexagonal phase in presence DTAB and MTAB in aqueous media for both relative concentration ratios, $([MTAB] + [DTAB])/[DNA] = \rho$, 1 and 5. Structures undergo a phase transition due to an influence of NaCl salt. The structures enter a super hexagonal phase in presence of a large amount of DTAB (wt %) in 300 mM NaCl solutions for ρ 1. The structures gradually obtain a square phase for increasing the amount of DTAB (wt %) in 300 mM NaCl solutions with ρ 5.

Introduction

Formation of surfactant-DNA complexes and its precipitation in aqueous media has many biological applications [1]. Up-taking of DNA complexes through cellular membranes, which can easily be commenced [2] in the processes of forming giant complexes as it enhances penetration ability of nucleic acids into cell membranes, is obviously known as gene delivery [3]. There are studies which confirmed that formation of DNA and cationic surfactant complexes depends on the length of surfactant alkyl chains. The surfactant-DNA complexes are mostly insoluble in aqueous media, this nature of the complexes leads to aggregation and precipitation of the complexes in media [4]. These precipitates have a range of internal structures such as hexagon or square or etc, which are being divulged by small-angle X-ray scattering (SAXS) [5]. In this article, we are reporting experimental investigation of phase behaviour for mixtures of surfactants, which are MTAB and DTAB, and DNA complexes in aqueous media and the salt effects on the phases of the complexes.

Experiments:

Materials and Methods

Dodecyltrimethylammonium bromide (DTAB), myristyltrimethylammonium bromide (MTAB), NaCl and Calf thymus DNA were procured from SigmaAldrich (India) to study phase behaviour in aqueous or NaCl media for various ρ . Samples were prepared in the following ways.



Fig. 1. Small angle x-ray scattering (SAXS) profiles of self-assembled complex structures of DNA and surfactants (DTAB and MTAB) in aqueous media for ρ 1 (a) and ρ 5 (b).

DTAB and MTAB were weighted according to requirement (wt %) maintaining ρ 1 or 5. The individual surfactants were dissolved in ethanol and then they were mixed properly in eppendorf tubes. The tubes were kept inside of a desiccator and its vacuum was monitored for a few days until ethanol alcohol evaporated completely. Millipore water or NaCl solutions were added to the mixtures and then kept in an conventional oven at 40 °C for two days. DTAB and MTAB solutions were cooled down to room temperature before adding 5 mg DNA to them.

SAXS experiments:

Results and Discussion

The relative peak positions in SAXS data for both values of ρ 1 and 5 in aqueous media confirm that the complex structures of surfactants-DNA complexes have hexagonal phases for small amount of DTAB but for large amount of MTAB (wt %) in aqueous media though higher order peaks are absent in

patterns (Fig. 1a). Comparison between Fig. 1a and 1b shows there are higher order peaks with relative



Fig. 2. SAXS patterns of complex structures of DNA and surfactants (DTAB and MTAB) in 300 mM NaCl media. The hexagonal lattice structure of the surfactants-DNA complexes turn into super hexagonal lattice for ρ 1 (a) but for ρ 5, lattice structures change to square lattice (b).

positions 1: $\sqrt{3}$:2 for lower values of DTAB (10 % and 30 %) and only for ρ 5. The first order peak gets broadened and higher order peaks disappear in the SAXS patterns with increasing concentrations of amount DTAB (wt %) and the structures enter into square phase with broad first order and second order peaks for both ρ 1 and 5 in the aqueous media. Salt effects on the surfactants-DNA structures have been carried out with 300 mM NaCl solutions for both o 1 and 5. Fig. 2a has conspicuous evidence that surfactants-DNA complexes acquire hexagonal phases with positions 1: $\sqrt{3}$:2. In the case for $\rho = 1$, the hexagonal phase is only possible for lower amounts of DTAB such as 33 %, 55 % and 66 % and then the structures enter into super hexagonal lattice phase with comparatively high lattice constant (Table 1) for high amounts of DTAB such as 75 %, 80 %, 90 % and 98 %. The super hexagonal profiles have higher order peaks with relative peak positions: $\sqrt{3}:2:\sqrt{7}:3$, however, the first order peak is absent in the X-ray pattern (Fig. 5a) [6].

Table 1. Lattice constants for structures of surfactants (DTAB and MTAB) and DNA complexes in 300 mM NaCl solution with $\rho = 1$.

% of DTAB	Lattice constant	Phase
	(nm)	
50	5.471	Hexagon
75	8.972	Super hexagon
90	8.971	Super hexagon

The structures attain square phase with comparatively small lattice constants for high amounts of DTAB such as 70 % and 90 % in solutions [6]. The SAXS profiles for square lattices have higher order peaks with relative peaks; the first and second order peaks become broad for 50 % of DTAB and phase is also not well-defined (Fig. 5b). Theoretical calculations of energy profiles for different complexed structures are carried out in Madhukar et al [7].

Conclusion

The lattice structures of surfactants-DNA complexes undergo phase transition for increasing amount of DTAB (wt %) but decreasing amount of MTAB (%) in the aqueous in presence of salt for both ρ 1 and 5. The structures acquire hexagonal phase in presence for small amounts of DTAB but large amounts of MTAB (wt %) in aqueous media for both ratios, ρ 1 and 5. At ρ 1, structures enter into super hexagonal phase in presence of 300 mM NaCl with increasing amount of DTAB (wt %). However, at p 5, structures gradually move to square phase with increasing amounts of DTAB (wt %). The square phase has more stability than other phases, and is more favourable for the small sized micelles. The hexagonal phase shows stability over a wide range of the micellar radius (big to small). Though hexagon of second type has capability of intaking more DNA molecules into itself, it also has to encounter more repulsion to stabilise the structures. Both phases have almost equivalent energy for bigger micelles, however, the hexagon of the second type becomes unstable for small micelles.

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Water Desorption Kinetics Of Poly(vinyl alcohol) Thin Films

Sonam Zangpo Bhutia, Shakshi Gupta, and Dillip K. Satapathy

Soft Materials Laboratory, Department of Physics, IIT Madras, Chennai, 600036, India

*szangpokaleon@gmail.com

Abstract

The water desorption kinetics in one-dimensional confined PVA thin films has been studied using temperature-dependent spectroscopic ellipsometry (SE) and in bulk PVA through thermogravimetric analysis (TGA). Two characteristic temperatures, T_{C1} and T_{C2} are identified that distinguish three different processes of desorption of unbound free water, thermal expansion, and desorption of tightly bound water that the film undergoes during its first heating. Interestingly, for the thinner film of 39 nm thickness, the magnitude of such thermal expansion becomes even more prominent in comparison to the 72 nm film. Further, through TGA, the presence of different phases of water desorption (three regions) has been confirmed and their corresponding activation energies are estimated.

Introduction

Poly(vinyl alcohol) (PVA) is a synthetic watersoluble polymer that has been extensively studied due to the presence of a high concentration of hydrophilic hydroxyl (-OH) groups resulting in its strong affinity towards water. So, along with the water sorption kinetics, the water desorption from PVA has also been of significant interest. The presence of three types of water has been revealed via calorimetric and gravimetric experiments[1]. These include the nonfreezable bound water that binds strongly with the polar or ionic sites of the polymer chain and the two freezable water, namely, the structured or bound water and the bulk-free water. The freezable bound water is affected by the polymer chain interactions, however, the freezable bulk-free water seems to be unbound and unaffected by the polymer matrix.

Here, we have reported water desorption kinetics in PVA thin films confined in one dimension using temperature-dependent SE. Despite the desorption of a large amount of water, PVA films undergo thermal expansion in the temperature range from T_{C1} to T_{C2} and it becomes even more significant for a thinner film. Along with this and the weight loss for bulk PVA obtained through TGA, has enabled us to understand the water desorption kinetics of two kinds of water with different activation energies.

Experiments

PVA was dissolved in deionized (DI) water at 60 °C for 6 hours and cooled down to room temperature. Different concentrations of PVA solutions (wt.%) were filtered and spin-coated onto piranha cleaned silicon substrates (1x1cm) to produce PVA thin films with various thicknesses. These films were stored in a vacuum desiccator.

Spectroscopic ellipsometer integrated with a heat cell was used to perform the temperature-dependent

measurements. The Ψ and Δ , which represent the amplitude ratio and the phase difference, were recorded in-situ while heating and cooling the PVA thin films at different temperatures varying from 30 to 250 °C. A constant heating and cooling rate at 2 °C/min, holding time of 3 min and temperature interval of 4 °C were maintained for each film. The ellipsometry raw data were fitted with a three-layer Cauchy model of PVA/SiO₂(2 nm)/Si substrate, to determine film thickness (d) variation as a function of temperature. Further, thermogravimetric analysis at a heating rate of 10 °C/min was used to determine the weight loss as a function of temperature for bulk PVA.

Results and Discussion

Temperature-dependent SE measurements for PVA films of 72 nm and 39 nm have been shown in Fig. 1. As the film is heated, the thickness is found to decrease initially, followed by a slight increase aided by thermal expansion before the final rapid reduction. Three different slopes for a 72 nm film, intersecting at two characteristic temperatures, $T_{C1} = 46$ °C and $T_{C2} = 194$ °C have been shown to indicate the water desorption, thermal expansion, and again the final water desorption processes. Such thermal expansion of the polymer film indicated by the increase in thickness becomes even more prominent for a relatively thinner 39 nm film with no significant changes in the characteristic temperatures, T_{C1} and T_{C2} .

Further, the TGA measurement was conducted on bulk PVA and Fig. 2 reveals the presence of three water desorption processes indicated by regions I, II, and III. The activation energy values for different kinds of water are evaluated to be 81 kJ/mol, 38 kJ/mol, and 152 kJ/mol, respectively. These values were evaluated following a well-established method previously reported for the chitosan water system[2].



Fig. 1. The ratio of change in the film thickness (Δd) to its initial thickness (d_0) vs. temperature plot for two PVA films. The solid red lines are linear fits to data and the two dotted vertical lines are indicating the characteristic temperatures (T_{C1} and T_{C2}).

An earlier report on pure PVA membrane describes the existence of water in different states[3]. So, regions I and II can be attributed to the desorption of unbound free water, i.e. the freezable bulk-free water. Water desorption observed in region III is associated with the water molecules that bind with the hydrophilic groups (-OH) of the PVA chains, i.e., the freezable bound water with high activation energy, 152 kJ/mol.



Fig. 2. Weight loss (%) vs. temperature during the first heating of the bulk PVA. The three regions (I, II, and III) corresponding to different slopes are indicated by different colors.

So comparing with the SE measurements shown in Fig. 1, we can attribute the initial thickness reduction to the unbound free water desorption. This desorption of free water might still be continuing between T_{C1} and T_{C2} . However, the net increase in thickness of the film between T_{C1} and T_{C2} suggests that the increase in thickness due to thermal expansion of the polymer is

higher than the decrease in thickness due to desorption of water. Finally, after T_{C2} , the desorption of tightly bound water initiates corresponding to region III.

Further to investigate the water desorption kinetics of the 72 nm film, after initial heating up to 250 °C, was cooled down to 30 °C without breaking the vacuum and then reheated up to 250 °C. During the second heating, the film thickness decreases slightly followed by a significant increase in between T_{C1} and T_{C2} (approx.). This indicated that the unbound free water has been completely desorbed during the first heating and the thermal expansion becomes even more significant. However, above T_{C2} , the bound water continues to desorb even during the second heating.

Polymer films undergo a reduction in thickness due to water desorption and enhancement due to thermal expansion during heating. The thermal expansion dominates for thinner films. This could be due to the comparatively low content of the unbound free water molecules in thinner films. When a similar study was performed for a 98 nm film, the magnitude of thermal expansion almost overlaps with the 72 nm film.

Conclusions

Our study revealed that upon heating, different kinds of water desorb from a PVA film at disparate rates. Two characteristic temperatures, T_{C1} and T_{C2} , distinguishes the process of desorption, thermal expansion, and further desorption, during the first heating of PVA films. The thermal expansion is found to be enhanced upon reduction of film thickness without any significant changes in T_{C1} and T_{C2} . The presence of various kinds of water and their activation energies are estimated from TGA measurements. Based on their activation energies, regions, I and II have been attributed to the unbound free water desorption and region III to the bound water desorption. For the 72 nm film, the thermal expansion between T_{C1} and T_{C2} becomes even more significant during the second heating.

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CO₂ Adsorption-Desorption Kinetics on Silica-Polyethyleneimine Microspheres obtained through Evaporation Induced Assembly

Swati Mehta^{1,2}, Jitendra Bahadur^{1,2*}, and Debasis Sen^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, India

> *Corresponding author: jbahadur@barc.gov.in Abstract

In the current scenario of global warming, mitigation of CO_2 remains a challenge to tackle with. However, amine-based solid adsorbents have provided a potential way to surmount this facet. In order to revamp the performance and design of CO_2 capture reactors study of adsorption/desorption kinetics is crucial. Such kinetics on microspheres with 20% amine loading is studied using thermo-gravimetric analysis at different temperatures under CO_2 flow. The kinetics of adsorption follows Avirami model, whereas desorption kinetics resembles to dose-response model for low adsorption temperatures and approaches exponential decay model at higher temperatures. Higher temperature results in homogeneous adsorption due to sufficient kinetic energy of CO_2 molecules and better accessibility of amine sites, which sequentially increases the sorption capacity.

INTRODUCTION

A significant attention has been drawn towards CO₂ capture as increasing levels of anthropogenic CO₂ emissions have precipitated serious environmental concerns. A wide range of technologies to capture CO₂ has been proposed¹. However, the current-state-of-art involves amine scrubbing, which suffers from several drawbacks, for instance, energyintensive process, corrosiveness of the utilized tools, volatilization and degradation of amines, disposal of the spent scrubber to mention a few. Overcoming these drawbacks engages the use of solid adsorbents where PEI based solid nano-adsorbents have acquired substantial attention due to their high selectivity for CO₂, tolerance to water vapor, lower regeneration heat requirement, etc². Physical impregnation and grafting of amine functional groups onto a substrate are the two avenues employed to prepare amine-functionalized nano-adsorbents. Howbeit, the CO₂ uptake and adsorption rate in both the approaches depends upon textural properties of the silica support and accessibility of the amine sites. In addition, the loading of PEI in the pores of silica matrix leads to the reduction in porosity and surface area which in turn affects the CO₂ capture capacity. Therefore, apart from the complex synthesis, existing solid adsorbents encounters scalability issues, inaccessibility of adsorption sites at high loading, aggregation of amine content on the external surface of support which hinders their practical applications. Consequently, a new approach of Evaporation Induced Assembly (EIA) of multi-component colloids has been utilized to obtain tuneable organic-inorganic hybrid microspheres.

However, in addition to high selectivity and CO_2 sorption capacity, the desired sorbents should have high CO_2 adsorption/desorption rate. In order to optimize the performance of the sorbents, understanding adsorption and desorption kinetics is very utilitarian as it explicate the dynamic behavior of adsorbents.

The present work investigates the adsorption/desorption kinetics of the silica-PEI microspheres obtained using bottom-up approach of EIA³ for 20% PEI loading(referred

as HS40-PEI(20)). The CO₂ uptake measurements have been carried out using thermo-gravimetric analysis under flow (15% CO₂ balanced by N_2).

RESULTS AND DISCUSSION



Fig. 1: FESEM images of HS40-PEI (20) with varying magnifications.

Electron microscopy images of HS40-PEI (20) are shown in Fig.1, where the formation of the spherical grains is evident. High resolution image depicts the cluster formation, giving rise to the interstitial pores on the surface of silica-PEI microspheres.

CO2 CAPTURE & KINETICS STUDIES

It is evident from Fig.2, nearly 80% of the capture is observed within a minute, where capture is done using TG flow. Fast desorption of the CO_2 illustrates the liberation of nearly 85% in 5 min which is quite good for regeneration of the microspheres and ascribes to the significant porosity and surface area of the silica microspheres despite the PEI loading.



Fig.2.CO₂ capture capacity of HS40-PEI (20) using TG flow at different adsorption temperatures.

Detailed analysis of the CO_2 adsorption/desorption kinetics of PEI-silica microspheres is desirable to determine its performance and to understand the adsorption and desorption mechanism. To model the adsorption-desorption kinetics Langmuir model, pseudo-first-order model, pseudo-second-order model, Avirami's model⁴ can be used. However, the fractional-order Avirami's kinetic model is found to be best suited to model the adsorption process of CO_2 onto amine-based adsorbents due to the involvement of occurrence of multiple adsorption pathways including competitive physisorption and chemisorption. The integrated form of Avirami model can be described as:

$$q_t = q_e (1 - e^{-(k_a t)^n})$$
(a)

 q_e and q_t are the capture capacity at equilibrium and at time t, respectively. Here, k_a is Avirami kinetic constant and n is Avirami exponent.

Avirami exponent provides an insight into the mechanism of the adsorption process, which involves nucleation and growth of the product during the reaction of CO₂ at the active sites of the amine⁴. The fit of the model to the data is shown in Fig. 3(a). n, is found ~1.5 for 30 °C and 50 °C, whereas n value decreases to 0.9 at 75 °C and 90 °C.



Fig. 3.(a) Avirami model for CO_2 adsorption, (b) dose-response model for desorption of HS40-PEI (20) microspheres at 30 °C and 50 °C and exponential model for 75 °C and 90 °C.

Thus, the adsorption of the CO_2 remains inhomogeneous due to the low kinetic energy of CO_2 and poor accessibility of active amine site at low temperature. n is found to be nearly 1.0 at higher adsorption temperature due to sufficient kinetic energy of the CO_2 and better accessibility of the active amine sites resulting in homogenous adsorption.

The value of enthalpy and entropy is calculated using Erying equation, where $\Delta H^{\ddagger} = -23.74 \text{ kJ} \text{ mol}^{-1}$ and $\Delta S^{\ddagger} = -335.1 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$. Negative enthalpy of activation implies the tight transition state with low potential energy, which can be achieved via a short-lived intermediate. The plausibility of the formation of intermediate during the reaction between amines and CO₂ is also confirmed by the Gibb's free energy, $\Delta G = 29 \text{ kcal/mol}$. Hence, this corroborates with the formation of the zwitterions being a transition state, during the reaction mechanism of amines with CO₂.

Desorption process involves the decomposition of the reaction species and the diffusion of CO_2 through the barrier induced by the reaction species. Therefore, the

nature of the adsorption and growth of the reaction species also dictates the nature of desorption. Low adsorption temperature desorption profiles are fitted by dose-response whereas higher adsorption temperature, model exponentially decaying model was used. The dose-response model can be described as $q_t = A_1 + (A_2 - A_1)/(1 + 10^{(\log t_0 - t)^p})$ (b)

Here, A_2 is the top saturation plateau and A_1 is the bottom saturation plateau. p is the Hill constant.

Whereas, an exponential decay model can be described as: $q_t = A_0 e^{-k_d t}$ (c)

 Table1. Parameters obtained from fitting for desorption

 profiles of HS40-PEI(20) microspheres

Ads. Temp (C)	(A2-A1) (mmol/g)	Hill const. p
30	1.29	-0.17
50	1.47	-0.19

As expected, the span (A_2-A_1) is more for higher adsorption temperature. The reduction in Hill constant depicts fast desorption kinetics. For the higher adsorption temperature, exponential decay model fits the data as shown in Fig. 3(b) and decay constant increases with the increase in temperature.**CONCLUSIONS**

In this work, silica-PEI microspheres for 20% PEI loading is used to study adsorption/desorption kinetics using the thermo-gravimetric flow method. A novel and facile approach of Evaporation Induced Assembly is utilized to obtain silica-PEI microspheres. The adsorption of CO2 on HS40-PEI(20) is successfully described by Avirami model. Systematic transition from inhomogeneous adsorption to homogeneous adsorption has been observed with the increase in the temperature as the accessibility of amines increases. Negative enthalpy substantiates the formation of a shot-lived intermediate during the reaction between CO₂ and amines. Dose-response model is used to study the desorption kinetics at lower adsorption temperature, exponential decay as the adsorption approaches temperature increased. Studying of desorption kinetics reveals desorption to be rapid.

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Recrystallization Of Poly(vinylidene fluoride) Membrane: Enhancement In The Spherulite Morphology

Shakshi Gupta, G Suresh and Dillip K. Satapathy

Soft Materials Laboratory, Department of Physics, IIT Madras, 600 036-Chennai, India

*shakshi.phy@gmail.com

Abstract

We report the temperature-dependent spherulitic growth and microstructural evolution of the non-crystallized and crystallized Poly (vinylidene fluoride) (PVDF) membranes. The recrystallization of the α -phase PVDF membrane leads to the formation of prominent spherulites and its reversibility is confirmed using *in-situ* temperature-dependent x-ray diffraction. Temperature-dependent *in-situ* optical microscopy revealed that the nucleation and growth of spherulites start at a higher temperature for α -PVDF and results in spherulites of much larger size during the recrystallization process.

Introduction

Poly(vinylidene fluoride) (PVDF) is a versatile polymer with various properties such as pyroelectric, ferroelectric, and piezoelectric and is a desirable candidate from both scientific research and industrial aspects. The flexible, biocompatible PVDF has a fast and dynamic response and can be used for touch sensors, infrared detectors, and thermal imaging devices [1-3]. Most of its characteristics, including the mechanical property, depend on its polymorphic phase composition, which can be tuned by different processing routes [6]. Extensive research is being conducted to understand the crystallization kinetics of PVDF, the correlation between the phase behavior and intrinsic morphology. PVDF crystallization is reported to be temperature-dependent, with an average Avrami exponent of 2.5, indicating its spherulitic growth followed by heterogeneous nucleation [4]. An increase in crystallization temperature is also found to influence its half crystallization time [5]. Silva et al. [6] studied the isothermal crystallization kinetics of PVDF membranes at different crystallization temperatures and revealed both alpha and gamma phase **PVDF** formation. In this work, we have investigated the crystallization kinetics and the resulting morphology of the α -phase PVDF membrane while cooling down from its melt state at 210 °C at a fixed cooling rate. It is found that recrystallization significantly influences the growth kinetics and the morphology of the spherulites and also improves the mechanical property.

Experiments

PVDF of average molecular weight 534000 g/mol and N,N-dimethylformamide (DMF) of ACS reagent grade are used as received from Sigma-Aldrich India.

A PVDF membrane (uncrystallized) and in α -phase PVDF are synthesized from a standard solution of 10 wt% in a miscible organic solvent (acetone + DMF in a ratio of 1:1). The PVDF membrane is synthesized by drop-casting the PVDF solution on a highly cleaned glass substrate. In contrast, the α -phase PVDF membrane is synthesized by instantly transferring the drop-casted PVDF membrane into an oven maintained at 210 °C for 20 minutes. Subsequently, the membrane was cooled down to room temperature via natural cooling. The formation of α -phase of the thermally treated membrane is confirmed by x-ray diffraction and polarized optical microscopy images. The in-situ crystallization as a function of controlled heating and cooling rates is studied using the Linkam hot stage integrated with a polarized optical microscope. The heating is carried out at a relatively faster rate of 10 °C/min while continuous cooling is carried out at a rate of 1 °C/min.

Results Discussion and The XRD profiles of α -phase PVDF membrane and during the recrystallization process are measured insitu by heating the membrane up to the melting temperature and subsequent cooling to room temperature and are shown in Fig. 1. The reversibility of the α -phase of PVDF during the recrystallization is confirmed from the XRD measurements. Further, a detailed study using polarized optical microscopy is carried out to understand the effect of recrystallization on the growth kinetics and overall morphological changes of the crystalline domains. Fig. 2(a) and (b) show the polarized optical images measured at different temperatures during cooling of the PVDF membrane and α-phase **PVDF** membrane. respectively.



Fig. 1. XRD profiles showing the α -phase evolution during recrystallization of α -phase PVDF membrane. The vertical dotted lines indicate the peak position for α -phase PVDF.

To eliminate the influence of any sample preparationinduced residual stresses, each sample is held for about 15 minutes at a temperature 210°C, far beyond its melting temperature. It is observed that, in the case of PVDF membranes, the nucleation of spherulites is initiated at lower temperatures with a relatively faster growth rate. The rapid growth rate results in a higher number of smaller size spherulites. On the other hand, during recrystallization of a-phase PVDF membrane, the nucleation started at a higher temperature with a reduced growth rate resulting in a smaller number of spherulites with enormous size. For the recrystallization of α -phase PVDF, the size of spherulites is found to be about four times larger than in the other case. We conjecture that the relatively slow growth rate of spherulites observed for the α phase of PVDF is primarily responsible for their larger size.

Conclusions

The growth kinetics and morphology of spherulites during the recrystallization process are investigated for a PVDF membrane using temperature-dependent XRD and polarized optical microscopy. XRD measurement unambiguously confirms the reversible nature of α -phase albeit with a different morphology. The temperature-dependent polarized microscopy measurement found that the morphology of spherulites during the recrystallization of the PVDF can be significantly enhanced by tuning the preparation condition. Recrystallization of PVDF membranes is a simple and promising method for obtaining α -phase PVDF membranes with enhanced spherulitic morphology.



Fig. 2. Temperature-dependent Polarized microscopy images of (a) PVDF membrane and (b) α -phase PVDF membrane during their in-situ crystallization while cooling down from their melt state with a constant cooling rate of 1°C/min.

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Water Vapor Triggered Rapid Actuation of Cotton Films

Aathira Murali*¹, P B Sunil Kumar¹ and Dillip K. Satapathy ²

¹Department of Physics, Indian Institute of Technology Palakkad, Kerala 678557, India, ²Soft Materials Laboratory, Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India

*Corresponding author: 221704001@smail.iitpkd.ac.in

Abstract

Stimuli-responsive soft actuators are gaining much research attention in recent years and remain a rapidly growing field with many applications. Here, we report the fully reversible and repeatable actuation characteristics of free-standing cotton films upon exposure to water vapor. Cotton has added advantage of being biopolymers that are biodegradable and sustainable. A minuscule quantity of water vapor is sufficient to generate significant macroscopic responses. The differential swelling-induced anisotropic strain generated across the thickness of the cotton film is the driving force responsible for the observed actuation characteristics.

Introduction

The stimuli-responsive materials show some visible change of form or shape upon exposure to specific stimuli. They constitute an excellent set of smart soft materials sought after for potential applications in emerging fields like programmable origami, soft sensors, soft robotics, and so on [1,2]. The triggers that could generate a macroscopic response can be the temperature, pH, light, electric or magnetic field, solvents, solvent vapor, etc. In this work, we report the water vapor responsiveness of a polymer film prepared from naturally available cotton, which is also biocompatible.

The vapor responsive systems have the inherent advantage of realizing rapid shape alterations without direct physical contact with the film. Since the actuation depends on the flux of external stimuli, the vapor concentration or the evaporation rate of a solvent can be used as the key control parameters to tune the response. Figure 1 shows a schematic for vapor responsive free-standing cotton film. It is reasonably well understood that the responsive systems must have some inhomogeneity either within the structure of the film or in the external trigger to show the actuation characteristics [3,4,5]. In our system, the cotton film is homogeneous, i.e., the composition and structure remain the same across the film thickness, and the stimuli are provided from only the bottom side of the film, which generates the required inhomogeneity of stimuli concentration.



Fig. 1. A schematic showing the shape transformation of vapor responsive free-standing film.

Material and Fabrication

The organic and inorganic dirt was removed from the cotton wools by immersing them in soap solution for about 30 minutes, followed by thorough rinsing with distilled water. The cleaned cotton wools were dried in a hot oven maintained at 80°C for about 40 minutes. Then a homogeneous cotton solution (1% w/v) was prepared by dissolving cotton fibers in Trifluoroacetic acid (TFA). For dissolving the fiber, the solution was continuously stirred using a magnetic stirrer for about 30 hours at room temperature (30°C). Next, the cotton solution was drop cast over a clean rectangular plastic sheet and dry under ambient conditions. The drying process was completed after about 1 hour, and the freestanding films were peeled off carefully.

Actuation Characteristics Measurement

A stationary platform for clamping free-standing film in a cantilever geometry (see Figure 1) and a computer controllable mobile stage for providing stimuli was set up to analyse the actuation characteristics. The videos were captured using a CCD camera connected to the PC. The videos recorded were later processed and analysed using the "Tracker" [6] software to obtain actuation kinetics. Here, we quantify the actuation using two-time scales, the response and relaxation time, which can be obtained from the measured temporal profiles. They are defined as the time taken to reach the maximum actuated position starting from the exposure to the stimuli and the time required to return to the initial position after turning the triggers off, respectively.

Result and Discussion

The fastest response obtained for a cotton film is obtained for a 5μ m thick film having an aspect ratio 2:1 (the size is length 10 mm and breadth 5 mm). The

snapshots recorded during the one actuation cycle with time labels and the measured bending angle as a function of exposure time are shown in Figure 2 (a) and (b) respectively. When the bottom surface of the film is exposed to water vapor, the film responds almost instantly and bends upwards, and attains a maximum actuated position corresponding to a bending angle of ~165° within about 0.13s (defined as the response time). The films continue to retain the state with the maximum bending angle until the vapor source is retrieved. After removing the stimuli, the film moves downward its initial position and attains an equilibrium position in about 0.70s (defined as the relaxation time).



Fig. 2. (a) Snapshots and (b) evolution of bending angle as a function of vapor exposure time the actuation of a 5μ m thick cotton free-standing film with dimension 10mm x 5mm.

The observed actuation phenomenon can be explained by taking into account the stresses generated by the differential swelling between the exposed and unexposed surfaces of the film. When the bottom side is exposed to water vapor, the bottom surface swells more by absorbing water than the top surface. For a film, the stretching energy is proportional to the initial thickness (t), whereas the bending energy varies as t^3 [7]. Hence, as the film thickness reduces to a few microns, the bending/curving deformation becomes energetically favourable. The actuation can be characterized by a purely geometric perspective using the Equation a) [8],

$$C \sim \frac{1}{h} (\varepsilon_e - \varepsilon_u)$$
 a)

where C is the curvature, h is the initial thickness of the film, ε_e and ε_u are the strains due to trigger-film interactions at the exposed and unexposed surfaces. Hence, any change that can impact ε_e and ε_u unequally may drive the actuator.

To analyse the thickness dependency on actuation times, we perform experiments for samples of the same aspect ratio but different thicknesses. The response time and relaxation time observed for different thicknesses are listed in Table. 1. We can see a distinct trend of increase in the response and relaxation time with the increase in film thickness. It is clear from our measurements that fast actuators can be realized solely by reducing the thickness of the film, but it may alter the mechanical stability of the film concurrently. Therefore, further optimization of the film's actuation characteristics and mechanical properties is required for practical usage.

Table 1. Actuation times with varying thickness of film

Thickness of film	Response time	Relaxation time
(µm)	(s)	(s)
5	0.13	0.70
10	1.61	1.84
15	6.65	14.26
22	7.55	17.01

Conclusions

We report the actuation characteristics of a novel biopolymer (cotton) based water vapor responsive smart material. The underlying mechanism of the macroscopic shape alteration is the anisotropic volume change arising upon the exposure to the stimuli within the material. The free-standing cotton film with thickness 5μ m exhibited a very rapid actuation with sub-second actuation time. The thickness dependency of response and relaxation times of cotton films were also investigated in detail.

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Phase Transitions In An Implicit Solvent Minimal Model Of Lipids: Role Of Head-Tail Size Ratio

Biplab Bawali¹, Jayashree Saha¹, and Alokmay Datta²

¹Department of Physics, University of Calcutta, 92 Acharya Prafulla Chandra Ray Road, Kolkata 700 009 ²Materials Characterization and Instrumentation Division, CSIR-Central Glass and Ceramic Research Institute, 196 Raja Subodh Chandra Mullick Road, Kolkata 700 032

*Corresponding author: <u>*fellow1@cgcri.res.in</u>; <u>alokmay.datta@saha.ac.in</u>; <u>alokmaydatta@gmail.com</u>

Abstract

We present Monte Carlo simulations under constant NVT conditions on a minimal 'three beads' coarse grained implicit solvent model of lipid molecules, with the hydrophilic head represented by one bead and the hydrophobic tail represented by two beads. We consider two lipids, one with the head and tail bead sizes equal and the other with the tail beads smaller than the head. When cooled to the ambient temperature from an initial isotropic phase at high temperature, the first lipid transforms spontaneously to a lamellar phase while the second lipid transforms to a micellar phase, showing the crucial role of the head-tail size ratio on lipid phases.

Keywords: Minimal coarse-grained model, implicit solvent model, lipid phases, head-tail size ratio

Introduction

Phase transitions in lipid assemblies have been at the centre of attention because of their association with biology and medicine [1-8]. Depending upon amphiphilic concentration, different phases like micellar, hexagonal, lamellar can be achieved in these systems. Other than lipid concentration, parameters like temperature, pH, the type of amphiphilic, water content and additives can change lipid phases.

From molecular structural perspectives, the lipid phase in a solvent depends on ratio of the size of head group to the aliphatic chain present in the amphiphilic lipid because the phase structures are dependent on the degree of curvature generated by the packing arrangement of the amphiphilic molecule. Low curvatures create lamellar phases whereas larger increment in curvature results in the formation of micellar phases.

The implicit solvent model accounts for the aqueous solvent by including its effects on the model lipid molecules. Here we present a minimal implicit solvent coarse grained model of lipids which is able to produce different phases by changing head to tail size ratio of the molecules.

Model

In this model each lipid molecule consists of three spherical atoms (Figure 1). The blue sphere represents the hydrophilic head group while the two red spheres represent the hydrophobic tail group. This model is a modified version of the model proposed by Cooke and Deserno [9]. By eliminating the finite extensible nonlinear bonds between the beads we have fixed the bond length which makes the model simpler.



Figure 1. The three atom coarse grained lipid model. Lipid 1 has longer tail on the other hand Lipid 2 has smaller tail. Variation in the length of the tail chain is modeled by varying the diameter of the tail beads.

In this model, the effects of the solvent on each molecule have been considered implicitly in the interaction of the molecules. To incorporate the hydrophilic and hydrophobic effect each bead interacts with others via Weeks-Chandler-Andersen (WCA) repulsive potential

$$\phi(r;\sigma_{ij}) = \begin{cases} 4\varepsilon \left(\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^6 \right) + \varepsilon, \ r \le r_c \\ 0, \qquad r > r_c \end{cases}$$
a)

To stabilize the lipid structure, an extra attractive potential between all tail beads are considered.

$$\begin{aligned} V_{tail-tail}(r) &= \\ & -\varepsilon &, r < r_c + w_f \\ & \left\{ 4\varepsilon \left[\left(\frac{\sigma_{ij}}{r - w_f} \right)^{12} - \left(\frac{\sigma_{ij}}{r - w_f} \right)^6 \right] &, r_c \le r \le w_f + w_{cut} \\ & 0 &, r > w_f + w_{cut} \end{aligned} \right. \end{aligned}$$

with $r_c = (2)^{1/6}\sigma$, where σ_{ij} is the effective diameter of each atom. We have considered two lipids (Lipid-1 and Lipid-2). For Lipid-1, σ_{ij} is chosen as $\sigma_{head,head} = 0.95\sigma$, $\sigma_{head,tail} = 0.975\sigma$, $\sigma_{tail,tail} = \sigma$ i.e. head and tails have same size. For Lipid-2, $\sigma_{head,head} = 0.95\sigma$, $\sigma_{head,tail} = 0.875\sigma$, $\sigma_{tail,tail} = 0.80\sigma$ i.e. tails are smaller than the head. Here σ is the unit of length and ε is the unit of energy. The value of $w_{cut} = 2.5\sigma$ and stabilization energy w_f is chosen as $w_f = 0.4\sigma$. It should be mentioned that Lipid-2 may represent a different conformation of Lipid-1 with bond disorder in the tails.

Result

We have a system of 800 lipid molecules within a cubic box of side21.0 σ . We carried out Monte-Carlo (MC) simulations on the system for the two different types of lipid, under constant NVT conditions. First we have achieved the isotropic phase at a sufficiently high temperature for both lipids (Figure 2(a)). We then started lowering the temperature until it reached the reduced temperature 1.0, corresponding to ambient temperature. We then kept the temperature fixed and simulate both systems further with larger Monte-Carlo steps under identical conditions and without changing any other parameter.



Fig. 2. Different phases of the system. (a) the isotropic phase (b) lamellar phase of Lipid 1 (c) micellar phase of Lipid 2.

The systems reduced to the lamellar phase for Lipid-1 (Figure 2(b)) and micellar phase for Lipid-2 (Figure 2(c)) after 8 lakh MC steps. No further change was observed.

Conclusion

Lipid mesophases depend crucially on the head-tail size ratio of the lipid molecule. Here, for Lipid-1 the effective sizes of the head and tail beads are equal, which create zero mean curvature and gives rise to the lamellar phase. For Lipid-2 the head group is larger than the tail beads. This causes a positive large curvature and a micellar phase is observed in case of Lipid-2. Our minimal coarse-grained implicit solvent model of lipid molecules shows spontaneous phase transitions based entirely on the head-tail size ratio, underscoring this dependence.

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Charged Active Particle in the Presence of Magnetic Field

M Muhsin and M Sahoo^{*}

Department of Physics, University of Kerala, Kariavattom, Thiruvananthapuram-695581, India

*Corresponding author: jolly.iopb@gmail.com

Abstract.

We consider the dynamics of a charged inertial active particle self-propelling in a 2D harmonic trap. The dynamics is further subjected to the presence of a magnetic field applied perpendicular to the plane of its motion. The particle is modeled as an active Ornstein-Uhlenbeck particle (AOUP) with exponentially correlated noise. We have exactly calculated both the position and velocity correlations and investigated the dynamical behavior in various time scales of the dynamics. The analytical results are in good agreement with the simulation and the inertia is found to have significant impact on dynamics. The influence of magnetic field on position and velocity correlation persists only in the inertial regime of the dynamics and disappears for highly viscous medium.

Introduction

The emerging field of active matter has recently attracted the attention of researchers in various fields. Active matter systems are a class of condensed matter systems that are inherently out of equilibrium. The imbalance between energy injected from the environment and the energy dissipated by the particle is the indicator of activity [1, 2]. The Stochastic motion of charged particles in a magnetic field is an interesting problem with potential applications in plasma physics and astrophysics. Even though the non-equilibrium features of active matter are an old problem, most of the studies focus on the overdamped limit of Brownian dynamics. But when the particle has a macroscopic size or gaseous medium is involved, then the inertial effects are not negligible. The inertia introduces new features to the system such as inertial delay [3] and coupling with the external magnetic field [4].

In this paper, we study an underdamped version of the active Ornstein-Uhlenbeck particle (AOUP). The particle is charged and moves inside a harmonic trap. A magnetic field is applied perpendicular to the plane of its motion. In the next section, we address the model under consideration in detail. The results are presented in the subsequent section and finally, we conclude.

Model

We consider an active particle with a charge |q|, confined in a 2D plane. The particle is at position $\mathbf{r}(t) = x(t)\mathbf{\hat{x}} + y(t)\mathbf{\hat{y}}$ and at velocity $\dot{\mathbf{r}} = \mathbf{v}$ at time t, where $(\mathbf{\hat{x}}, \mathbf{\hat{y}})$ are the unit vectors along x and y. It is trapped in a 2D harmonic potential $U(x, y) = \frac{1}{2}k(x^2 + y^2)$, where k is the spring constant. The particle is subjected to an external constant magnetic field $\mathbf{B} = B\mathbf{\hat{z}}$ where $\mathbf{\hat{x}}$ is the unit vector along z. The

motion of the particle is given by the Langevin equation,

 $m \ddot{\mathbf{r}} = -\gamma \dot{\mathbf{r}} - k\mathbf{r} + \frac{|q|}{c} (\dot{\mathbf{r}} \times \mathbf{B}) + \sqrt{D} \boldsymbol{\xi}(t) \quad (1)$

Here m is the mass of the particle. The third term in the RHS represents Lorentz force caused by the magnetic field which couples x and y. $\xi(t)$ represents the colored noise, satisfying the properties

$$\langle \xi_{\alpha}(t) \rangle = 0, \ \left\langle \xi_{\alpha}(t) \xi_{\beta}(t') \right\rangle = \frac{1}{2t_c} \delta_{\alpha\beta} e^{\frac{-|t-t|}{t_c}}$$
(2)

Where D is the strength of the noise, which is related to the self-propulsion velocity, and t_c is the correlation time of the noise. This Eq. [1] with the moments of noise given by Eq. [2] models an active Ornstein-Uhlenbeck particle (AOUP). Using $\Gamma = \frac{\gamma}{m}$, $\omega_c = \frac{|q|B}{mc}$, $\omega_0 = \sqrt{\frac{k}{m}}$ and introducing a complex variable z(t) = x(t) + iy(t), one can rewrite the Eq. [1] in terms of z(t) [4]:

$$\ddot{\mathbf{z}}(t) + \Gamma \dot{\mathbf{z}}(t) - j\omega_c \dot{\mathbf{z}}(t) + \omega_0^2 \mathbf{z}(t) = \epsilon(t) \quad (3)$$

Where $j = \sqrt{-1}$ and $\epsilon(t) = \frac{\sqrt{D}}{m} \left(\xi_x(t) + j \xi_y(t) \right)$.

The two important physical parameters for investigating the dynamical behavior of the systems are position and velocity correlation. The position correlation of the particle in the steady state is defined as:

$$C_x(t) = \lim_{t \to \infty} \langle \boldsymbol{r}(t') \cdot \boldsymbol{r}(t'+t) \rangle \tag{4}$$

Similarly, the long-time velocity correlation is defined as

$$C_{\nu}(t) = \lim_{t' \to \infty} \langle \boldsymbol{\nu}(t') \cdot \boldsymbol{\nu}(t'+t) \rangle$$
(5)

It is to be noted that in $t_c \rightarrow 0$ limit, $\xi(t)$ becomes delta correlated white noise and the dynamics simply represents the case of a passive Brownian particle.

Simulation of the dynamics has been carried out using Heun's method algorithm with a time step of 10^{-3} . The active noise is modelled with an improved method of Fox et al. [5]. The simulation is carried out for 10^3 seconds and an average of 10^4 realizations are taken after ignoring the initial transient time.

Results and Discussion

The dynamics of the particle is mainly controlled by four time scales: (i) $\frac{\gamma}{m}$, or inertial time scale; (ii) $\frac{1}{\omega_c}$, due to influence of magnetic field; (iii) $\frac{1}{\omega_0}$, corresponding to the harmonic confinement, and (iv) t_c , the correlation time of activity. Solving Eq. [3] for z(t) and using Eq. [4], the steady state position correlation is found as:

$$C_{x}(t) = Re\left\{\sum_{i=1}^{2}\sum_{j=1}^{2}\frac{a_{i}a_{j}^{*}D}{2m}\left[\frac{t_{c}e^{\frac{-t}{t_{c}}}}{(t_{c}s_{i}-1)(t_{c}s_{j}^{*}+1)} - 2\frac{e^{s_{j}^{*}t}}{(s_{i}+s_{j}^{*})(1-t_{c}^{2}s_{j}^{*2})}\right]\right\}$$
(6)

The velocity correlation is similar to Eq. [6] with a_i and a_j^* are replaced by b_i and b_j^* . Here, the values of s_i 's are given by:

$$s_{1} = \frac{-(\Gamma - i\omega_{c}) \pm \sqrt{(\Gamma - i\omega_{c})^{2} - 4\omega_{0}^{2}}}{2}$$
(7)

With a_i 's and b_i 's are given by:

$$a_1 = \frac{1}{\pm s_1 \mp s_2}; \quad b_1 = s_1 a_1$$
 (8)

Fig. 1 shows the position and velocity correlations for different parameter regimes of the model. Increase of t_c reflects the persistent of activity for longer time, which further suppress the influence of the magnetic field in the dynamics. With increase in ω_c the correlation functions show an oscillatory behavior which is a consequence of the response of the charged particle to the magnetic field. Similar behaviour is observed with different Γ . For very small Γ , the inertia plays a major role in the dynamics of particle. With increase in ω_c , oscillations increase with decrease in magnitude and for large Γ the correlation shows an exponentially decaying behaviour, which is a characteristic of overdamped Brownian particles. Moreover, for very large Γ both the position and velocity correlations are found to be independent of the presence of magnetic field.



Fig. 1. The position correlation [Eq. [4]] (left) and velocity correlation [Eq. [5]] (right) with time: **First row:** for different values of t_c along with the simulation (dotted lines), **second row:** for different values of ω_c and **third row:** for different values of Γ . All the variables other than those mentioned in the plots are set to unity.

Conclusions

In conclusion, we have explored an active Ornstein-Uhlenbeck particle (AOUP) trapped in a 2D harmonic potential in the presence of magnetic field. We have investigated both the position and velocity correlations both analytically as well as using numerical simulation. The analytical results are in good agreement with the simulation. We observe the crucial role of inertia in the dynamics. When inertial effects are negligible, the dependence of the applied magnetic field on correlation disappear.

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Dynamical Heterogeneity in Deep Eutectic Solvents

H Srinivasan^{1,2}, V K Sharma^{1,2}, and S Mitra^{1,2*}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai – 400 085 ²Homi Bhabha National Institute, Mumbai – 400 094

*Corresponding author: smitra@barc.gov.in

Abstract

The quest for a green solvent media in various industrial processes has been a hot pursuit. Deep eutectic solvents (DESs) are one of the recent additions to this repository. The transport properties of these solvents play a decisive role in their applications. At the microscopic level, they exhibit strong heterogeneity in their dynamics owing to extensive hydrogen bond interactions. In this study, we employ neutron scattering technique to explore the dynamical heterogeneity in acetamide + lithium salt based DESs. The extent of heterogeneity is characterized by deviation from the Gaussian nature of the diffusive dynamics in the system. Among the different salts used, it is found that lithium perchlorate is the least heterogenous and lithium bromide the most.

Structural Investigation of Quantum Dots Mixed Lipid Membranes

Subhadip Chowdhury^{*} and Mrinmay K. Mukhopadhyay

SPMS Division, Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata-700064, India

*Corresponding author: subhadip.chowdhury@saha.ac.in

Abstract

Use of quantum dots (QDs) instead of organic dyes for the biological application has several advantages. Here we report the Langmuir monolayer studies of phospholipids mixed with QDs to determine the assembly and the bio-conjugation of the QDs in the membrane. The x-ray reflectivity and AFM studies of the mixed phase monolayer, transferred on to the solid substrate by inverted Langmuir–Schaefer reveal the lipid head group specific attachment mechanism of QDs with the lipid membrane.

Introduction

Over the past few years, QDs are being used as an alternative for the biotechnological applications where conventionally fluorophores was used as the probe in cell and animal biology. A few notable advantages of the QDs over the fluorophores is the tuneability of the absorption and emission spectra just by changing QDs size, quantum yield, high dynamic range, stability and the decay rate. The molar absorption coefficient at the first absorption band of QDs are generally large as compared to organic dyes, typically it is ~ 100,000-1,000,000 M-1cm-1for QDs and ~ 25,000-250,000M-1cm-1for the organic dyes [1]. Similarly, the florescence lifetimes for the organic dyes are close to 1 - 5 ns but in case of ODs the lifetime can be even greater than 100 ns [1,2]. But one major drawback in using the QDs as the bioprobe is the bio-conjugation of the molecules with the cell environment [3,4]. Here we are presenting the results from the assembly of phospholipid membranes after its attachment with one such coreshell QDs. For this purpose, the Langmuir monolayers of phospholipids mixed with the QDs were prepared. The pressure-area $(\Pi$ -A) isotherm studies and the structure of the monolayer after its transfer on the solid substrate using x-ray reflectivity and AFM are presented.

Experiment

Langmuir-Blodgett films of lipids were prepared on freshly cleaned and hydrophobized silicon substrates from the monolayer of 1,2-dimyristoyl-sn-glycero-3-phosphocholine(DMPC) and 1,2-dimyristoyl-sn-glycero-3-phosphoamin (DMPE) on water surface. CdSe/ZnS core-shell QDs (R<4nm, λ =510 Å) were purchased from Sigma-Aldrich and mixed with chloroform solution of the lipids and subsequently the films were deposited on Si substrates using inverted Langmuir-Schaefer (LS) film deposition technique at Π = 30 mN/m and sub-phase T =25°C. Stock solution of 0.118 mg/ml for the lipids and 0.11

mg/ml for the QDs have been prepared first and then these two solutions are mixed together at the ratio of 2:1 in volume. The x-ray reflectivity (XRR) measurements were carried out with SmartLab diffractometer using Cu K α .

Results and Discussion

The surface pressure-area (Π -A) isotherm study is a very efficient technique to understand the surface activity and the interaction of the constituent molecules in the monolayer. The isotherms of DMPC. DMPE and their mixture with ODs at room temperature are shown in Fig.1. Inset shows the surface elasticity $[=-A(\partial \Pi/\partial A)_T]$ calculated from the monolayer isotherm. Initially the Langmuir layer passes through a series of phases, gaseous phase, liquid-expanded (LE), LE - liquid condensed (LC) phase and finally to the LC phase upon compression. The mean molecular area (MMA) for the DMPC + QDs monolayer is significantly more than the pristine DMPC monolayer but the change is not that significant for DMPE monolayer. The surface elasticity curves also indicate that the lipid monolayers become less elastic after the QDs attachment and DMPC + ODs is more elastic compared to DPME + QDs out of these two mixed monolayers. The decrease in elasticity after addition



Fig.1. Isotherms of DMPC, DMPE monolayer and their mixture with QDs.

of QDs can be attributed to the continuity in surface organization in the monolayer [4]. To investigate this, we transferred the monolayer on Si substrates by inverted LS technique after making the substrate hydrophobic. It is to be noted that the horizontal deposition with hydrophilic substrate was not giving a good film possibly due to the hydrophobic expose surface of the lipids on water. The XRR measurements of the deposited films are shown in Fig.2 along with the fits using Parratt's recursive method. The insets show the extracted electron density profiles (EDPs) which indicate that the total thickness is coming out to be equivalent to a bilayer formation of the lipid molecules with tail-head-headtail configuration on the substrate. The little high density for the head regions in the middle of the EDPs is clearly visible in the case of DMPC molecules [Fig.2(a)]. It is found that the ODs are mainly attached to the lipids in the tail region resulting in increase in total thickness of the bilayer assembly. Simultaneously a little drop in density of the tail regions is also evident in the EDP which may be the result of extra space occupied by the QDs in lipid tail region of the membrane. But the attachment



Fig. 2. Experimental data (symbols) of XRR along with the fits (line) of(a) DMPC (red) and DMPC with QDs (pink) (b) DMPE (green) and DMPE with QDs (yellow) on the hydrophobic Si substrates. Curves for DMPC and DMPE with QDs are shifted down by100 for clarity.

of the QDs with the DMPE lipids is quite different as can be seen from the analysed EDP in Fig. 2(b). In this case, we have not found any change in the total thickness even after QDs attachment, only a little increase in density at the top and bottom surface of the films has been observed. AFM image and corresponding histogram of the transferred film of lipids and lipid with QDs are shown in Fig: 3. The double peaks at the histogram corroborates the observations form the XRR analysis on the films. Even though the DMPE + QDs show two peaks in the histogram, the total thickness is almost the same as the pristine DPME layer as found from XRR.



Fig.3. AFM images of (a) DMPC, (b) DMPC with QDs, (c) DMPE and (d) DMPE with QDs layer on hydrophobic Si substrate and corresponding histogram in the inset.

Conclusion

The isotherm, XRR and the AFM studies indicate that the head group specific attachment mechanism of the QDs with the lipid molecules. The QDs prefer to stay in the tail region of the lipids due to hydrophobic match of the encapsulation of the QDs with the tail region of the lipids. It is also clear that the PC head group membrane has better compatibility with this core-shell QDs than the PE head group containing membrane. The reason for such difference of bioconjugation is not clear yet and we will be investigating that in future.

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Observation of Spherical to Non-spherical Transition of Micelles by Different Means

Himanshi Singh^{1,2} and Vinod K. Aswal^{1,2*}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094

*Corresponding author:vkaswal@barc.gov.in

Abstract

The non-ionic surfactantC12E10in aqueous solution self-assembles to form core-shell spherical micelles. Different means (temperature, salts and alcohols) have been examined to induce spherical to non-spherical transition of micelles using small-angle neutron scattering (SANS). The dehydration from micellar shell leads to spherical to non-spherical transition in the cases of increasing temperature and selecting salt (e.g. KF). On the other hand for alcohols, spherical to non-spherical micellar transition arises for long chain length alcohols CnOH (n> 5) because of the mixed micelles formation of alcohol with surfactant. The structural parameters of micelles have been determined from the form factor SANS analysis.

1. .

ModifyingHeat-Induced Protein Gelation by Addition of Tetravalent Counter-Ions

Sugam Kumar, Debasish Saha, Debes Ray, Sohrab Abbas, and Vinod K. Aswal

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.

*sugam@barc.gov.in

Abstract

Proteins are known to undergo unfolding on heating due to disruption of the hydrogen as well as disulphide bonds and exposure of hydrophobic groups. This results into the hydrophobic attraction driven gelation of the proteins at significantly high temperatures. We show that the gelation of the protein can be restricted by modifying inter and intra-protein interactions through addition of tetravalent (Zr^{+4}) counter-ions. In the absence of any counter-ions, bovine serum albumin (BSA) protein solution (5wt%, pH ~ 4) transforms into gel, at about 70°, keeping for nearly 2 hours. On the contrary, the BSA solution in the presence of Zr^{+4} does not gel even on heating upto higher temperatures and longer times. Such effect has not been observed to be arising for mono and divalent ions and believed to be originating due to ion-ion correlations, strongly prevailing in case of multivalent ions.

Biopolymer based Sodium Ion Conducting Ecofriendly Electrolyte for Electrochemical Energy Storage Applications: Ionic Conductivity and CV Analysis

S. Ishwarya, S. Seeniammal, S. Jayanthi*

Department of Physics, The Standard Fireworks Rajaratnam College for Women (Autonomous), Sivakasi - 626123.

*Corresponding author: jayanthi-phy@sfrcollege.edu.in

Abstract

A new series of sodium ion conducting biopolymer electrolyte were prepared using solution casting technique. I – Carrageenan and sodium bromide were used as biopolymer matrix, an electrolyte respectively. Both the concentrations of I – carrageenan and sodium bromide were varied. AC impedance spectroscopy result showed that the system with I – carrageenan (0.5 wt%)/sodium bromide (0.5 wt%) exhibited a maximum ionic conductivity of $4.4567 \times 10^{-4} \text{ Scm}^{-1}$ at room temperature. From CV analysis, the cyclic stability of the high ionic conducting sample was found to be good.

Surfactant induced stabilization of AOT/Water/Dodecane nano emulsion droplet

Sohrab Abbas^a, Sugam Kumarand V. K. Aswal

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

*Corresponding author: <u>abbas@barc.gov.in</u>

Abstract

SANS measurements have been used to investigate and tune thestructure and inter droplet interactions of AOT/Water/dodecane nanoemulsions droplets under varying macromolecular environment around the droplets. The macromolecular environment around droplets was effectively controlled using nonionic surfactant (C12E10), anionic sodium dodecyl sulfate (SDS) and cationic dodecyl trimethyl ammonium bromide (DTAB) surfactants.

AFM and Variable Range Hopping Conductivity Studies of Silver Sulfide Filled PVA-PEG Polymer Hybrid Material

Shruti S. Devangamath¹ and Blaise Lobo^{1*}

¹Department of Physics, Karnatak University's Karnatak Science College, Dharwad-580001, Karnataka, India

*Corresponding author: <u>blaiselobo@kud.ac.in</u>

Abstract. Polymer hybrid films were synthesized by solution casting method, using polyvinyl alcohol-polyethylene glycol (PVA-PEG) polymer blend as the organic host matrix, while the inorganic component, silver sulfide (Ag₂S), was prepared in situ in the polymer blend matrix in the absence of sunlight. Surface morphology of the prepared hybrid films was investigated using atomic force microscopy (AFM) technique. Highest value of average surface roughness (S_a) of 62.50 nm was seen for the hybrid film with Ag₂S particles in their micro form. Temperature dependent direct current (DC) electrical measurements were carried out using two probes setup and the data was analyzed using Greave's three dimensional (3D) variable range hopping (VRH) model. Pure polymer blend film has got the highest values of range of hopping (R_{hop}) and hopping energy (W_{hop}).

INTRODUCTION

The field of hybrid materials is widely investigated due to the potential applications of these materials in various fields. Numerous multifunctional hybrid materials have been developed which have major impact on future applications in fields such as, electronics, optics, optoelectronics, mechanics, ionics, coatings and sensors [1]. Strategies to combine the organic and inorganic domains in order to synthesize advanced materials are of paramount interest. The aim is to get synergic materials with properties of polymers such as, being lightweight, flexible and easily processable as well as having superior electronic, optical, mechanical properties of inorganic filler particles in a single novel material.

EXPERIMENTAL

Polymer hybrid films were synthesized in the laboratory by simple solution casting method [2]. In fact, 3 g of PVA powder (molecular weight (MW) =140,000 g/mol) and 1 g of PEG powder (MW of 6000 g/mol), were dissolved in 40 ml of double distilled water (DDW). This mixture was stirred on a magnetic stirrer in order to form homogeneous blend solution. For in situ formation of Ag₂S in PVA-PEG blend, standard solutions of precursors (silver nitrate (AgNO₃) and sodium sulfide (Na₂S)) were prepared by dissolving them in DDW. Measured volumes of AgNO₃ and Na₂S solutions (taken in 2:1 ratio, with little excess of Na2S) were added drop wise to polymer blend solution (in the absence of sunlight). Various volumes of precursors (see Table 1) were added to obtain hybrid films with various amounts of Ag₂S. All the solutions (in glass petri-dishes) were allowed to dry in oven (at 40°C), in order to obtain polymer hybrid films of uniform thickness.

AFM images were recorded using Nanosurf Easyscan2 atomic force microscope of SINSIL International, Bangalore. Scans were obtained using a tapping cantilever Tap 190Al-G. Temperature dependent DC electrical measurements were carried out for hybrid films of dimensions 1 cm×1 cm (coated with conducting silver paste on both sides), using a research grade two probe set up. A constant voltage of 6.1 V was set in the power supply and the sample was heated from RT up to 60°C using PID controlled oven [3].

RESULTS AND DISCUSSIONS

Three dimensional (3D) AFM images of pure and Ag₂S filled PVA-PEG hybrid films, are shown in Fig. 1(a-d). In Fig. 1a, it can be seen that AFM image of pure PVA-PEG blend film exhibits inhomogeneous or elevated surface features which may be attributed to partial immiscibility of the blend components. Presence of both bright and dark features indicates the semi crystalline nature of PVA-PEG blend film. Bright and elevated features correspond to the presence of Ag₂S filler in AFM images of hybrid films. Roughness parameters, such as average roughness (S_a) , root mean square roughness (S_a) were obtained using the NanoSurf software. It can be noticed from Table 1 that, there is an increase in the values of S_a and S_g for Ag₂S filled hybrid films when compared to that of pure blend film. This increase in the roughness value indicates interaction between polymer blend matrix and filler particles leading to complex formation [4]. It can be seen that, values of S_a and S_q for PPS1 hybrid film are highest when compared to that of remaining films. Increase in values of S_a and S_g is also an indication of decrease in the degree of crystallinity of the polymeric films.



Fig. 1. AFM images of **a**. pure PVA-PEG blend film and **b**. PPS1 **c**. PPS3 **d**. PPS4 polymer hybrid films.

 Table 1. Sample codes and Surface roughness parameters.

Sample code	Volume of precursor solutions (AgNO ₃ :Na ₂ S)	Surface roughness parameters (in nm) (with standard deviation values)		
	in ml	S_a	$\mathbf{S}_{\mathbf{q}}$	
Pure	0.0:0.0	11.36±1.56	14.62±1.74	
PPS1	1.0:0.5	66.90 ± 5.04	79.17±2.94	
PPS3	3.0:1.5	34.45±3.38	44.85±3.38	
PPS4	4.0:2.0	19.65±1.73	23.09±3.42	

These results are in agreement with scanning electron microscopy (SEM) and X-ray diffraction (XRD) results which have been published by us earlier [3]. PPS3 film with uniform distribution of nanoparticles of Ag₂S shows intermediate values of surface roughness. PPS4 film shows uniformly distributed sharp and bright elevated features along with some pores on the surface of the film. The presence of pores facilitates mobility of charge carriers and is responsible for enhanced ionic transport in this material and is evident by our earlier studies [2].

According to Greave's VRH model, dependence of σ on temperature follows the Eqn. (1) [5],

$$\sigma\sqrt{T} = \sigma_0 \exp\left\{-\left(\frac{T_0}{T}\right)^{\gamma}\right\} \tag{1}$$

where σ_0 is pre-exponential factor, *T* is absolute temperature, T_0 is characteristic temperature (in K) which is considered as the measure of degree of disorder and $\gamma = \frac{1}{D+1}$, where D = 1, 2 or 3, for 1D, 2D and 3D VRH charge transport respectively. Applicability of 3D-VRH model is confirmed by $\ln(\sigma T^{1/2})$ versus $(\frac{1}{T})^{\gamma}$ plots with best fit for $\gamma = \frac{1}{4}$, for the obtained experimental data (Fig. 2). Various parameters, such as electronic density of states (localized) at Fermi level ($N(E_f)$), activation energy (E_a), range of hopping (R_{hop}), and hopping energy (W_{hop}) are also calculated (see Table 2).



Fig. 2. Linear fit of $\ln(\sigma T^{1/2})$ vs. $(\frac{1}{r})^{1/4}$ plots.

Values of E_a , R_{hop} and W_{hop} obtained at various temperatures are averaged to obtain $\langle E_a \rangle$, $\langle R_{hop} \rangle$ and $\langle W_{hop} \rangle$ for the prepared hybrid films. Pure PVA-PEG blend film with highest value of $\langle E_a \rangle$ shows the least value of $N(E_f)$. PPS4 film with lowest value of $\langle E_a \rangle$ shows the highest value of $N(E_f)$. Higher the value of $N(E_f)$, lower is the value of $\langle E_a \rangle$. High value of T_0 indicates strong localization of charge carriers. Higher the value of T_0 , higher will be the values of $\langle R_{hop} \rangle$ and $\langle W_{hop} \rangle$. Pure blend film shows the highest values of $\langle R_{hop} \rangle$ and $\langle W_{hop} \rangle$ whereas PPS4 film shows the lowest values of $\langle R_{hop} \rangle$ and $\langle W_{hop} \rangle$ when compared to other hybrid films and this may be attributed to its porous morphology.

Table 2. Parameters obtained by applying 3D VRH model.

	, II , 8-						
Sample	Parameters obtained by applying 3D VRH model						
code	$< E_{a} >$	$< R_{hop} >$	$\langle W_{hop} \rangle$	T_{θ}	$N(E_F)$		
	(eV)	(nm)	(eV)	(×10 ¹¹	$(\times 10^{21})$		
				K)	eV ⁻¹ m ⁻³)		
Pure	1.84	30.24	7.36	16.60	4.02		
PPS1	1.71	29.72	7.15	15.29	4.36		
PPS3	1.38	22.64	5.50	5.22	12.80		
PPS4	1.12	18.53	4.51	2.33	28.60		

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Ionic Surfactant-inducedTuning ofBlock Copolymer Self-assembly

D. Ray¹, D. Saha¹, S. Kumar¹, and V. K. Aswal^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India, ²Homi Bhabha National Institute, Mumbai 400 094, India

*Corresponding author: debes@barc.gov.in

Abstract

The role of anionic surfactant sodium dodecyl sulfate (SDS) on the self-assembly behavior of poly(ethylene oxide)poly(propylene oxide-poly(ethylene oxide) PEO-PPO-PEO triblock copolymer [P85 ($EO_{26}PO_{39}EO_{26}$)] in aqueous solution as a function of temperature has been studied using small-angle neutron scattering (SANS). The measurements have been carried out for fixed concentrations (1 wt%) of block copolymer and surfactant. Each of the individual components (block copolymer and surfactant) and the block copolymer–surfactant mixed system has been examined at varying temperatures. The block copolymer P85 remains as unimer at lower temperature, forms spherical micelles at room temperature whereas shows sphere-to-rod like micelle transition at higher temperatures. On the other hand, surfactant SDSforms ellipsoidal micelles over a wide temperature range. Interestingly, it is found that phase behavior of mixed micellar system (P85 + SDS) as a function of temperature is drastically different than that of the rich phase behavior of P85, giving the control over the temperature-dependent structural transition of block copolymers.

Preferential binding of ionic surfactant in protein-ionic-nonionic surfactants complex and the resultant structure

Debasish Saha¹, Sugam Kumar¹, Debes Ray¹, and Vinod K. Aswal¹

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.

*Corresponding author: debiitm@gmail.com

Abstract

Proteins are known to interact electrostatically as well as hydrophobically with ionic surfactants and undergo unfolding, whereas they show weak interaction with nonionic surfactants. However, the nonionic surfactants bind hydrophobically to ionic surfactants, resulting in the formation of mixed surfactant micelles in the aqueous solution. In the present work, we have investigated the preferential binding of an ionic surfactant [sodium dodecyl sulfate (SDS)] in the protein [bovine serum albumin (BSA)]-ionic-nonionic surfactants [polyoxyethylene 10 lauryl ether (C12E10)] ternary system using Small-angle neutron scattering (SANS). It has been demonstrated the preferential binding of SDS strongly depends on the nonionic-to-ionic surfactant molar ratio. At lower ratios, the strong electrostatic interaction and co-operative binding between the BSA and SDS, leading to the formation of the beads-on-a-string-like complexes with the co-existence of individual C12E10 micelles. On the other hand, at higher ratios, the hydrophobic interaction of SDS-C12E10 overcomes the interaction between BSA-SDS, leading to the formation of mixed ionic-nonionic surfactant micelles co-existing with the native protein.

Introduction

The complex of protein and surfactant find important applications in protein purification, cosmetics industry, detergent industry, etc. [1]. Ionic surfactants exhibit strong interaction with proteins, resulting in the denaturation of proteins even at much lower concentrations compared to other denaturants such as guanidinium chloride or urea [2]. On the contrary, the nonionic surfactants either do not or weakly interact with proteins. The recent studies show that the hydrophobic and electrostatic interactions are equally important in protein unfolding and formation of the resultant complexes with surfactant [3]. Thus, the understanding of the relative importance of different interactions and control of the resultant structure is an important aspect for different applications.

The structure of protein-ionic surfactant complexes is defined by the beads-on-a string-like cluster, where the ionic surfactant micelles are randomly distributed along the unfolded polypeptide chains of protein [4]. Recently, the interaction of a globular protein has been studied with respect to the different self-assembled structures of oppositely charged ionic surfactants, where both surfactants also have the tendency to independently interact with the protein in the aqueous solution. The results suggest that a number of proteins wrap around the different microstructures (ellipsoid, rod-like, bilayer vesicles, etc.) formed by oppositely charged surfactant and thus, controlling the resultant structure formation [5]. The scenario is the opposite in the case of nonionic surfactants with protein. They coexist as the individual entities in the aqueous solution. However, the nonionic surfactants form mixed micelles with the ionic surfactants due to the hydrophobic interaction. Thus, the preferential interaction of ionic surfactant in the ternary solution of BSA, ionic and nonionic surfactants would be interesting as the ionic surfactant could interact with both of them.

Herein, bovine serum albumin (BSA) as a model protein, polyoxyethylene 10 lauryl ether (C12E10) as a nonionic surfactant, and sodium dodecyl sulfate (SDS) as an ionic surfactant have been used. The hydrophobic interaction between ionic-nonionic surfactants has been optimized by using different molar fractions of these surfactants. The interaction of BSA with mixed ionic-nonionic surfactants has been probed by Small-angle neutron scattering (SANS). The interparticle interactions in the system were minimized by using 0.5 M NaCl and fixing the pH of the solution at a value (acetate buffer solution at pH 5.5), which is close to the isoelectric pH of BSA.

Experimental

Small-angle neutron scattering experiments were carried out on the SANS-I instrument at the Swiss Spallation Neutron Source SINQ, Paul Scherrer Institute, Switzerland. The differential scattering cross-section per unit volume $(d\Sigma/d\Omega)$ as a function of Q for monodisperse interacting particles is given by,

$$\left(\frac{d\Sigma}{d\Omega}\right)(Q) = N_P P(Q)S(Q) + B$$

where Np is the particle number density. P(Q) and S(Q) are the form factor and structure factor, respectively, and B is the incoherent background.

Results and Discussion

Fig. 1 shows the SANS data of 1wt% BSA with 0-50 mM SDS. The result reveals that at lower concentrations, SDS molecules electrooptically bind to the oppositely charged patches of BSA. With increasing concentration, the hydrophobic interaction also plays a crucial role and above the critical aggregation concentration (CAC), the connected protein decorated micelle (beads-on-chain) like complexes are formed. The opening up of the folded polypeptide chains of BSA in presence of SDS leads to the unfolding of the protein. Such unfolded structure of BSA has been treated by the random flight model with constant step size [4]. This model provides information about the size of the individual micelle, the distance between the two nearest micelles, and the number of micelles per complex. The results suggest that with at 20 mM SDS, ~3 micelles per complexes are formed, where the micelles are separated by a step size of \sim 5.0 nm. The increase in the SDS concentration leads to the formation of elongated micelles separated by a longer distance. In addition, the number of micelles per complex is decreased at higher SDS concentrations. At 50 mM SDS, the number of micelles per cluster is decreased to 1.1, suggesting that the cluster is replaced by a single elongated micelle. On the contrary, C12E10 coexists with folded BSA structure in the aqueous solution.



Fig. 1. SANS data of 1wt% BSA with varying concentration of SDS (0-50 mM).

The interaction of mixed ionic-nonionic surfactants has been examined for different molar ratios of two surfactants. The molar ratio of C12E10 is defined as X=[C12E10]/([C12E10] + [SDS]) and is varied from 0 to 0.8 to optimize the interaction. The interaction of different molar ratios of mixed surfactants has been examined 1wt% BSA (Fig. 2). The results show that at lower X (0-0.2), the structure of protein-mixed surfactant complexes is completely dominated by the beads-on-a-string-like complex, formed by BSA-SDS. The nonionic surfactant coexists as individual micelles in the system. However, at higher X (0.6-0.8), the resultant structure is majorly defined by the mixed surfactant complex formed by SDS-C12E10. In the intermediate X (0.4), the structure is observed to be the mixture of unfolded BSA with mixed SDS-C12E10 micelles.

In general, at lower X, the BSA-SDS complexes formation is preferred as the electrostatic and hydrophobic interaction between these constituents overruled the hydrophobic interaction between SDS-C12E10. However, the hydrophobic interaction between ionic-nonionic surfactants happens to be increased with increasing X. Therefore, at higher X, the formation of mixed micelles is preferred over the unfolding of BSA. Interestingly, in such conditions, BSA protein retains its native structure. Thus, the preferential binding of SDS has been tuned by changing the molar fraction of C12E10.



Fig. 2. SANS data of ternary complexes of 1wt% BSA with SDS-C12E10 mixed at different molar ratios.

Conclusions

We show the preferential binding of SDS in ternary complexes and the resultant structure formation using SANS. Such preferential binding of SDS with C12E10 could be utilized for the refolding of prevent unfolding of BSA protein.

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Computer Simulation Study on Polar Biaxial Liquid Crystal Phases

Soumalya Bhowmick, Jayashree Saha

Department of Physics, University of Calcutta, 92, A.P.C Road, Kolkata-700009

*Corresponding author: soumalya555@gmail.com

Abstract

Computer simulation study on a system of polar biaxial ellipsoid particles is performed. Dipole-dipole interaction is taken as polar interaction along with a new kind of elliptic contact potential (ECP) interaction acting between the molecules. Generation of different polar biaxial liquid crystal phases depending on the temperature are reported.

Introduction

Polar liquid crystal molecules can show different liquid crystalline phases due to their positional arrangement in layer and orientation with respect to the layer normal. Biaxial liquid crystal phase generation in the system of polar molecules is another important topic for interdisciplinary science community apart from the uniaxial one. The long axis of the uniaxial molecule tend to orient along a particular direction known as director, \hat{n} . In nematic phase uniaxial molecule has only long range orientational order along the director. In biaxial nematic ordering there can be one or two other directions apart from director along which molecules can also have orientational ordering [1]. Uniaxial molecules arrange themselves in layer in smectic phase along with orientational order in the direction of layer normal. In biaxial ordering, other similar axes remain parallel for each molecules. Polar biaxial molecules can arrange themselves to generate smectic partial bilayer phase $(SmA_d)[2]$.

Computer simulation is one of the most efficient technique to study microscopic interactions among the molecules. There are various models to study such systems like full atomic, united atom, site-site, single site interaction models etc. Single site model is computationally most efficient as liquid crystal phase generating molecules are complex. These highly nonspherical [3] molecules can be considered as ellipsoidal for computational efficiency. We will consider such coarse grained model to study different phases generated by the system of polar biaxial ellipsoidal molecules.

Model

We consider a system consisting of polar biaxial ellipsoidal molecules, where each molecule is embedded with permanent dipole moment placed at a distance $d = \sigma_0$ along the principal axis of the ellipsoid as shown in Fig. 1.



Fig. 1. Modeling of polar biaxial ellipsoid molecule, length of the three axes of the molecule are not same

The angle between dipole moment and the principal axis is 90° and is directed towards the shortest molecular axis. The interaction between polar parts is dipole-dipole electrostatic in nature. The dipole-dipole interaction potential can be written as

$$U_{dd} = \frac{1}{r_d^3} \left[\overrightarrow{\mu_{d_1}}, \overrightarrow{\mu_{d_j}} - \frac{3}{r_d^2} \left(\overrightarrow{\mu_{d_1}}, \overrightarrow{r_d} + \overrightarrow{\mu_{d_j}}, \overrightarrow{r_d} \right) \right]$$

Where $\vec{r_d}$ is the vector connecting two points of *ith* and *jth* molecule at which point dipole is embedded in molecule. $\vec{\mu_{d_i}} = \mu^* \hat{u}_{d_i}$ and $\vec{\mu_{d_j}} = \mu^* \hat{u}_{d_j}$ are the dipole moment vectors of *ith* and *jth* molecule respectively. Here, $\mu^* = (\frac{\mu^2}{\sigma_0^3})^{\frac{1}{2}}$. Long range effect of dipole has been taken in consideration using reaction field method[4].

Non-polar part of the molecule is of the shape of an ellipsoid whose length of three axes are different. Apart from extensively used Gay-Berne potential [5] a new kind of elliptic contact potential (ECP) [6] has been considered to represent non polar interactions part of biaxial ellipsoidal molecules. The potential is of the following form

$$U = 4\varepsilon_0 \varepsilon_1^{\nu}(\widehat{\alpha}, \widehat{\beta}) \varepsilon_2^{\mu}(\widehat{\alpha}, \widehat{\beta}, \widehat{r}) \left[\left(\frac{\sigma_0}{r - \sigma(\widehat{\alpha}, \widehat{\beta}, \widehat{r}) - \sigma_0} \right)^{12} - \left(\frac{\sigma_0}{r - \sigma(\widehat{\alpha}, \widehat{\beta}, \widehat{r}) - \sigma_0} \right)^6 \right]$$

Where ε_0 is a constant, ε_1 is a function of the orientation of the two molecules and ε_2 is a function of \hat{r} in addition to the molecular orientation. μ , ν are two adjustable parameters. By adjusting values of them one can get different well depth for different configurations. σ_0 is the length of smallest semi axis and σ is the orientation dependent contact distance between two ellipsoids when they are at their closest. Here, \hat{r} is the unit vector along the line connecting the center of two molecules. Thus the effective potential is the sum of two kind of potentials.

 $U_{eff} = U + U_{dd}$

Simulation and Result

In this NVT [7, 8] molecular dynamics simulation we have taken 500 biaxial molecules embedded with dipolar head having dipole strength $\mu^* = 1.1$. Here, $\sigma_x: \sigma_y: \sigma_z = 1: 1.5: 4.5$ and corresponding values of I_{xx}^* , I_{yy}^* , I_{zz}^* are 1.125, 1.062, 0.16 respectively. Energy strength parameters are chosen as $\frac{\epsilon_x}{\epsilon_z} = \frac{1}{30}$, $\frac{\epsilon_y}{\epsilon_z} = \frac{1}{7}$ with $\nu = 2, \mu = 1$. Value of ϵ_0 is taken as 1. In this simulation, molecules are initially arranged at FCC lattice points at the density $\rho^* = \rho \sigma_0^3 = 0.175$ considering minimum image convention. To get the isotropic configuration, we melted it to a reduced temperature $T^* = \frac{k_B T}{\epsilon_0} = 5.0$ where k_B is the Boltzmann constant. We reduced the temperature of this isotropic configuration gradually and measured forces and torques using leap-frog algorithm. Time step size is taken as $\partial t^* = \frac{\partial t}{(\frac{m\sigma_0^2}{\epsilon_0})^{\frac{1}{2}}} = 0.001$. Biaxial

nematic ordering obtained at $T^* = 1.0$ and partial bilayer phase obtained at $T^* = 0.4$ as shown in Fig. 3.



Fig. 2. Pair correlation function of center of masses of molecules along director axis g(z*) is plotted against z^*



Fig. 3. Nematic bilayer at $T^* = 1.0(\text{left})$ and Smectic A_d phase at $T^* = 0.4(\text{right})$. The snapshots were generated by graphics software Ovito[9]

Conclusion

Our computer simulation on ellipsoid molecules interacting via new kind of ECP can generate different biaxial phases depending on temperature. Due to introduction of dipolar interaction, this system of molecules exhibit polar biaxial phases at different temperature. At higher temperature it generates biaxial nematic phase. Smectic partial bilayer phase is found due to dipolar interaction at lower temperature. So, our simulation can generate technologically important novel biaxial smectic A_d phase. Plot of pair correlation function of center of masses of molecules along director axis g(z*) against z* is shown at Fig. 2.

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Phase Behaviour of Dihexadecyldimethylammonium Bromide Bilayer Jyoti Gupta^{1,3}, V. K. Sharma^{1,3*}, H. Bhatt^{2,3}, H. Srinivasan^{1,3}, S. Mitra^{1,3}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085

²High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ³Homi Bhabha National Institute, Mumbai, 400085

*Corresponding author: sharmavk@barc.gov.in

Abstract

Dihexadecyldimethylammonium bromide (DHDAB) lipids form bilayer in aqueous media exhibiting a rich phase behaviour. In this work, by using Differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy, we have characterised the phase behaviour of DHDAB bilayer. It is found that in the heating cycle, the system goes from coagel to fluid phase via an intermediate phase. However, the intermediate phase is not observed in the cooling cycle, as the system goes back from fluid to coagel phase directly. DHDAB results have shown very contrast to dioctadecyldimethylammonium bromide (DODAB) bilayer which differs only in the tail length.

A Quantum Mechanical Prediction of C₂₄ Fullerene as a biosensor for Adenine Nucleobase

Sourav Kanti Jana¹, Darshil Chodvadiya¹, Narayan N. Som², Brahmanada Charkraborty^{3,4}, and Prafulla K. Jha¹

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, 39002-India

²Materials Design Division, Faculty of Materials Science and Engineering, Warsaw University of Technology, 141 Wołoska Str., 02-507 Warsaw, Poland

³High pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay Mumbai, 400008-India and ⁴Homi Bhabha National Institute, Mumbai, 40009-India

*Corresponding author: kantisouravphysics@gmail.com

Abstract

In this work, we have explored the potential of C_{24} fullerene for the applicability of adenine sensing using density functional theory. Among the different orientations, P1 site found to be minimum energetic configuration. The adsorption energies, interactions distances, NBO analysis, dipole moments and DOS are calculated to understand the impacts of adenine adsorption over C_{24} fullerene. The adsorption energy is -1.16 eV of adenine adsorption over C_{24} with P1 geometry. Our results indicate suitability of C_{24} fullerene in bio-sensing of the adenine molecule.

Position and Velocity Correlation of Inertial Self Propelled Particle

Arsha N, K P Jepsin, S Achuthan and M. Sahoo*

Department of physics, University of Kerala, Kariavattom, Thiruvananthapuram,695581 *Corresponding author: jolly.iopb@gmail.com

Abstract

We have studied the dynamics of an inertial active particle moving in a solvent with active Ornstein Uhlenbeck process. We have exactly solved the dynamics and calculated the position and velocity correlation functions for the case when the particle is freely propelling as well as when it is confined in a harmonic trap. When the self propelling time is of the order of the inertial delay time of the freely self propelling particle, the velocity at two different times are decorrelated. The correlation corresponding to the deviation in position is the athermal contribution and depends on the activity of the self propelled particle.

Introduction

The Physics of self propelled or active particles constitute an interesting area of research in the recent years. Self-propelled particles can move actively in a solvent where the frictional forces are more dominant¹. The active Brownian particle (ABP) constitute persistent self-propulsive forces and repulsive interaction² and has application in drug delivery systems, cargo transport etc. The active motion can be found in colloidal systems as well as in gaseous medium. Depending on the medium, it can be micro swimmers or microflyers³. More recently, models of fluctuating self- propelled particles are studied using Active Ornstein Uhlenbeck process (AOUP) which was initially used to study passive particles in the presence of colored noise⁴. This has become an appropriate way to study the active particles

Motivated by the dynamical behavior of inertial self propelled particles, in this paper, we have explored the activity of an Active Ornstein Uhlenbeck particle. We have exactly calculated the position correlation and velocity correlation in both free particle case as well as harmonically confined case. The paper is organized as follows. In the next section, we will explain our model which will be followed by the result and discussion.

Model

The dynamics of an inertial active particle is given by,

$$m\frac{dv}{dt} + \gamma v = \sqrt{D} \eta(t) . \qquad (1)$$

Here $m\frac{dv}{dt}$ is the inertial force with 'm' as the mass of the particle, γ is the viscous coefficient of the medium, D is the strength of exponentially correlated noise, $\eta(t)$. The moments associated with noise are given by the relations,

$$<\eta(t)=0> \text{ and } <\eta(t_1)\eta(t_2)>=\frac{1}{2t_c}e^{\frac{-|t_1-t_2|}{t_c}}$$
 (2)

Where t_c is the self propulsion time. The angular brackets <...> represent the ensemble average over noise. By solving the dynamics, the velocity at any instant of time can be calculated as,

$$v(t) = v_0 e^{\frac{-\gamma t}{m}} + \frac{\sqrt{D}}{m} \int_0^t e^{\frac{-\gamma(t-t')}{m}} dt' \qquad (3)$$

Where v_0 is the initial velocity of the particle.

The velocity auto correlation function at two different times t_1 and t_2 can be obtained as,

$$\langle v(t_1)v(t_2) \rangle = v_0^2 e \frac{-\gamma(t_1 + t_2)}{m} + \frac{Dt_c}{2(\gamma^2 t_c^2 - m^2)} \left\{ e^{\frac{-(t_1 - t_2)}{t_c}} - e^{\frac{-t_2}{t_c} \frac{\gamma t_1}{m}} - e^{\frac{-t_1}{t_c} \frac{\gamma t_2}{m}} + e^{\frac{-\gamma(t_1 + t_2)}{m}} \right\} + \frac{Dm}{2\gamma(\gamma^2 t_c^2 - m^2)} \left\{ e^{\frac{-\gamma(t_1 + t_2)}{m}} - e^{\frac{-\gamma(t_1 - t_2)}{m}} \right\}$$

$$(4)$$

The steady state correlation $C_v(t) = \langle v(0)v(t) \rangle$ can be calculated as,

$$C_{\nu}(t) = \frac{D}{2(m^2 - \gamma^2 t_c^2)} \left[\frac{m}{\gamma} e^{\frac{-\gamma t}{m}} - t_c e^{\frac{-t}{t_c}} \right]$$
(5)

Similarly the position auto correlation function is,

$$C_{\chi}(t) = x_0^2 + \frac{2x_0 m v_0}{\gamma} + \left(\frac{m v_0}{\gamma}\right)^2 + \frac{Dt}{\gamma^2} - \frac{Dm}{\gamma^3} - C_{\chi}^T$$
(6)

Where C_x^T is the correlation corresponding to the deviation in position and is given by,

$$C_{x}^{T} = \frac{Dt}{\gamma^{2}} - \frac{Dm}{\gamma^{3}} - \frac{Dt_{c}^{2}}{\gamma^{2}} + \frac{Dm}{4\gamma^{3}t_{c}\left(\frac{\gamma^{2}}{m^{2}} - \frac{1}{t_{c}^{2}}\right)}e^{\frac{-\gamma t}{m}} - \frac{D}{2\gamma^{2}}e^{\frac{-t}{t_{c}}}\left(t_{c} + \frac{1}{\left(\frac{\gamma}{m} + \frac{1}{t_{c}}\right)}\right)$$
(7)

Using Kubo's theorem, we have also calculated the steady state diffusion coefficient D_f as,

$$D_f = \int_0^\infty \langle V(\tau) V(0) \rangle,$$

$$D_f = \frac{D}{2\gamma^2}$$
(8)

which is same as the case of a passive Brownian particle.

For the case when the particle is confined in a harmonic well with potential $\frac{1}{2}m\omega_0^2 x^2$, the position correlation can be obtained as ,

$$= \frac{D}{4m^2} \left\{ \frac{e^{\frac{-t}{t_c}}}{\sqrt{\left(\left(\frac{1}{t_c} + \frac{\gamma}{2m}\right)^2 + \omega_1^2\right)\left(\left(\frac{\gamma}{2m} - \frac{1}{t_c}\right)^2 + \omega_1^2\right)\right)}} \right\} \\ + Ae^{\frac{-\gamma t}{2m}} \left(\frac{\cos(\omega_1 t)f_1(\omega_1) + \sin(\omega_1 t)f_2(\omega_1)}{\sqrt{\left(\left(\frac{1}{t_c^2} - \frac{\gamma^2}{4m^2} + \omega_1^2\right)^2 + \omega_1^2\right) + \frac{\gamma^2 \omega_1^2}{m^2}}\right)} (9) \\ \text{Here } f_1(\omega_1) = \frac{-3\omega_1\gamma^2}{m^2} + \frac{4\omega_1}{t_c^2} + 4\omega_1^3, \\ f_2(\omega_1) = \frac{2\omega_1^2\gamma}{m^2} - \frac{\gamma^3}{m^2} + \frac{2\gamma}{mt_c^2} + \frac{16\gamma\omega_1^2}{m}, \\ A = \frac{D}{16m^2\gamma\omega_1\omega_0^2} \text{ and } \omega_1 = \sqrt{\omega_0^2 - \frac{\gamma^2}{4m^2}} \right\}$$

In the $t_c \rightarrow 0$ limit, the particle is simply a passive particle in the presence of a white Gaussian noise. In this limit the correlation corresponding to the deviation is same as already obtained in⁵.

Result and Discussion

Fig.1 shows the plot of $C_{\nu}(t)$ as a function of $\frac{t}{t_c}$ for different values of inertial delay time, $\frac{m}{\gamma}$ for the case when the particle is not confined. The decay of $C_{\nu}(t)$ depends on two time scales, inertial delay time and the persistent time. When the persistent time is of the order of the inertial delay time, the correlation vanishes, reflecting the decorrelation of velocities at two different times. In the steady state limit, the diffusive behavior of the particle is same as the case of a passive particle in the presence of white Gaussian noise.



Fig1: $C_{\nu}(t)$ [Eq. (5)] as a function of $\frac{t}{t_c}$ for different values of $\frac{m}{\gamma}$. The other parameters are fixed as unity

The $C_x(t)$ for particle confined in harmonic well [Eqn. 7] also have two time scales of $\frac{m}{\gamma}$ and t_c and these time scales can contribute to the activity of particle

Conclusions

In this work, we have explored the dynamical behavour of an active particle by investigating the position and velocity correlations. The inertial delay time and the persistent time or the self propulsion time are found to have impact on the decay of velocity correlation. The decorrelation happens when the inertial delay time matches with the persistent time scale or self propelsion time scale. The correlation corresponding to the shift relative to average position of the particle is found to be athermal and depends on the activity of the particle. The steady state diffusion is found to be independent of the activity and it depends on the strength of the noise.

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Structural Reorientations and Stability of Curcumin-Chitosan Drug Formulations Embedded to Silica Nanoparticles

Himal Bhatt^{1,4,*}, J. Bahadur^{2,4}, R. Checker^{3,4} and D. Sen^{2,4}

¹High Pressure & Synchrotron RadiationPhysics Division,²Solid State Physics Division,³Radiation Biology & Health Safety Division, Bhabha Atomic Research Centre, Mumbai, 400085 ³Homi Bhabha National Institute, Mumbai, 400094

*Corresponding author: hbhatt@barc.gov.in

Abstract

Efficient drug delivery formulations to address low solubility, bioavailability and hence sustained release applications of Curcumin (yellow bioactive component of turmeric), a potential anti-cancer, anti-viral drug, merit detailed structural investigations. Here, curcumin, hydrogen bonded to the polymer chitosan, a well-known drug delivery vehicle was encapsulated in microspheres formed by the scaffolds of silica nanoparticles under varying chemical environments, and investigated using infrared spectroscopy at ambient and *in-situ* high temperature conditions. Noticeable spectroscopic features have been shown which highlight the subtle molecular reorientations under varying chemical environments that eventually dictate the structural assembly. The microspheres are found to show good stability upon heating upto 60°C.

Effect of low dose 200 keV N⁺ ion beam irradiation on dielectric and polarization properties of free-standing, flexible films of PVDF-HFP

Mandeep Jangra^a, Abhishek Thakur^a, Siddhartha Dam^a, K. Saravanan^a, Souvik Chatterjee^b,

N. V. Chandra Shekar^{a,c,} Shamima Hussain^a*

^a UGC-DAE CSR, Kalpakkam Node, Kokilamedu, Tamil Nadu-603104, India (Affiliated to University of Madras) ^b UGC-DAE CSR Kolkata Centre Kolkata, West Bengal-700106, India

^c Material Science Group, IGCAR, HBNI, Kalpakkam, TN-603102, India

*corresponding author: shamimah1@gmail.com; sh@csr.res.in, Phone no.044-27480500-21914

Abstract

Dielectric studies and polarization studies were carried out on low dose N⁺ (200 keV) ion beam irradiated free-standing, flexible films of Poly(vinylidene fluoride-hexafluoropropylene) (PVDF-HFP). Effect of the irradiation on the physical properties of the films were studied using Field Emission Scanning Electron Microscopy, X-Ray Diffraction, Raman, and Fourier-transformed infrared spectroscopic studies. The dielectric constant of the pristine films was found to reduce to ~16 from ~21 while the remanent polarisation reduced to $3 \times 10^{-4} \,\mu\text{C/cm}^2$ from $4.8 \times 10^{-3} \,\mu\text{C/cm}^2$, upon irradiate ion with a dose of $5 \times 10^{12} \,\text{ions/cm}^2 \,\text{N}^+$ ions.

Introduction

Amorphization due to irradiation is a well-known phenomenon in materials [1]. In polymers, this happens due to cross-linking as a consequence of scissoring of the main chains of polymers. This modifies the physical and chemical properties. PVDF-HFP is a non-reactive thermoplastic fluoropolymer with good chemical and physical stability. Flexible films of PVDF-HFP find applications due to their high piezoelectric and dielectric properties [2]. Modulation in the dielectric properties of PVDF-HFP composites by electron beam irradiation have been reported by researchers [3-4].

In this article, we report the effect of N^+ ion irradiation on free-standing flexible films of PVDF-HFP.

Experimental

Free-standing, flexible films of PVDF-HFP were synthesized using the sol-gel method. A 15 wt.% PVDF-HFP sol in N, N- Dimethylformamide was prepared at 60°C. Films were spin-coated from this sol on clean glass substrates. The films were then annealed in a microwave oven for 3 minutes to obtain free-standing flexible films. The thickness of the films was found to be ~14 μ m measured using a digital micrometer. The synthesized films were then irradiated using an ion accelerator with N⁺ (200 keV) ion beam at a fluence of 5 × 10¹² ions/cm². **Results and discussion**

Changes in the morphology due to irradiation were observed from FESEM studies Fig. 1(a-b). Fig.

1(a) reveals the porous and fibrous morphology of asdeposited PVDF-HFP films. Pores of ~100 nm size dominant the surface. Upon irradiation an increase in the porosity of the films with decreased pores size was observed. Since, irradiation causes scissoring of polymer chains a rearrangement in the polymer chains might be the reason for decreased pore size (Fig. 1(b)). Therefore, the reduced length of the fibre might be an indication of decreased crystallinity of the polymer, investigated through XRD (Fig.2).







Figure 2. XRD patterns for pure PVDF-HFP and Irradiated films recorded 20 from 10 to 30 $\,$

The peak corresponding to the α (2 θ ~20.3°, 26.4°), β (2 θ ~20.8°,) and γ (2 θ ~18.5°) phases of PVDF were observed. Upon irradiation, with N⁺ ion the slight

decrease in the intensity of peaks were observed due to amorphization [5-6]. Since the beam used is of low Z ions (N^+), not much decrease in the intensity is observed.



Figure 3. FTIR spectra for pure PVDF-HFP and Irradiated films plotted between from 740 cm⁻¹ to 860 cm⁻¹.

Similar, observation was recorded in the FTIR studies too (Fig.3). The peak corresponds to the α (763 cm⁻¹, 796 cm⁻¹, 854 cm⁻¹), γ (811 cm⁻¹) and the β + γ (840 cm⁻¹) phases of PVDF were observed [5-6]. Fraction of electroactive phase (EA) was calculated using equation 1 found to be decreased from 44% to 43% [5]. A slight decrease in the intensity of peaks were observed. Additionally, the intensity of the β + γ peak was found to decrease after irradiation, indicating a decrement in electroactive phase fraction.



Figure 4. Dielectric constant vs frequency graph for pure PVDF-HFP and Irradiated films.

PVDF-HFP is of primary interest due to its dielectric properties. The dielectric constant of the films was determined from impedance spectroscopy. The dielectric property is related to the polarizability of the dipoles [4]. A decrease in dielectric constant from ~21 to ~16 was observed upon irradiation. This could be as upon irradiation, a decrease in the number of dipoles would be observed due to scissoring of chain and their possible rearrangement. The increased porosity is an indication for the same.

To further confirm the charge distribution, P-E loop measurements were carried out (Fig.5). The P-E loop study is a measure of the number of dipole moments polarized per unit area upon application of the electric field. As seen from Figure 5 the area under the curve falls drastically, for irradiated samples. This indicates a decrease in the concentration of charges i.e., the number of dipoles. The remanent polarization decreases from $4.8 \times 10^{-3} \,\mu\text{C/cm}^2$ to $3 \times 10^{-4} \,\mu\text{C/cm}^2$ which is an indication of a decrease in the dipole polarizability. Similar, a decrease in saturation polarization was also observed.



Figure 5. P-E loop studies of pure PVDF-HFP and Irradiated films

Conclusion

Effect of irradiation of low ions on free-standing, flexible films of PVDF-HFP explored. A remarkable increase in porosity with irradiation was observed. Decrease in the intensity of XRD and FTIR spectra, along with the reduction in the fraction of EA phase by 1% was observed. Reduction in the dielectric constant and polarizability was also observed. Scissoring of the polymer chains with possible crosslinking has been attributed as the cause of these changes.

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Surfactant dependent interaction of aminoglycoside antibiotic with metal nanoparticles

Amritpal Kaur* and Rajesh Kumar

Departmentof Physics, Panjab University Chandigarh, 160014, India

*Corresponding author: kamritpal59@gmail.com

Abstract

Silver and gold nanoparticles were synthesized by chemical method in the presence of different surfactants. Trisodium citrate was used to study its role as a binder between metal nanoparticles (AgNPs and AuNPs) and aminoglycoside antibiotic named amikacin. Analytical techniques such as UV-Visible absorption spectroscopy, and X-ray diffraction have been used to investigate the interaction mechanism between drug and nanoparticles surface. It has been observed that in case of AgNPs, citrate is not a good linker for amikacin to bind with nanoparticle surface as silver lost its SPR after the addition of amikacin due to formation of unstable sulphur compounds. However, in case of AuNPs, citrate could be used as a linker between drug and nanoparticle surface.

Gamma Ray Induced on Synthesis of SF-AgNPs: Characterization

Madhukumar R^{1,*}, Mohan N R², and Sangappa Y³

¹Department of Physics, R.T.E.Society's Arts, Science and Commerce Degree College, Ranebennur, 581 115, India ²Assistant Adviser, National Assessment and Accreditation Council (NAAC), Bangalore, 560 072, India ³Department of Physics, Mangalore University, Mangalagangotri, Mangalore 574 199, India

*Corresponding author: nwwton@gmail.com

Abstract

In this work *Bombyx mori* silk fibroin (SF) films were prepared by solution casting method. Gamma irradiation of protein biopolymer films were carried out in dry air at room temperature using Co - 60 source, and radiation doses are in the range of 0-60 kGy. The unirradiated and irradiated films were characterized by the resultant products have been confirmed to be Ag-NPs was carried out based on UV-Vis spectroscopy (427 nm). The UV-visible spectra showed that the characteristic surface plasmon resonance (SPR) band at around 424 nm and high-resolution transmission electron microscopic (HR-TEM) measurements. From this study, it was found that the increasing the radiation dose increases the rate of reduction and decreases the particle size. The size of the AgNPs can be tuned by controlling the radiation dose.

Introduction

Silk is a natural fiber and semicrystalline biopolymer. *Bombyx mori* silk contains a fibrous protein termed fibroin (both heavy and light chains) that form the thread core and glue-like proteins termed sericin that surround the fibroin fibers to cement them together. The fibroin is an insoluble protein containing up to 90% of the amino acids glycine, alanine, and serine leading to significant content of antiparallel β -pleated sheet formation in the fibers [1], Recent interest in the use of reprocessed silks such as fibroin in biotechnological materials and in biomedical applications originate from the unique mechanical properties of the silk fibers as well as their biodegradability and biocompatibility [2],

In recent years noble metal nanoparticles synthesis has attracted much attention of many researchers. The development of clean synthetic procedures for the synthesis of metal nanoparticles have been the area of focused researches due to their interesting catalytic, optical, electrical, and magnetic properties [3]. The metal nanoparticles, therefore, have potential uses in technological applications. Silver is a nontoxic inorganic material well known for possessing an inhibiting effect towards 650 types of microbes growth [4]. Silver exhibits the highest electrical and thermal conductivities among all the metals. A quite large number of methods are available for synthesis of silver nanoparticles for example, chemical reduction, sol gel, hydrothermal, electrochemical synthesis, thermal decomposition, sonochemical, photo reduction in reverse micelles, bacterial synthesis and microwave irradiation method [5]. All the above listed methods used for the synthesis of nanoparticles, involve the usage of environmentally toxic or biologically hazards chemicals as reducing agent. Therefore, for an environmental sustenance, the development of clean, eco-friendly, green route approach for synthesis of silver nanoparticles is very much needed.

Experimental

Preparation of SF-AgNPs solution and gamma irradiation: 10 mg of AgNO3 powders were added into 10 mL of 1 wt% SF solution to form a transparent SF-AgNO₃ mixture solution. And then mixture solution was exposed to gamma radiation. The samples were irradiated in the dose ranging from 0-80 kGy in step of 10 kGy at CARRT center, Mangalore University, India. The synthesized silver nanoparticles were confirmed by UV-vis absorption, TEM. The UV-visible absorption spectra of SF-AgNPs solution have been recorded using UV-visible spectrophotometer (Shimadzu UV-1800, Japan) in the wavelength range 190-800 nm.The morphology of the silver nanoparticles was studied using transmission electron microscope (TEM), which was performed at 200 keV using JEOL JEM2010.

Results and Discussions

UV-visible spectroscopy is one of the commonly used tools for the analysis of silver nanoparticles. The UV-visible absorption spectra of SF and SF-AgNPs samples are presented in Fig. 1. The recorded spectra of SF sample display absorption at λ =275 nm (not shown), which was attributed to the presence of the Tyr, Phe and Try residues in the silk fibroin (SF) chain [6-8]. The formation of the silver nanoparticles in the aqueous RSF solution was evidenced with the change in colour. The initial SF-AgNO₃ solution was colourless, but after the exposure to the gamma radiation the colour turned to yellowish, then to the dark brown colour. Such a change was attributed to the size and shape dependent surface plasmon resonance (SPR) of AgNPs formed in the solution in the visible region (Fig.1). The surface Plasmon absorption band with a maximum of 424 nm indicates the presence of spherical or nearly spherical silver nanoparticles and this was also confirmed by TEM images.



Fig. 1. UV-Vis absorption spectra of Silk fibroin and SF-AgNPs.

TEM analysis: Fig.2. shows the TEM images of silver nanoparticles formed in the SF solution. Most of the silver nanoparticles were roughly spherical in shape with smooth edges. The structures were identical to those of the silver nanoparticles produced from the green route method **[9-10].** The HRTEM images (Fig 2) further illustrated the nature of silver nanoparticles. The overall morphology of the silver nanoparticles produced by reduction of Ag^+ to Ag^0 with 0.1mg/mL, 60 kGy irradiated sample is composed of almost uniform nanoparticles. The local elemental composition was confirmed as Ag by EDX SEM analysis and was given in Fig.2.



Fig 2. (a) TEM images of AgNPs biosynthesized using the Silk fibroin, showing that particles are well dispersed (scale bar: 100 nm, 10nm) and Typical selected area electron diffraction of AgNPs biosynthesized using Silk fibroin (scale bar: 5 1/nm).

Conclusions

In this study, silver nanoparticles were synthesized by an eco-friendly bio based green route method. Bombyx morisilk fibroin has acted as a reducing and stabilizing agent for the synthesis of silver nitrate into silver nanoparticles under gamma radiation environment. Synthesized silver nanoparticles were confirmed by colour change which was observed by UV-visible spectra at 424 nm. Photoluminescence analysis showed that, the intensity loss indicates the oxidation of tyrosine in silk fibroin. The synthesized silver nanoparticles were spherical in shape and their morphology was confirmed by TEM images. From this investigation, it was found that the increasing the radiation dose increases the rate of reduction and decreases the particle size, and thus the size of the silver nanoparticles can be tuned by controlling the radiation dose.

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Nonlinear Refraction and Absorption in Semiconductor Core-Shell Quantum Qots

Bhupendra Kumar^{1,*} Sanjeev Gupta² and P. K. Sen¹

¹Department of Applied Physics, Shri G S Institute of Technology & Science, Indore - 452 003. ²Department of Physics, St. Xavier's College, Ahmedabad, Ahmedabad, Gujarat 380009 <u>*bhu.msu@gmail.com</u>

Abstract

We present the results of the numerical analysis of the theoretical formulations to examine the occurrence of optical nutation in semiconductor quantum dot of GaAs/AlGaAs subjected to ultra-fast pulsed coherent radiation. The transient values of $\chi_r^{(3)}(t)$ and $\chi_i^{(3)}(t)$ enables one to analyze both nonlinear refraction and nonlinear absorption in the quantum dots. The transient nonlinear optical responses have been over a wide range of photon energy for strongly confined excitonic features of the QDs.

Keywords: Semiconductor, Quantum dots, Screened Columbic electron-hole interaction **PACS:** 68.55.ag, 68.65.-k

INTRODUCTION

The question of what happens when light interacts with single atom or molecule has been and still is an active area of research in physics. At this point in our understanding of such phenomena, we know very well what happens in normal situations where the light is not very intense. In such cases, it turns out that the light has a very small effect on what happens inside the atoms or molecules themselves, that is to say it just tickles them as it passes through, with the effect that they may absorb or scatter some of the light, but in such a way so as to leave the optical properties of the material itself unchanged [1-2].

We propose to make analytical studies of the nonlinear optical processes viz, nonlinear refraction and nonlinear absorption in core-shell quantum dots of direct band gap semiconducting materials belonging to III-V or II-IV direct gap crystal classes [2-3]. We will include the effects arising due to the presence of the bound electron-hole pairs, properly known as exciton with electronic properties similar to those of a Hydrogen atom.

Under higher exciton density regime, we will also make an attempt to investigate the nonlinear optical processes when H_2 -molecules type of bi-excitons are formed due to the binding of two electron-hole pairs with a finite binding energy. We have also examined exotically the role of the shape or size non-uniformity in the on the optical nonlinearties in the semiconductor QDs.

THEORETICAL FORMULATIONS

The only screening considered is included in the screened Columbic electron-hole interaction energy in

the crystal with a dielectric constant and the absolute permittivity and the static dielectric constant of the crystal, respectively is given by [3-4],

$$\chi_r^{(3)}(t) = \frac{N\mu^4 \Delta \omega e^{-\gamma t}}{16\varepsilon_0 |\beta|^2 \hbar^3 (\Delta \omega^2 + \gamma^2)} \sin(\Delta \omega t + \frac{\Omega_R^2 \Delta \omega t}{(\Delta \omega^2 + \gamma^2)})$$

$$\chi_i^{(3)}(t) = -\frac{N\mu^4 \gamma e^{-\gamma t}}{16\varepsilon_0 |\beta|^2 \hbar^3 (\Delta\omega^2 + \gamma^2)} \sinh(\gamma t - \frac{\Omega_R^2 \gamma t}{(\Delta\omega^2 + \gamma^2)})$$

Above equations clearly shows the both real and imaginary parts of the third-order optical susceptibility of the QD are time dependent and one can make use of these two equations to study the phenomena of transient nonlinear refraction and transient nonlinear absorption in the QDs.

RESULTS AND DISCUSSION

Figure 1 illustrates the behavior of the real part of the transient third-order optical susceptibility $\chi_r^{(3)}(t)$ of the crystal. This shows the occurrence of the material dispersion for damping constant much smaller than the detuning frequency as a function of time t. The oscillatory nature of $\chi_r^{(3)}(t)$ establish the occurrence of dispersive type optical nutation. The sinusoidal nature of curve shows that, at zero damping the optical susceptibility is time dependent with constant amplitude that periodically switches polarity



Figure 1: Optical nutation in GaAs/AlGaAs QDs with negligible damping.

Figure 2 illustrates the behavior of the real part of the transient third-order optical susceptibility $\chi_r^{(3)}(t)$. On comparing the two optical nutation signal of GaAS in the presence of damping. We can conclude that the amplitude of the real part of the susceptibility decreases where as its frequency of oscillations increases with increase radius of GaAs quantum dots. In the graph, we observe that there is approximately two fold decrease in the frequency of $\chi_r^{(3)}(t)$ by slightly increasing the radius of QD (11nm from 10nm).



Figure 2: Optical nutation in GaAs/AlGaAs QDs in presence of damping.

Figure 3 illustrates the damped oscillatory behavior of $\chi_r^{(3)}(t)$ as a function of input frequency. The graph shows that the rate of decrease of amplitude is decreasing with input frequency.



Figure 3: Optical nutation in Galas/AlGaAs QDs ir presence of damping



Figure 4: Optical nutationinin(figaAs/AlGaAs QDs in presence of damping.

While the frequency of $\chi_r^{(3)}(t)$ increases with input frequency. Figure 4 illustrates the behavior of the imaginary part of the transient third-order optical susceptibility $\chi_i^{(3)}(t)$ of the crystal. The Imaginary part of $\chi_i^{(3)}(t)$ increase sharply with time attaining peak at 30fs and then start decreasing with time. The optical signal reaches zero after 150fs.

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Evidence of Giant Magnetic Moment Clusters and their Disintegration into Small Clusters in a Cobalt Carbide Nanocomposite

Nirmal Roy, Suprotim Saha, S. S. Banerjee

Indian Institute of Technology Kanpur, Kanpur, 208016, Uttar Pradesh India

*Corresponding author: satyajit@iitk.ac.in

Abstract

We study the magnetic properties of cobalt carbide nanocomposite with a mixture of Co₂C and Co₃C phases in a 1:1 ratio (volume). *M*-*H* hysteresis measurements ascertain the presence of significant hysteresis up to room temperature (*T*). Using a modified Langevin analysis of M(H) curves, we observe that at room temperature, the nanocomposite behaves as a collection of giant magnetized clusters, with each cluster possessing a large average magnetic moment of ~ 4200's μ_B . Each cluster comprising a few hundred Co₃C molecules behave as a single unit exhibiting a giant moment. At high *T*, there are small numbers of these large-sized magnetized clusters. Below 100 K, the number of clusters increases significantly while the size of each cluster decreases, and the average moment per cluster also decreases rapidly down to 30 μ_B . Thus, it appears that there is a fine-graining disintegration transition of these clusters around 100 K. We explain our results by considering that the nanocomposite with clusters possesses a mixture of Co₃C-Co₂C, interspersed with primarily Co₂C rich regions. The strong exchange coupling is mediated within the heterogeneous clusters through free electrons at high *T*, leading to a giant moment. The exchange coupling in these clusters weakens below 100 K leading to the fine graining transition.

Introduction

The magnetism at the nanoscale is very different from that of the bulk counterpart of materials. The properties at the low dimension differ significantly due to an increase in the surface-to-volume ratio. The reduced coordination number at the surface of nanoparticles (NPs) results in drastic modification in the band structure and scenarios related to the localization of electrons, leading to enhanced moments[1,2]. It is known that the average magnetic moment of few atom clusters of ferromagnetic transition metals increases with cluster size and applied magnetic field[3]. At the nanoscale, ferromagnetic materials show the modification of coercivity and anisotropy energy with respect to the bulk. It is essential to study these magnetic NPs because they find varied applications in high-density data storage devices, high-tech industries, and nanomedicine[4-6]. Recently, the nanomaterials of transition metal carbide, particularly cobalt carbide NPs, have received attention due to their high remanence, coercivity at room temperature, along with their cost-effective synthesis routes, making them a prospective candidate for rare-earth-free permanent magnets[7-9].

Cobalt carbide has two stable forms, viz., Co_2C and Co_3C . Electronic band structure calculations showed that bulk Co_2C is paramagnetic and strongly metallic [10]. Recent theoretical studies on few atom clusters

of Co₂C and Co₃C showed emergent magnetic behavior[9] of phases with the magnetic moment of 0.99 μ_B /atom (Co₂C) and 1.67 μ_B /atom (Co₃C), respectively. Studies on pure Co₃C nanoparticles show unusually large magnetic anisotropy ~ 7.5×10^5 J/m³ with 8 nm-sized ferromagnetic domain and a T_C of 573 \pm 2 K [8]. More recently, admixed nanocomposite of Co₂C and Co₃C showed a transformation from a magnetically coupled state (at $T \ge 100$ K) with delocalized spin-wave to a magnetically decoupled state (at $T \leq 100$ K) with localized spin-wave.[11]. It is worthwhile studying the behavior of the average moment of these nanoparticle clusters around the coupling-decoupling transition. Using a modified Langevin analysis of the initial magnetization curves of admixture of Co₂C and Co₃C, we show that there are a small number of large-sized clusters, with each cluster possessing a large average magnetic moment ~ 4200 μ_B at high temperature. With reducing T, the number of clusters increases rapidly below 100 K while the average magnetic moment per cluster decreases to about 30 μ_B at low T. We estimate that each cluster at room temperature has a few hundred molecules which seem to be strongly exchangecoupled, leading to a large net moment. These clusters begin disintegrating with the lowering of T. The above phenomenon suggests a fine graining transition in the

nanocomposite. We explain that the nanocomposite with a heterogeneous mixture of Co_3C-Co_2C is interspersed with primarily Co_2C rich regions. There is strong exchange coupling in the heterogeneous clusters at high *T*, favoring giant moment cluster units. The exchange coupling in the clusters diminishes rapidly below 100 K leading to the fine graining transition. We believe that the strong exchange interaction is mediated by free electrons available in the heterogeneous clusters.

Results and Discussion

Sample preparation and X-ray diffraction (XRD) analysis of the as-prepared sample are described in detail in Ref.[11] XRD analysis indicates the presence of a 1:1 ratio of Co₂C and Co₃C. The nanoparticles size is estimated to be 40 ± 15 nm, as shown in the Transmission Electron Microscope (TEM) image in Fig. 1



Fig. 1. TEM image of the nanoparticles

This nanocomposite's magnetic hysteresis M(H) is measured using a SQUID magnetometer, Cryogenic, UK. Figure 2 shows M(H) loops at different temperatures. In order to determine the average magnetic moment for our nanocomposite, instead of fitting the M(H) data using a simple Langevin function

 $(L(\frac{\mu H}{k_B T}))$ which implicitly assumes a uniform distribution of magnetic moments (μ), we use a modified Langevin form [12]. The modified Langevin form considers variance in the values of magnetic moments (μ) in the nanocomposite, explicitly a lognormal distribution [12] $f(\mu) = \frac{1}{\mu s \sqrt{2\pi}} \exp(-[\ln(\mu/\xi)]^2/2s^2)$, where *s* is the variance and ξ is related to the average magnetic moment through, $\mu_{avg} = \xi \sqrt{e^{s^2}}$. The *M*(*H*) of Fig. 2 is fitted to



Fig. 2. The *M*-*H* loops at different temperatures.

the modified Langevin form, $M(H) = N_{cluster} \int_0^\infty \mu f(\mu) L(\frac{\mu H}{k_B T}) d\mu$, where $N_{Cluster}$ is a

number density parameter. Using N_{Cluster} , s, and ξ as the fit parameters, Fig. 3(a) shows that the M(H) data at different T fits well to the modified Langevin form with a regression R of 0.998 (the value of s is nearly constant at about $0.25\pm.06$ in the fit). Figure 3(b) shows that the μ_{avg} on each particle in the nanocomposite monotonically decreases with reducing T. The figures also show an unusual behavior; $N_{Cluster}$ is roughly constant at ~ 10¹⁷ (per gram) for high T, increases rapidly to about 10^{19} below 100 K. Note that at 300 K, the μ_{avg} is large in the range of 4200 μ_B while it decreases down to ~ 30 μ_B at 2 K. It may be mentioned that some reports in the past have also indicated to systems where large magnetic moment values have been observed[13,14]. We believe the number density parameter $N_{Cluster}$ in the fit corresponds to the number density of giant magnetic clusters in the nanocomposite, where each cluster has an average *n* number of magnetized molecules. Our earlier report on magnon confinement in the admixture of Co₃C- Co₂C indicated a cluster size of ~ 6 nm at low T[11]. Recall Co₃C is a well-known ferromagnetic system, with a magnetic moment of 1.67 μ_B /Co atom. At 2 K, the $\mu_{avg} \sim 30 \ \mu_B$ suggests that the number of Co₃C molecules which are coupled in each cluster are quite small, i.e., $n \sim 6 [=30\mu_B/(3 \times 1.67\mu_B)]$. The increase of μ_{avg} to $4200\mu_B$ at a high T of 300 K corresponds to an increase of $n \sim 840$ molecules for each cluster. Thus, at low T, there are a large number of clusters ($N_{Cluster} \sim 10^{19}$), with each cluster possessing an average of 6 Co₃C molecules and an average net moment of 30 μ _B. At high *T* (300 K), the individual

phase transition. Many aspects of this system are highly intriguing and worthy of future theoretical and experimental investigations.



Fig. 3. (a) Initial magnetization curves at different temperatures and solid line is fitted data with modified Langevin function with log-normal distribution of magnetic moments. (b) Number of nano-particles Cluster ($N_{Cluster}$) (blue) and average magnetic moment (dark yellow) with temperature.

cluster size increases with ~ 840 coupled Co_3C molecules having an average net moment of 4200 $\mu_{\rm B}$. Thus, each giant cluster having almost 840 Co₃C molecules behaves like a single giant particle with one large average magnetic moment ~ $4200 \mu_B$ at room T. Below 100 K, the giant magnetized clusters disintegrate into a large number of smaller-sized clusters with each cluster having a lower average magnetic moment. We conjecture that the clusters in the nanocomposite possess a heterogeneous mixture of Co₃C-Co₂C interspersed with primarily Co₂C rich regions. A strong exchange coupling mediated by free electrons in the heterogeneous clusters at high T favors giant moment cluster units. The exchange coupling in the clusters diminishes rapidly below 100 K leading to the fine graining transition with a low average magnetic moment.

Conclusion

Co₃C-Co₂C In conclusion, we believe the nanocomposite appears to exhibit the formation of giant magnetized clusters, behaving as a single unit at high T. These clusters are almost extensions of the quantum mechanical picture of individual atoms with an associated magnetic moment. Each giant magnetic moment cluster is free to move about and rotate at high T, exchanging energy with the environment. However, with decreasing T, the clusters begin to disintegrate due to the changing electronic density of states within each cluster. These clusters shrink, and so does their average moment. This shrinkage is like a second-order

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Synthesis and characterization of Spherical shaped silver nanoparticles from extremophilic bacterium Deinococcus radiodurans

Velmurugan Sekar¹ Kavitha N S¹, Velmathi G¹ and Amutha Santhanam^{1*}

¹Nano Biotherapeutics Laboratory, National Centre for Nanoscience and Nanotechnology, University Of Madras,

Guindy Campus, Chennai 600025.

*E-mail: amutha1994santhanam@gmail.com

Abstract

In Nanotechnology, the biosynthesis of metal nanoparticles has potential applications in many fields. The particle synthesis from Extra cellular substances of bacterial cells have low cost and eco - friendly, while it can produce with controlling parameters like pH, biomass and growth phase. The extremophile bacteria *Deinococcus radiodurans* that possesses the power to resist very high radiation and desiccation stress has been utilized for the synthesis of silver nanoparticles (AgNPs) during this study. Since it's having distinctive size-dependent properties, silver nanoparticles offer the chance to develop new therapeutics. This work is aimed to synthesis AgNPs from the cell free extract of *Deinococcus radiodurans* and also the silver nanoparticles confirmed through UV-Visible spectrometry, FT-IR, DLS, SEM - EDAX.

Key words: Deinococcus radiodurans, silver nanoparticles, UV, FT-IR, SEM, DLS & ZETA POTENTIAL.

INTRODUCTION

Nanomaterial acts as a bridge between bulk materials and molecular, atomic structures. They exhibit fully new and improved properties in comparison with the majority material. Silver nanoparticles (AgNPs), are incontestable to possess various potential applications. Currently, several ways are according for the synthesis of AgNPs victimisation chemical, physical, photochemical, and biological routes. To cut back the dreadful effects of chemical synthesis and to get novel nanoparticles at a less expensive rate, inexperienced synthesis is more and more being explored [1]. An eco-friendly solvent system and availability of biocompatible reducing and capping agents are the fundamental requirements for green synthesis. Additionally, biological ways are inexhaustible, economic, and might be operated at ambient temperature and pressure conditions. varies microbes are legendary cut back to scale the silver (Ag+) ions to create AgNPs, most of which are found to be spherical particles. The extremophilic microorganism *D. radiodurans* was able to accumulate AgNps in medium beneath varied conditions, and process optimization was administered earlier in our laboratory with reference to time, temperature, pH, and concentration of silver salt. In this work we synthesized silver nanoparticles from this bacterium and AgNPs were characterised victimisation UV/vis spectrum analysis, scanning microscopy, Fourier transform infrared spectroscopy, DLS and ZETA potential [2].

Preparation of Spherical AgNPs

In the synthesis of bacteria based spherical AgNPs was synthesized. The chemicals used are analytical grade with 99% purity of sigma Aldrich. The bacterium *D. radiodurance* was grown in TGY broth (Tryptone, Glucose, Yeast extract) in 100 ml and the pH 7.0 is maintained and sterilized. After sterilization, the culture was inoculated with single pure colony of bacterium and incubated at 36° C for 8 hr in a rotary shaker. The extracellular synthesis of AgNps was carried out. The grown culture of *D. radiodurance* was kept for overnight and centrifuged at 6000 rpm for 10 minutes to separate pellet and supernatant. Then the filtrated solution was mixed with 1mM of silver nitrate precursor. In this ratio of 1:1 and the color change were absorbed at after regular intervals. The colour changes indicate the presence of nanoparticles in the solution.

RESULTS AND DISCUSSION

UV-Visible Spectrophotometer Analysis

The UV-Visible of pure AgNPs synthesized by bacteria mediated biosynthesis is shown in figure.1. A strong and broad surface plasmon peak located at 426 nm was observed and it showed the indication of silver nanoparticles synthesized using *D. radiodurance* cell free extract solution. The silver nanoparticles indicating the surface plasmon resonance cantered at 426 nm, confirming the extracellular accumulation of silver nanoparticles in the solution.



Fig.1. The UV-Vis absorption spectrum of AgNP

Fourier Transform Infrared Spectroscopy [FTIR]

FTIR measurements were performed to spot the possible biomolecules accountable for bio-reduction, capping, and/or stabilizing the AgNPs synthesized using *D. radiodurans*. so as to get good S/N of AgNPs, the spectrum was taken within the range 500 - 4500 cm⁻¹. The prominent intensity peaks at 3297 cm⁻¹, 2118 cm⁻¹and 1630 cm⁻¹ The functional groups like C–H stretch, CH₃ - R, N–H, C–O–C, aromatic C–C skeletal vibrations, –COO, –NO₃, thioester, and S–S stretch were observed. The reported functional groups like –C–O–C–, –C=C–, and –COO is derived from heterocyclic compounds like proteins present within the bacterial extract and are capping ligands of nanoparticles. In our study, the amide linkage and other functional groups revealed through the FTIR analysis may probably play a task within the interaction of synthesized nanoparticles with the proteins and peptides of *D. radiodurans*, there by stabilizing the AgNPs. The strong band at 3432 cm⁻¹ could also be assigned to the stretching vibration of OH, NH groups present in carbohydrates or proteins. The bands at 665 cm⁻¹ appreciate P–O–C stretching vibrations indicating the interaction between phosphoprotein and therefore the AgNPs surface. Moreover, the band at 1121 cm⁻¹ may be ascribed to the methylene scissoring vibration in proteins during the formation of AgNPs [3,4].



Fig.2. Shows the FTIR Spectrum of AgNPs

Scanning electron microscopy and Energy dispersive spectroscopy

Scanning electron microscopy was employed to visualize the size and shape of AgNps is shown in fig.3 (a, b, c). The particles showed cantered spherical with the diameter of 20 nm to 5 nm. The SEM image of AgNps was due to interactions of hydrogen bond and electrostatic interactions between bioorganic capping molecules bound to the AgNps. The AgNPs were of spherical, pseudo-spherical and irregular shapes which were observed on the surface layer and were more evident in the image of the prepared AgNPs. Energy dispersive spectroscopy micro analysis was performed by measuring the energy and intensity of X-ray signals generated by a focused electron beam on a specimen. Fig.3(d, e) shows the clear elemental composition profile of the synthesized AgNps. In this study it was used to confirm that the nanoparticles suspension contains silver.



Fig.3. SEM images a, b, c pure AgNPs and d, e shows the EDAX of AgNPs

Dynamic Light Scattering

The particle size and zeta potential of AgNPs were further measured using the DLS measurement. The observed plot depicts the formed AgNPs were highly monodispersed, and therefore the average size of the AgNPs was 88 nm while the dimensions of the very best percentage of AgNPs, which matched with the dimensions of nanoparticles observed by SEM [5]. The zeta potential value -33.5 mV with the polydispersity index at pH 7of AgNPs indicated that the AgNPs were stable.



Fig.4. Shows the (a) DLS and (b) Zeta Potential of AgNPs

Conclusion

The present work has been enunciated the facile, eco-friendly bacterial mediated biosynthesis of AgNps nanoparticles using *Deinococcus radiodurans* bacterium. SEM images confirmed the structure and morphology of AgNps. FT-IR spectrums clearly represent that interaction of biogenic molecules and bacterial extraction contributed during the AgNps synthesis. DLS shows the size of the nanoparticles and zeta potential shows the stability of the silver nanoparticles. The UV – visible spectrum shows the broad spectrum at 426 nm and it conforms the silver nanoparticles.

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Facile Synthesis of *Terminalia chebula* and *Strychnos potatoram* mediated Titanium Dioxide (TiO₂) Nanoparticle and Its Nano bio application: Comparative study

Niveditha N¹, Kavitha N S¹, Muthulakshmi V¹, Amutha Santhanam^{1*}

¹Nano Biotherapeutics Laboratory, National Centre for Nanoscience and Nanotechnology, University of Madras, Guindy Campus, Chennai 600025. *E-mail: amutha1994santhanam@gmail.com

ABSTRACT

Recently there has been increasing interest in developing potent non-toxic drugs in medicine which is widening the chances for studying the usage of nanostructures in nanomedicine. The present work reports a method for a facile and an eco-friendly synthesis of titanium di oxide nanoparticles (TiO₂ NPs) using *Terminalia chebula* fruit extract (TCE) and *Strychnos potatoram*. In the selection of herbal scenario for current usage, *Terminalia chebula* (Kadukkai) and *Strychnos potatoram* (Thettan Kottai), are the oldest herbal medicinal plant which is called as the King of the Medicine's, and they contain a number of chemical constituents like chebulic, ellagic acid, tannic acid, alkaloids, flavonoids', saponins, etc. Hence the main aim of this work is to facile synthesis of TiO₂ NPs from the aqueous extract of *Terminalia chebula* and *Strychnos potatoram*. The obtained Titanium Dioxide nanoparticle has been characterized by UV Visible Spectrophotometer, Fourier Transforms Infra-Red Spectrophotometer, SEM, Dynamic light scattering and Zetapotential. In addition, a comparative study of its antioxidant activity was analysed.

Key words: Strychnos potatoram, Terminalia chebula, nanoparticle, Characterization, Antioxidant, Antimicrobial etc.,

INTRODUCTION

Nanoparticles and nanomaterials associated with technology have brought great advances in the field of nanotechnology applied in the life sciences. Nanomaterials are classified into different types to synthesis the inorganic metal oxide nanoparticles. They are always listed first in the Ayurvedic Materia medica because of their extraordinary power of healing with a wide spectrum of biological activity. The biosynthesis method has received great attention in recent years due to its capability and ability to produce alternative and safer, less toxic, and energy efficient routes towards synthesis. These routes have been associated with the rational utilization of various nanoparticle preparation and synthesis. Several studies reveal that this metal oxide contains several properties like Antibacterial, Antidiabetic, Antioxidant activities Nanoparticles are very small-sized particles that are being exploited increasingly in medicine as in other sciences. Generally, the properties of nanoparticles depend on size, shape, composition, morphology, and crystalline phase. There are few sorts of metal oxide nanoparticles like CuO, TiO₂, ZnO, MgO, NiO, etc. Among all the Titanium Dioxide [TiO₂] Nanoparticle has been extensively used as an environmentally harmonious agent and a clean photocatalyst [1].

Titanium Dioxide nanoparticle are also called the Ultrafine Titanium dioxide nanoparticle. The Titanium dioxide nanoparticle has an optical property of high chemical stability and nontoxicity. This nanoparticle is used in the green synthesis of plants and their parts. The biosynthesis of the nanoparticle is used in a wide range by a synthetic route using plants [2]. The green synthesis of titanium dioxide nanoparticle has more advantages due to its less consumption of chemicals, a cost-effective and eco-friendly method [3]. The aim of the present study is to synthesis titanium dioxide nanoparticle using green synthesis from the aqueous seed extract of *Terminalia chebula* and *strychnos potatoram* and to characterize with the UV visible spectrophotometer, FTIR, DLS, Zeta potential.

Preparation and Synthesis of Titanium Dioxide Nanoparticle

The fresh seeds of terminalia chebula and strychnos potatoram are identified and washed with deionized water. The seeds were dried at room temperature and made into fine powder. The prepared powder of terminalia chebula and strychnos potatoram were and stored in an air-tight container for further analysis. About 10 g of powder of terminalia chebula and strychnos potatoram was mixed with each 100ml of deionized water and kept in a boiling water bath for 20 mins. The obtained extracts of Terminalia chebula and Strychnos potatoram were filtered using Whatman's filter paper and both the samples were washed several times and centrifuged at 2000 rpm for 20 mins, and then the powder was sealed properly and kept at 4 °C for further use [4].

The required amount of fine seeds powder of terminalia chebula and strychnos potatoram were washed and boiled to make the aqueous extract. The synthesis of Titanium dioxide nanoparticle is carried out using the aqueous extracts of the Terminalia chebula and Strychnos potatoram. The 1mm of TiO_2 was weighed and mixed with each 80 ml of distilled water and then a mixture of 20 ml of prepared extract of the herbal seeds was added separately. The samples were kept for 24 hrs for incubation. The sample's color changes to orange, then both the samples were centrifuged and the collected powder was dried in a hot air oven [5]. The dried powder was further used for other characterization techniques and antioxidant activity.

RESULTS AND DISCUSSION

UV-Visible Spectrophotometer

In order to confirm the presence of TiO_2 nanoparticle in the resulting solutions, the UV visible spectroscopy was characterized and the broad maximum peak denotes the presence of Titanium dioxide nanoparticle in both the samples. *Terminilia chebula* shows the peak at 330 nm. *Strychnos potatoram* showed the peak at 316 nm. The UV visible absorption spectra for TiO_2 nanoparticle are between 200 to 400nm. Both the peaks indicates the presence of TiO_2 .



Fig.1. Shows the UV of (a) $TiO_2 T.C$ and (b) TiO_2 in S.P

Fourier Transform Infra-Red Spectroscopy

FTIR is a technique used to obtain an infrared spectrum of absorption or emission of solid liquid gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide range of spectrum. In order to confirm the presence of TiO₂ the peaks range from 430 to 850 cm⁻¹ corresponds to the vibration of metal-oxygen. Moreover, prominent peaks in the 450 to 800 cm⁻¹ range are due to Ti-O & Ti-O of stretching vibrations, confirming the formation of TiO₂ nanoparticle in Terminalia chebula showed the peaks at 506 cm⁻¹ corresponds to the Ti-O bonds. A broad band nearly stretching at 3302 cm⁻¹ is because of its O-H stretching vibration of the inter layered molecule. Strychnos potatoram showed its peaks at 491 cm⁻¹ corresponds to H – bonded alcohols and phenols. The bands at 1637 cm⁻¹ that indicates the presence of C-O stretching alcohols, carboxylic acids. Both the samples prove the presence of TiO₂


Fig.2. Shows the FTIR spectra of (a) $TiO_2 T.C$ and (b) TiO_2 in S.P

Dynamic light scattering and Zeta potential

Dynamic Light Scattering technique is an efficient method to measure the particle diameter. This size is not only connected with the metallic core of the nanoparticles but it is also influenced with all substances adsorbed on the surface of the nanoparticles. The DLS study of Terminalia chebula indicates at 583. And Strychnos potatoram shows at 748. DLS shows the size of the nanoparticles and zeta potential shows the stability of the titanium dioxide nanoparticles.



Fig.3. Shows the DLS of (a) T.C of TiO_2 and (b) S.P of TiO_2

 TiO_2 NPs have a positive zeta potential at low pH in contrast to the negative zeta potential at high pH due to the protonation and deprotonation process. A unique finding is that TiO_2 nanoparticles shaped by sodium dodecyl sulphate (SDS) have double isoelectric points (IEPs), while other shape-controlled TiO_2 nanoparticles have only one IEP. The ZP study of Tio2 for terminalia chebula was found to be -58.9 mV and the Strychnos potatoram showed at the peak at -55.9 mV.



Fig.4. Shows the Zeta potential of (a) T.C of TiO₂ and (b) S.P of TiO₂

CONCLUSION

The synthesis of Titanium dioxide nanoparticle from the aqueous extract of Terminalia chebula and Strychnos potatoram which acts as a reducing and stabilizing agent and was carried out using the green synthesis method. The prepared TiO_2 were characterized using UV, FTIR, DLS, ZP. Both the samples showed a peak which indicates the presence of Titanium dioxide nanoparticle present in the aqueous extracts of both the herbal seed extract. The FTIR spectrum indicated the role of nitro compounds and O-H group in the synthesis of TiO_2 NPs. This simple, low cost, eco-friendly method for synthesizing stable TiO_2 NPs provides a valuable alternative approach for large scale synthesis.

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Fluorescence Emission Enhancement Of Copper Nanoclusters (CuNCs) In The Presence Of Ascorbic Acid

Subhankar Pandit*, Sarathi Kundu

Soft Nano Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Vigyan Path, Paschim Boragaon, Garchuk, 781035, Assam, India

*Corresponding author: subhankarphysics@gmail.com

Abstract

An environment friendly chemical synthesis method is used to synthesize lysozyme templated ultra-small copper nanoclusters (CuNCs). The as-synthesized NCs shows an UV-Vis absorption around 365 nm and an emission at around 449 nm corresponding to this absorption. The fluorescence emission of CuNCs enhances with increasing concentration of ascorbic acid. The interaction of surface lysozyme with ascorbic acid may be the reason behind such enhancement. Due to interaction, the NCs possibly form aggregates and the aggregation induced enhancement in emission is observed.

Introduction

Ultra-small metal nanoclusters (MNCs) have tremendous potential in the field of bioscience and engineering due to their unique properties, such as, biocompatibility, size-dependent fluorescence, and photostability. MNCs are composed of several to tens of atoms showing the molecule like electronic transition rather than surface plasmon resonance (SPR) [1]. In last few decades, MNCs of copper, gold, platinum, and silver were synthesized using different techniques and have been utilized in sensing, imaging, drug delivery, etc. Among different MNCs depending on synthesis procedure and use of template material, protein templated MNCs have drawn special attention among others due to its nontoxicity, stability and excellent fluorescence properties [2].

The fluorescence emission of MNCs generally quenched in the presence of ions, solvent, pH etc., and this property is used in various applications. Though, instead of quenching, in some cases the emission of fluorescent MNCs can be enhanced depending upon the physicochemical environment. The fluorescence enhancement of MNCs can be helpful in sensors, light emitting devices, photosensitizers, etc [3]. Fluorescence emission of MNCs is enhanced by doping other materials, aggregation, dissolved ions, solvent, biomolecules, pH, temperature, etc [3,4]. One of the drawbacks of the MNCs is the unavailability of high quantum yield (OY). The emission enhance mechanism can solve this drawback. The doping of a different metal to a MNCs such as doping of Ag in AuNCs can significantly affect the fluorescence properties [5]. The emission of the MNCs can be enhanced upon aggregation. Aggregation may restrict the nonradiative relaxation and enhance the fluorescence. Selection of the appropriate solvent can result in aggregation [4,6]. MNCs can be self-assembled or assembled with the template and can give rise to fluorescence enhancement. Among different MNCs, CuNCs are less studied though it has large abundance and it can also show excellent emission behavior.

In this work, lysozyme templated CuNCs were synthesized and characterized. After that the optical absorption and emission behaviors of the CuNCs in the presence of ascorbic acid was studied. In the presence of ascorbic acid, the enhancement in fluorescence emission is observed. The emission enhancement may be due to the aggregation of CuNCs in the presence of ascorbic acid.

EXPERIMENTAL DETAILS

Lysozyme (catalogue no. 62971) and sodium borohydride (NaBH₄) (catalogue no. 480886), and ascorbic acid (catalogue no. A7506) were purchased from Sigma, whereas copper chloride (CuCl₂·2H₂O) (catalogue no. 1.93691.0521) was purchased from Merck and were used as received. Before use, all solutions were freshly prepared using double-distilled water from the Millipore Milli-Q system. CuNCs were prepared using the chemical synthesis method. First, 15 mg/ml lysozyme solution was stirred at a constant 500 rpm speed at room temperature (25°C). After that, the aqueous solution of CuCl₂ was added to the solution, followed by a tiny amount of NaBH₄. The final concentration of CuCl₂ and NaBH₄ in the solution was fixed at 5 and 8 mM, respectively. After nearly 15 hours, the solution became pale green, which is the indication of the formation of CuNCs. The solution was stored at 4°C for characterizations and other studies. For the emission enhancement study, CuNCs concentration was fixed at 15.2 mg/ml

whereas, the ascorbic acid concentrations were varied from 0-250 μ M and incubated for 30 mins. Absorbance of the samples was observed through UV-Vis absorption spectrophotometer (Shimadzu UV-1800) within a range of 190 – 1000 nm. Corresponding fluorescence emission spectra were recorded using JASCO FP 8500 fluorescence spectrophotometer within 290 – 700 nm with a slit width of 5 nm.

RESULTS AND DISCUSSION

The optical properties of the lysozyme templated CuNCs was characterized. The UV-Vis absorption spectrum is recorded and shown in Fig.1. The CuNCs show an absorption at around 365 nm. The fluorescence emission corresponding to this excitation is also shown in Fig.1. The maximum emission intensity of CuNCs is observed at around 449 nm. This emission is due to the transition from HOMO to LUMO as no other SPR peak is observed in far red region.



Fig. 1. UV–vis absorption (black line) and fluorescence emission (red line) of lysozyme templated CuNCs.

The emission behavior of CuNCs in the presence of ascorbic acid is also studied and shown in Fig.2.



Fig. 2. Fluorescence emission spectra of CuNCs in the presence of different concentration of ascorbic acid. Inset: The change of maximum emission intensity as a function of ascorbic acid concentration.

It is observed that in the presence of ascorbic acid the fluorescence emission increased almost two times without changing the peak position or peak shape. The variation of maximum emission intensity with the ascorbic acid concentration is shown in the inset of Fig.2. The ascorbic acid may co-ordinate strongly with the amines of the lysozyme present on the surface of the CuNCs. This may lead to the aggregation of the NCs. Due to the aggregation, the rotational and vibration movement of the system is restricted and as a result non-radiative decay is reduced and fluorescence enhancement occurs [6].

CONCLUSIONS

The lysozyme templated CuNCs was synthesized using chemical synthesis route and optical properties are studied. The UV-Vis absorption and corresponding fluorescence emission is observed at 365 nm and 449 nm respectively. The interaction of CuNCs with the ascorbic acid is studied through fluorescence spectroscopy. Around two times of fluorescence emission enhancement of CuNCs in the presence of ascorbic acid is observed. Due to the strong interaction of the acid with the surface lysozyme the CuNCs aggregate and the aggregation induced emission enhancement occurs.

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Impact of Thermal Treatment on Surface Morphology and Band Gap Modification of In₂O₃/SiO₂ Nanocomposite

Neelam Rani^{1*}, Bindiya Goswami² and Rachna Ahlawat³

^{1,2,3}Department of Physics, Material Science Lab., Chaudhary Devi Lal University, Sirsa, Haryana (India) Pin-125055.

*Corresponding author: neelam.rani.sardiwal@gmail.com

Abstract

In the present study, we have demonstrated the impact of thermal treatment on surface morphology and band gap modification of In_2O_3/SiO_2 nanocomposite using sol-gel technique. The powder samples are calcined at various temperatures those are further examined by famous characterization tools. The cubic phase of prepared sample is confirmed by XRD and microstructure details are obtained from SEM study. The surface interactions play a crucial role in determining the morphology and crystal phase which further modify the band gap of prepared In_2O_3/SiO_2 nanocomposite.

Introduction

Indium oxide (In_2O_3) is a vital n- type semiconductor with a large band gap range about (3-3.5 eV) having potential use in optoelectronic appliances and gas sensing applications [1-2]. In₂O₃ is mainly used to prepare nanostructures owed to their less cost, easy to manufacture, high and long-term stability [3]. In the last few ages, many attempts have been made to regulate the structure and morphology of In₂O₃ to enhance its physical properties. Several In₂O₃ nanostructures as like nanoparticles, nanocubes, nanowires, nanotubes and few microstructures have been effectively prepared via either physical deposition or chemical methods [4-5].

Nanocrystalline In_2O_3 is an important member of inorganic materials semiconductor, whose shape, size, phase and constituents impart a major role in their performance. Keeping this in view, structural and optical performance of In_2O_3/SiO_2 nanocomposite has been demonstrated in this work. The impact of annealing on surface morphology and modification in band gap energy is also given.

Sample Formation and Characterizations

The chemical used in synthesis of indium doped silica were TEOS, purity >98%, C_2H_5OH 99.8%, In_2O_3 , double distilled water catalyzed by HCl with TEOS: H_2O : HCl = 1:6:1.4. Ageing process were done for 1 week and finally dried in stages from 30°C to 110°C for 5 days to yield the as-groomed sample Z1. Z1 sample was transferred into a crucible and then placed in furnace at 300°C, 600°C and 900°C for 3 h named as Z2, Z3 and Z4.

The data of XRD were received by XPERT-PRO XRD machine run at the voltage 45 kV and current 40 mA, via radiation of Cu K α wavelength 1.5406 Å.

JEOL-JSM-6100 scanning electron microscope (SEM) was used to study surface topography and constituent elements were identified with an energy dispersive X-ray spectrometer (EDX). Samples were diffused in ethanol to record optical absorption spectra in range of 200–900 nm by Lambda 750 (Perkin Elmer) spectrophotometer.

X-ray Diffraction (XRD) Analysis

The phase and structure of the prepared nanocomposite are determined by XRD.



Fig. 1. XRD sequence of all prepared samples with corresponding W-H plot.

Figure 1 defined the main 20 values ~ 21.43° , 30.41° , 35.42° , 37.20° , 42.22° , 45.45° , 50.97° , 55.78° and 60.65° matching with JCPDS card no. 06-041 for all annealed samples [2]. The observed peaks are corresponding to XRD miller indices (211), (222), (400), (411), (332), (431), (440), (611) and (622) which belongs to cubic crystal structure of In_2O_3

having space group Ia $\overline{3}$. The unit cell parameters for this cubic phase have values a = b = c = 10.16 Å and $\alpha = \beta = \gamma = 90^{\circ}$. Average nanocrystallite size is calculated for annealed samples Z2, Z3 and Z4 that is evaluated as 9.81, 14.73 and 15.87 nm respectively via famous Debye-Scherrer's formula:

$$D = \frac{\kappa \lambda}{\beta \cos \theta} \qquad \qquad a)$$

Further the effect of micro-strain could be evaluated by well-known Williamson-Hall plot for annealed samples given by following equation:

$$B_{hkl}Cos\theta_{hkl} = \frac{K\lambda}{D} + 2\varepsilon Sin\theta_{hkl}$$
 b)

In the annealed samples Z3 and Z4 micro strain have negatives values i.e., -0.005 and -0.0126 corresponding to compressional strain developed in nanostructures due to high thermal treatment.

SEM Microscopy (SEM) Analysis

It gives the information regarding surface or topography of the prepared samples. Here, we have presented the most crystalline micrograph corresponding to highest annealed sample (Z4). The micrograph has small and large size nanoparticles.



Fig. 2. EDX spectra for sample Z4 with SEM micrograph.

EDX spectrum gives elemental compositional percentage for the prepared sample. Large intensify peak of oxygen and silica were recorded 50.54 wt % and 48.16 wt % respectively. The less intensified peak of indium is due to less amount (1.31 wt %) present at starting level of the prepared sample [3].

Ultraviolet-Visible Spectroscopy (UV-Vis.) Analysis

Figure 3 displays the absorption spectra of all prepared sample Z1, Z2, Z3 and Z4. As we can easily see that band edge is observed at 320, 315, 320 and 324 nm for prepared sample Z1, Z2, Z3 and Z4 respectively. This fact is in accordance with the excitonic transition from lower band to upper band. Blue shift occurs in absorption changing point due to thermal treatment. Tauc's plot of In_2O_3/SiO_2 nanocomposite is attained by plotting graph between $(\alpha hv)^2$ vs hv and the symbols v, α , h are respectively used for frequency, absorption coefficient and

Planck's constant. The variation of the plots provided band gap values 2.79, 3.24, 3.29 and 3.37 eV for Z1, Z2, Z3 and Z4 sample of In_2O_3/SiO_2 nanocomposite, respectively. The observed values are higher than the bulk band gap values of In_2O_3 (3 eV) [2]. The trend of results highlighted the quantum size effect that is significantly observed in prepared nanocomposite In_2O_3/SiO_2 . Increase in band gap energy with increase in temperature is due to removal of defects, hydroxyl ions etc. and pure In_2O_3 nanocrystalline are formed which are homogeneously dispersed in silica matrix.



Fig. 3. Absorption plots and corresponding band gap energy of In_2O_3/SiO_2 nanocomposite sample.

Conclusions

studied synthesized In₂O₃/SiO₂ We have nanocomposite and impact of thermal treatment on surface morphology and band gap. Average nanocrystallite size is obtained 9.81, 14.73 and 15.87 nm for Z2, Z3 and Z4 sample by Debye-Scherer formula. Sharp and intensified peaks of XRD pattern evident the cubic phase of In₂O₃. SEM micrograph exhibited agglomerated nanoparticles with their specific elemental composition. Optical properties through Uv-Visible spectra shows blue shift in absorption edge corresponding to increase in band gap energy with thermal treatment. The results have emphasized suitable applications of In2O3/SiO2 nanocomposite in field of electronics, photonics, optical amplification and solar cells.

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Optical, AC conductivity and dielectric properties of pure and Ag doped TiO₂NPs prepared by microwave-assisted synthesis method P. Suriya, K. Jagannathan*

Depart. of Physics, SRM Institute of science and technology, Vadapalani campus, Vadapalani, Chennai, TN, India

*Corresponding author: kjagan81@gmail.com

Abstract

Pure and Ag doped (0.04 mol%) TiO₂ nanoparticles (NPs) were prepared by microwave-assisted method, and were characterized by XRD, UV and dielectric techniques. XRD plots of both samples confirmed the presence of anatase tetragonal structure with the proper incorporation of Ag at TiO₂ lattice. UV spectral analysis showed that optical energy gap of TiO₂ was reduced with increased Urbach energy by Ag doping. The dielectric measurements showed that the dielectric constant increased as frequency of applied field increases. The a.c. conductivity of both samples followed Jonscher's power law. The Nyquist plots of both samples suggested that conduction process took place predominantly through grain boundary in both samples; however, influence of grain boundary in Ag-TiO₂ NPs is reduced. These results were discussed by correlating optical and dielectric properties of TiO₂ and Ag doped TiO₂ NPs which gave broad understanding to device fabrications successfully.

Introduction

Dilute Magnetic Semiconductors (DMS) in nanoregime are attracted researchers and engineers by having wide variety of applications. Among various DMS nanoparticles (NPs), TiO₂ is a conventional n-type semiconductor, but still it is an essential multifunctional material by offering significant integration advantages [1]. However, there are two main disadvantages in TiO₂ while using it for device fabrication: (i) Energy band gap (E_{α}) of TiO₂ NPs is 3.2 eV and 3.0 eV for anatase and rutile phases respectively [2], which restricts its photoactivity in the visible light region; (ii) external energy of photons supports the recombination of electron and hole pair which limits photocatalytic degradation rate. These two discrepancies must be removed to achieve the best quality device which is possible by doping process in parent lattice. Doping of metal NPs in the TiO₂ system will reduce particle size, and so charge carrier density will be automatically increased, and it will improve trapping of electrons to prevent electron-hole recombination during irradiation [3]. Among the various metal NPs, the silver (Ag) nanoparticles have outstanding ability such as excellent chemical with high stability, and conductivity [4]. It can accelerate the chemical reaction process as activating analyte too.

Particle size will be influenced by several synthesis conditional parameters such as selection of precursors, sintering temperature, sintering duration etc. Still, there is a lack in the course of selecting and optimizing the methods to prepare pure as well as Ag doped TiO_2 nanoparticles. Here, we have prepared pure TiO_2 and Ag- TiO_2 (0.04 mol%) nanoparticles by microwave-assisted method. This method provides good amount of fine particles of samples in short

period of time by easy process. The structural, optical and dielectrical properties of prepared samples are systematically characterized, and the observed data are comparatively analyzed.

Results and Discussion



Fig. 1.XRD patterns with Rietveld refinement of synthesized (a) TiO₂ and (b) Ag-TiO₂ nanoparticles

 Table 1: Lattice Parameters of prepared TiO2 and Ag-TiO2 NPs

Sample	Lattice Parameters			
_	from GSAS fittings			
	a=b (Å)	C (Å)	Volume (Å ³)	
TiO ₂	3.7737	9.4545	134.64	
Ag-TiO ₂	3.7701	9.4525	134.38	

Fig. 1(a-b) shows the XRD patterns of synthesized TiO_2 and Ag- TiO_2 NPs. It confirms that both samples are in best quality nanolevel crystalline and the XRD pattern of TiO_2 matches with JCPDS card no. 15-4601, which exhibits anatase tetragonal structure. The retrieved lattice parameters and unit cell volumes from these refinements uding GSAS refinement are given in Table 1. The lattice

parameters and the volume of Ag-TiO₂ are slightly smaller than that of pure TiO₂. This is due to the fact that the substitution of larger Ag atom (172 pm) at smaller Ti (147 pm) atomic places increases the d planer spacing [5], and so lattice parameters too.



Fig.2: (a) UV-Vis Spectra of synthesized TiO_2 and Ag-TiO₂ NPs [Insets: Tauc plots from main graphs]

In UV spectra for both samples, the strong absorption peaks are observed around 350 nm, and plots shows red shift by Ag doping. Optical bandgap (Eg) of both samples are 3.34 and 3.21 eV for pure TiO_2 and Ag- TiO_2 respectively. The doing of Ag increases the oxygen vacancies and creates shallow defect bands, and the narrowing of the band gap while Ag doping in TiO_2 .



Fig. 3. (a) ε' vs f, (b) ε' 'vs fof synthesized TiO₂ and Ag-TiO₂ NPs; (c) σ_{ac} vs f of synthesized TiO₂ and Ag-TiO₂ NPs (green lines are Jonscher power law fitting); (d) Nyquist plot of synthesized TiO₂ and Ag-TiO₂ NPs (green lines are Non Linear Least Square fitting)

The ε' of TiO₂ and Ag-TiO₂ NPs are 236 and 388 F/m [Fig. 3(a)]. The dielectric constant of both samples decreases with the increase in frequency. The external electric field with low frequency moves the charge carriers across the grains, but grain boundaries prevent this process. So, the dielectric constant is high to low frequency region. But, the external electric field with low frequency supports hopping of charge carriers between grains due to the rapid fluctuations of alternating field. Dielectric constant is increases while doping. It might due to fact that the improvement in particle size increases the

dielectric constant automatically [6]. Fig. 2(b) shows the dispersion for dielectric loss also. As the energy required for migration of charge carriers through grains is high at low frequency, energy loss will also be high at low frequency. ε' at higher frequency region is small which is due to that migration of electrons is well easy as the grain resistance dominates at high frequency. As the high potential barrier height of Ag-TiO₂ NPs prevents the accumulation of charge carriers at grain boundaries, dielectric loss is so high in low frequency region of Ag-TiO₂ NPs.

As the frequency of applied field supplies energy to free charge carrier and stimulate hopping process, and then liberate the charge carriers from localized atoms. Hence, the conductivity of both samples increases with frequency [Fig. 7(c)], but of course, in slow rate at lower frequency and very faster rate in higher frequency. σ_{ac} of Ag-TiO2 NPs at higher frequency region is higher than of TiO₂ NPs. Conductivity of Ag-TiO₂ NPs is increased at higher frequency. Jonscher power law fitting on σ_{ac} plots provide the values of n for TiO2 and Ag-TiO2 NPs as 1.20 and 0.87 respectively. It confirms that hopping process of charge carrier is through localized hopping in TiO₂ NPs, whereas through sudden translation motion in Ag-TiO₂ NPs. The mobility value of Ag-TiO₂ NPs are much higher than of TiO₂ NPs, that is obviously confirms the high conductivity of Ag-TiO₂ NPs. A single semicircular arc was observed in Nyquist plots of both samples [Fig. 7(d)] those are corresponding to grain interior (bulk) effect only. The lack of the grain boundary contribution is might be due to the tightly packed nature of the pellet.

Summary

The TiO_2 and Ag- TiO_2 NPs were prepared by microwave-assisted method. The substitution of bigger Ag atom at smaller Ti sites reduces the lattice parameters as well as the volume of the system. But, crystalline size is decreased, but grain Size is increased by Ag doping in Ag- TiO_2 NPs. This variation increase electrical conduction process mainly through grain boundary in both samples.

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Transport And Optical Properties Of Selenium Rich MoSe₂ Nanospheres

C Malavika, and E S Kannan

Department of Physics, BITS-Pilani K. K. Birla Goa Campus, Zuarinagar, Goa-403726, India.

*Corresponding author: 12malavikac@gmail.com

Abstract

In this work, we investigated the transport and optical properties of Molybdenum diselenide (MoSe₂) nanospheres synthesized using hydrothermal technique. Temperature dependent resistance measurement revealed two conduction regimes, one dominated by degenerate electrons contributed by excess Se and the other by phonons and impurities. The transport regime dominated by degenerate electron was observed from 300 to 70 K, with conductivity decreasing with decrease in temperature. From the Arrhenius plot, the activation energy for the electrons is found to be ~0.5 meV which is the activation energy for the electrons from uncompensated Se atoms. In the low temperature regime (below 70 K) the nanosphere exhibited a metallic like behavior with conductivity increasing with decrease in temperature indicating that the electron transport is dominated by impurities and phonons. Our findings revealed that hydrothermally synthesized MoSe₂ is Se rich and has the characteristics of a degenerate semiconductor.

Introduction

Materials such as graphene, boron nitride, and transition metal dichalcogenides (TMDCs) have attracted wide interest as they are likely to be preferred as a material of choice for future electronics [1]. Numerous scientific investigations have revealed that the properties of these materials vary significantly depending on their geometry, preparation technique, stoichiometric ratio and the nature of defects and impurities [2]. It is also experimentally demonstrated that metallic, superconducting, semiconducting or insulating phases can be achieved in TMDC by varying the polytype and the number of transition metal d electrons [3]. Increasing or decreasing the stoichiometric ratio of transition metals with respect to chalcogenides changes the electronic band structure leading to opening of band gap that spans from visible to near infra-red portion of the electromagnetic spectrum [4]. All these results even though exciting was predominantly carried out in 2D nanosheets and it is natural to ask whether such characteristics exist in TMDCs with other morphologies. Most of the studies on TMDCs with nanosphere or nanorod like geometry focused on their ability to sense various gases and as photocatalyst for environmental application. There is scarcely any report on transport and optical properties of MoSe₂ nanoparticles. In this work we hydrothermally synthesized MoSe₂ nanoparticles and investigated their optical and transport properties.

Experimental

MoSe₂ nanospheres were synthesized by hydrothermal technique. Sodium molybdate(VI) dihydrate, selenium powder and sodium borohydride were dissolved in 50 ml of the mixture of DI water and absolute ethanol and stirred for 10min. The mixture was transferred into a stainless-steel autoclave, sealed and heated at 200°C for 48h in an oil bath. The solution was then filtered and washed with absolute ethanol and distilled water. It was then dried in an oven at 60°C for 8 h. The synthesized sample was then characterized using X-ray diffraction (XRD) and Field emission scanning electron microscopy (FESEM). Temperature dependent current-voltage (I-V) measurement was carried out by loading the sample in a variable range closed cycle cryostat. Keithley 4200 semiconductor characterization system was used for the conductivity measurement.

Results and Discussion

Figure 1(a) shows the SEM image of as synthesized $MoSe_2$ nanospheres. The surface of nanospheres consist of tangled and closely networked fibrous nanostructures with length scales of the order of tens of nanometers. The size of the nanospheres appears fairly uniform with a size distribution of 100 ± 30 nm. Crystallographic phase of the nanosphere was determined from the XRD analysis. All the observed diffraction peaks can be indexed to the hexagonal phase of MoSe₂. The crystallite size obtained by using Debye-Scherrer equation for the two prominent peaks corresponding to (004) and (103) planes are 31.5 and 81.6nm respectively. The Debye-Scherrer equation is given by:

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta} \qquad \qquad \text{a)}$$

Where, τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain

size, K is a dimensionless shape factor, with a value close to unity, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle. No peaks from other impurities are detected in the XRD pattern, indicating that the prepared sample is of high purity. Several experimental trials using the same recipe were performed to ascertain the fact that MoSe₂ prepared using hydrothermal technique is always Se rich. The excess Se will create interstitial defect in the MoSe₂ lattice and the electrons released from the uncompensated Se atoms tend to increase the overall conductivity of nanospheres. The activation energy of energy for electrons released from Se interstitial sites was determined by carrying out temperature dependent resistance measurements on the nanospheres.



Fig. 1. (a) SEM images of MoSe₂ nanospheres. (b) X-Ray Diffraction was performed on MoSe₂nanospheres and a scan angle $10^0 \le \theta \le 60^0$ SEM images of MoSe₂ nanospheres.

Figure 2 shows the variation of resistance as a function of temperature. Two distinct conduction regimes were observed from the temperature dependent resistance characteristics of MoSe₂ nanosphere. The first regime is observed from 300 to 70 K, where the transport was dominated by electrons released from Se interstitial. In the second regime below 70 K, the conduction was dominated by phonon and impurity scattering. In the first regime, the conductivity decreased exponentially with decrease in temperature. The activation energy of electrons from Se interstitial is determined by using the Arrhenius equation:

$$R_t = R_0 * \exp\left(\frac{E_a}{KT}\right)$$
 b)

Where R_t is resistance at particular temperature, R_0 is the resistance at room temperature, E_a is the activation energy, K is the Boltzmann constant and T is the temperature in kelvin. An Arrhenius plot was constructed by taking logarithm of (R_t/R_0) in the y axis and the reciprocal of the temperature, 1/T on x-axis. From the slope the activation energy (E_a) for the electrons (above 80K) is found to be ~19.4 meV which is the activation energy for the electrons from uncompensated Se atoms. In the low temperature regime (below 70 K) the nanosphere exhibited a metallic like behavior (between B and C) with conductivity increasing with decrease in temperature as the phonon scattering decreases. From C to D, resistance remains almost constant with temperature which a typical signature of transport being dominated by impurity scattering.



Fig. 2. Resistance vs temperature of MoSe₂ nanospheres at various temperatures

Our findings revealed that hydrothermally synthesized $MoSe_2$ is Se rich and has the characteristics of a degenerate semiconductor.

Conclusion

In this work MoSe₂ nanospheres were synthesized using hydrothermal synthesis method. The degenerate nature of as synthesized MoSe₂ nanospheres were confirmed through low temperature I-V measurements. Our findings revealed that hydrothermally synthesized MoSe₂ is Se rich and has the characteristics of a degenerate semiconductor.

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Efficient Broad-Spectrum UV attenuation By Defect Engineered ZnO Nanodots Synthesized By A Facile Wet Chemical Batch Process

Sayoni Sarkar¹, Rohit Srivastava², and Ajit R. Kulkarni^{3*}

¹Centre for Research in Nanotechnology and Science, ²Department of Biosciences and Bioengineering, ³Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay, Mumbai, 400076,

India

*Corresponding author: ajit.kulkarni@iitb.ac.in

Abstract

Defect engineered ZnO nanodots (E-NDs) exhibiting high quantum yield with efficient UV attenuation were synthesized by a novel facile wet chemical approach in a batch reactor with enhanced reaction kinetics. This synergistic effect of fast nucleation-growth facilitates the enrichment of singly ionized oxygen vacancy defects (V_0). The E-NDs exhibited high photostability with long-lasting photoluminescence, narrow particle size distribution of its stable dispersion and superior radical scavenging characteristics.

Keywords: Oxygen vacancies, UV attenuation, ZnO nanodots, visible photoluminescence, photostable

Introduction

Nanodots (NDs), exhibiting fascinating structureproperty correlation, are a distinctive class of nanomaterials that have garnered immense attention. The size-dependent quantum confinement effect in the NDs alter their fundamental properties and surface chemistry remarkably. Besides, ZnO NDs with their unique defect chemistry can appreciably fine-tune the optical, electrical, biological properties thus enriching its functionality. The fairly open structure of ZnO is amenable to create surface defects which under oxygen-deficient conditions, is dominated by the singly charged oxygen vacancies (V_o). These V_o play a crucial role in enhancing the photoluminescence quantum vield (PLQY) by acting as radiative centers. Luminescent ZnO NDs have found a place in exigent fields of catalysis, bio-imaging, drug delivery, therapeutics, solar cells and energy storage applications.^[1] Apart from the characteristic UV emission, ZnO nanostructures also exhibit visible photoluminescence which is ascribed to the presence of Vo. However, this domain of defect-induced visible emission in nanostructured ZnO remains a highly debatable field even after years of extensive research. The plausible mechanism for the Vo related visible emission as has been reported in the literature advocates the recombination of electrons in V_o with a hole in the valence band of ZnO NDs. Therefore, incorporating more V_o is essential for devising novel defect engineered ZnO NDs (E-NDs) which will also nurture its potential as an efficient broad-spectrum UV attenuator with high photostability and quantum yield.

Over the years, the commercial considerations of ZnO NDs and their applications have taken an upward

trajectory, leading to numerous hi-tech innovations. Advancements in the frontiers of a facile synthesis with rapid nucleation-growth kinetics have become an absolute necessity for the enrichment of defects in ZnO NDs. The concentration of defects increases under kinetically favoured non-equilibrium reaction conditions. Thus, in this paper, a facile wet chemical approach in batch reactor set-up has been adopted for the synthesis of E-NDs to achieve strong visible photoluminescence for enhanced UV attenuating efficacy.

Experimental Details

The wet chemical synthesis of E-NDs was performed in a batch reactor set-up. The raw precursors (Zn(CH₃COO)₂) (Sigma Aldrich, USA, 99.99 %), lithium hydroxide (LiOH) (Sigma Aldrich, USA, \geq 98%, analytical grade) and absolute ethanol (Analytical Reagent, Assay: 99.99 %) were used as received without any additional purification. The batch synthesis consisted of an RBF (round-bottomed flask) with an ethanolic solution of Zn(CH₃COO)₂ in it and was placed in a pre-heated oil bath with precise temperature control. The optimized heating rate of $Zn(CH_3COO)_2$ solution (0.1M) in the RBF was 0.18°C/sec to achieve a temperature of 75°C. For initiation of the reaction, a precursor solution of LiOH (0.1M) was added at a rapid rate to facilitate fast nucleation and the reactor was sealed to ensure minimal oxygen zone during the synthesis. The [Zn]/[OH] molar ratio was maintained at 1:1 and the solution was subjected to high magnetic stirring for 1 min to obtain a clear solution of E-NDs. After reaction completion, the RBF was immediately taken out of the

hot oil bath and air-quenched to room temperature. The photoluminescence emission spectra and excitation spectra were recorded using HORIBA JobinYvon Fluorolog 3 and HORIBA Fluoromax-4 Spectrofluorometer respectively. For the DLS Analysis ZetaSizer Nano- ZS, Malvern Instruments, Malvern, UK was used.

Results and Discussion

A comparative study of the visible emission observed in the PL spectra (Fig. 1.) of the luminescent E-NDs with that of the control-ZnO NPs elucidate that the presence of engineered V_0 in the former helps it in bypassing the characteristic UVA emission at ~370 nm thereby increasing its efficacy for biological applications where this UVA is found to be detrimental for the body. Further, the PLQY measured for the E-NDs with quinine sulphate in 0.1N H₂SO₄ as standard was estimated to be 0.41 and this high value is attributed to the increased surface V_o (luminescence centres) concentration owing to the accelerated nucleation-growth kinetics. Interestingly, these nanodots were also found to be highly photostable thus overcoming one of the most prevalent problems of poor luminescence stability when it comes to its advanced applications as smart nanomaterials.



Fig. 1. Comparison of efficient UV-attenuation by E-NDs with respect to control ZnO NPs (left) PLQY of E-NDs with quinine sulphate as standard (right) (OD fixed at 0.08)

The average hydrodynamic diameter of E-NDs dispersed in ethanol were estimated to be 7.67 nm using the Dynamic Light Scattering (DLS) measurements. Additionally, DLS also manifested the monodispersity observed for the size of E-NDs from the size distribution plot as shown in Fig. 2. Fascinating enough the polydispersity index (PDI) calculated was found to remain the same even after 4 months revealing the high stability of colloidal E-NDs with no agglomeration. These results are in good agreement with the narrow FWHM observed in the PL spectra and substantiates the colloidal stability further.



Fig. 2. PL spectra comparison for the photostability studies of E-NDs over a period of four months (left). Stability study of E-NDs dispersed in ethanol by DLS measurements. The average value was determined after measuring in triplicate. (right)

A hydrogen peroxide (H_2O_2) assay of varying H_2O_2 concentration (60-240 µM) was added to 100µg/mL of E-NDs to investigate the fluorescence quenching of defect (V_o) incorporated ZnO nanodots exhibiting radical scavenging behaviour. The Stern-Volmer (SV) plot implies the excellent radical scavenging behaviour of E-NDs against H₂O₂ illustrated in Fig. 3.^[3] The mechanistic study reveals that alleviation of the V_0 occurs due to the reaction of H_2O_2 with $ZnO_{(1-x)}$ which is evident from the decrease in the intensity of the defect emission bands in the PL spectra. The quenching effect evinces the high V₀ concentration in the engineered ZnO NDs which fosters good photostability, radical scavenging activity and efficient broad spectrum UV filtering properties.



Fig. 3. Stern-Volmer plot showing fluorescence quenching (Integrated PL intensity of defect emission) at varying $[H_2O_2]$ (**p* <0.05). The digital images (λ_{ex} = 365 nm) of the E-NDs having different [H₂O₂] showing time-dependent quenching. (right)

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Structural and Colloidal Stability Studies of PVA Functionalized Greigite

A R Aarathy¹, J V Lakshmi², and S Savitha Pillai^{3,*}

Department of Physics, University of Kerala, Thiruvananthapuram - 695581

*Corresponding author: savitha@keralauniversity.ac.in

Abstract

Surface functionalized magnetic nanomaterials are significant due to their increased chemical stability and biocompatibility. The present work is involved in synthesizing ferrimagnetic Greigite (Fe_3S_4) nanoparticles by solvothermal method and its surface functionalization by Poly vinyl alcohol (PVA). The XRD patterns reveal the formation of the phase Greigite. The increased hydrodynamic size indicates that PVA is coated effectively on the surface of nanoparticles. The slight increase in the Zeta potential for the coated sample indicates that PVA enhances the colloidal stability of the Greigite.

Introduction

The advancement of nanotechnology in the field of nanoparticle-mediated magnetic hyperthermia encouraged researchers to explore a wide variety of magnetic nanomaterials with high heating efficiency and biocompatibility [1]. Iron oxide nanoparticles are widely studied for magnetic hyperthermia among various magnetic nanomaterials due to their suitable structural, colloidal, and magnetic properties with less toxic effects. The biocompatibility is achieved by the surface functionalization of the nanoparticles. Among the polymer coatings, PVA (Polyvinyl alcohol), Dextran and PEG, etc., are regarded as safe and proved biocompatibility [2]. Greigite (Fe_3S_4) is an iron sulfide mineral analogous to magnetite has an inverse spinel structure. It is one of the promising magnetic materials due to its biocompatibility and high magnetic heating efficiency and needs to be explored a lot in magnetic hyperthermia.

Experimental Method

Greigite nanoparticles (NPs) are synthesized by the solvothermal method [3]. The procedure for the PVA coating of Fe_3S_4 is as follows. 0.1M PVA is prepared in 50ml of deionized water and stirred for about 1 hr. 0.05g of Fe_3S_4 is added to the above solution and further stirred for 1 hr, and kept overnight at room temperature. PVA-coated Greigite is collected by discarding the supernatant solution and dried at 70°C for 1.5 hr.

Results and Discussion

The XRD patterns for Fe_3S_4 and Fe_3S_4/PVA are demonstrated in Figure 1. The prominent peaks for bare Fe_3S_4 match well with the standard one of Fe_3S_4 (JCPDS No.89-1998, cubic phase), indicating that the obtained sample is Greigite. For Fe_3S_4/PVA , the characteristic peaks correspond to (101), (311), (132), and (440) planes. For Fe_3S_4/PVA , the peaks became broader, and the intensity has reduced due to the addition of PVA. It is due to the domination of amorphous PVA [3].



Fig. 1. XRD patterns of bare Fe_3S_4 and Fe_3S_4/PVA

The morphological characteristics of bare Fe_3S_4 and Fe_3S_4/PVA were determined by FESEM and are shown in Figure 2. The bare Fe_3S_4 nanoparticles were spherical, while Fe_3S_4/PVA was observed as nanoflakes. The average size of Fe_3S_4 and Fe_3S_4/PVA nanoparticles was 11.626 nm and 62.487 nm, respectively.

Figure 3 represents the FTIR spectra of Fe_3S_4 , PVA, and Fe_3S_4 /PVA. The bands observed 673 cm⁻¹ and 676 cm⁻¹ of Fe_3S_4 and Fe_3S_4 /PVA, respectively, are related to the stretching vibrations of Fe-S bonds [4]. There is a decrease in the intensity of peaks for Fe_3S_4 /PVA compared to the bare Fe_3S_4 . This is due to the presence of PVA and indicates the irreversible adsorption of PVA on the surface of Fe_3S_4 particles. The bands at 1082 cm⁻¹ and 1084 cm⁻¹ of PVA and Fe₃S₄/PVA, respectively, indicate the C-O stretching vibration of PVA.



Fig.2. SEM images and the particle size distribution of Fe_3S_4 (a and b) and Fe_3S_4 /PVA (c and d)

In Fe₃S₄/PVA, the bands at 2892 cm⁻¹, 3270 cm⁻¹ respectively represent the C-H stretching band and O-H stretching bands for free alcohol. These observed bands indicate the presence of a PVA layer on the surface of PVA-coated greigite nanoparticles.



Fig.3. FTIR spectra of Fe₃S₄, PVA and Fe₃S₄/PVA

The average hydrodynamic diameters of the bare Fe_3S_4 and Fe_3S_4/PVA were 153.4 nm and 210.7 nm, respectively. The increase in the hydrodynamic size for Fe_3S_4/PVA is due to chemisorbed PVA through its hydroxyl groups on the surface of the nanoparticles [6]. The zeta potential measurements determined the surface charge of the prepared NPs and gave an idea about the stability of the colloidal system. The zeta potential of Fe_3S_4 and Fe_3S_4/PVA was found to be -6.3mV and 9.9mV, respectively. The values are slightly lower when compared to Fe_3O_4/PVA [6]. Zeta potential becomes more positive with decreasing P_H values [7]. The positive zeta

potential value of Fe_3S_4/PVA may be due to the addition of PVA, which reduced the P_H of the particle. The zeta potential values of Fe_3S_4 and Fe_3S_4/PVA show some agglomeration and are evident from SEM images [6]. But when compared to bare Fe_3S_4 , PVA-coated NPs have a high zeta potential value. This indicates a higher repulsion between the coated nanoparticles and is more stable than bare Fe_3S_4 nanoparticles.

Conclusion

Greigite (Fe_3S_4) nanoparticles were synthesized by the solvothermal method. The peaks obtained from XRD confirmed the presence of Greigite as well as the peaks obtained for coated NPs confirmed the presence of PVA layer on the surface of bare NPs. The average particle size for Fe_3S_4 and Fe_3S_4/PVA from SEM analysis is 11.626 nm and 62.487 nm, respectively. The functional groups obtained by FTIR analysis showed Greigite (Fe₃S₄) and polyvinyl alcohol (PVA) in the coated nanoparticles. The increased hydrodynamic size indicates the effective coating of PVA on Greigite NPs. The high zeta potential value of coated NPs compared to that of bare NPs suggests better colloidal stability for the coated NPs. The results indicate that PVA coating can effectively enhance the colloidal stability of greigite (Fe₃S₄) nanoparticles.

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Heat-Induced Silver Nanoparticles Inside Poly(vinyl alcohol) Film

Sanjib Sau* and Sarathi Kundu

Soft Nano Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Vigyan Path, Paschim Boragaon, Garchuk, Guwahati, Assam 781035, India

*Corresponding author: sanjibsaumid@gmail.com

Abstract

Poly(vinyl alcohol) (PVA)-silver (Ag) nanocomposite films are prepared for different heating periods and their structure, optical and mechanical properties are investigated. UV-visible absorption spectrum shows localized surface plasmon resonance peak at around 433 nm due to the formation of silver nanoparticles. XRD spectrum also indicates the incorporation of silver salt inside PVA matrix. The size of the spherical silver nanoparticles formed inside PVA-Ag composite film heated for 15 min is obtained as 26.3 ± 0.6 nm. Loading-unloading test shows decreasing hysteresis loop area with increasing the number of cycle.

Introduction

Metal nanoparticles are enormously utilized in the fields of photonics, electronics, chemical and biological sensing and catalysis [1]. Recently, metalpolymer nanocomposites have achieved immense attention due to its tuneable characteristics. The optical, electrical, thermal and mechanical properties of the metal-polymer nanocomposites depend on the size and shape of the nanoparticles, the distribution of nanoparticles within the host polymer and the nature of the used polymer [2]. Noble metal nanoparticles, i.e., silver (Ag) and gold (Au) nanoparticles, exhibit unique features such as localized surface plasmon resonance (LSPR) extinction and self-assembly under specific conditions [1]. Due to the specific tuneable properties, polymer-silver nanocomposites are regarded as promising functional materials. Therefore, these nanocomposites have potential applications in the fields of antibacterial agents, biosensors, surface-enhanced Raman scattering (SERS) substrates, catalysts and optical filters [1-3].

Poly(vinyl alcohol) (PVA), polyvinyl pyrrolidone polyurethane (PVP), (PU) and polymethyl methacrylate (PMMA) are generally used as host polymer for the preparation of polymer-silver nanocomposites [3]. Interestingly, PVA (CH₂CHOH) has attained great attention due to its superior properties like low toxicity, good film forming capability, biocompatibility, water solubility, optical transparency and good mechanical behaviours [4]. However, many researchers have reported different aspects of PVA-silver nanocomposites using in situ and ex situ methods. Structural and morphological modifications of PVA-Ag nanocomposites were investigated with thermal annealing treatment and the film thickness [5]. In this study, AgNO₃ is mixed with PVA polymer which acts as a reducing agent for Ag ions. Ag nanoparticles are formed under heat treatment for different heating periods.

Experimental details

Materials

Poly(vinyl alcohol) (PVA) (catalogue no. 8.43866.1000, M.W. = 60000 g mol⁻¹, 99% purity) and silver nitrate (AgNO₃, M.W. = 169.87 g mol⁻¹, 99.5% assay) were purchased from Merck. Double-distilled water (resistivity $\approx 18.2 \text{ M}\Omega$ -cm) from the Millipore Milli-Q system was utilized for the experiments.

Film preparation

All the films were prepared using solution casting method. For the preparation of 10 wt% pristine PVA film, first homogeneous solution of PVA was prepared at 90°C by continuous stirring for 3 h and next solution was casted on polystyrene petri dish followed by drying at room temperature for 72 h. To prepare 5 wt% AgNO₃ composite film, AgNO₃ was mixed with homogeneous PVA solution by stirring 1 h followed by casting and next it was dried at room temperature for 72 h. As prepared dried composite film was heated for 5 min and 15 min at 130°C.

Characterization techniques

X-ray diffraction measurements were performed using D8 Advanced, Bruker, AXS X-ray diffractometer (XRD). UV-visible absorption spectra were taken using Shimadzu UV-1800 spectrometer. The surface morphological studies were performed by field emission scanning electron microscopy (FESEM) (SIGMA 300, ZEISS). Mechanical studies were performed using Tinius Olsen (Model-H5KL) setting gage length ≈ 10 mm for 4 successive cycles.

Results and discussion

The formation of noble metal nanoparticles, e.g., silver nanoparticles (AgNPs) is confirmed from the

UV-visible absorption spectra, which is shown in Fig. 1(a). For pristine PVA, two absorption bands are observed at around 280 and 330 nm indicating $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively due to the resonating carbonyl group (>C = O) [6]. For 15 min heated of the PVA-Ag composite film, a shoulder peak is observed at around 306 nm indicating Ag⁺ ions. LSPR peak is observed at around 433 nm indicating the formation of AgNPs as a part of the silver ions are reduced to nanoparticles under heat treatment.



Fig. 1. (a) UV-visible absorption spectra, and (b) XRD spectra of pristine PVA film and 5 wt% PVA-Ag nanocomposite film for 15 min heating.

XRD spectra shown in Fig. 1(b), shows three peaks of semi-crystalline pristine PVA polymer at $2\theta = 19.5^{\circ}$, 22.5° and 40.5°, which occur from (101), (200) and (202) reflection planes respectively [7]. For 15 min heated PVA-Ag composite film, all the peak intensities are reduced indicating the successful grafting of Ag nanoparticles inside PVA matrix.



Fig. 2. SEM images of (a) pristine PVA film and 5 wt% PVA-Ag nanocomposite films for (b) 5 min and (c) 15 min heating. (d) EDAX spectrum, (e) histogram plot with Gaussian fitting and (f) loading-unloading plot of 5 wt% PVA-Ag nanocomposite film for 15 min heating.

From SEM images shown in Fig. 2(a)-(c), it is clear that the pristine PVA has smooth surface, while with incorporation of silver salt and different heating periods such as for 5 and 15 min, spherical silver

nanoparticles are homogeneously evolved inside PVA. With longer period of heating, number of nanoparticles are increased. EDAX spectrum of the composite film, which is heated for 15 min, is shown in Fig. 2(d), which implies the typical peak of silver nanoparticles at around 3 keV [8] and also indicates the presence of good amount of silver in the film. For this composite film, the size of the AgNPs is obtained around 26.3 ± 0.6 nm (shown in Fig. 2(e) histogram plot).

Loading-unloading loops shown in Fig. 2(f) are taken for the composite film, which is heated for 15 min at 25% strain. It is evident that the first cycle has significant hysteresis loop indicating huge energy dissipation. With increasing the number of cycle, loop area decreases and ultimately collapses with each other.

Conclusions

In this work, formation of silver nanoparticles inside PVA is revealed through heat treatment. LSPR peak is observed at around 433 nm due to the formation of AgNPs. XRD indicates the grafting of silver inside PVA. SEM images show the homogeneous distribution of spherical Ag nanoparticles inside PVA matrix. Loading-unloading test shows the decrease of hysteresis loop area with increasing the number of cycle.

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Non-Linear Optical Properties of PMMA Doped ZnO Thin Film

Zeeshan Khan¹, Shafi ul Islam¹, Imran Ahmad Salmani¹, Javid Ali¹, Mohd. Shahid Khan^{1*}

¹Laser and Molecular Spectroscopy Lab, Department of Physics, Jamia Millia Islamia, New Delhi 110025 India

*Corresponding author: <u>mskhan@jmi.ac.in</u>

Abstract

In the present work, ZnO nanoparticles were synthesized using sol gel method. Polymethyl methacrylate (PMMA) doped ZnO thin film was casted by drop-casting method. Using XRD the average grain size found to be 34 nm. To study the bonding nature of the ZnO nanoparticles FTIR study was done. The linear optical properties were studied by UV-Visible spectra. Nonlinear absorption of prepared thin film was examined using open aperture z-scan technique at different intensities. We found that the nonlinear absorption coefficient (β) decreases on increasing the intensity.

Introduction

The Nonlinear optical properties of semiconductor are the current topic of research nowdays. Among the various semiconducting materials, ZnO a wide band gap (3.37 eV) material has gained much attention due to its good nonlinear optical properties due to which they can be used in many optical devices like uv emitters, random lasers etc. Binding energy of ZnO is 60 meV which is very high at room temperature [1-3]. Also, nowadays nanocomposites of polymer and inorganic nanomaterials are in focus. PMMA is one of the polymers which is famous for its properties like good transparency in visible region, rigidity, and low optical absorption [4-5]. Nonlinear optical properties of composite films having semiconductor nanoparticles find many practical switching applications like optical and [6]. optoelectronics devices ZnO-PMMA nanocomposites have shown good results for application like optical limiting against intense laser pulses [7].

In this research paper we investigated the NLO properties of PMMA/ZnO thin film and reported nonlinear absorption coefficient (β) evaluated by open aperture (OA) z-scan technique.

Experimental

Firstly, the ZnO nanoparticles were synthesized using Sol-gel technique [8]. After that PMMA doped ZnO thin film was casted. Firstly 10 wt% solution of PMMA/Chloroform was prepared by magnetic stirring for 2 hrs at room temperature. Then ZnO with concentration of 1 wt% was added to above mixture and sonicated for 15 mins. Then the mixture was stirred for 2 hrs to get homogeneous solution. On glass petri dish at 27° C PMMA/ZnO solution was poured. After 2-3 hours film was pulled out from petri dish easily. To solidify this thin film, it was kept at 30 °C for one day.

Results and discussion

Fig.1 shows XRD pattern of ZnO. All the peaks matched with wurtzite structure of ZnO having hexagonal phase (JCPDS No.36-1451). Particle size was calculated using Scherrer's formula and found to be 34.76 nm.



Fig. 1. XRD pattern of ZnO.

In FTIR spectrum of ZnO nanoparticles, shown in Fig. 2, due to the presence of water vapours, the peaks 3452.30 cm⁻¹ and 1119.15 cm⁻¹ are because of O-H stretching and deformation, respectively. Peaks detected at 1634 and 620.93 cm⁻¹are due to Zn-O stretching and deformation [9].



Fig.2 FTIR Spectra of ZnO nanoparticles

The absorption for PMMA/ZnO thin film is in the range of 300-400 nm as shown in Fig. 3(a). The direct band gap of ZnO is estimated from the Tauc plot of $(\alpha hv)^2$ versus hv, Fig. 3(b) where hv is the

photon energy and α is the linear absorption coefficient, band gap is found to be 3.14 eV.



Fig.3(a) &(b) UV-visible spectrum of ZnO and Tauc plot.

Nonlinear optical properties were studied using open aperture (OA) z-scan technique with CW solid state laser of 405 nm wavelength. Pure PMMA thin film shows insignificant absorption. PMMA doped ZnO thin film shows sharp dip at the focus with transmittance decreasing confirming reverse saturable absorption (RSA) phenomenon present in the film. As we can see in Fig.4, transmission is symmetric about z=0 and minimum at focus. Transmission at focus decreases with the increase in input intensity. Calculated values of non-linear optical parameters of PMMA/ZnO thin film are presented in Table 1. The collected data of OA z-scan is best fitted to equation (1) [10].

$$T(z) = 1 - \frac{\beta L_{eff} I_0}{2^{3/2} (1 + (z^2/z_0^2))}$$
(1)

Where nonlinear absorption coefficient is β , I_o is the intensity at beam centre given by $I_0=2P/\pi w_0^2$, this P is the power of the laser and w_o beam waist.



Fig. 4(a,b,c,d) OA z-scan curves of PMMA/ZnO film at different intensities.

Power (mW)	Beam waist (µm)	Intensity (×10 ⁶) (W/m ²)	β(×10 ⁻²) (m/W)		
5	70.0	0.644	1.67896		
10	67.5	1.397	0.79914		
15	65.0	2.261	0.53656		
20	62.5	3.261	0.38083		

Table 1. NLA coefficient β of PMMA/ZnO thin film

Conclusions

ZnO nanoparticles were synthesized by sol gel method and thin film of ZnO doped PMMA was prepared with concentration of 1% ZnO as filler. Different characterizations of ZnO were done, like XRD, which showed that the size of the nanoparticles was 34 nm and FTIR for the information of metal oxide bond formation. In optical characterization, UV-Visible was done which shows very less absorption in visible range. The Energy Band gap of ZnO comes out to be 3.14 eV. Nonlinear absorption coefficient (β) was studied at four different intensities using OA zscan. We found the decrease in the nonlinear absorption coefficient (β) on increasing the intensity. This shows the presence of sequential two-photon absorption in ZnO.

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Formaldehyde Gas Sensing Properties of Hafnium Oxide Nanopowders Synthesized by Sol-Gel Method

Anamitra Chattopadhyay¹ and Jhasaketan Nayak²

Oxide-Semiconductor Laboratory, Department of Physics, Indian Institute of Technology (Indian School of Mines), Dhanbad - 826004, Jharkhand, India

*Corresponding author: anamitra.ism@gmail.com

Abstract

This work reports the development of an interesting chemiresistive formaldehyde gas sensor based on hafnia (HfO₂) nano-powder. Monoclinic HfO₂ nano-crystals were synthesized by sol-gel route at two different calcination temperature viz. 500 °C and 700 °C. The gas sensing characteristics of HfO₂ were studied by employing formaldehyde gas at four different concentrations ranging from 1000 to 30000 ppm. HfO₂ sensor shows high response under formaldehyde exposure. Also, the shorter reaction and recovery time and linear response suggest that HfO₂ could have a potential application in formaldehyde gas sensor fabrication.

Introduction

Along with the development of industrialization, air pollution causes by widespread use of volatile organic compounds became a serious environmental problem. Formaldehyde is a typical volatile organic compound and has extensive use in chemical industry, pharmacology, food, paint, hygiene and cosmetic production. High level of formaldehyde exposure can damage the immune system, central nervous system and blood cells. Therefore, development of a real time and effective method to detect and monitor the formaldehyde gas concentrations, especially at ppm level, is very important for safety of human life and environment.

In this work, we are interested to synthesize crystalline hafnia powders. Also, we will study the gas sensor characteristics of the prepared nanomaterials at various formaldehyde gas concentrations.



Fig. 1. XRD patterns of sol-gel synthesized HfO₂ powders calcined at 500 °C (S1) and 700 °C (S2) respectively.

Experimental

Hafnia powder were synthesized by sol-gel process using citric acid, hafnium tetrachloride and ethylene glycol as described by González et al. [1]. All the precursors were purchased from Sigma-Aldrich India. The prepared powders had been calcined at 500 °C (S1) and 700 °C (S2) for 2 h in a muffle furnace and pressed into 11 mm diameter pellets. The pellets were sintered at 1100 °C for 4 h and employed to gas sensing measurements. A home-built testing chamber were used for the gas sensing measurements using Keithly SMU 2450 as described by Ahmadipour et al. [2]. The response of the sensor is defined by $\Delta I/I_a$, Where, $\Delta I=$ I_g - I_a , I_g and I_a are the electrical currents of the sensor in target gas and dry air respectively. The structures of the powders were studied by PAN alytical X-ray diffractometer equipped with Cu-K α radiation (λ = 1.5406 Å).



Fig. 2. Dynamic gas sensing response and recovery curve of HfO_2 to different concentration of formaldehyde at room temperature and 40 % RH.



Fig. 3. The logarithmic plot of responses of S1 and S2 sensor at different concentration (ppm) of formaldehyde.



Fig. 4. Response time of S1 and S2 sensor under the exposure of formaldehyde gas at different concentrations (ppm).



Fig. 5. Recovery time of S1 and S2 sensor under the exposure of formaldehyde gas at different concentrations (ppm).

Results and discussions

Fig. 1 depicts the XRD patterns of S1 and S2. Formation of monoclinic phase (m-phase) of hafnia with space group P21/c is confirmed by the XRD peak analysis (JCPDS file no. 01-078-0049). The responses of HfO₂ sensors (S1 and S2) to formaldehyde are measured from 1000-30000 ppm as shown in Fig. 2. The responses of S1 to formaldehyde are 0.5, 1.5, 3.1 and 4.9 at 1000, 6000, 15000 and 30000 ppm respectively. Similarly, the responses of S2 are 0.9. 2.9, 4.6 and 11.1 at 1000, 6000, 15000 and 30000 ppm respectively. At these concentrations S2 shows 44.4 %, 48.2 %, 32.6 % and 55.8 % more response as compared to S1. It is found that with increasing the formaldehyde concentrations the sensor response also increases. Fig. 3 shows the linear variation of sensing response with formaldehyde gas concentrations in logarithmic scale. This linear response is very important in case of practical gas sensors. The obtained linearities are 0.99 and 0.96 for S1 and S2 respectively. For high-performance gas sensors, response and recovery times are two important parameters. It is observed that both response and recovery time increases with increasing the formaldehyde concentrations as shown in Fig. 4 and Fig. 5. The average response times for S1 and S2 are ~ 29 s and 23 s respectively. Similarly, the average recovery times are ~11 s and 13 s for the same. Therefore, S2 sensor has smaller response time as compared to S1 sensor.

Conclusions

In summary, monoclinic HfO_2 -based highperformance formaldehyde gas sensor had been successfully prepared by sol-gel method. HfO_2 nanopowder synthesized at 700 °C (S2) exhibit higher crystallinity, greater sensing response and possess smaller response time as compared to the powder synthesized at 500 °C (S1). These results suggest that S2 could be a promising candidate for fabrication of formaldehyde gas sensor.

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ANALYSIS OF CINNAMON ZEYLANICUM BARK EXTRACT INFUSED NICKEL OXIDE NANOPARTICLES AS EFFICIENT DRUG DELIVERING AGENT

J.Rinita¹, Riya Jose¹, N.S.Nirmala Jothi^{1*}

¹Department of Physics, Loyola college Chennai-34, India.

*Corresponding author: jmjnirmala@yahoo.co.in

Abstract

Nickel Oxide Nanoparticles takes a special place and interest for its various application in optoelectronics, magnetism, catalysis, solar cells, sensors and many other environmental and biological applications Because of their exceptional properties, these NiO nanoparticles are being studied extensively. Antiferromagnetism is another significant strategic property of NiO nanoparticles, which leads to increased biosystems applications. The bark of Cinnamon. zeylanicum has been shown to have impressive pharmacological effects in the treatment of type 2 diabetes and insulin resistance. With regard to biomaterial dosage and pH, we have discussed the drug delivering efficiency of NiO nanoparticles using C. zeylanicum bark powder extract (CBPE). Keywords: Nickel oxide, biosystem, Cinnamon zeylanicum, Drug delivery

Structural and Dielectric Studies of Bi₄Ti₃O₁₂ Plate-like Nanomorphology Prepared By Low Temperature Molten Salt Method

Priyanka Mitra¹ and B. Harihara Venkataraman^{1*}

¹Birla Institute of Technology and Science-Pilani, Jawahar Nagar, Shameerpet, Hyderabad - 500078, India

*Corresponding author: hari@hyderabad.bits-pilani.ac.in

Abstract

Abstract. Polycrystalline ceramic samples of Bi₄Ti₃O₁₂ (BIT) have been synthesized at low temperature by adopting molten salt (MSS) route using high purity oxides and NaCl as a flux. The X-ray diffraction studies confirmed the formation of single phase BIT ceramics with orthorhombic crystal structure. The scanning electron micrographs (SEM) revealed the presence of plate-like morphology of the layered structure BIT. The energy dispersive X-ray analysis (EDAX) showed the stoichiometric ratio of the constitute elements present in BIT nanoceramics. The dielectric constant, as well as loss factor, measured at 300K exhibited the dispersion behaviour at low frequencies. The observed high value of dielectric constant and low valve of loss factor at 300K might establish this ceramic as a promising material for capacitor based devices.

Keywords: Bismuth titanate, Molten salt synthesis, Nanoceramics, Plate-like morphology and Dielectric properties.

INTRODUCTION

In the era of nanotechnology, bismuth layered structured ferroelectrics (BLSFs) have attracted significant attention for their potential application in the field of high-temperature sensors [1]. An extensive study on the polycrystalline bismuth titanate (Bi₄Ti₃O₁₂) exhibited a large dielectric constant with low loss, high Curie transition temperature (675°C), excellent resistance to depolarization and fatigue, which established it as a well-known lead free material among Aurivillius family of layered structures [2,3]. Januari et. al reported the plate-like BIT particles formed at 900°C for a longer synthesis duration by adopting MSS method [4]. Molten salt synthesis method is one of the effective fabrication routes for synthesizing ceramic powders at relatively lower temperatures. The presence of salt in MSS method helps to accelerate the reaction process at lower temperature as compared to high temperature activated synthesis processes. In this present work, a systematic study has been carried out on the structural, microstructural and dielectric properties of single phase Bi₄Ti₃O₁₂ nanoceramics.

EXPERIMENTAL DETAILS

The polycrystalline $Bi_4Ti_3O_{12}$ nanoceramics were prepared by molten salt synthesis method. The stoichiometric mixture of high purity Bi_2O_3 and TiO_2 oxides added with NaCl; where oxide to salt ratio was maintained at 1:3. These raw materials were mixed thoroughly for 2h in pestle and mortar and subsequently calcined at 700°C for 4h in alumina crucible. These calcined powders were then filtered with distilled water to remove the alkali metal salt and the residue was kept for drying. Further, this mixture was cold pressed at 300K for few minutes at the pressure of 225kg/cm² and subjected to the conventional sintering process at 750°C for 4h.

The structural and phase confirmation of the calcined powder as well as sintered pellet were carried out by X-Ray Diffractometer (Rigaku Ultima - IV). The surface morphology and chemical composition of these samples were examined by using FESEM with EDAX characterization technique. The sintered pellets were coated with silver paste as electrodes to determine the dielectric properties as a function of frequency using Wayne Kerr LCR meter with a signal strength of 1 V_{rms}.

RESULT AND DISCUSSION

Figure 1 (a,b) shows the X-ray diffraction pattern of the calcined powder as well as sintered pellet of $Bi_4Ti_3O_{12}$ samples. All the diffraction peaks are well matched with the standard pattern of BIT (JCPDS 73-2181), which confirmed the phase formation of orthorhombic structure with space group Fmmm. A negligible trace of impurity was observed in the calcined sample (Fig. 1(a)), but this phase was not appeared in the sample sintered at 750°C.



FIGURE 1: XRD pattern of $Bi_4Ti_3O_{12}$ samples (a) calcined at 700°C and (b) sintered at 750°C.

In order to estimate the crystallite size (D) and micro-strain (ϵ) of BIT samples, the Debye-Scherrer and Williamson-Hall method [5] have been adopted. The calculated D and ϵ values are listed in Table. 1.

Table 1. Structural and microstructural parameters of BIT

Crystallite size		Strain	Elements	%Atomic
D-S (nm)	W-H (nm)	ε (x 10 ⁻⁴)	(from EDX)	
			Bi	21.70
46	58	17	Ti	16.59
			0	61.71

The FESEM micrographs of $Bi_4Ti_3O_{12}$ ceramic samples are shown in Figure 2(a,b). The surface morphology of calcined powder (Fig. 2(a)) and sintered pellet (Fig. 2(b)) of BIT clearly indicated the formation of plate-like morphological grains which are anisotropic in nature. The EDAX analysis of $Bi_4Ti_3O_{12}$ ceramics contained the stoichiometric elements of Bi, Ti and O only as listed in Table. 1



FIGURE 2: FESEM images of $Bi_4Ti_3O_{12}$ for (a) calcined and (b) sintered samples.

with atomic percent of the constitute elements.

Figure 3 shows the variation of the dielectric constant and loss tangent with frequency at 300K.

The dispersive behavior of the dielectric constant of BIT ceramics could be attributed to the space charge relaxation effect [6]. It is also noticed that a low amount of energy for electron transfer between multivalence states in BIT ceramics especially at higher frequencies which led to the reduction in dielectric loss.



FIGURE 3: Variation of dielectric constant and loss tangent of Bi₄Ti₃O₁₂ ceramics.

CONCLUSION

From the above studies, it is concluded that a single phase of $Bi_4Ti_3O_{12}$ nanoceramics was successfully synthesized at low temperature by using molten salt route. The FESEM images revealed the well packed plate shaped grains of uniform microstructure. The frequency dependent dielectric behavior of $Bi_4Ti_3O_{12}$ nanoceramics has been studied at 300 K.

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Microstructural and Optical Properties of Electrochemically Etched Silicon Nanowires (SINWs)

P. Nath^{1,a)} and **D.** Sarkar¹

¹CMP Research Laboratory, Department of Physics, Gauhati University, Guwahati, Assam, 781014, India

^{a)}Corresponding author: pranjalnath741@gmail.com

Abstract

Silicon nanowires (SINWs) are fabricated by electrochemical etching of silicon using metal-assisted route on silver electroplated silicon (Si) wafer at room temperature. Morphology and optical properties of the prepared samples are investigated through field emission scanning electron microscopy (FESEM), UV-visible reflectance spectroscopy, photoluminescence (PL) and Raman studies respectively. FESEM shows alignment of SINWs in the vertical direction with average length of 24 µm. UV-Visible shows considerably low reflectance of SINWs to that of Si wafer. PL shows an intense peak at around 450 nm. Raman studies complements the FESEM results by showing the peak shifting of SINWs to that of Si wafer due to nano Si structure. Optical properties reveal that SINWs could be a better candidate for optoelectronic applications.

Introduction

In recent years, SINWs draws a huge attention among the research community due to its outstanding electrical, mechanical and optical properties with environmental friendly nature [1-3]. SINWs shows considerably low reflectance over the solar spectrum substituting typical multilayer antireflection coatings on solar cells [4, 5].

There are many ways to fabricate SINWs based on top down or bottom up approaches. Bottom up approach needs high temperature, high vacuum with hazardous gas which makes the process expensive to perform. Top down approach minimizes some of the issues involved in bottom up approach to a great extent. Among top down approaches metal-assisted electrochemical etching is one of the most efficient methods which can produce large number of SINWs at a singe go. In the present work, SINWs are prepared with this particular method. Structural and optical properties of these SINWs are studied to throw some light on its application potentiality.

Experimental

The boron doped p-type <100> Si wafers of thickness ~375 μ m with resistivity 1-10 Ω cm are used for fabrication of SINWs. The wafers are treated with RCA treatment prior to etching. The RCA treated Si wafers are dipped in a mixture of HF and AgNO₃ for Ag electroplating over Si wafer. For the fabrication of SINWs, Ag electroplated Si wafers are loaded in the electrochemical cell consisting of platinum cathode and aluminum counter electrode and a mixture of HF and H₂O₂ is used as an electrolyte. Etching current density (dc) is maintained at 22.07 mA cm⁻² through Agilent 6634B dc power

supply. After electrochemical etching the wafers are dipped in HNO₃ solution to remove anyremnant Ag.

Results and Discussion

The visual observation of silicon wafers after electrochemical etching becomes black in color which infers the formation of SINWs over Si surface.

Fig.1 (a, b) illustrates the planar and cross sectional view of SINWs respectively. Fig.1 (a) shows presence of large number of SINWs which are bunched and the surface appears porous. From the cross sectional view of FESEM of Fig.1 (b) the average length of the SINWs is estimated as $24 \mu m$.



Fig.1. FESEM micrograph of SINWs (a) Planar (b) cross sectional

Fig.2 illustrates UV-Visible reflectance spectra of Si wafer and SINWs. The reflectance spectra are recorded at an incidence angle of 8^0 to the surface of the film. SINWs shows considerably low reflectance compared to that of bare Si wafer, which is due to the light trapping that happened on the sidewalls of the SINWs via multiple reflections.



Fig.2. UV-visible reflectance spectra of SINWs and Si wafer

Fig. 3 depicts the PL spectra of SINWs for excitation wavelength of 340 nm. This gives an intense PL peak at 440 nm due to quantum confinement in Si nanostructure 6]. PL intensity depends on the size and orientations of the nanowires formed over Si surface.



Fig.3. PL spectra of SINWs

Fig.4. shows the Raman Spectra of Si wafer and SINWs. SINWs shows more intense broadened peak compared to that of the bare Si wafer. On decovolution of the spectra, two peaks can be visualized, one is due to the nano Si structure for which the peak is red shifted due to phonon confinement [7]. The other peak arises from Si. Raman scattering from SINWs is mostly based on phonon confinement model (PCE). Nanowire diameter plays a vital role in controlling the confined modes [7, 8]. On the other hand, Fano effect (i.e electron-phonon interaction) controls the asymmetric Raman line shape broadening [9, 10]. The significantly intense Raman signal of SINWs compared to that of the bare Si wafer is due to partial localization of exciting light via multiple elastic scattering on the side walls of SINW arrays.



Fig. 4. Raman spectra of SINWs and Si wafer

Conclusion

SINWs are successfully fabricated by metal-assisted electrochemical etching. Morphological study shows fine alignment of SINWs in vertical direction with porous structures on surface view. Optical studies indicate SINWs are optically active material and could be explored for optoelectronic device potentiality.

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Defect-mediated Photoluminescence Properties of Transitional Metal ions-doped ZnO Nanoparticles

Jagriti Gupta¹*, K. C. barick^{1,2}, and P. A. Hassan^{1,2}

¹Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai – 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai – 400094, India *Corresponding author. jagritigupta@iitb.ac.in*

Abstract

Transition metal (Ni and Co) ions doped ZnO nanoparticles (TM doped ZnO NPs) were synthesized via a soft-chemical approach. The structural, microstructures, and photoluminescence properties of TM doped ZnO NPs were investigated thoroughly by various characterization techniques. The successful doping of metal ions was evident from chemical analysis and electron mapping using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), respectively. X-ray diffraction and transmission electron microscopy analyses of doped ZnO NPs showed the formation of single-phase wurtzite structure without any impurities. X-ray photoelectron spectroscopy further confirmed the doping of metal ions into the ZnO matrix. The photoluminescence study showed that doped ZnO NPs exhibited the defect-dependent photoluminescence behavior.

Structural and Electrical Properties of Ba_{0.9}Sr_{0.1}Ti_{0.9}Mn_{0.1}O₃.

Mehroosh Fatema¹, Shahid Husain^{1*} and Anand Somvanshi¹

¹Department of Physics, Aligarh Muslim University, Aligarh(INDIA),202002.

*Corresponding author: s.husaincmp@gmail.com

Abstract

Nanocrystalline sample of $Ba_{0.9}Sr_{0.1}Ti_{0.9}Mn_{0.1}O_3$ has been synthesized using solid state reaction route. Raman spectroscopy indicates that the sample exists in tetragonal phase at room temperature. The Raman modes shift towards the higher wavenumber indicating the presence of compressive strain with blue shift. Impedance analysis highlights the non-Debye behaviour of the sample. The imaginary part (- $Z''(\omega)$) for the material exhibits a sharp decrease with frequency indicating the absence of relaxation at room temperature. The a.c. conductivity follows the Jonscher law.

Heterostructures of Carbon Nanocomposites and Engineered Resonator Arrays for Wide-band Electromagnetic Shielding

Vivek Kale, Shravani Kale, BV Bhaskara Rao, S.N. Kale*

Department of Applied Physics, Defence Institute of Advanced Technology, Girinagar, Pune 411025, INDIA

*Corresponding author: sangeetakale2004@gmail.com

Abstract

Electromagnetic shielding is one of the important areas of research due to the requirement being crucial for Radar applications and data security. Variety of design strategies and exploration of new materials are adopted continuously to ensure the effective shielding of precious objects (such as aircrafts, UAVs and data storage / computing devices). From the materials perspective, light-weight, flexible and adhesive (to metal surfaces, mainly) materials are highly desirable so that they could be coated on aero-chassis or on any such protective enclosures. In this context, micro-assembled, engineered thin film structures of silver arrays have been used along with different carbon nano composite thin films on flexible substrates for shielding in the X-Band (8.2 GHz to 12.4 GHz) radar range of the electromagnetic spectrum. Micron sized antenna structures of silver are stacked with nanocomposite films of multiwall carbon nanotubes (MWCNTs) in polyvinyl dimethyl fluoride matrix to obtain wide band electromagnetic shielding. Shielding in entire X-band with the power loss of 27 dB (99.98 % loss) and a minimum of 21 dB (99.92 % loss) is demonstrated here, for MWCNT. A strong interplay of carbon nanocomposites with the array of resonators of varied resonant frequencies shows concomitant suppression in the incident electromagnetic power; the results of which are supported by simulation (CST Microwave Studio) studies as well. This work opens up a strategy to obtain wide band shielding using a combination of optimized nanomaterial composites, heterostructured with engineered metallic resonators.

Introduction

Carbon nanocomposites have been explored for various applications 1,2, of which electromagnetic shielding is one prominent. On the other hand, in the domain of electronics and material science, resonators have been conventionally used for antenna applications ³. Split ring resonators (SRRs) were first introduced by Pendry et al. to produce magnetic material with negative permeability in the vicinity of its resonant frequency⁴. X-band, which is a wellknown Radar band, needs protection from defence of-view.In surveillance pointthis context. multiwalled carbon nanotubes (MWCNTs) were used along with polyvinylidene difluoride (PVDF) matrix to form thin flexible films of nanocomposites. On other side, silver ink was used to print SRRs of various unit cell dimensions. The dimensions and their responses were carefully ascertained using simulation software. Four resonators of same unit cell dimensions were used as a single layer and such layers of various unit cells were stacked with nanocomposite thin film to evaluate their X-band electromagnetic response. Extremely high EMS in entire X-band (8.2 GHz to 12.4 GHz) with the power loss of 27 dB (99.98 % loss) and a minimum of 21 dB (99.92 % loss) was observed.

Simulation and Experimental studies

An array of silver patterns on polyester flexible substrates was simulated and designed using CST Microwave Studio. The transient solver was used. One standard SRR structure with its parameters is shown in the inset of Figure 1. The SRR samples consisted of patterned silver films of thickness 35 microns on the surface of a polyester substrate (0.15 mm thick). The geometry of SRR was defined by following parameters: distance between two ring resonators within a SRR (d) was 0.4 mm, thickness of each SRR (c) was 0.3 mm, gap in each SRR (g) was 0.2 mm and the distance between two SRRs was 1 mm (D). An array of SRRs (4-unit cells) was treated as periodic lattice, and the stacks were created by varying the structures via their lattice constant variation from 2.3 mm to 2.8 mm (6 layers).

The systematic shifts in transmission frequency as well as magnitude were observed with various values of lattice constants, the results are shown in Figure 1 The resonance frequency was calculated using the standard equivalent LCR circuit formula:

$$\omega = 2\pi f = \frac{1}{\sqrt{LC}}$$

Where, ω is resonant frequency, L and C are the equivalent inductance and capacitance of SRR respectively.

Experimental Results and Discussion

Silver SRR structures were printed on commercially available Polyester film (ε_r =4.0, thickness= 0.15 mm). These were printed on a single polyester sheet and four SRRs of a=2.3 was cut to get one sheet of EMS material. Similarly other sheets were also cut till the maximum of a= 2.8 mm.

Therefore, for one experiment, 6, (4x1 matrix) sheets of printed polyester films were used and stacked together to observe their response in the X-band of electromagnetic spectrum. On the other hand, our earlier results ⁵ had reflected that the flexible sheets of nanocomposites of mutiwalled carbon nanotubes (MWCNTs) and polyvinylidene difluoride (PVDF) matrix yield EMS as highas 23.3 dB (99.93%). This sheet was used along with the layers of resonator arrays to yield a single flexible system which was evaluated for EMS applications. One layer of MWCNT-PVDF 900 micron film and 6 layers of silver resonator arrays were pressed together using hydraulic press, to ensure that there are no air gaps between the individual layers. The data was collected for individual resonators, individual nanocomposites as well as combined stacks. For this, the X-band



Figure 1 shows simulated (S21) data of SRRs of different lattice constants. The inset shows two SRR structures explaining the various parameters of their dimensions and spacing between two SRRs.

waveguide was chosen which was active in 8.2 to 12.4 GHz range. This waveguide was connected to a Vector Network Analyzer (PNA N522A ranging from 10 MHz to 26.5 GHz) supported by 85071E material measurement software, to record the data.

Figure 2 (I) shows the response of individual resonator arrays, which were of increasing unit cell values. It was seen that the rejection band (resonant frequency) power increased (in terms of negative values) monotonously with the increase in the unit cell dimensions. The EMS values changed from 0.75 dB to 2.75 dB with the change in "a" from 2.3 mm to 2.8 mm. The dip in resonance frequencies showed no specific selectivity. Figure 2 (II) shows the response of the layered (nanocomposite and SRR structures together) film. Concomitant change on the basic response of resonators was observed due to the presence of the nanocomposite layer. The threshold improved to -24.5 dBat 8 GHz, which was ~99.964%

loss. This was further improved by about 2.5 dB to yield -27 dB loss at 8 GHz, which is about 99.98% loss. Second observation, which is also very important, is this that the entire range of X-band showed prominent rejection, with the minima going to -21 dB (99.92 % loss) which was indeed negligible fall. The data projects a highly shielding layered material system, which is also flexible. The shielding is via the combination of the EMS property of nanocomposite and the cascaded, tuned multi-layered SRR structures.



Figure 2 shows shielding effectiveness of (I) silver SRR structures with different lattice constants (length of the outer resonator), namely 2.3 (a), 2.4 (b), 2.5 (c), 2.6 (d) 2.7 (e) and 2.8 (f);(II) shows the response of individual MWCNT nanocomposite film (a) and the final multi-layered system of nanocomposite and six layers of 4x1 matrix resonator arrays together (b).

Conclusion

In conclusion, a wide range electromagnetic shielding film has been demonstrated in the entire X-band of electromagnetic spectrum. The shielding as high as 99.98% has been achieved by combining nanomaterials along with engineered matrix of array of resonators.

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Hydrothermal Synthesis and Photoluminescence Study Of Anhydrous Polyhalite K₂Ca₂Mg(SO₄)₄

Shiva H B^{1,2}, Madhura N T¹, Chandrakala S S¹, Pradeep T M¹ and Gnana Prakash A P^{1*}

¹Department of Studies in Physics, University of Mysore, Manasagangotri, Mysuru, 570006, India ²Department of Physics, SHDD Government First Grade College, Paduvalahippe, Hassan, 573211, India

*Corresponding author: gnanaprakash@physics.uni-mysore.ac.in

Abstract

Nanoparticles of anhydrous Polyhalite $K_2Ca_2Mg(SO_4)_4$ are synthesized by hydrothermal method. The synthesized sample is characterized by powder X-ray diffraction (XRD) to confirm its triclinic crystal structure and to get average crystallite size of the nanoparticles. The UV-Visible spectroscopy is used to estimate the optical band gap energy. The scanning electron microscopy (SEM) is used to study the surface morphology. The photoluminescence study shows that PL emission intensity is found to be 310, 385 and 560 nm.

Introduction

The mineral Polyhalite $K_2Ca_2Mg(SO_4)_4 \cdot 2H_2O$ is found in the nature as a marine evaporite mineral. The earlier studies on Polyhalite throw a light on its crystal structure [1] and thermal stability [2]. There is hardly any literature on synthesis of Polyhalite using hydrothermal method. In this article we are providing the details of synthesis of anhydrous Polyhalite using hydrothermal method and its photoluminescence behaviour.

EXPERIMENTAL PROCEDURE

The chemical compounds Potassium Sulphate (K₂(SO₄)), Calcium Sulphate (Ca(SO₄)) and Magnesium Sulphate (Mg(SO₄)) were taken in a stoichiometric ratio and water was used as a solvent. All the compounds were mixed together in a 50 ml beaker for stirring using a magnetic stirrer for 2 hours. After rigorous stirring, the mixture was transferred to 50 ml Teflon liner tube until it was filled to 60 percent which was then kept into a stainless steel autoclave. This autoclave was kept inside a muffle furnace which was maintained at 180°C temperature for 16 hours. After removing from the furnace, autoclave was cooled at room temperature. The filtered product from the Teflon liner tube was washed thoroughly using ethanol twice and the obtained solid sample was dried. Finally the sample was calcined at temperature 400°C for 3 hours. Then the obtained sample was ground to fine powder using mortar and pestle in order to make it ready for characterization.

CHARACTERIZATION

The powder X-Ray diffraction analysis of the synthesized sample was performed by Rigaku

SmartLab X-Ray Diffractometer with Cu-K α radiation (λ =1.5406 Å). The UV-Visible Spectrophotometer (DU 730) was used to analyze the absorption spectra and to determine the band gap energy. The photoluminescence spectra is analyzed using JASCO Fluorescence Spectrometer (FP-8300). The morphological study has been done using Scanning Electron Microscope (EVO LS 15) Zeiss, Germany.

RESULTS AND DISCUSSION

Fig.1 shows XRD pattern of the $K_2Ca_2Mg(SO_4)_4$ obtained at $180^{\circ}C$ for 16 hours hydrothermal reaction. It is clear from this XRD pattern that the position of the diffraction peaks is in good agreement with those of a XRD pattern provided by G. Wollman *et al.* [1]. The presence of broader peaks confirm the formation of nanoparticles.



Fig. 1. Powder XRD pattern of anhydrous Polyhalite.

The crystallite size (D) of the synthesized nanoparticles is calculated using Debye Scherrer's formula,

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad \text{a}$$

Where k is the constant (0.9) called shape factor, λ =1.5406 Å is the wavelength of incident X-rays, β is the full width at half maximum intensity of the diffraction peak and θ is the glancing angle. The smallest crystallite size is found to be 16.14 nm at $2\theta = 21.37^{\circ}$. The largest crystallite size is found to be 98.9 nm at $2\theta = 22.98^{\circ}$. The average crystallite size is found to be 50.52 nm.

The UV-Visible spectrum is shown in Fig.2. It shows the presence of prominent absorption peak at 200 nm. It indicates that the sample absorbs UV light to the greater extent. By plotting Tauc Plot and by extrapolating the linear region of the curve we get the energy gap of 6.08 eV which infers that this material is colourless i.e., there is no absorption of visible light.



Fig. 2. UV absorption Spectra and Tauc Plot

The Fig.3 shows the Photoluminescence spectra of anhydrous Polyhalite. The sample was excited at a wavelength of 200 nm in order to study the photo



Fig. 3. PL Spectra of anhydrous Polyhalite

luminescent behaviour and the corresponding emission spectra shows two prominent peaks in the medium wavelength UV region and longer wavelength UV region or near band edge region of UV at 310 nm and 385 nm respectively. It also shows a peak at 560 nm which corresponds to green colour in the visible spectra which is shown in Fig.3.

The images taken from scanning electron microscopy (SEM) with different magnifications provide the surface morphology of synthesized anhydrous Polyhalite is shown in Fig.4. From these pictures we can clearly see the formation of agglomerated nanoparticles and triclinic crystal structure of Polyhalite (Fig.4.a).



Fig. 4. SEM images of synthesized anhydrous Polyhalite

CONCLUSIONS

The nanoparticles of anhydrous Polyhalite $K_2Ca_2Mg(SO_4)_4$ were successfully synthesized by hydrothermal method. The powder XRD pattern of the synthesized sample confirmed the triclinic crystal structure with mean crystallite size of 50.52 nm. The band gap energy is found to be 6.08 eV. The SEM images showed the agglomerated nanoparticle formation. The photoluminescence spectra showed good emission intensity confirming the suitability of the synthesized sample for display devices.

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Structural, Dielectric and Magnetoelectric properties of Bi³⁺ doped NiFe₂O₄ nanoparticles

Sobi K Chacko¹, M. T Rahul¹, Jini K Jose¹, Karthik Vinodan¹, and B. Raneesh¹

¹ Department of Physics, Catholicate College, Pathanamthitta, Kerala-689 645, India

*Corresponding author: raneesh.b@gmail.com

Abstract

Abstract. Trivalent Bi-ion doped Nickel ferrite nanoparticles exhibiting room-temperature multiferroic properties have been derived using the sol-gel method. The X-ray diffraction pattern is used to confirm the phase purity and lattice parameter of the synthesized samples. Frequency-dependent dielectric properties and magnetoelectric properties of the samples were analyzed. Excellent multifunctional properties show that, it could be a promising candidate for magnetoelectric sensing, memory devices etc.

INTRODUCTION

Multiferroics, as the term, indicates the materials having two-or-more ferroic orders are of great interest due to their wide range of applications in various fields [1]. The existence of different ferroic orders in a single material is rare, which makes multiferroicity unique. Ferrites are of never ending interest due to their excellent physiochemical properties. Nickel ferrite (NFO) is one of the most established soft magnetic materials among them. It has been exploited in various technological applications ranging from EMI shielding to magnetic data storage applications[2-4].

In this work, we have prepared the bismuth (Bi³⁺) doped NFO nanoparticles and studied the role of Bi doping in the structural, electrical and magnetoelectric properties of the Nickel ferrite.

EXPERIMENTAL SECTION

NiFe₂O₄ (NFO) and Ni_(1-x)Bi_xFe₂O4 (x=0.05) (NBFO) nanoparticles have been prepared using Polyvinyl alcohol (PVA) assisted simple sol-gel method. Nickel nitrate, Ferric nitrate and Bismuth oxide were taken as the precursors. Bismuth oxide was dissolved in HNO₃, to obtain Bismuth nitrate. A stoichiometric amount of precursors were taken and dissolved in Deionized water. Aqueous solutions were mixed and sonicated at room temperature. PVA was added to the solution, having weight the same as that of the metallic ions in the precursor solution. The solution was subjected to continuous stirring and kept at a temperature range of 70-80^oC. The resultant gel was ground and calcined at 500^oC for 3 hours.

Phase purity and crystallinity of the prepared samples were analyzed using X-ray diffractometer Bruker AXS D8 Advance. To measure the dielectric and magnetoelectric properties of the samples, prepared powders were pelletized and sintered at 500^{0} C. Dielectric properties of the samples were

studied using Agilent E4980 precision LCR meter. Magnetoelectric voltage and coupling coefficient have been studied using ME-Lock in amplifier setup.

RESULT AND DISCUSSION

X-ray Diffraction (XRD)

XRD patterns of the NFO and NBFO are shown in Fig.1. The cubic structure and fundamental reflection planes are confirmed (JCPDS 89-4927) from the XRD data. No impurity peaks have been detected, which confirms the structural purity and well dissolution of Bi ions in the samples. Broadening in the diffraction peaks with increasing dopant concentration indicates the reduction in the average crystalline size due to the increase in strain originated by the addition of Bi ions [3]. The average crystallite size of the NFO and NBFO is found to be 20 and 12 nm, respectively, from the Scherrer equation. The unit cell parameter shows a slight increase with the addition of Bi ions. It increases from 8.3244 to 8.3298 Å.

Dielectric Studies

Room temperature dielectric properties of NFO and NBFO in a frequency range of 100 Hz to 2 MHz have been studied and the plots of dielectric constant and dielectric loss tangent are shown in Fig. 2. and Fig. 3 respectively. NBFO shows a lower dielectric constant than NFO. However, both the samples exhibit a high value of dielectric constant at lower frequency region. A decrease in dielectric constant with increased frequency and attained a stable state at a higher frequency range. This trend can be explained on the basis of space charge polarization. By increasing the frequency of the field, the space charge carriers fail to keep up with the change in frequency. This will result in the reduction of the dielectric constant. Similar behavior in the dielectric loss tangent have been reported for ferrites previously. This is due to the hoping of iron ions. When the frequency of the applied field matches with the hopping frequency, dielectric loss tangent peaks occur[5]. As this system exhibits excellent dielectric constant value and low dielectric losses, these materials are potential candidates for device applications



Fig. 1. XRD patterns of the prepared NFO and NBFO samples.



Fig.2. Frequency dependence of Dielectric constant of NFO and NBFO at room temperature.



Fig.3. Frequency dependence of Dielectric loss tangent of NFO and NBFO at room temperature.



Fig.4. ME voltage Vs AC magnetic field for NBFO

Magnetoelectric studies

Fig.4. shows the dependence of induced ME voltage with AC magnetic field. The AC measurements are taken for a fixed DC biased field of 1500 Oe. ME voltage shows a linearly increasing trend with AC magnetic field. The prepared NBFO sample exhibit a ME coupling coefficient (MECC) of 8.881mV/cm.Oe for 1500 Oe.

CONCLUSION

Phase pure Bi-doped Nickel ferrite nanoparticles have been synthesized. Structural, dielectric and magnetoelectric studies of the prepared samples have been done. The doped system shows a MECC value of 8.81mV/cm.Oe.

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Laser Synthesis of Anionic Cadmium Sulfide Cluster Ions: Cd_mS_n⁻

T. Jayasekharan

¹Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay Mumbai-400085

*Corresponding author: jsekhar@barc.gov.in

Abstract

Cadmium sulfide cluster ions, $Cd_mS_n^-$ of different stoichiometry have been generated from $CdS_{(s)}$ target material using pulsed laser ablation/desorption ionization technique. The negative ions generated during the laser-matter interaction processes have been analyzed by Time-of-Flight Mass spectrometry. Analysis of the mass spectral data indicates the formation of 6 different binary cluster ion series *viz.*, $(CdS)_n^-$, $Cd_nS_{n+1}^-$, $Cd_nS_{n+2}^-$, $Cd_nS_{n+4}^-$, $Cd_nS_n^-^-$ along with abundant S_n^- .

Introduction

Semiconductor nanocrystals in the size range from 1-10 nm (<100 atoms) exhibit unique size-dependent optoelectronic properties due to their quantum confinement effects and thus finds application in the fabrication of optoelectronic and quantum devices.¹ However, the preparation of pristine semiconductor nanomaterials with specific sizes and dimensions is still challenging. Pulsed laser deposition (PLD) is an efficient and versatile physical vaporization technique employed in the production of high-quality thin films and multilayer. The laserinduced ablation plasma plume is a vital component in PLD where most of the physical transformation and chemical reaction takes place at transient high temperature. The chemical composition of the plasma plume and its spectroscopic properties are essential to evaluate the nature and quality of the thin films and multilayer. Therefore, it is paramount important to know the composition and dynamics of the ejected plume to estimate the energy exchanged during laser ablation, the evolution of the plume process, and the nucleation characteristics of the ejected materials.

Cadmium sulfide (CdS) is a direct semiconductor material with a bandgap of 2.42eV at 300K and has excellent thermal and chemical stability along with strong optical absorption. CdS are used in solar energy conversion devices, nonlinear optical devices, light-emitting diodes, lasers, transistors, and optical switches. PLD of CdS/ZnS thin films on Si (100) substrate by a nanosecond laser show wavelength-dependent particle aggregation.² In situ monitoring of the CdS laser ablation plume by optical emission spectroscopy (OES) and quadrupole mass spectrometer (QMS) show the formation of low mass atomic/molecular species, $S^{0/+}$, $S_2^{0/+}$, $S_3^{0/+}$, $S_4^{0/+}$, Cd^{0/+}, and CdS^{0/+}.³ However, mass analysis by time of flight analyzer shows the formation of abundant neutral/cationic clusters at different wavelengths $(\lambda = 266, 532, 355, 1064 \text{nm})$ of excitation above and below the bandgap at a wide fluence (F=17-330 mJcm⁻²). ^{4.6} However, the nature of the negative ions present in the same ablation source has not been reported. In this work, the anionic species formed from the laser ablation of the CdS_(s) target have been investigated with a pulsed UV laser beam whose single photon energy ($E_{\rm hv}$ =3.492eV) is above the bandgap energy.

Experiment

 $CdS_{(s)}$ target have been irradiated with pulsed laser light of λ =355nm ($\tau \approx$ 5ns) from an Nd: YAG laser. The negative ions present in the laser-induced plasma plume have been mass analyzed by a home built TOFMS.^{7,8}

Result & Discussion

Figures 1-2 show the mass spectra of negative ions obtained from the $\mathrm{CdS}_{(s)}$ target in different mass ranges.



Fig. 1. Mass spectra of $Cd_mS_n^-$ cluster anions in the low mass range.



Fig. 2. Mass spectra of $Cd_mS_n^-$ cluster anions in the high mass range.

The difference between the observed and the calculated mass is within ± 0.1 amu in lower mass range and is ± 0.5 *amu* in higher mass range. Cadmium has 8 stable isotopes, ¹⁰⁶Cd(1.25%), ¹⁰⁸Cd(0.89%), ¹¹⁰Cd(12.49%), ¹¹¹Cd(12.80%), ¹¹²Cd(24.43%), ¹¹³Cd(12.22%), ¹¹⁴Cd(28.73%), and ¹¹⁶Cd (7.49%). Sulfur has 4 stable isotopes, ³²S (94.93%), ³³S (0.76%), ³⁴S (4.29%), and ³⁶S (0.02%). The isotopic profile of the observed ionic amonion The isotopic profile of the observed ionic species matches well with the calculated isotopic profile. The mass spectral data show the formation of 7 different ion series viz., (CdS),, CdnSn+1, CdnSn+2, CdnSn+3, $Cd_nS_{n^{+}4}^{-},\ CdS_n^{-}$ and $S_n^{-}.$ In pure metal clusters, no anions are observed due to their poor electron affinity. Sulfur clusters, $S_n^{\ -}$ show 5 members in the anion spectra. The formation of S⁻ in this ion series evidences dissociation of CdS into Cd⁺ and S⁻. The observation of sulfur clusters, S₂⁻, S₃⁻, S₄⁻, and S₅⁻ indicates the formation of sulphur allotropes in the ablation plume. Among the 6 binary cluster ion series, stoichiometric anion series, (CdS)_n⁻ show only 3 members indicating poor electron affinity of (CdS)_n while the corresponding cation series show long progression up to $(CdS)_{n=1-34}^{+.6}$. The $Cd_nS_{n+1}^{-.5}$ series show progression up to 20 members while Cd_nS_{n+2} series show long progression up to n=35. Similarly, the $Cd_nS_{n+3}^{-}$ series also show more numbers in anions while $Cd_nS_{n+4}^{-}$ series show only three members. The observation of Cd_nS_{n+1} , Cd_nS_{n+2} , Cd_nS_{n+3} , and $Cd_nS_{n+4}^{-}$ ion series indicates that the stoichiometric (CdS)_n cluster is susceptible for further reaction with sulfur and its allotropes $S_2^{-}/S_3^{-}/S_4^{-}$ rather than

electron attachment. In addition the above ion series, cadmium polysulfides, $CdS_{n=1-7}^{-}$ is also noted evidencing the greater binding affinity of Cd for sulfur ligands. Table I lists the positive and negative ions formed during laser laser– $CdS_{(s)}$ interaction. The observation of different ion series in the plasma plume indicates that CdS in the vapor phase aggregates rapidly and form stoichiometric and off-stoichiometric clusters. These clusters contribute significantly in the properties of CdS thin films and multilayer prepared by PLD technique.

Table I. Distribution of $Cd_m S_n^{\pm}$ cluster ions in the laserinduced plasma plume of CdS (5) target.

Positive Ions ⁶	Negative Ions
$Cd_{n}S_{n-1}^{+}{}_{(n=1-9)}$	XXX
$(CdS)_{n}^{+}_{(n=1-36,44)}$	$(CdS)_{n}^{-}_{(n=1,3,4)}$
$Cd_nS_{n+1}^{+}_{(n=1-20,40)}$	Cd_nS_{n+1} (n=1-20, 33,36)
$Cd_{n}S_{n+2}^{+}(n=1-20)$	Cd_nS_{n+2} (n=1-35, 39,41)
XXX	Cd_nS_{n+3} (n=1-15, 33,37,38,40,42,43)
XXX	$Cd_{n}S_{n+4}(n=1,3,4)$
$\operatorname{CdS}_{n (n=1-4)}^{+}$	CdS _n (n=1-7)
$\operatorname{Cd}_{n}^{+}_{(n=1-3)}$	XXX
$S_{n}^{+}_{(n=2,3)}$	S _n (n=1-5)

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Substitutional Modification on the Properties of Sr-doped BiFeO₃ Ceramics Synthesized by Molten Salt Method

N.Jahangeer^{1,2}, B. HariharaVenkataraman^{1,*}

¹Department of Physics, Birla Institute of Technology and Science, Pilani, Hyderabad, 500078 ²Department of Physics, Sreenidhi Institute of Science and Technology, Hyderabad, 501301

*Corresponding author:hari@hyderabad.bits-pilani.ac.in

Abstract: Sr doped BiFeO₃ samples with the stoichiometric ratio of $Bi_{1-x}Sr_xFeO_3$ (x=0.0, 0.05, 0.10, 0.15, 0.20, mol%) were prepared by molten salt synthesis route using NaCl as a flux. The X-ray diffraction studies of these samples confirmed the phase formation ofperovskite type rhombohedral structure of BiFeO₃. Furthermore, it also showed the presence of secondary phase of bismuth iron oxide (Bi₂Fe₄O₉) in all Sr doped BiFeO₃ samples. The XPS analysis revealed the dominance of Fe³⁺ oxidation state in these ceramic samples. The frequency dependent dielectric constant measurements were performed at 300K for x = 0.05 and 0.20 samples from 1kHz to 1MHz which showed the decrease in the value of dielectric constant with increase in Sr concentration.

Keywords: Multiferroics, Molten salt flux method, Nanoceramics, Dielectric constant

INTRODUCTION

In recent years, multiferroic materials capture great attention for their potential applications in various multifunctional devices. BiFeO₃(BFO) is a well-known multiferroic material that possesses ferroelectricity ($T_{C}=$ 1100K) and anti-ferromagnetism ($T_N = 640K$) at room temperature. It belongs to rhombohedrally distorted perovskite structure with space group R3c. It has been reported that the substitution of A or B-site ions by divalent metal cations (Ca^{2+} , Pb^{2+} , and Ba^{2+}) enhanced the magnetic, dielectric, optical and magneto-electric properties. In this regard, Sr²⁺ has been chosen as an appropriate choice for the substitution at Bi-site due to the difference in the ionic radii of Sr²⁺(1.18Å) and Bi³⁺ (1.03Å) ions [1,2&3]. This substitution would create a charge imbalance that might be compensated in two possible ways: (i) partial conversion of Fe^{3+} to Fe^{4+} state and (ii) creation of oxygen ion vacancies. In this work, molten salt (MSS) method was employed to synthesize different compositions of Sr-doped bismuth ferrite compound and studied its influence on various physical properties to exploit it especially for memory device application.

EXPERIMENTAL PROCEDURE

Pure and Sr doped BiFeO₃ (Bi_{1-x}Sr_xFeO₃; x = 0.0, 0.05, 0.10, 0.15 and 0.20) nanoparticles were synthesized by molten salt method. The stoichiometric ratio of Bi₂O₃, Fe₂O₃and SrCO₃ were used as the raw material and this mixture was ground in the pestle and mortar for 2h rigorously with 1:3 NaCl flux mole ratio. Subsequently, these powders were transferred into high purity alumina crucible and calcined at 650°C for 4h. These calcined powders were washed with distilled water until no precipitate appeared by the titration with AgNO₃ solution and then the residue was dried at 85°C for 24h. These dried powders were pressed into pellets of 10mm diameter and 1mm thickness and sintered at 700°C for 4h.

CHARACTERIZATION

The crystal structure of these prepared ceramic samples was examined by X-Ray Diffractometer (Rigaku Ultima-IV) over a 2 θ range of 20-70°C using Cu K α radiation. The morphological features of these samples were characterized by using field emission scanning electron microscope (FESEM, FEIAperoLoVac). The chemical valence states of these samples were determined by X-ray photoelectron spectroscopy (XPS,Thermo Scientific K-Alpha). The room temperature dielectric measurements were carried out on theseceramic pellets polished on both sides with silver pasteas a function of frequency using Wayne Kerr LCR meter with a signal strength of 1 V_{rms}.

RESULTS AND DISCUSSION

The XRD patterns of all the calcined samples are shown in Fig.1(a). Interestingly, these patterns indicated the formation of rhombohedral perovskite structure related to BFO, as all the major peaks were well matched with the JCPDS data file (PDF 86-1518). A less intense impurity peak related to Bi₂Fe₄O₉phase (marked as*) was also seen in these XRD patterns.



Fig. 1(a&b) XRD pattern of the samples calcined at 650°C.
Fig.1(b) showed the magnified view of the Bragg peak (104) at 20~32 for Bi_{1-x}Sr_xFeO₃ (x = 0.00 to 0.20) samples. It is clearly observed that the diffraction peaks (104) and (110) were merged into a single peak with increasing Sr-content due to the structural phase transformation [1&2]. The crystallite size (D) of these prepared samples were calculated by using Scherrer's relation and it varied from 38 nm to 44 nm as the Sr content increases from x = 0.0 to x = 0.20. $D = \frac{0.9\lambda}{2}$

$$D = \frac{\beta}{\beta \cos\theta}$$

The morphological analyses of the sintered samples were done by the field emission scanning electron microscopy technique for x = 0.05 & 0.20 samples and are depicted in Fig. 2 (a&b). The micrographs of these samples



Fig.2(a&b): SEM images of x = 0.05 and 0.20 samples.

revealed the spherical shaped grains and the porosity of these samples decreased with increase in Sr doping concentration.

The deconvoluted core level XPS spectra of x = 0.20 composition are presented in Fig. 3(a-d). Fig. 3(a) shows that Bi4f doublet consisting of two peaks, Bi4f_{7/2} and Bi4f_{5/2} at 158.4eV and 163.8eV respectively, which are from Bi-O bonds. Fig. 3(b) depicts the Fe2p doublet also consisting of two wide peaks, Fe2p_{3/2}~709.8eV and Fe 2p_{1/2}~723.45 eV, which are mainly ascribed to Fe-O bonds. Also, spin-orbit splitting energy is equal to 13.6 eV, which is comparable to that of the theoretical value of Fe2p for Fe₂O₃[1]. In Fig. 3(c), the O 1s peak is deconvoluted



Fig. 3(a-d): Deconvoluted core level XPS spectra of (a) Bi 4f, (b) Fe 2p, (c) O 1s & (d) Sr 3d of x = 0.20 composition.

into two peaks which are attributed to the oxygen present in the lattice of BFO. The Sr 3d spectra (Fig. 3(d)) was deconvoluted into two wide peaks of Sr $3d_{5/2} \sim 132.4$ eV, Sr $3d_{3/2} \sim 133.9$ eV and the associated broad hump could be attributed to Sr-O bonds in BFO lattice.

Fig. 4 shows the variation of the dielectric constant and loss of x = 0.05 and x = 0.20 compositions measured at 300K in the frequency range of 1kHz to 1MHz. It is observed that the dielectric constant decreased with increase in frequency and it becomes almost independent at higher frequencies in both the compositions. The decrement in dielectric constant with increase in frequency is considered to be the dielectric relaxation phenomenon in multiferroic related materials. Also, the dielectric constant decreases with increase in Sr composition in all the frequencies under study which might be ascribed to the difference in the ionic radii of Sr and Bi ions [2&4]. Similarly, there is a gradual decrease in the dielectric loss of these two compositions with increase in frequency which is shown as an inset of Fig. 4.



Fig.4: Variation of dielectric constant and loss of x = 0.05 & 0.20 composition.

CONCLUSION

Bi_{1-x}Sr_xFeO₃ nanoceramics were successfully synthesized by the molten salt method. The XRD, FESEM, XPS and dielectric studies were carried out to investigate the structure-dependent evolution of properties of perovskite Bi_{1-x}Sr_xFeO₃ ceramics. The XPS spectra indicated a slight increase in the oxygen ion vacancies with increase in Sr content of BFO samples. The dielectric constant and loss could be tuned as a function of Sr content in BFO ceramics.

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Electrochemical Study of Nanosized Co_{0.5}Zn_{0.5}Fe₂O₄ Synthesized by Hydrothermal Method

K. Sarkar^{1,*}, R. Mondal², D. Majumdar³, S. K. Bhattacharya⁴ and S. Kumar¹

¹Department of Physics, Jadavpur University, Kolkata-700032, India, ²Department of Electronics, Barrackpore Rashtraguru Surendranath College, Kolkata-700120, ³Department of Chemistry, Chandernagore College, Chandannagar, West Bengal 712136, ⁴Department of Chemistry, Jadavpur University, Kolkata 700032

*Corresponding author: koyelsarkar9@gmail.com

Abstract

Herein, we report the electrochemical study of nanosized $Co_{0.5}Zn_{0.5}Fe_2O_4$ synthesized by hydrothermal method. Structural and microstructural characterization has been carried out by powder x-ray diffraction (PXRD) and transmission electron microscopic techniques. UV–vis diffuse reflectance spectroscopy has been performed to analyze the optical property of the sample. The PXRD study suggests that the sample has crystallized as a single-phase cubic spinel ferrite with Fd3m symmetry. The average particle size is ~ 19 nm. The band gap of the sample is 1.75 eV. The sample exhibits maximum specific capacitance of 85.5 F/g at 10 mV/s scan rate. The pseudocapacitive behavior of the sample can be ascertained from the non-rectangular shape of cyclic voltammetry curves. The sample can act as a supercapacitor.

Introduction

In the fast-growing world, development of energy storage devices is gaining special attention in order to sustainably harness the depleting energy resources. Supercapacitors are emerging as the most promising next-generation energy storage devices due to their high-power density and longer cycling life [1]. The supercapacitor performance is mainly governed by the surface morphology and electrical properties of electrodes [1]. Nanosized ferrites are appearing as potential candidates for supercapacitor application owing to their high surface to volume ratio, low price, environmental benignity and large abundance [1]. But, electrochemical properties of mixed ferrites have not been explored abundantly [1]. In this regard, investigation of electrochemical properties of nanosized Co_{0.5}Zn_{0.5}Fe₂O₄ and accessing their application as supercapacitor appears promising.

Experimental

The nanosized $Co_{0.5}Zn_{0.5}Fe_2O_4$ (CZ5050) has been synthesized by hydrothermal method maintaining proper stoichiometric ratio following the procedure described in our earlier work [2].

The powder X-ray diffraction (PXRD) data and high-resolution transmission electron micrograph were recorded using Bruker D8 Advanced Diffractometer and Jeol2100 HRTEM, respectively. The diffuse reflectance spectroscopy (DRS) spectrum of the sample was recorded by a PerkinElmer UV–vis spectrometer (Lambda 35). The working electrode for cyclic voltametric measurements was fabricated by adopting the procedure described in our earlier work [1] and measurements were carried out using a potentiostat instrument (Digi-ivy, model No. DY2300).

Results and Discussion

Structural and microstructural characterization

The PXRD pattern of CZ5050 (Fig. 1) match well with JCPDS ICDD card numbers 22–1086 and 82–1049 for Co and Zn ferrite, respectively. The data has been refined using MAUD2.33 package [3] and the values of structural, microstructural and refinement parameters are presented in Table 1.

Table 1. Crystal data and refinement parameters	
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Parameters	CZ5050
Crystallite size (nm)	17
Microstrain	3.76×10 ⁻³
Lattice parameter (a(Å))	8.372
Density (g cm ⁻³)	5.304
Rwp	0.008
Rexp	0.005
GOF	1.21

The TEM micrograph of CZ5050, given in Fig. 2, suggest that the constituent particles are non-spherical in shape and possess a size distribution. The average particle size of CZ5050 obtained by fitting with lognormal distribution function is 19 nm, which is slightly greater than the crystallite size due to strong tendency of agglomeration.

Study of Optical Properties

The UV-vis diffuse reflectance spectrum (DRS) of CZ5050 shown in Fig. 3 displays an absorption edge

at around 705 nm. The band gap of CZ5050 is 1.75 eV (shown in inset of Fig.3), as estimated from the intercept of the $(\alpha h\nu)^2$ versus hv plot (Kubelka–Munk plot), where α is the absorption coefficient [4].



Fig. 1. PXRD pattern of CZ5050



Fig. 2. TEM micrograph of CZ5050



Fig. 3. UV-DRS spectrum of CZ5050 and $(\alpha hv)^2$ versus hv plot (inset)

Electrochemical performance study

The cyclic voltammograms (CV) of CZ5050 electrode at scan rates of 10, 20, 50, 100 and 200 mV/s in the potential range of ± 0.3 V with reference to the saturated calomel electrode are illustrated in Fig. 4.

The deviation from the rectangular shape of the CV curves can be ascribed to the pseudocapacitive behavior of CZ5050 originating from the transfer of charges between electrode and electrolyte through electrosorption and intercalation processes. The values of specific capacitance (C_S) have been calculated from the CV plot using formula described elsewhere [1]. C_S values for CZ5050 at scan rates of 10, 20, 50, 100 and 200 mV/s are 85.5, 56, 25, 20 and 17 F/g, respectively. At higher scan rates, ions get attached to the atoms of the electrode escalating obstruction in the charge transfer process leading to the drop of capacitance. Further, the area of the CV curves increases with the sweep rate, keeping the shape of the curves unaltered, reflecting good electrochemical response of the sample [1].



Conclusion

The PXRD and TEM suggest that CZ5050 is a well crystalline, single phase spinel ferrite with average particle size ~ 19 nm. CZ5050 exhibits good electrochemical performance due to its nano size, morphology and lower band gap energy and can act as a supercapacitor.

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Control of Ferroelectric Dipole Orientation in Ultra-thin Polymer Film for Enhanced Piezoelectric Response

Zinnia Mallick, and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali-140306, Punjab, India

*Corresponding author: dmandal@inst.ac.in

Abstract

Effect of annealing in thin-film poly(vinyledene-trifluoride), P(VDF-TrFE) in terms of molecular chain orientation and localized ferroelectric response was investigated systematically. The grazing incidence reflection absorption spectroscopic results indicates the preferential tendency from face-on to edge-on molecular chain orientation upon selective annealing techniques. Piezoresponse force microscopy measurement validates the superior ferroelectric and piezoelectric response in annealed films with vertical piezoelectric coefficient, $d_{33} \sim 16 \text{ pm/V}$ compared to as-spun films of $\sim 6 \text{ pm/V}$. Furthermore, the dependency on piezo- and ferro-electric responses depending on different types of annealing techniques are also undertaken.

found that the converse piezoelectric coefficient was increased upon thermal annealing.

INTRODUCTION

fluoride) (PVDF) Poly(vInyledene and it's poly(vinylidene copolymer of fluoridetrifluoroethylene) (P(VDF-TrFE) has been of special interest in the applications of ferroelectric memory due to their low cost and easy processing conditions.¹ The parent polymer PVDF is a semi-crystalline polymer with five different crystalline polymorphs of α , β , γ , δ and ϵ .² The β phase with all-trans (TTTT) conformation is of highest polarity and hence is the focus of interest for electronic applications. The copolymer P(VDF-TrFE) is known to be directly crystallized into the polar β phase. Hence P(VDF-TrFE) has long been treated as a model polymer to study nanoscale piezo and ferroelectric properties. For memory applications the data writing capability (1 and 0) has been utilized by switching the C-F dipole orientation (up and down) under external applied bias by invoking the property of bistable polarization in ferroelectric materials. In terms of device performance for memory applications, crystallinity of P(VDF-TrFE) along with the molecular dipole and chain orientation is important. If the dipole orientation is parallel to the surface (face-on) then the polarization switching is ineffective. Hence the requirement is the dipoles to preferably to orient perpendicular to the surface (edge-on orientation).³

Here in this work, we have studied the role of thermal annealing to induce favourable edge-on molecular dipole orientation in the spin-coated thin films of P(VDF-TrFE). The effect of annealing on local piezoelectric properties were also studied and it was

EXPERIMENTAL DETAILS

P(VDF-TrFE) (75/25) (piezotech-Arkema) was dissolved in Methyl ethyl ketone (CDH Pvt. Ltd.) in 4 (w/v %). The solution was then spin-coated onto cleaned ITO coated glass substrates at 4000 rpm in presence of N₂. Further, the as- spun thin films were subjected to annealing at 140 °C in vacuum oven for 2 hrs resulting into thickness of ~ 90 nm. The molecular chain and dipole orientation were studied using Fourier transform infrared spectroscopy (FTIR) grazing incidence reflection absorption in spectroscopy (GIRAS) mode (Thermofisher scientific iS20 with Pike Technologies Veemax III assembly) with spectral resolution of 4 cm⁻¹ and 128 number of scans. The nanoscale ferroelectric properties were investigated using Piezoresponse force microscopy mode using Bruker multimode 8 using Pt/Cr coated conductive AFM probe ElectriMulti 75-G.

RESULTS AND DISCUSSIONS

The GIRAS-FTIR is one of the most reliable, nondestructive techniques to investigate the molecular dipole and chain orientation in thin polymer films predominantly in the direction perpendicular to the substrate. Fig. 1(a) depicts the qualitative spectra of GIRAS-FTIR revealing the characteristics β phase vibrational bands at 1292 cm⁻¹ and 845 cm⁻¹ for both the as-spun and annealed P(VDF-TrFE) thin films confirming the presence of all trans (TTTT)



Fig. 1. GIRAS-FTIR spectra of as-spun and annealed P(VDF-TrFE) thin films.

electroactive β phase. P(VDF-TrFE) is known to get crystalized into edge-on and face-on orientation where the molecular dipoles (CF_2) are perpendicular and parallel to the substrate respectively as shown in the schematic diagram Fig. 1(b)). Hence, for several electronic applications edge-on orientation is of interest due to its ease of dipole switching along the applied electric field direction (along the thickness). Considering the vibrational bands of P(VDF- TrFE). the band at 1411 cm⁻¹ (B₁) is attributed to the $v_{as}(CC)$ coupled with $\omega(CH_2)$ (dipole parallel to molecular chain) and 1292 cm⁻¹ band (A₁) to the $v_s(CF_2)$ coupled with $v_s(CC)$ and $\delta_s(CCC)$ vibration for which dipoles are perpendicular to the molecular chain.⁴ The dipolar orientation can be determined by considering the relative absorbance intensity of the A₁ and B₁ bands. If the molecular chains are parallel to surface, that means the CF₂ dipoles are perpendicular to surface as consequence A₁ band intensity increases indicating edge-on orientation, or else if molecular chains are perpendicular to the surface the B₁ band intensity increases (face-on orientation). The as-spun film shows higher intensity of 1400 cm⁻¹ band (B₁) compared the 1292 cm⁻¹ band (A_1) depicting a face-on orientation. However, in the annealed films the intensity of the 1292 cm⁻¹ (A₁) increased significantly These results indicates that during thermal annealing molecular chain reorientation took place and converted the chain orientation from face-on to edge-on.

PFM spectroscopic phase and amplitude hysteresis loop is illustrated for the as-spun film (Fig.2 (a) and (b)). and annealed film (Fig. 2(c) and Fig. 2(d) respectively. However, the annealed sample depicted a well saturated hysteresis loop, whereas the as-spun sample showed a distorted one. The reason can be attributed to the low crystallinity of the as-spun samples causing a non-uniform applied field distribution. Upon thermal annealing crystalline region formation as well as molecular chain reorientation from face-on to edge on alignment gave rise to better ferroelectric properties. Hence, it can be concluded that thermal annealing plays a major role on the ferroelectric properties of P(VDF-TrFE). The converse piezoelectric coefficient (d₃₃) was calculated



Fig. 2. Local piezoresponse amplitude and hysteresis loop for as-spun (top panel) and annealed (bottom panel) films.

from the amplitude hysteresis curve and found to be 6 pm/V for the as-spun sample, whereas it increased by ~ 1.7 times and achieved a value of 16 pm/V for the annealed films. Again, this improved piezoelectric properties of the annealed samples can be accredited to the enhancement of crystallinity due to thermal annealing.³

In conclusion, thermal annealing was found to be an important step to improve molecular chain orientation as well as the nanoscale piezoelectric properties of P(VDF-TrFE) thin films.

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Synthesis and Characterization of ZnO and Graphene-ZnO Nanorods for NO₂ Sensing

Suraj Patil¹, Gouri Wadkar¹, Shradda Kumbhar¹, Sanjay Bhongale¹ and Sarfraj Mujawar¹

¹Department of Physics, Yashavantrao Chavan Institute of Science (Autonomous), Satara, 415001

*Corresponding author: surajpatil@ycis.ac.in

Abstract

ZnO and Graphene doped ZnO thin films with nanorod structure were synthesized by effective and low cost reflux method. X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), study the properties of prepared samples. Well defined hexagonal shaped vertically aligned nanorod morphology is observed from SEM micrographs. Z axis oriented structure of ZnO rods are confirmed by XRD pattern, NO₂ sensing mechanism and Comparative study of NO₂ sensing of ZnO and Graphene-ZnO films were studied and various parameters were evaluated.

Study of Structural and Optical Properties of ZnFe₂O₄ Nanoparticles Prepared by High Energy Ballmilling

Ishfaq Ahmad Parray¹, Anand Somvanshi² and Syyed Asad Ali^{1*}

¹Department of Applied Physics, Aligarh Muslim University, Aligarh, 202002 ²Department of Physics, Aligarh Muslim University, Aligarh, 202002

*Corresponding author: <u>asadsyyed@gmail.com</u>

Abstract

A fine powder of zinc ferrite $(ZnFe_2O_4)$ was prepared by high energy ball milling, milled for 10 hours, with the balls to powder ratio 8:1 and molar percentage ratio between ZnO and Fe₂O₃ as 1:1. Solid state diffusion between the precursor materials starts the Zinc ferrite formation. The process of mechano-synthesis of $ZnFe_2O_4$ at room temperature led to the formation of $ZnFe_2O_4$. XRD is used to study the phase formation of zinc ferrite and estimated the average crystallite size by using Scherrer's formula. FTIR data reflected proper occupation on Zinc oxide on octahedral site and FeO on tetrahedral site. Optical properties of the synthesized nanoparticles was studies by analysing UV-Vis spectroscopic data.

Study of photocatalytic activity of pure and CTAB assisted cadmium oxide nanoparticles

Deepak Singhwal¹, Amita Khatri¹, and Pawan S. Rana^{1*}

¹Deenbandhu Chhotu Ram University of Science & Technology, Murthal, Sonipat 131039, Haryana, India

*Corresponding author: drpawansrana.phy@dcrustm.org

Abstract

Pure and CTAB assisted CdO nanoparticles have been synthesized via co-precipitation method. X-Ray Diffraction (XRD) spectra confirm the formation of nanoparticles. Formation of oxygen vacancies or defects can be seen from the photoluminescence spectra. Photocatalytic performance of pure and CTAB assisted CdO in the degradation of Methylene Blue (MB) dye in UV light can be seen from the absorbance spectra.

Introduction

Environment pollution has become major concern for human health. Among various types of pollution, water pollution is the major cause for the spreading of various hazardous diseases among humans as well as animals. It contains various pollutants which are carcinogenic in nature. Carcinogenic dyes cover the major part of these pollutants [1]. Among various methods for removing these pollutants, advanced oxidation process is very efficient. In advanced oxidation process, photocatalytic process is very simple and effective [2]. Role of photocatalyst is very crucial in this process because it provides the stage for this process to take place. Nanomaterials as a photocatalysts are emerging as a boon in this process. In nanoscale their properties drastically change in comparison to bulk especially surface area. Surface to volume ratio of nanoparticles in comparison to bulk is more. In photocatalytic process when there is irradiation of the catalyst takes place then production of electrons and holes take place. These electrons and holes produce free hydroxyl radicals and superoxide ions which are highly reactive. These reactive groups randomly attack the molecules of carcinogenic dyes to distort their structure so that they are no more toxic. Now for an effective photocatalyst it should have band gap in visible range so that solar light photon can be used for production of electrons and holes. For this purpose, CdO is an effective photocatalyst because its band gap lies in visible region (2.2-2.5 eV). There are various methods for the production of nanomaterials i.e. sol-gel, hydrothermal etc. but in this work, co-precipitation is used because of its good production yield and non complexity. Surfactant plays a crucial role in the formation of nanoparticles. In this work, how varying concentration (0.04M, 0.08M and 0.12M) of CTAB affect the photocatalytic activity of CdO nanoparticle has been reported.

Results and discussion

X-Ray Diffraction

Figure 1. is showing X-Ray Diffraction pattern of prepared samples. Formation of pure, 0.04M, 0.08M and 0.12M is confirmed by X-Ray Diffraction peaks (111), (200), (220), (311) and (222) which are appearing at angles 33.04°, 38.34°, 55.32°, 65.94° and 69.30° respectively. According to JCPDS card no 05-0640, this diffraction pattern of CdO confirms the formation of cubic structure [3].



Fig. 1. XRD spectra for pure and CTAB assisted CdO nanoparticles.

Calculation of Crystallite size (D) is done with the help of Debye-scherrer's equation:

$$D = \frac{k\lambda}{\beta \, Cos(\theta)} \tag{1}$$

Here, *D* represents crystallite size, k = 0.94 is a constant, λ is the wavelength of X-ray which is 1.54 Å, β stands for full width at half maximum (FWHM) and θ is the half of angle at which peak is located. Crystallite size for pure, 0.04M, 0.08M and 0.12M are found to be 23.89 nm, 30.13 nm, 40.76 nm and 47.79 nm respectively.

Photoluminescence Spectra

Photoluminescence spectra of prepared samples were measured at the excitation wavelength of 470nm.Spcetra of the material is shown in the Fig. 2. Spectra comprises of peak positioned at ~521 nm which is emission peak of recombination of hole produced from photon and oxygen vacancy. 521nm lies in the range of green emission which is due to interstitial vacancies and oxygen vacancies [4]. Addition of surfactant is not affecting the intensity of the peak because it is not creating any defects in the crystal. Surfactant aligning the particles in particular direction rather than creating defects or oxygen vacancies.



Fig. 2. PL spectra of pure and CTAB assisted CdO nanoparticles.

Photocatalytic Activity

Photocatalytic ability of the cadmium oxide nanoparticles is assessed by deterioration of dye (MB) with the help of UV light source. Absorbance range of MB dye is from 500 to 700 nm. In the Fig. 3(a-d) showing absorbance spectra of MB dye with time when treated with pure, 0.04M, 0.08M and 0.12M respectively. Degradation efficiency is found in the order of 83% with pure, 82% with 0.04M, 70% with 0.08M and 74% with 0.12M. Main contribution in degradation of dye by a photocatalyst is of photon. As we know when we irradiate the sample with radiation having energy equivalent or higher from band gap of the material electron from valence band jump to conduction band leaving behind hole in valence band. Due to more numbers of electron and hole pairs photocatalytic efficiency also increase.

Degradation (%) is calculated from the formula: $\frac{(A_0 - A_t)}{(A_0)} \ge 100$ (2)



Fig. 3. Photocatalytic performance of pure and CTAB assisted CdO nanoparticles.

Conclusion

Pure CdO nanoparticles synthesized with feasible coprecipitation method performed highly efficient in comparison to CTAB assisted CdO nanoparticles in degradation of MB dye in 1 hour. Hydrophobic interactions between surfactant molecules play a vital role in aligning the particle in particular direction. Therefore, this study indicate that surfactant can be used as potential material to change the morphology of the particles.

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Impact of Co doping on Mg-Zn Spinel nano-ferrites

Garima Rana¹, Gagan Kumar², Arun Kumar³ and Pooja Dhiman^{1*}

¹ School of Physics and Materials Science, Shoolini University of Biotechnology and Management Sciences, Bajhol, Solan (H.P.) 173229,

> ² Department of Physics, Chandigarh University, Gharuan, Punjab, 140413, India ³Department of Physics, Kurukshetra University, Kurukshetra, Haryana 136119, India

> > *Corresponding author: dhimanpooja85@gmail.com

Abstract

Co-doped Mg-Zn spinel ferrite nanoparticles were prepared via the facile solution combustion method. The crystal structure, lattice parameter, crystallite volume, and the formation of prepared nanoparticles were investigated via XRD. The microstructure and vibrations of tetrahedral or octahedral sites were carried out by TEM and FTIR spectra. VSM analyses are used to study the magnetic properties of the papered samples which revealed the highly magnetic nature of samples.

Protonation mediated intercalation of selenium in g-C₃N₄ for the enhanced sunlight driven photocatalytic degradation

Y. N. Teja, R. Mithun Prakash, K. Gayathri, P. P. Adarsh Chandran, and M. Sakar*

Centre for Nano and Material Sciences, Jain University, Bangalore 562112, Karnataka, India.

*Corresponding author: <u>m.sakar@janiuniversity.ac.in</u>

Abstract

In this study, protonation mediated intercalation of selenium in graphitic-carbon nitride (g-C₃N₄) has been demonstrated. The observed changes in the XRD and ATR-IR peaks revealed the successful intercalation and improved exfoliation of g-C₃N₄ layers. A relative red-shift in the optical absorption and emission is observed for protonated Se/g-C₃N₄, which also found to effectively degrade the rhodamine B dye molecules under sunlight irradiation. This observed enhancement is attributed to the improved surface properties and rich surface-active sites due to the protonation induced intercalation of selenium in g-C₃N₄ layers.

Introduction

Ever since the report by Wang et al. on the application of graphitic carbon nitride (g-C₃N₄) - a metal-free polymer semiconductor possessing visible light responsive band gap structure for photocatalytic water splitting application, g-C₃N₄ has become a focal point of various photocatalytic studies.¹ Apart from its narrow band gap energy, g-C₃N₄ also carries advantages such as low-cost, ease of synthesis, chemical stability, non-toxicity, etc. However, the practical application of pristine g-C₃N₄ is hindered due to its limitations including rapid recombination of photogenerated charge carriers and less-surface active properties and eventually, various efforts have been made to overcome these drawbacks.² In this context, herein, we have developed a strategy to intercalate the selenium in the layers of g-C₃N₄ via protonation. This protonation-mediated intercalation enhances the separation and transportation of charge carriers in the system and improves the surface-active sites in $g-C_3N_4$ (GCN).

Experimental

In this synthesis process, a required amount of selenium dioxide and melamine was taken and thoroughly mixed and grounded using a mortar-pestle and thermally polymerized at 550 °C for 4 h in a muffle furnace. Then, this obtained product was dispersed in 37% conc. HCl and stirred for 2 h and washed with deionized water and ethanol for several times to attain pH ~7 and dried at 80° C overnight.

Results and discussion

XRD pattern of bare $g-C_3N_4$ shows characteristic peak at 27.64° (002) and 12.9° (100) corresponding to its interplanar and layer-stacking structure (Fig. 1). The observed peak-narrowing for Se-GCN and peakbroadening for protonated Se-GCN along with suppression of peak at lower 2θ in both cases indicated that there could be an interlayer grafting of selenium into the GCN layers, while the protonation further enhances their exfoliation with intercalation.



Fig. 1. XRD pattern of the bare and modified g-C₃N₄.



Fig. 2. ATR-IR spectra of bare and modified g-C₃N₄.

The obtained ATR-IR spectra (Fig. 2) showed the typical N-H, C-N heterocycle stretching and heptazine unit in the region of 3500-3000, 1200-1600

and at 800 cm⁻¹, respectively corresponding to the protonated Se-GCN, which is similar to the bare-CGN. This indicated that the backbone structure of GCN is remained unaltered upon the chemical modifications. However, the observed peak distortion and especially, the emergence of new peaks in the region of 3500-3000 cm⁻¹ for both the modified GCN could be attributed to the interaction of selenium and protonation induced modification in the structure of parent GCN as observed from the XRD results.³



Fig. 3. (a) UV-Visible absorption spectra and (b) Tauc's plots of the synthesized bare and modified $g-C_3N_4$.

The optical absorption spectra of both Se-GCN and protonated Se-GCN showed a clear red-shift (Fig. 3a), indicating that there could be a slight shift in the HOMO-LUMO edge positions due to the stacking of GCN layers via intercalated selenium that kept the layers intact. Accordingly, the corresponding bandgap energy of Se-GCN and protonated Se-GCN is decreased to 2.52 and 2.48 eV as compared to the bare GCN, which is 2.61 eV (Fig. 3b). Similarly, the emission peak for protonated Se-GCN is found to be red-shifted as compared to the Se and bare-GCN (Fig. 4a). This indicates that both the protonation and selenium intercalation modified the band structure of GCN via shifting their relative band edge potentials.⁴



Fig. 4. (a) PL spectra and (b) Photocatalytic degradation efficiency (C/C_0 ratio plot) of bare and modified g-C₃N₄.

For the photocatalytic studies, 10 mg of catalyst was dispersed in 10 ppm rhodamine B (RhB) dye solution and stirred under dark for 30 min. Then, the solution was exposed to sunlight. Dye degradation was monitored using UV-visible-abs spectrometer by withdrawing a small amount of solution for every 30 min. It is observed from the obtained C/C_0 ratio that the protonated Se-GCN, bare Se-GCN and bare-GCN

degraded ~92, 84 and 71% of dye, respectively in 120 min (Fig. 4b).



Fig. 5. Schematic illustration of protonation mediated selenium intercalation and their photocatalytic mechanism.

As described based on the characterization results, Se interacts with the inter-layers of GCN and the protonation process further leads to intercalation of Se in the inter-layers of GCN thereby this intercalated structure improves the separation of charge carriers and promotes them to the surface for the redox reactions. Such intercalated structure also facilitates an improved surface properties for GCN, which enhances the proximity of photocatalysts surface and dye molecules. This close interaction through surface charges paves ways for the effective response of the dyes for the redox reaction and their degradation as shown in Fig. 5.

Conclusion

It was observed that the protonation improves the selenium intercalation in $g-C_3N_4$ layers. Accordingly, the observed changes in the XRD and IR spectra confirmed the possible intercalated structure in GCN. Such process improved the absorption and emission properties of the system through inter-layer interaction of Se in GCN, which ultimately resulted in the improved photocatalytic efficiency towards the degradation of rhodamine B dye under sunlight.

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Correlation between absorption features and optical transitions from SWCNT based thin film coatings

Sonia Saini^{1,2}, S Reshmi³, Girish M. Gouda² and Kuntala Bhattacharjee^{1,3,*}

¹Indian Institution of Space Science and Technology (IIST), Thiruvanthapuram, 695 547, India

²Laboratory for Electro-Optics Systems (LEOS), ISRO, Bengaluru, 560 058, India

³Institute of Physics, Sachivalaya Marg, Bhubaneswar 751005, Odisha, India

*Corresponding author: <u>kbhattacharjee@iopb.res.in</u>, Kuntala.iopb@gmail.com

Abstract. In this work, we report correlation between absorption and optical signatures of one dimensional (1D) single walled carbon nanotubes (SWCNTs) as a manifestation of electronic transitions occurring within the sharp van Hove states of valence band, v_2 to conduction band, c_2 . These sharp transitions arising within the van Hove singularities due to the unique 1d structures of SWCNTs correspond to the energy band E_{22} . We demonstrate unique way of correlating 7 absorption energy features with 8 optical transitions depending on the tube diameter and chirality. This assignment has been carried out based on empirical calculations according to the tight binding model approximation. This finding can have direct impact in tuning the bandgap of SWCNTs of specific diameter and chirality for nanoelectronics and nanophotonic applications.

Introduction

Single walled carbon nanotubes (SWCNTs) which are first reported in 1993¹ have unique electronic and optical properties because of their distinctive onedimensional (1D) structure. SWCNTs as a rolled-up graphene sheet is described with a set of chiral indices (n, m) which correlate its diameter (d_t) and chiral angle $(\theta)^2$. Optical absorption and photoluminescence (PL) are two non-destructive characterizations to study SWCNT properties which can be tunable according to the applications. In this study, we correlate various transitions happening within the absorption band in the energy range 1.8 to 2.3 eV with the PL optical transitions in the visible spectral range of energy 1.8 to 2.2 eV for the SWCNT based coated films. Optical and absorption properties of SWCNTs are very sensitive to the (n, m) values which are expressed by sharp van Hove peaks. Van Hove transitions occurring between valance band v_2 to conduction band c_2 correspond to E_{22} energy band for SWCNTs with specific (n, m) structures³. In our previous work, high absorptance of the order of 97-98 % was obtained from the SWCNT based coatings in the visible spectral range⁴. Here, we discuss optical signatures corresponding to the electronic transitions in the same spectral range. Tight binding (TB) approximation defines inverse correlation between the van Hove singularities to the d_t . For the particular energy band E_{22} , the relation is given by

$$E_{22} = \frac{4\gamma_0 a_{\mathcal{C}-\mathcal{C}}}{d} \tag{a}$$

where γ_0 is C-C tight-binding overlap energy (2.9 eV), a_{C-C} is the nearest neighbor C-C distance (~0.142 nm) and d is the diameter of nanotube. In our

studies, we are assigning diameter values for different chiral SWCNTs according to E_{22} absorption and optical transition energies. We find composite SWCNTs of different chiral index exhibiting transitions within the energy band E_{22} .

Experimental section

SWCNTs, produced by high-pressure carbon monoxide (HiPCO) method were obtained from NoPo Nanotechnologies India Pvt. Ltd. Bengaluru which have the diameter and length in the range between 0.6 to 1.1 nm and ~ 400 to 1000 nm respectively. Postsynthesis chemical purification is done to eliminate the contaminants present in the as-prepared CNTs. Purification process involves wet oxidation at 300 °C followed by an acid wash using concentrated hydrochloric acid (HCl) and then annealing at 900 °C in an inert environment. For coated sample, acid treated CNTs mixed with polymer binder and solvent was hand sprayed over Al substrate⁴. Absorption properties of the spray-coated samples were analyzed using a UV-VIS-NIR spectrometer, PerkinElmer Lambda 950 in the wavelength range of 500 to 750 nm. The optical signatures of purified and spray-coated samples were obtained by subjecting them to photoluminescence (PL) spectroscopy analysis using Lab Ram HR 800 instrument.

Results and discussion

The absorption band corresponding to the E_{22} energy range and various optical transitions happening within the band are shown in Figure 1. The fitting of the absorption data was performed using Voigt line profiles. From the fitting, we obtained 7 contributions corresponding to SWCNTs of specific (n, m) and dt. The dt values obtained from the transitions within the absorption band using equation (a) is in the range between 0.7 to 1 nm (table 1). Table 1 shows the energy - diameter correlation according to the TB approximation discussed by Bachilo et al^2 .



Fig. 1. Voigt line profile fitting of the absorption spectrum obtained for the coated film in the energy range 1.8-2.4 eV which corresponds to *E*₂₂ band.

Table 1 Diameter	assignment to	the correspond	ling
absorption energy	transitions.		

Energy (eV)	Diameter (nm)/ Chirality (n, m)
1.80	1.04 (12,2)
1.89	0.89 (7,6)
1.97	0.94 (10,3)
2.06	0.84 (8,4)
2.14	0.69 (6,4)
2.22	0.81 (9,2)
2.29	0.79 (10,0)

In similar way, we have performed Voigt line fittings of the PL data in the energy range between 1.8 - 2.3 eV (Figure 2) for the SWCNT based coated films with different chiral indices. We observe total 8 optical signatures within the PL transitions which corresponds to the visible spectral range of 550 - 700 nm.



Fig. 2. PL transitions in the energy range 1.8-2.3 eV after performing Voigt function fitting of the coated film.

Each energy transition is attributed to a particular set of SWCNTs with specific (n, m) and d_t^5 . These optical signatures cover the diameter range from 1.8 - 2.2 nm (Table 2). Table 2 depicts the energy - diameter correlation for the coated film along with assigning their chiral index.

Table 2 Diameter assignment to the corresponding
Voight line fit energy transitions of PL data.

Energy (eV)	Diameter (nm)/ Chirality (n. m)
1.79	0.76 (9,1)
1.84	0.98 (9,5)
1.94	0.83 (7,5)
1.97	0.65 (7,2)
2.01	0.92 (11,1)
2.03	0.92 (11,1)
2.14	0.69 (6,4)
2.16	0.69 (6,4)

Conclusion

Identification of SWCNTs can be done effectively with the study of absorption spectroscopy and PL transitions. We have observed total 7 absorption and 8 optical transitions within the specific energy range between 1.8 to 2.3 eV. Absorption spectrum obtained from the coated film reveals absorptions from the SWCNTs of dt 0.8 to 1 nm. Similarly, PL spectrum obtained from the coated film exhibits various optical transitions from the SWCNTs of dt approximately 0.8 to 1 nm in the energy range around 1.8 to 2.2 eV. Hence, in a unique way, we are able to correlate the optical transitions with the absorptions happening within the absorption band depending on the SWCNTs chirality and dt. This is an important finding to tune the energy bandgap of specific SWCNTs according to the applications e.g. in fabrication of photodetectors and optoelectronic devices. This understanding will open up a new era in the field of nanotechnology related to the research based on SWCNTs.

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Bessel Beam Probed Silver Nanostructures Employed As Plasmonic SERS Substrates For Trace Level Detection Of Real-time Explosive and Dye

Dipanjan Banerjee¹, A. Mangababu², R. Sai Prasad Goud², Venugopal Rao Soma^{1*}

¹Advanced Centre of Research in High Energy Materials (ACRHEM), ²School of Physics University of Hyderabad, Hyderabad 500046, Telangana, India

*Corresponding author: soma_venu@uohyd.ac.in

Abstract

In this work, we report the fabrication of exotic silver (Ag) nanostructures (NS) employing a ultrafast Bessel beam utilizing a picosecond (30 ps, 10 Hz) laser pulses. Subsequently, an improved Surface Enhanced Raman Scattering (SERS) response from the Ag NS were thoroughly explored for trace level detection of an explosive (Picric Acid-500 nM) and one dye (MB-5 nM) molecule.

3D Visualization of Crystallography Information of Hydrothermally Synthesized 2H-MoS₂ Nanocrystalline Material

Piyush Siroha¹, Naveen Kumar², Rajesh Kumar², Davender Singh¹, and Jitendra Gangwar^{1*}

¹Department of Physics, RPS Degree College, Balana, Mahendergarh, Haryana, 123029, India ²Department of Physics, Panjab University, Chandigarh, 160014, India

*Corresponding author: njitendrag127@gmail.com

Abstract

In this work, we demonstrate the visualization of atomic arrangement of crystal structures and lattice planes of 2H-phase of MoS_2 nanocystalline material prepared via inexpensive hydrothermal method. The phase identification and crystallography information are examined through powder X-ray diffraction technique and VESTA-3D theoretical tool. The associated crystal planes are created and displayed. This work is to be useful in modern structure-property relationships.

Introduction

Progress over the past decades has been made for understanding of manifold aspects of MoS₂ nanomaterials, including its processing, growth mechanism and structure-property relations. Based upon the coordination environments, MoS₂ crystal exhibits both stable phase (2H-MoS₂) and various metastable phases (1T, 1T', 1T", 1T"', 1H, 3R and etc.), where the letters T, H and R correspond to trigonal, hexagonal and rhombohedral, respectively and the digits indicate the number of monolayers in unit cell. The tunable crystallographic structure of nano MoS₂ materials has aroused significant research interests among distinct scientists, engineers and researchers. Either experimental or theoretical works have extensively studied about the crystal structure information however they turn the attention to probably crystallographic, atomic and/or electronic structure analysis and synthetic approaches involve sophisticated instruments and chemical precursors. A simple and safe strategy to synthesize MoS₂ nanomaterial, therefore, is essential for technological applications and fundamental understandings about the visualization of distributions of atoms and lattice planes in unit cell at atomic level.

Herein, 2H-MoS₂ nanocrystalline material prepared by unique hydrothermal approach and theoretic predictions for crystallography properties such as phase identification, crystallinity, orientation factor and 3D-visualization of the crystal lattice plane is summarized.

Synthesis of Nanocrystalline MoS₂

 MoS_2 nanocrystalline material was synthesized by a safe and facile hydrothermal method using $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and NH_2CSNH_2 as starting material. In a typical procedure, 1.2 and 2.2 gm of (NH₄)₆Mo₇O₂₄·4H₂O and NH₂CSNH₂, respectively were dissolved in 40 ml Millipore water under continuous stirring for 1 hour. After that, the formed solution was transferred into stainless steel Teflon-lined autoclave and further kept at 240 °C for 6 hours. After natural cooling, resultant black precipitate was washed four times with Millipore water and absolute ethanol and lastly dried in oven at 80 °C for 24 hours to produce black MoS₂ powder.

Characterization of Nanocrystalline MoS₂

Structural analysis was carried out using X-ray diffraction (XRD; PAN analytical X'pert pro, Netherlands) with Cu-k_{al} radiation ($\lambda = 1.54$ Å) in the 2 θ range of 10-70°. 3D-visualization of crystal structure and lattice planes was created through Visualization for Electronic and STructural Analysis (VESTA) software.

Results and Discussions

Fig. 1 (a) shows the XRD pattern of the assynthesized MoS_2 material. As shown in Fig. 1(a), XRD pattern demonstrate (002), (101), (103) and (110) crystal planes are observed which confirmed the crystalline structure of 2H phase of MoS₂ with hexagonal crystal system (S.G.: P63/mmc, a = b =3.14 and c = 12.54 Å, standard JCPDF No.: 01-075-1539). The prominent peak intensity corresponds to (002) plane reveals the maximum numbers of atoms are aligned in z-direction. Inset in Fig. 1 (a) shows the hexagonal crystal structure of MoS₂ indicating stacking layers of molybdenum (Mo) atoms lie in zplane and sulfur (S) atoms situated in between these layers and form covalent bond with neighboring Mo atoms resulting crystalline 2H-MoS₂ structure. Fig. 1 (b) indicates the crystallite size (D) and orientation

factor (O_{hkl}) analysis. Crystallite size was calculated from Debye-Scherrer's equation (eqⁿ 1) using the FWHM obtained from XRD pattern to be within the range of 3.5 nm to 8.9 nm authenticate the formation of nanocrystalline MoS₂ material.

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad \dots (1)$$

 O_{hkl} was evaluated from observed intensity (I_{obs}) and standard intensity (I_{std}) by using eqⁿ 2.

$$O_{hkl}(\%) = \frac{I_{obs}/I_{std}}{\sum \left(\frac{I_{obs}}{I_{std}} \right)} \times 100 \qquad \dots (2)$$



Fig. 1. (a) XRD pattern, (b) Bragg's position *versus* crystallite size and orientation factor curves of MoS₂ nanocrystalline material. Inset (in a) provides the crystal structure of MoS₂. Color code: inset (in a) Large (Violet) balls indicate Mo atoms and Small (Green) balls indicate S atoms, (in b) Black (Hollow) and Blue (Solid) triangles shows crystallite size and orientation factor, respectively.

Table 1 illustrates the observed crystallite size and orientation factor analysis for different sets of crystal lattice planes (*hkl*) at various identified peak positions and relative intensities.

Table 1. crystallite size and orientation factor analysis.					
2θ (°)	Plane (hkl)	I _{obs} (a.u.)	I _{std} (a.u.)	Crystallite size (nm)	O _{hkl} (%)
14.03	(002)	1166	1000	8.95	11.46
33.73	(101)	673	124	8.38	53.38
39.46	(103)	434	658	3.54	6.62
59.22	(110)	397	137	5.40	28.52

Fig. 2 (a-d) shows the schematic representation of distinct crystal lattice planes (002), (101), (103) and (110) as observed in XRD pattern.



Fig. 2. Three-dimensional (3D) schematic representation showing (a) (002), (b) (101), (c) (103) and (d) (110) crystal lattice planes as observed in XRD pattern.

Conclusions

In the present study, 2H-phase of MoS_2 nanocrystalline material was successfully synthesized by using hydrothermal method. Crystallographic identification revealed the obtained MoS_2 material crystallized in hexagonal symmetry within the size range 3.5 to 8.9 nm. It was found that the orientation factor was observed to be within the range of 6-53%. 3D visualization on the crystal structure and lattice planes is created to demonstrate atomic arrangement of 2H-MoS₂. It is believed that this study will be of interest in future to understand the structure-property relationships in the research area of both Condensed Matter Physics and Materials Science.

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Modified Young's Modulus of Carbon Nanotubes With Vacancies: A Molecular Dynamics Approach

Keka Talukdar

Department of Physics, Nadiha High School, Durgapur-713211, West Bengal, India

*Corresponding author: keka.talukdar@yahoo.co.in

Abstract

 Sp^2 bonding between the carbon atoms inside carbon nanotubes (CNTs) has imparted them astonishing mechanical properties which can be exploited in building super-strong composite materials. A critical study on the variation of their properties under different conditions is necessary to extract their maximum efficiency as filler materials for preparing composites. In the present work the Young's modulus of an armchair, a chiral and a zigzag single-walled CNT of almost same diameter with a number of vacancies at different positions are computationally analyzed to predict their mechanical behavior.

Low-Temperature Synthesis of Nanocrystalline Silicon-Oxycarbide Thin Films

Sukalyan Shyam and Debajyoti Das*

Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India

*Corresponding author: erdd@iacs.res.in

Abstract

Intrinsic nanocrystalline silicon-oxycarbide (nc-SiO_xC_y:H) thin films are prepared by conventional PECVD at a low temperature zone around 170–180 °C, using ~1.6% (SiH₄ + CO₂ + CH₄) in (H₂ + He) diluent, at moderate rf power ~260 W. Crystallinity, grain size and conductivity, in general, improves at elevated substrate temperature. Films possessing adequate crystallinity ~40 %, with (220) crystallographic orientation, good conductivity ~ 10^{-3} S cm⁻¹ and low activation energy ~140 meV, grown at such low temperature seem appropriate for utilization as the window layers in *p-i-n/n-i-p* nc-Si solar cells.

Structural and Optical Properties of Sm Doped a-MnO₂

Deepti Gangwar¹ and Chandana Rath^{*1}

¹School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi, 221005, India

*crath.mst@itbhu.ac.in your@emailaddress.in

Abstract

Hydrothermal synthesis of bare and Sm doped α -MnO₂ demonstrates the presence of a pure tetragonal phase with space group I4/m. However, after incorporating Sm, the crystal structure of α -MnO₂ rests tetragonal, but the crystallinity reduces. Doping of Sm also increase the number of oxygen vacancies, as measured by X-ray photoelectron spectroscopy. Bare and Sm doped α -MnO₂ have gap of 1.95 and 1.85 eV respectively, as determined by absorption in the UV region. The bandgap in visible region and increase in oxygen vacancy suggest that it could be used as both, a photocatalyst and an electrode in supercapacitors, respectively.

Development of Diamond-Like Carbon Films with Prominent Nano-diamond Phase

Brijmohan Paramanik and Debajyoti Das^{*}

Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India.

*<u>Corresponding author: erdd@iacs.res.in</u>

Abstract

Diamond like carbon (DLC) films were grown on inexpensive glass substrates, without its pre-treatment or applying dc bias, at a moderate power ~500 W in MW-PECVD. Using C₂H₂ as the precursor gas and utilizing the CH₃ ions extracted by MW plasma decomposition, we have been able to grow DLC films with significant fraction of nanodiamond phase at substantially low temperature of 300 °C. The existence of diamond peak and t-PA peaks, the maximum magnitudes of I_{Dia}/I_G (~1.05), and minimum magnitude of I_D/I_G ratio (~1.0) in the Raman spectrum indicate good quality of the nano-diamond phase, identified with its <111> orientation in the optically transparent DLC film.

Optical Properties of Silicon Nanowires Fabricated by Ag- Assisted Chemical Etching

Smruti Medha Mishra and Biswarup Satpati

Surface Physics and Material Science Division, Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata 700064, India

*Corresponding author: smruti.mishra@saha.ac.in

Abstract

Silicon and its different nanostructures are already being used extensively in the field of optics, electronics and photovoltaics. Here we have successfully fabricated silicon nanowires on pre-fabricated pyramidal Si substrate (P-Si) by metal assisted chemical etching (MACE) method and the metal used here is silver (Ag). The synthesized nanowires were investigated by Transmission Electron Microscopy (TEM) and its optical properties by PL Spectroscopy and UV-VIS spectroscopy. The NWs on pyramidal Si (P-Si) substrate shows less reflectance compared to planer Si substrate. The PL enhancement has been recorded for P-SiNWs by a factor of 1.3 in comparison to planar SiNWs. All these properties like high aspect ratio structures, enhancement of optical properties taken all together have a great influence on the photovoltaic applications.

Introduction

Silicon nanowires (SiNWs) in ensembles have attracted much attention in the last few years to serve as future building blocks in solar cells, sensors, transistors, and photodetectors. The silicon-based approaches are certainly preferred because of material richness and nontoxicity at a high level of materials control.

Due to the high surface to volume ratio and exclusive quasi one-dimensional structure, silicon nanowire-based devices have gained a lot of attention nowadays [1]. Metal assisted chemical etching based upon the electro-chemical redox reactions is a selective etching methods that allow to obtain vertical SiNWs [2]. It has been shown that SiNWs, which were obtained by MACE are found to possess remarkable optical properties like visible photoluminescence (PL), exceptionally low reflection. Silicon nanowires exhibit strong anti-reflective properties and are capable of enhancing optical absorption over that of bare silicon [3].

In this work, we studied the optical properties of the as-synthesised silicon nanowires on pre-fabricated pyramidal Si (P-Si) and planar Si by MACE and compared the result with virgin Si. The structures of the SiNWs are discussed based on TEM studies.

Experimental Details

This method involves electro-less (silver) deposition on the Si wafer followed by chemical etching. In a typical MACE process, a Si substrate covered by a noble metal is subjected to an etchant composed of HF and an oxidative agent. Typically, the Si beneath the noble metal is etched much faster than

the Si without metal coverage. As a result, the noble metal sinks into the Si substrate, generating Si wires.

SiNWs synthesised upon planar and pyramidal Si wafer were studied in cross-sectional mode using TEM (FEI, Tecnai G2 F30, S-Twin microscope) operating at 300 kV equipped with a high-angle annular dark field (HAADF) detector from Fischione (Model 3000). For PL measurements, a Kimmon Coha IK series He-Cd laser with excitation power of 100 mW operating at 325 nm was used as the excitation source.

Results and Discussion

Detailed structural study has been done by crosssectional TEM (X-TEM) analysis. The SiNWs possess a diameter of about 140 nm to 180 nm and length of about 1.75μ m to 1.93μ m.



Fig. 1. TEM image of (a) SiNWs (b) P-SiNWs (c) SAED pattern of (a), (d) HRTEM image and inset shows the FFT pattern which confirms the growth direction to be <100>.

The SAED pattern taken along [110] zone axis of Si which shows crystalline nature of the nanowires. The growth direction is found to be < 100 > from SAED pattern as well as from FFT pattern on a single nanowire as shown in figure Fig. 1(c) and inset of Fig. 1(d), respectively.



Fig. 2. Photoluminescence spectra obtained for SiNW and P-SiNW

After the formation of silicon nanowires on P-Si substrate, we noticed improvement in the PL intensity. The escape of photons from P-Si was facilitated by texturing the surface, because the surface scattering phenomenon occurred strongly on the textured surfaces [4]. SiNWs on P-Si surface may lead to such enhanced scattering. In addition, PL shifts towards high energy region and short wavelength may be ascribed to the recombination of electrons trapped at the states due to the quantum confinement effect [5].



Fig. 3. UV-VIS spectra showing the % reflectance

Figure 3 shows reflectivity of the samples such as planar silicon substrate and the SiNWs on the planar Si and pyramidal Si substrates. The reflectivity decreases to around 4% in the wavelength range 200 nm-800 nm for P-SiNWs as compared to around 7% for planar SiNWs and around 10% for the planar substrate without any texture.

Conclusion

A facile fabricating method was used for the silicon nanowire arrays via the established two step Agassisted chemical etching (MACE). We obtained SiNWs those are straight and perpendicular to the wafer surface via a preferred < 100 > direction using Si (100) and that of pyramidal Si substrate as the starting wafer. P-SiNWs exhibit a strong decrease in reflectance to near about 4% in comparison to the other samples taken. The PL intensity is affected by the surface morphology of the nanowires. And all these characteristics put influence on the applications towards solar cells or PV cells.

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Magnetic Control of Dielectric Permittivity and Electric Polarization Voltage of Polymer Based Nanocomposite Film

Sonali Pradhan^{1,2}, Pratik Deshmukh^{1,2}, S. K. Majumder^{1,2} and S Satapathy^{1,2*}

¹Laser Biomedical Application Division, Raja Ramanna Centre for Advanced Technology, Indore, 452013, India ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India

*Corresponding author: srinu73@rrcat.gov.in; srinusatapathy@gmail.com

Abstract

Magnetodielectric and magnetoelectric materials are technologically demanded due to desirable control of dielectric properties and electric polarization. In this work, NiFe₂O₄/P(VDF-TrFE) nanocomposite films (40 μ m) were synthesized using solution casting technique. The magnetodielectric and magnetoelectric properties of these nanocomposites are presented here. Magneto-dielectric study in DC magnetic field range 0-7000 Oe shows increase in permittivity with magnetic field. In addition, room temperature magnetoelectric study shows maximum coupling voltage of 136.4 mV/Oe-Cm at 1.21 kOe DC magnetic field and both the effect was attributed to the presence of mechanical coupling in magnetostrictive and piezoelectric phase.

INTRODUCTION

Tuning of dielectric properties and electric polarization of materials with magnetic field attract current research for the design of multifunctional devices [1]. Single phase materials show ME (magnetoelectric) effect at low temperature whereas room temperature ME coupling is required for device applications which lead attention towards composite materials [2,3]. Among the composites, nano sized ferrite embedded polymer-based nanocomposites show high strain mediated ME and MD (magnetodielectric) effect due to of coupling enhancement mechanical between magnetostrictive phase (ferrite nanoparticles) and ferroelectric phase (polymer) [4].

In this work, 0-3 type particulate NiFe₂O₄/P(VDF-TrFE) nanocomposite film was investigated for high ME and MD effect. NiFe₂O₄ nanoparticles (NFO NPs) of approximately 50 nm size were synthesized using auto combustion technique [5]. The inverse spinel structure of NFO NPs was confirmed from X-ray diffraction analysis. These NPs with different volume % (0.2, 0.5, 1, 1.5 and 2) were incorporated in P(VDF-TrFE) matrix to prepare nanocomposite film (40 μ m) by solution casting technique. XRD patterns of the nanocomposite films confirm the presence of β -phase of polymer as well as NFO phase.

The frequency dependent dielectric study shows the existence of permanent dipole in the frequency range 100 Hz to 1MHz. The nanocomposite films show room temperature well-saturated ferroelectric loop and magnetization versus magnetic curve carried out by P-E loop tracer (Marine India) and SQUID S700X magnetometer respectively. To confirm the coupling between electric and magnetic order parameters, ME and MD measurement were carried out at room temperature.

MAGNETO-DIELECTRIC (MD) PROPERTIES

Room temperature MD measurements within frequency 100 Hz to 1 MHz were performed for electric poled nanocomposite films with increasing magnetic field from

500 Oe to 7000 Oe. The dielectric permittivity was observed to be gradually increasing with increasing magnetic field. These nanocomposites give rise to MD property due to interface coupling between magnetostrictive and piezoelectric phases. In the present case, the MD coupling arises due to the strain induced by NFO NPs to the polymer which causes increase in dipolar mobility with an electric field and so increase in permittivity. The magnetostrictive effect of NFO NPs orient the spin configuration which leads to change in charge and dipole configuration of P(VDF-TrFE), thus change in polarization.



Fig. 1. Magnetic field induced permittivity for 0.5% NFO/P(VDF-TrFE) nanocomposite.

The variation of permittivity with applied magnetic field is characterized by MD constant defined as

MDE (%) =
$$\frac{\varepsilon'(H) - \varepsilon'(0)}{\varepsilon'(0)} \times 100$$
 a)

where $\varepsilon'(H)$ and $\varepsilon'(0)$ are the permittivity in the presence and absence of the applied magnetic fields respectively [6]. A significant change in MDE (%) was observed from 0.8% to 1.79% with increasing DC magnetic field from 500 Oe to 7000 Oe as high magnetic field will create higher mechanical interaction between the two phases.

MAGNETO-ELECTRIC (ME) MEASUREMENT

The transverse magnetoelectric voltage coefficient for electrically poled (900 volt) 0.5% NFO/P(VDF-TrFE) nanocomposite film at 10 kHz is shown in figure (2). The voltage coefficient was observed to be increasing initially with the applied DC magnetic field (both in positive and negative field) up to a maximum value and then decreases with further increase in magnetic field. The maximum coupling voltage at an optimum magnetic field indicates the saturation of magnetostriction of NFO NPs which was followed by fall of the coupling at higher magnetic field.



Fig. 2. Transverse magnetoelectric voltage coefficient versus DC magnetic field for 0.5% NFO/P(VDF-TrFE) nanocomposite film.

Due to application of external DC magnetic field, strain is generated in NFO NPs (negative magnetostriction) which transfers to the polymer due to elastic interaction between NFO NPs and polymer phase leading to output voltage. The magnetoelectric voltage coefficient (α) is quantified using the empirical formula

$$\alpha = \frac{\partial V}{t \times \partial H}$$
 b)

where, ∂V is the output voltage in mV, t is the thickness of the film in Cm and ∂H is the applied DC magnetic field [7]. The maximum magnitude of the ME voltage coefficient was found to be 136.4 mV/Oe-Cm at 1.21 kOe DC magnetic field for 0.5% NFO/P(VDF-TrFE) nanocomposite film. The

magnitude of ME voltage coefficient for 0.2, 0.5, 1, 1.5 and 2 volume % NFO/P(VDF-TrFE) films has given in the Table 1.

Table 1. Transverse ME voltage coefficient		
Sample name	Transverse ME voltage coefficient (α_v^{31}) mV/Oe-Cm	
0.2 %	128.5	
0.5 %	136.4	
1 %	126.6	
1.5 %	121.5	
2 %	85.5	

CONCLUSIONS

The room temperature Magnetodielectric effect and Magnetoelectric coupling coefficient measurement were performed for NFO/P(VDF-TrFE) nanocomposite films. The existence of electric and magnetic order was confirmed in these nanocomposites. The magnetic field-controlled dielectric permittivity (MD effect) and electric polarization (ME coupling) were achieved by mechanical coupling (strain induced) between the magnetostrictive phase and piezoelectric phase. Room temperature significant ME coupling voltage and MDE (%) explored in these nanocomposite films will be helpful for device applications.

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Preferential <220> Crystalline Growth of Boron Doped Nanocrystalline Silicon Thin Films by ICP-CVD

Chandralina Patra and Debajyoti Das^{*},

Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India

*Corresponding author: erdd@iacs.res.in

Abstract

B-doped nc-Si thin films are successfully grown in inductively coupled plasma (ICP) CVD without using additional H₂ dilution to the SiH₄ plasma, by lowering the substrate temperature from 400 °C to 30 °C. The *p*-nc-Si thin film with dominant <220> crystallographic orientation of the nanocrystallites, providing a significantly wide optical band gap (>1.88 eV) and high electrical conductivity (> 10^1 S cm⁻¹) appears suitable for the nc-Si heterojunction solar cell fabrication.

Optimization of Process Parameters to Fabricate Uniform, Beadfree Cobalt Ferrite Fibers Through Electrospinning Technique

P Durga Prasad¹ and J Hemalatha²

^{1, 2}Advanced Materials Lab, Department of Physics, National Institute of Technology, Tiruchirappalli-620015.

*Corresponding author: hemalatha@nitt.edu

Abstract

The process parameters to fabricate uniform, bead-free cobalt ferrite fibers through electrospinning technique are optimized. To obtain the best quality, bead-free fibers, various electrospinning process parameters such as polymer solution concentration, tip to collector distance, flow rate, and applied voltage were optimized to be 12 wt%, 14 cm, 05 ml/h and 20 kV, respectively. The as spun fibers were then calcined at various heating rates. SEM, TEM, and AFM were used to examine the fiber morphology. Fibers calcined at 800°C with a heating rate of 2°C/min produced bead-free continuous fibers with a fiber diameter of 200 nm. The XRD pattern confirmed the cubic spinel crystalline structure of cobalt ferrite with a crystallite size of 34 nm.

Carambola-like NiCoP Nanostructure for Efficient OER Activity

Pijush K. Gan^{1#}, Arnab Pal^{1#} and Kuntal Chatterjee^{1*}

¹Department of Physics, Vidyasagar University, Midnapore-721102, WB, India

**Corresponding author: <u>kuntal@mail.vidyasagar.ac.in</u> # Authors have equal contribution*

Abstract. Inexpensive and highly efficient electrocatalysts from earth abundant transition metals are the demand of the hour for renewable energy production. Here we report the successful synthesis of carambola-like nickel cobalt phosphide (NiCoP) through a two-step hydrothermal process followed by the solid-state reaction and its promising employment as an electrocatalyst for oxygen evolution reaction (OER). The as prepared NiCoP exhibits excellent OER activity in 1.0 M KOH solution by reaching 10 mA cm⁻² current density at significantly small overpotential of 288 mV. It also showed a relatively small Tafel slope of 83.26 mV dec⁻¹ and high durability. The performance is better than the benchmark RuO₂ catalyst and the study opens up new possibilities of electrocatalytic OER activity.

Introduction

The increasing demand of clean renewable energy sources for a green-technology based future are driving the scientific community to explore various sustainable environment-friendly energy sources^{1, 2}. Electrocatalytic water splitting is currently drawing the attraction of the scientific community for its efficiency to generate uninterrupted hydrogen and oxygen with satisfactory level of energy conversion and without any emission³. Electrochemical water splitting consists of two half reactions, hydrogen evolution and oxygen evolution. Among them, achieving efficiency in OER is more challenging because of the required high overpotential and sluggish kinetic rate due to the complex proton coupled electron transfer process⁴. Electrocatalysts like RuO₂ and IrO₂ are proven their best for OER, however their high cost and low earth abundance force the scientific community to search non noble metal based low cost electrocatalysts. Low cost as well as earth abundant transition metals like nickel and cobalt based compounds such as oxides⁵, chalcogenides⁶ and phosphides⁷ are emerging as new low cost and efficient electrocatalysts. It was earlier reported that phosphorization process in transition metals played an active role to improve the electrocatalytic activity for OER⁸. Structural morphology also plays a key role in OER⁹. Herein we report the synthesis of nickel cobalt phosphide (NiCoP) via two step hydrothermal process accompanied by solid state reaction. The unique carambola like structure provides NiCoP large active surface area which helps it to achieve 10mA cm⁻² current density at a low overpotential of 288 mV in alkaline medium. The low Tafel slope, 83.26 mV dec-1, also exhibits its efficient electron transfer process. The performance is superior to reported RuO₂ and some of the other contemporary works. Thus, we propose, with further detailed study, carambola like structured NiCoP will become a promising electrocatalyst for OER and play a crucial role in green energy-based technology.

Experimental Details

Standard hydrothermal process was performed to prepare Ni-Co hydroxide followed by the standard solid-state reaction to achieve NiCoP as shown in Figure 1(a). The X-ray diffraction of the powder sample was done with Rigaku Mini-Flex X-ray diffractometer using Cu Ka radiation of wavelength 1.5406 Å. Scanning electron microspcopy (SEM) was performed with MERLIN (Carl Zeiss). The electrochemical performance was tested with Autolab PGSTAT204. The linear sweep voltammetry for OER was performed at a scan rate 5mV/sec in 1.0 M KOH solution in a three-electrode system with Pt wire as counter electrode, Ag/AgCl as reference electrode and glassy carbon with 5mm diameter as working electrode. All potentials were measured with respect to reversible hydrogen electrode (RHE) and iR correction has been made for LSV curves. The ink for the electrochemical test was prepared with 2mg NiCoP dissolved in a solution of 70µl Isopropyl alcohol (IPA), 130 µl of DI water and 20 µl of 0.5% nafion. The electrochemical impedance spectroscopy was performed in the frequency range 0.1 to 10^5 Hz at 1.567V vs RHE.

Results and Discussions

The crystal structure ascertained from X-Ray analysis in Figure 1(b) revealed the presence of (111) plane of NiCoP³ at 41⁰ along with the signature of (011) plane of CoP¹⁰ at 31.6⁰. Figure 1(c) depicts the SEM images, where a unique carambola-like structures have been observed with enhanced surface area and that is beneficial for the electrocatalytic activity. Figure 1(d) represents the elemental mapping of NiCoP which presents almost equal presence of Ni and Co with well phosporization of the overall sample. This is in good agreement with NiCoP phase found in our XRD result.



Fig. 1. (a) Schematic diagram, (b) XRD, (c) SEM, (d) Elemental mapping.

Electrochemical OER result, Figure 2(a), exhibits excellent performance with overpotential value of 288mV and 409 mV to reach 10 and as high as 150 mA cm⁻² current density respectively. Low Tafel slope of 83.26 mV dec⁻¹ shown, in Figure 2(b), indicates a fast charge transfer process. The sample-performance is superior than RuO₂¹¹ and it also outperformed some contemporary works^{3, 12}. The contribution of GC is negligible, shown in Figure 2(a). The Figure 2(c) represents the well stability of NiCoP in 1.0M KOH medium with slight shift of onset potential (7 mV) after 2000 cycles of voltammetry.



Fig. 2. Electrochemical activity (a) LSV curves (b) Tafel slopes of NiCoP and RuO₂ (c) Durability and Chronoampiometry (Inset) of NiCoP, (d) EIS of NiCoP

Figure 2(c) inset also supports the robustness of the sample with chronoamperometry performed at 1.518 V vs. RHE which gives a stable 10mA cm⁻² current density for 10 hours. To get an insight on charge

transfer mechanism electrochemical impedance spectroscopy was performed at 10^5 to 0.1 Hz frequency range, shown in Figure 2(d). It reveals a low charge transfer resistance $R_{ct} \sim 4.74$ ohm, which establishes the faster charge transfer rate helping to overcome the usual sluggish kinetic rate of OER.

Conclusion

In summary, we have successfully synthesized carambola-like NiCoP through a facile and scalable two-step process. The sample demonstrate commendable performance towards OER activity in base medium with very low overpotential (288 mV), low Tafel slope 83.26 mV dec⁻¹, and high durability outperforming the benchmark RuO₂ and some contemporary reported samples. The carambola like unique morphology of NiCoP provides higher surface area which in turns provides active catalytic sites to facilitate efficient charge transfer process enhancing OER activity. Thus, with further detailed study, NiCoP has the potential to be a leading electrocatalytic candidate for OER in future.

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Morphological transition of the ZnO hexagonal nanowires to cylindrical nanowires

Priyanka Sharma*, Sanjiv Kumar Tiwari and P.B. Barman,

Department of Physics and Materials Science, Jaypee University of Information Technology, Waknaghat, Solan, HP- 173234

*Corresponding author: sharmaps94@yahoo.in

Abstract

Current research paper represents ZnO nanowires (NW's) synthesis by simple chemical method on the seeded quartz substrate. The ZnO NW's were characterized by field emission electron microscopy (FESEM) and X-ray diffraction (XRD) spectroscopy. Morphological evolution of the ZnO NW's from hexagonal to cylindrical with the growth time was observed. The growth mechanisms of the NW's as the growth time proceeds were also discussed in this paper.

Introduction

ZnO NW's with controllable parameters and morphology have wide range of electric and optoelectronic applications. Morphology of these nanostructures affects its properties the most. ZnO can grow into several nanostructures such as nanorods, nanowires, nanoflowers, nanopetals, nanosheets and nanopetals Different etc. nanostructures have different optical and electric properties due to the variation in the surface to volume ratio. Out of all these nanostructures 1-D nanostructures attracts the special attention due to their high surface to volume ratio. These nanostructures can be prepared by various methods such as pulsed laser deposition, chemical bath method, hydrothermal method and Rf-magnetron sputtered method etc. In the present case, we choose the simple chemical method at low temperature for the synthesis of NW's. Morphological evolution of the NW's from the hexagonal to cylindrical shape was investigated.

Material and methods

ZnO nanowires (NW's) were grown on quartz substrate. The synthesis process was done in two steps, in the first step seeded substrate was prepared by thermal decomposition of zinc acetate Zn $(Ac)_2$ on the substrate followed by drying for 20 min at 350°C in the muffle furnace. In the second step, ZnO nanowires (NW's) were grown on the seeded substrate. NW's were grown by taking the equimolar concentration (0.04M) of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) mixed for 1 hour at 70-80°C. Later on, the seeded substrate immersed in solution for 20 and 24 hours at 60-70°C and oven dried for 16 hours at 75-85°C. The resultant nanowires were typically of ~411nm- 560nm in

diameter and $\sim 2.42 \mu m$ - $4.476 \mu m$ long. The following reaction represents the growth of ZnO NW's within the solution ⁴.

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (1)$$

$$NH_3 + H_2 0 \to NH_4^+ + 0H^-$$
(2)
$$20H^- + Zn^{2+} \to Zn(0H)_2$$
(3)

$$20H^{-} + Zn^{2+} \rightarrow Zn(0H)_{2} \qquad (3)$$

$$\rightarrow ZnO(s) + H_{2}O$$

Results and Discussions

Field emission scanning electron microscopy (FESEM)

Figure 1 represents the FESEM images of ZnO nanowires grown on ZnO seeded quartz substrate at two different growth times (20h and 24h). It can be clearly observed that morphology of nanowires were different in both the samples. Distribution of nanowires width is represented in inset of figure 1. Nanowires grown in the solution transformed from hexagonal to cylindrical structured wires as the growth time proceeds. It has been observed from the figure 1 that diameter affects least as compared to the length with change in growth time.



Fig. 1. FESEM images of ZnO NW's at 20h (a) and 24h (b) growth time

Growth mechanism for transformation of ZnO nuclei

In the present case, ZnO nuclei were formed in the solution containing zinc nitrate hexahydrate and HMTA. As the time proceeds, the evolution of the nuclei starts as shown in figure 2. After 2 h, ZnO acquire nano prism type morphology, which evolves towards hexagonal morphology and finally resulted to cylindrical nanowires with increase in growth time. This might be due to change in the amount of ammonia in the solution with the growth time. The whole process was carried out under constant temperature of $75-85^{\circ}$ C, so as the time proceeds the evaporation of the NH₃ from the solution occurs and changes the pH of the solution and thus affects the morphology of the resultant products. It was also reported that HMTA is responsible for the 1-D nanostructured formation⁶.



Fig. 2. Morphological evolution of ZnO nanostructure in the growth solution.

Crystal structure of the Nanowires

Crystal structure and preferred orientation of the grains of ZnO NW's were observed by X-ray diffraction (XRD) using the Cu-K α (λ =1.54056 Å) at 45kV and 40mA. A diffraction spectrum was recorded with the step size of 0.02⁰ from 10.01⁰ to 90.07⁰ (2 θ). It clearly confirms the formation of wurtzite hexagonal structure of nanowires as their diffraction peak reflection perfectly matched with the standard JCPDS (JCPDS- 36-1451, a=b=3.24982, c=5.20661, α = β =90⁰, γ =120⁰) shown in figure 3. The reflection peaks observed were (100), (002), (101), (102), (110), (103), (200), (112) and (201).



Fig. 3. Rietveld refinement of X-ray spectra of ZnO nanowire grown at growth time 24h

Conclusion

The current research article emphasizes on ZnO NW's synthesis through simple chemical route. Furthermore, morphological behavior of the NW's with respect to the growth time was also investigated. Present study reveals that morphology of ZnO NW's changes from hexagonal to cylindrical with growth time from 20 h to 24 h.

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Optical And Sensing Properties of Multi-core Gold@Silica Coreshell Nanoparticles

Suman Dey and Biswarup Satpati

Surface Physics and Material Science Division, Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata 700064, India

*Corresponding author: suman.dey@saha.ac.in

Abstract

Multi-core Au@SiO₂ core-shell nanoparticles were prepared successfully via simple chemical synthesis method. The structure and morphology of the synthesized nanoparticles were studied using transmission electron microscopy (TEM) and their optical properties by UV-vis spectroscopy. A coupling effect on UV-vis spectra was observed due to multiple cores of Au. The electrocatalytic activity of multi-core Au@SiO₂ core-shell nanoparticles was investigated by using cyclic voltammetry technique and it can detect small changes in concentration of glucose. Our present study highlights the influence of multiple Au cores in Au@SiO₂ core-shell nanoparticles and application in the field of glucose sensing.

Introduction

The interest in the production of different types of nanoparticles is growing, since they have distinctive properties and potential applications, depending on their structures. Core-shell type of nanoparticles are particularly getting special attention as they offer more stability and multi-functionality. Gold (Au) nanoparticles (NPs) show remarkable optical properties like surface plasmon resonance (SPR), surface-enhanced Raman scattering (SERS) and are also used in sensing and biomedicine. Interestingly, there is a coupling effect in the plasmon resonance when more than one particle is in proximity [1]. Our main focus in this research is to investigate the coupling effect of multiple gold (Au) cores that are encapsulated within silica (SiO₂) shell. Silica shell is used here for enhancing the stability of the Au nanoparticles in aqueous solvents [2]. Silica is biocompatible and non-toxic. Moreover, silica is chemically inert and optically opaque in nature. Due to these properties, it does not have a major effect on the optical properties of Au cores.

In this part of work, we have studied the structural properties of multi-core $Au@SiO_2$ core-shell nanoparticles using transmission electron microscopy. Uv-vis spectroscopy was done to see how optical properties of Au NPs change when multiple Au cores are coated with SiO₂ shell. We have performed cyclic voltammetry study for their use in glucose sensing.

Experimental Details

Au nanoparticles were synthesized via Frens method [3] with slight modifications. Silica shell has grown on the Au cores by adding Au colloids into Stöber system [4] which consists of ethanol, ammonium hydroxide (NH_4OH), H_2O and tetraethylorthosilicate (TEOS).

The structural properties and morphology of the resulting nanoparticles are observed using a FEI Tecnai G² F30-ST transmission electron microscope (TEM) with operating voltage 300 kV, equipped with several attachments like high-angle annular dark field (HAADF) detector from Fischione (Model 3000) and energy dispersive X-ray (EDX) detector. Assynthesized multi-core Au@SiO₂ core-shell nanoparticles were drop-casted on carbon coated copper grids of 300 mesh for TEM study. The UV-vis spectra were collected from a Jasco V-770 UV-vis-NIR spectrometer with а unique single monochromator. All spectra were acquired in water medium at normal room temperature using a quartz cuvette of 1 cm optical path length. To find out electro-catalytic activity for glucose sensing, cyclic voltammetry (CV) was performed with a CHI 660C (CH Instruments, USA) electrochemical workstation. which consists of three electrodes: a Pt wire counter electrode, an Ag/AgCl reference electrode and a glassy carbon working electrode (GCE) on which the multi-core Au@SiO2 core-shell NPs were deposited. CV was performed using 1/16 M Phosphate-buffered saline (PBS) as electrolyte.

Results and Discussion

Bright-field TEM images of multi-core Au@SiO₂ are shown in Fig.1(a) and Fig.1(b). The Au cores have an average diameter of 46 ± 6 nm. In Fig.1(c), we have shown the HRTEM image of Au core. In the inset, we have shown the fast Fourier transform (FFT) pattern from the red box area shown in Fig.1(c). The corresponding Inverse Fourier filtered

image is shown in Fig.1(d). The lattice spacing of 2.35 Å in the Inverse Fourier filtered image corresponds to the (111) interplanar spacing of Au (JCPDS 65-2870).



Fig. 1. (a) and (b) Bright-field TEM images of multi-core Au@SiO₂ NPs, (c) HRTEM image of Au core with an FFT pattern of the selected area in the inset, (d) IFFT image.

Fig.2. shows the UV-vis absorption spectra of the dispersed Au NPs and multi-core $Au@SiO_2$ coreshell NPs in aqueous solution. The peak of the absorption spectra of Au NPs is at 519 nm.



Fig. 2. Uv-vis absorption spectra of Au NPs and multicore Au@SiO₂ core-shell NPs in aqueous medium.

When multiple Au cores are coated with SiO_2 shell, the peak is slightly red-shifted to 521 nm as the refractive index of SiO_2 is little more than that of water. However, an additional peak appeared at 650 nm, attributed to the aggregation of the Au NPs inside SiO_2 shell.

Fig.3. shows CV plots of different concentrations of glucose at multi-core Au@SiO₂/GCE in 1/16 M PBS. Scan rate is 20 mV/s. It is observed that multicore Au@SiO₂/GCE can detect the small changes in glucose concentration in PBS. So, there is no doubt that multi-core $Au@SiO_2$ core-shell nanoparticles can act as a sensitive glucose sensor.



Fig. 3. CV of 0.05 mM, 0.10 mM and 0.35 mM glucose at multi-core Au@SiO₂/GCE in 1/16 M PBS. Scan rate: 20 mV/s

Conclusions

In summary, we have successfully synthesized multi-core $Au@SiO_2$ core-shell NPs by a facile method and characterized by transmission electron microscopy. We have also done UV-vis spectroscopy and saw a remarkable change in absorption spectra due to multiple Au cores inside SiO₂ shell. We have performed CV and concluded that multi-core Au@SiO₂ core-shell NPs can be used as a sensitive glucose sensor.

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Structural And Absorbance Study Of Sm³⁺ Doped Ca₃(VO₄)₂ Phosphors.

Vaibhav Chauhan^a, Prashant Kumar Pandey^a, Prashant Dixit^a, and Praveen C. Pandey^a*

^aDepartment of Physics, Indian Institute of Technology (Banaras Hindu University),

Varanasi - 221005, (U.P.) India

*Corresponding author: pcpandey.app@iitbhu.ac.in (Praveen C Pandey),

Abstract

In this paper, we report the synthesis of Sm^{3+} (0, 1, 4, and 5%) doped $Ca_3(VO_4)_2$ phosphor by the urea-assisted combustion process. All the samples are characterized by X-Ray diffraction (XRD), Ultraviolet-visible (UV-vis) spectroscopy, and Fourier Transform Infrared (FTIR) spectroscopy. The XRD result ascertains the rhombohedral crystal structure of all the samples. Absorption analysis manifests that all samples have near UV absorption at 290 nm. The bandgap analysis reveals a decrease in bandgap after Sm^{3+} doping in $Ca_3(VO_4)_2$ phosphor. The FTIR analysis confirms all the infrared modes present in the phosphors. We have explained the effects of Sm^{3+} doping on the structure and absorption of $Ca_3(VO_4)_2$ phosphor. Thus, our analysis of Sm^{3+} doped $Ca_3(VO_4)_2$ phosphor ascertains that it has potential application in lightning devices.

Synthesis and characterization of sheet shaped MgO nanostructures using paper as a novel solid support

Somesh Chandra^{1,2}, S Ganesamoorthy³, Arindam Das³, Shamima Hussain¹, G. M. Bhalerao^{1*}, N. V. Chandra Shekar³

¹UGC-DAE CSR, Kalpakkam Node, Kokilamedu, Tamil Nadu-603104, India ²University of Madras, Chennai, TN-600005, India ³ Material Science Group, IGCAR, HBNI, Kalpakkam, TN-603102, India

*corresponding author: gmbhalerao@csr.res.in, gmbhalerao@gmail.com Phone no.044-27480500-21917

Abstract

In the present work we report a novel synthesis and characterization of MgO sheet shaped nanostructures, using simple paper as a solid support. As-synthesised sample was characterized by Powder X-Ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and UV-Visible Spectroscopy (UV-Vis). The XRD results confirmed the formation of cubic phase of MgO. FE-SEM micrographs established the formation of MgO sheets like structures in the agglomerated nanoparticles. UV-Vis spectrum reveals absorption property of the MgO sheets. The optical band gap was calculated to be 3.5 eV, which is less than the bulk MgO value. These results corroborate the formation of MgO sheet shaped nanostructures.

Introduction

Synthesis of MgO has been receiving great attention due to their interesting properties like sensing properties, photo-catalytic properties, optical properties and its wide band gap [1-3].

Many researchers used different techniques to prepare nanostructures of MgO such as, thermal evaporation technique, microwave assisted sol-gel synthesis, hydrothermal method, solvent mixed spray pyrolysis technique, combustion technique and green synthesis etc. [4-9].

In the present work, sheet shaped MgO nanostructures were synthesised by a facile and ecofriendly combustion method using filter paper as a novel solid support. As-synthesised sample was characterized by XRD, FE-SEM and UV-Vis Spectroscopy.

Material and methods

Magnesium acetate hydrate tetra $Mg(CH_3COO)_2 \cdot 4H_2O$ with purity $\geq 98\%$ was purchased from Merck India, and used as precursor for synthesis. De-ionised water was used as a solvent. Whatman Grade 41 ash less filter paper was used as the solid support. 0.1 M aqueous solution of the precursor was loaded on the paper support by fully drenching into solution and left for 24 hours of dry, under normal conditions. Dried filter paper was burnt in air, leaving a white solid residue of the MgO material. This residue was used for further characterizations.

Characterization

In order to investigate the phase purity and crystallinity, powder X-ray diffraction (XRD) of the prepared sample were performed by GNR APD 2000 PRO powder X-ray diffractometer with Cu-K_a radiation (λ =1.5406 Å) in 2 θ range 30°- 85° with the step size of 0.05°. Surface morphology was investigate with the help of CERL ZEISS SUPRA 55 Field-emission scanning electron microscopy with working voltage 5 kV. For the FE-SEM ethanol and deposited on Si-substrate and the gold coated. The optical absorption properties were investigated with the help of AVANTES UV-Vis spectroscopy in the range of 200 to 750 nm range. For the UV- Vis spectroscopy, the nanomaterial was dispersed in deionized water by ultrasonication.

Results and discussion

XRD pattern of the synthesized sample is shown in Fig. 1.It shows two prominent peaks at 43.05° , 62.40° and a small peak at 78.85° corresponding to



Fig. 1. XRD pattern of MgO nanostructures.

(200), (220) and (222) planes of cubic MgO [JCPDS 65-0476]. XRD confirms the crystalline nature of MgO and crystallite size was calculated by Scherrer equation,

$$\beta_{hkl} \cos\theta = \frac{K\lambda}{D}$$

The average crystallite size of MgO nanostructure was found to be 30 nm.



Fig. 2. FE-SEM image of sheet shaped MgO nanostructures. EDS spectrum is shown in Fig. d.

FE-SEM micrographs of the synthesised material are shown in Fig. 2(a-c). Fig. 2(a, b) indicate the formation of sheet shaped morphology of MgO nanostructures. Fig. 2c suggests that the sheets are formed by a predominant two dimensional agglomeration of MgO nanoparticles. Energy dispersive x-ray spectroscopy (EDS) shown in Fig. 4d. It shows that only the Mg, Si, Au and O elements are present, in which Si and Au come from the Sisubstrate and the gold coating, respectively. Mg and O are from the specimen with the fractional elemental composition of 29.02 and 28.09% respectively. This 1:1 mole ratio of Mg and O shows that the composition of the material is MgO, corroborating the finding from XRD. Most importantly, absence of any other impurity elements is noted, it further support the XRD.



Fig. 3. UV-Vis spectra of MgO nanostructures and tauc plot shown in inset of the figure.

The absorption spectrum of MgO sheets was recorded in 200-750 nm range, as shown in Fig. 3.The absorption band near 230-250 nm indicates the formation of MgO nanostructures [10]. Further, the absorption spectrum was used to determine the energy gap of the MgO sheets using Tauc's relation given by $(ahv) = A (hv - Eg)^n$, where v, a, h represents the photon frequency, absorption coefficient and Planck's constant respectively. A is a constant, E_g is the energy gap (Tauc gap), **n** is a constant equal to 1/2 for the direct band gap. Band gap was calculated by extrapolating the curve plotted between hv and $(\alpha hv)^2$. Band gap of sheet shaped MgO nanostructure obtained from Tauc plot is 3.5 eV which is significantly lower than 7.8 eV of bulk MgO [11]. However it closely matches to the predicted value for monolayer of MgO [12] Thus, synthesis of MgO nanostructures using novel ash less filter paper results to the growth of two dimensional sheet shaped nanostructures with a low band gap which suggests tenability of electronic properties for further applications.

Conclusion

Our present study suggests the formation of sheet shaped MgO nanostructure using an eco-friendly method with paper based solid support. XRD results confirm the cubic phase of MgO nanostructures with typical crystallite size of about 30 nm. SEM and EDS analyses reveal the formation of impurity free MgO sheets comprised of dominantly two dimensional agglomeration of MgO nanoparticles. UV-Vis absorption spectrum of MgO sheets shows an optical band gap of 3.5 eV which suggests its uses in photo catalysis and optical devices.

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Magnetic Study of Ni doped CdTe Nanoparticles

Sayantani Das^{1,3,*}, Vishal Bhardwaj² and T. P. Sinha³

¹Department of Basic Science and Humanities, Gargi Memorial Institute of Technology, JIS group, Baruipur, Kolkata 700144, West Bengal, India

²Magnetics and Advanced Ceramics Laboratory, Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016, India

³Department of Physics, Bose Institute, 93/1, Acharya Prafulla Chandra Road, Kolkata-700009, India

* Corresponding author: <u>sayantanidas22@yahoo.com</u> (Sayantani Das)

Abstract

Pure and nickel (Ni) doped cadmium telluride (CdTe) nanoparticles have been synthesized by chemical route. The X-ray diffraction patterns at room temperature show the cubic phase of the samples. The average crystallite size of pure and doped CdTe is found to be ~ 15 nm using Debye-Scherrer formula. The field dependent (M-H) and the temperature dependent (M-T) magnetization of the samples have been considered at room temperature and low temperature (2 K). M-T measurement at 500 Oe has been carried out under zero field cooled (ZFC) and field cooled (FC) conditions. There is a sharp peak in M-T measurement for pure CdTe nanomaterials shows the magnetic transition temperature from diamagnetic to ferromagnetic transition.

Structural and Optical Properties of Green Synthesized Zirconium Oxide Nanoparticles

Nadar Jebamerlin Selvaraj Janaki¹ and P. Sumithraj Premkumar¹

¹Post Graduate and Research Department of Physics, St. John's College, Palayamkottai, Tirunelveli, Tamilnadu –

627 002, India

*Corresponding author:psumithraj@gmail.com

Abstract

Green synthesis method was adopted to prepare the zirconium oxide nanoparticles. The prepared zirconium oxide nanoparticles were characterized by powder X ray diffraction, Raman Spectroscopy and UV-visible spectroscopy to investigate the structural and optical properties respectively. The powder X- ray diffraction data showed that the green synthesized zirconium oxide nanoparticles belong to cubic structure and the lattice parameter was determined. Raman Spectrum of the green synthesized zirconium oxide nanoparticles confirmed that the prepared samples are cubic crystalline structure. Optical absorbance of the green synthesized zirconium oxide nanoparticle was studied from the diffuse reflectance spectra and it showed that the prepared nanoparticles are opaque in the ultraviolet light region.

Introduction

Zirconium oxide (ZrO₂) is a material of great technological importance that enjoys a wide range of diverse applications in the field of solid oxide fuel cells, oxygen gas sensors, optic fibers etc [1]. The crystal structure of ZrO₂ significantly influences its physical properties. Even the performance of the ZrO₂-based devices considerably depends on the crystal structure of ZrO2.ZrO2 powders with nanostructured particles have been synthesized by various techniques such as sol-gel, vapor phase, spray pyrolysis, hydrothermal etc [2-3]. However, these methods faced many limitation factors such as complicated procedures, high reaction temperature, longer action time, toxic reagents and by-products used which made it difficult to prepare. Recently, bio inspired green synthesis method has been used in syntheses of several metal oxide nanomaterials for environment friendly as no toxic material discharges in to the drainage system.

In the present investigation, we discuss the green synthesis of ZrO_2 nanoparticles using zirconyl nitrate as a precursor. Structural analysis of the nanostructures is performed by X-ray diffractometry techniques. Raman spectral analysis and the vibration mode assignment of the nanostructures are discussed. UV–vis absorption spectroscopic properties are also investigated.

Materials and Methods

Analytical reagent grade Zirconyl Nitrate (99.5%), *Melia dubia* leaves (Common Name: Malabar Neem) and deionized water were used for the preparation of zirconium oxide nanoparticles. Ethanol was used for the purification of the as-synthesized nanoparticles.

A fresh, cleaned Melia dubia leaves were collected and added to deionized water in a beaker. Then it was heated on a hot plate to get the extract by means of double boiling method. After prepared, the required amount of zirconium nitrate was added to 100mL of Melia dubia leaf extract in the beaker. The solution was stirred constantly at a temperature of 80°C for 5 hours in order to get the precipitate. Then the solution was centrifuged and the obtained precipitate was washed twice with deionized water, ethanol. The obtained precipitate was dried in Hot Air Oven for 1 hour at a temperature of 60°C. Finally, it was calcined in a muffle furnace at 800°C for 2 hours. The as-obtained white zirconium oxide nanoparticles were stored in the vial under ambient conditions for further characterization.

Powder diffraction patterns were recorded on Xray diffractometer (Bruker D2 Phaser) in the range of 2θ from 20° to 90°. The absorption characteristics of the synthesized NPs were analyzed by UV-Visible spectrophotometer ((UV-2600 Shimadzu, Japan) in the wavelength range between 200 and 900 nm with a resolution of 2 nm. Raman spectroscopic analysis (BRUKER RFS 27 MultiRAM FT Raman Spectrometer) of the nanoparticles was performed at room temperature.

Results and Discussion

The structural studies of zirconium oxide nanoparticles were analyzed using the result obtained from powder X-ray diffraction and Raman Spectroscopy. Powder x-ray diffraction pattern showed that the synthesized zirconium oxide nanoparticles were crystalline in nature. As reported that pure ZrO₂ exists in three polymorphic phases at different temperatures: monoclinic, tetragonal, and cubic [4]. Hence, the obtained XRD pattern of zirconium oxide nanoparticles were compared with JCPDS data [File Nos: 37-1484, 89-2340, 81-1551] to identify the structure. The as-synthesized ZrO₂nanoparticles in the present study are well matched with the JCPDS file [81-1551] as all the peaks were prominent. Thus, the synthesized ZrO₂ nanoparticles belong to cubic structure and the space group $Fm\bar{3}m(225)$. The indexed PXRD pattern of the as-synthesized zirconium oxide nanoparticles is displayed in figure 1.



Fig.1.PXRD pattern of zirconium oxide nanoparticles

The lattice constant and unit cell volume of the green synthesized zirconium oxide nanoparticles are calculated to be 5.3 Å and 148.88 Å³ respectively. The average particle size of the green synthesized zirconium oxide nanoparticles is estimated to be 22 nm.



Fig. 2.Raman spectra of zirconium oxide nanoparticles

Figure 2 presents the Raman spectra ZrO_2 nanoparticles, which shows the sharp Raman peak at 146, 266, 313, 458, 600, and $642cm^{-1}$. The similar observations were noted for the cubic structure of ZrO_2 nanoparticle [5]. However, one additional peak at 146cm⁻¹ was observed. It may be due to the formation of cubic structure with low calcinations temperature with fractions of impurities. The broadening of Raman peak indicates the low dimensionality of the sample.

Optical absorption characteristics of green synthesized zirconium oxide nanoparticles were analyzed from the diffuse reflectance spectroscopy. Figure 3 shows the absorbance of the green synthesized zirconium oxide nanoparticles. The maximum absorption by the ZrO_2 nanoparticles was recorded at 262nm and 371nm.



Fig. 3.UV-vis studies of zirconium oxide nanoparticles

The band gap was determined by extrapolating the linear portion of the curve. The band gap of green synthesized zirconium oxide nanoparticles was found to be 3.97 eV.

Conclusion

Zirconium oxide nanoparticles were synthesized using *Melia dubia* leaf extract. PXRD and Raman spectra confirmed that the synthesized ZrO_2 nanoparticles belong to cubic structure. UV-Visible spectra show that the synthesized ZrO_2 nanoparticles were opaque in the ultraviolet light region.

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Characterization of TiO₂ and Zn doped TiO₂ Nanofibers for DSSC applications

Vijayanand S, T Raguram and K S Rajni

Department of Sciences, Amrita School of Engineering, Coimbatore, Amrita Vishwa Vidyapeetham, India

*Corresponding author: ks_rajani@cb.amrita.edu

Abstract

We have synthesized one dimensional TiO₂ nanofibers using electrospinning technique and $Zn2^+$ ions are doped over the TiO₂ nanofibres through a simpler impregnation technique. Both the undoped TiO₂ nanofibres and Zn doped TiO₂ nanofibers were analyses for their structural and optical properties. The fabricated TiO₂ and Zn doped TiO₂ photoanodes are used in DSSC and its photo conversion efficiency (PCE) was found to be 3.47 and 2.51%.

Introduction

DSSCs are popular photovoltaic devices, which are cheap and non-hazardous [5]. The key component in a DSSC is the photo anode (TiO₂), sensitizer (N719), electrolyte (LiI/I) and counter electrode (Pt). The internal structure of the photoanode is important in facilitating efficient electron transportation. Recent advances in overcoming the surface defects of the photoanode is the introduction of 1D porous TiO₂ nanofibres [1]. In this work, 1D rod shaped TiO₂ and Zn-doped TiO₂ nanofibres (NF) are prepared by electrospinning technique.

Experimental Techniques

7.1 g of PVP (MW = 40,000 g/mol) added to 13.85 ml of ethanol, 3.3 ml of glacial acetic acid and 1.6 g of TTIP. The films annealed at 500 °C and then dipped in 10 ml of 3.5 M of Zinc Nitrate aqueous solution. N719 dye is used as sensitizer. The effective area of the cell is 0.5 X 0.5 cm.

Results and Discussion

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2theta (deg.) **Fig. 1.** XRD pattern of TiO2 and Zn-TiO₂ NF From the fig. 1, It is noted that The diffraction peaks matches with anatase (card No. 89-4203) and the

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rutile phase of TiO₂ (card no. 89-4920). A peak corresponding to ZnO (JCPDS no. 36-1451) is also observed. A smaller shift in the main peak position (101) reflect the incorporation of Zn in TiO₂ [2]. The average crystallite size of the Zn doped TiO₂ is found to be 13.95 nm which is slightly greater than the undoped TiO₂ (13.09 nm) due to the Zn doping.

3.2. Optical Analysis



Fig. 2. UV-Vis. absorbance spectra of TiO_2 and $Zn\text{-}TiO_2$ NF

Optical absorption spectra of TiO_2 NF shows the absorption around 380 nm (fig 2.). The optical absorption edge of Zn-TiO₂ NF is shifted towards the visible region around 550 nm due to the increase in zinc doping concentration [3]. It is noted that this absorption increases with increase in doping concentration. From the inset of Fig. 2, the optical band gap of TiO₂ and Zn–TiO₂ NF was found to be 3.01 eV and 3.88 eV, respectively. It is inferred that the increase in visible light absorption is due to the introduction of the new energy levels in the band gap due to doping [3].

3.3. Photoluminescence Analysis

Fig. 3 shows a major peak at around 380 nm, which indicates the band-to-band recombination as it

appears to be a near band edge luminescence. The peaks 470 and 542 refers to that of the oxygen vacancies. The higher PL peak intensity recorded for Zn-TiO₂ NF refers to the reduction in the electron-hole lifetime, indicates the faster recombination rate [3]. The reduced intensity for the TiO₂ NF is due to the inhibition occurring in photo-generated electron recombination from the conduction band to the valence band of TiO₂.



Fig. 3. PL emission spectra of TiO₂ and Zn-TiO₂ NF

3.4 FESEM and EDS Analysis

From the Fig 4, it is noted that the structure of the film is continuous, randomly oriented, and had good fibrous morphology. The diameter of the nanofibre was found to vary from 28 nm to 34 nm. From EDS (inset Fig. 4) analysis, the presence of Zn is confirmed.



Fig. 4. FESEM image and EDS spectrum of Zn-TiO₂ NF

3.5 J-V Analysis

DSSCs were prepared using both the TiO_2 nanofibers and Zn-TiO₂ nanofibers as photoelectrodes. Table 1 and Fig. 5 shows the results. It is noted that the TiO_2 NF displayed higher energy conversion efficiencies. Because the photoelectrodes were highly porous and possessed a fibrous form, many electron-transport paths were produced, enhancing the adsorption of dye and the ability of the material to harvest sunlight [4]. The PCE was found to be 3.47 and 2.51% for TiO₂ and Zn-TiO₂ NF. This is due to the formation of Zn²⁺ with the dye complexes, for higher Zn doping concentration, resulting in hindered dye absorption and electron transportation [1] and hence the efficiency is decreased.



Fig. 5. J-V Characteristics of $TiO_2 NF$ and $Zn - TiO_2 NF$

 Table 1. J-V parameters of DSSC using TiO2 and Zn-TiO2

 NF photoanodes

Sample	V _{oc} (V)	J _{SC} (mA/cm ²)	FF	η (%)
TiO ₂ NF	0.5956	11.5379	0.5054	3.47
Zn-TiO ₂ NF	0.5582	9.4996	0.4735	2.51

4. Conclusion

The XRD analysis confirmed the presence of both the anatase and rutile forms of TiO₂. The increase in the crystallite size is due to the Zn doping over the TiO₂ NF. A shift in the bandgap 3.3 to 3.75 eV is observed in optical analysis. From PL analysis, it is noted that recombination of photo electrons has been greatly reduced. Zn^{2+} formed dye complexes at higher doping concentration is reduced the light absorption and hence the efficiency 2.51% compared to the undoped one (3.47%).

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Structural And Optical Studies Of Dy³⁺ Doped ZnMoO₄ Phosphors.

Prashant Dixit^a, Prashant Kumar Pandey^a, Vaibhav Chauhan^a, and Praveen C. Pandey^a*

^aDepartment of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi – 221005, (U.P.) India

*Corresponding author: pcpandey.app@iitbhu.ac.in

Abstract

In this work, un-doped and Dy^{3+} doped ZnMoO₄ phosphors have been prepared via a facile auto-combustion method. The diffraction peaks of the XRD pattern confirm the triclinic phase of doped and un-doped ZnMoO₄. Optical studies have been investigated via UV-Vis analysis and photoluminescence analysis. UV-Vis absorbance spectra of ZnMoO₄ and Dy^{3+} doped ZnMoO₄ confirm the shift in bandgap with Dy^{3+} doping. Photoluminescence excitation spectra represent a broad excitation band centred at 302 nm for host phosphor, corresponds to $[MoO_4]^{-2}$ band. Photoluminescence emission spectra represent broad emission spectra centred at 518 nm corresponds to $[MoO_4]^{-2}$ energy band. Some intense peaks are observed at 495nm, 575 nm, and 661 nm, corresponds to $^{4}F_{9/2}\rightarrow^{6}H_{13/2}$, and $^{4}F_{9/2}\rightarrow^{6}H_{11/2}$ transitions of Dy^{3+} ion under the host's excitation at 302 nm. The chromaticity coordinate (CIE) of the Dy^{3+} doped phosphor represents the overall emission in the yellowish-white color which suggests that Dy^{3+} doped ZnMoO₄ phosphors can be a better candidate to realized in white light-emitting diode (w-LED).

Study of Structural and Optical Properties of Europium Ion Activated Bismuth Oxide Nanophosphors

Prashant Kumar Pandey, Vaibhav Chauhan, Prashant Dixit, and Praveen C. Pandey*

Department of Physics, Indian Institute of Technology (BHU), Varanasi – 221005, U.P., India.

*Corresponding author: pcpandey.app@iitbhu.ac.in

Abstract

This paper presents a study of structural and optical properties of un-doped and a series of Eu^{3+} ion doped bismuth oxide nanophosphors synthesized via a facile, low-cost and room temperature co-precipitation method. X-ray diffraction (XRD) analysis confirms the monoclinic crystal structure of the samples without any trace of impurity. Optical properties of the samples have been investigated using UV-Vis and photoluminescence (PL) spectroscopy. A slight increment in the band gap has been observed in the doped samples (2.79-2.81eV) as compared to the bismuth oxide host (2.77eV). The emission intensity has been augmented sufficiently in 7 mol% Eu^{3+} doped Bi_2O_3 nanophosphor. Thus, our study corroborates an evident red-shift in the aforementioned optimized composition and suggests that it is a potential candidate for lightning and display devices.

Interband Transition in Plasmonic Nanomaterials and its Application for UV Light Harvesting

Santanu Podder^{1*}, Jyotisman Bora¹, and Arup R. Pal¹

¹Plasma Nanotechnology Laboratory, Physiacal Sciences Division, Institute of Advanced Study in Science and Technology, Guwahati, Assam-781035

*Corresponding author: santanu.podder13@gmail.com

Abstract

In this study, we have shown the applicability of interband transition generated charge carriers in plasmonic nano-system for the fabrication of highly responsive and ultrafast UV photodetectors. Two different devices are fabricated – one with gold nanoparticles (Au NPs) and the other with titanium nitride (TiN) nanoparticles. In both the devices, plasmonic interband transition generated photocurrent is coupled with the excitonic-pyroelectric current of non-centrosymmetric wurtzite zinc oxide (ZnO) and as a result, the performance of the devices enhances significantly. Both the devices show very promising performance in selfpowered mode. However, the Au NPs based device shows very high performe in the photoconductive mode also.

Introduction

During the last decade, the field of plasmonics have grown tremendously specially for the application in opto-electronics. The Localized Surface Plasmon Resonance (LSPR) or the intraband transition phenomena in plasmonic nanomaterial is the main driving mechanism for the charge carrier generation in such materials.¹ With the progression of this technology, the field also expands its material base beyond noble metal nanoparticles such as Au, Ag etc. towards transition metal nitrides, transparent conductive oxides etc.² But, in most of these materials, the LSPR occurs in the visible to near infrared (NIR) range and light harvesting utilizing these materials is confined in that region only. However, there is ample scope of utilizing the UV portion of the electromagnetic spectrum for the fabrication of various opto-electronic devices and unfortunately this area was not touched by the plasmonic community rigorously. So, this lag can be converted into opportunity by utilizing another important property of plasmonic materials - that is interband transition as most of the plasmonic materials show this transition in the UV region. In plasmonic materials, the interband transition i.e. transition of electrons from the inner d to the sp band has the capability to produce efficient charge carriers.³ So, in this study we have shown the applicability of the interband transition effect of plasmonic materials (Au and TiN) for the fabrication of UV photodetectors.

In this study, we have combined the plasmonic materials (Au and TiN) with non centrosymmetric ZnO thin films to fabricate highly responsive and ultrafast UV photodetectors. Due to the wide bandgap, ZnO shows interband transition i.e. transition of electron from valance band to conduction band in the UV region. This region coincides with the interband transition region of both Au and TiN. So, upon proper UV illumination, charge carriers are generated in both the semiconducting and plasmonic component of the fabricated device and thereby enhances the photodetection performance. The incorporated ZnO thin film has an additional advantage - its pyroelectric nature which is originated from its non-centrosymmetric crystal structure. So, apart from the photo induced current, pyroelectric current is also generated in the device which not only increases the overall performance but also responsible for the ultrafast response of the fabricated devices.

Experimental Details

We have fabricated two UV photodetectors one with plasmonic Au nanoparticle and another with plasmonic TiN nanoparticles. In both the devices, the plasmonic contributions are coupled with the excitonic-pyroelectric effect of ZnO. The configuration of the fabricated devices are ITO/Au NPs/ZnO/Au film and ITO/TiN/ZnO/Au film respectively. The photoactive components i.e. ZnO and plasmonic materials are sandwiched in between ITO and Au film electrodes. All the photoactive components are synthesized by pulse DC magnetron sputtering technique. The plasmonic materials are synthesized in the form of nanoparticles and the ZnO as a nanostructured thin film.

Results and Discussion

Both the fabricated devices show very promising photo response in the UV region. Fig. 1(a) shows a comparative Photoresponsivity study of the fabricated devices in self-powered mode along with a pristine device without the incorporation of any plasmonic material. The study clearly shows that the performance of the devices enhances tremendously after the incorporation of plasmonic material. This superior photo response is coming from the combined contribution of interband transition of plasmonic material and the excitonic-pyroelectric effect of ZnO. Fig. 1(b) shows the comparative I-t response of the fabricated devices in self-powered mode. In both the devices, spikes in currents are observed when the devices change its state from on to off or vice versa. These rapid current generation within very short time is the outcome of the induced pyroelectric effect in ZnO and it is responsible for the ultrafast response of the device. From the figure it is also clear that the pyro current is dominant in the TiN based device whereas photo current is the dominant one in the Au based device. The generation of these two types of currents can be clearly understood from their energy level diagrams as discussed in the later section.



Fig. 1. Photoelectrical characterization of the fabricated devices (a) Photoresponsivity study, (b) Transient photoresponse study.

In spite of showing little less performance than the TiN based device, the Au NPs incorporated device is more advantageous because apart from selfpowered mode, the device also shows very promising performance in the photoconductive mode. Fig. 2 shows the bias dependent study of the Au based device. The photoresponsivity of the device increases with increasing applied bias and it registered a photoresponsivity as high as 4.65 A/W at an applied bias of -4V and after that it gets saturated. Fig 2(b) shows the bias dependent I-t response of the device which shows remarkable increment of the on-off ratio with increasing applied bias. The study also shows that the photovoltaic current is the main driving force and pyroelectric current loses its strength in the biased mode operations.



Fig. 2. Bias dependent study of the Au NPs based device (a) Photoresponsivity study, (b) Transient photoresponse study.

To understand the device working mechanism, energy level diagrams of both the devices are constructed and shown in Fig. 3. It is observed that, in the Au NPs incorporated device, a strong schottky barrier is formed in between Au and ZnO. This barrier generates an in-built electric filed within the device which is responsible for the photovoltaic nature of the device. On the other hand, the barrier between TiN and ZnO is not strong enough to produce significant photovoltaic effect.



Fig. 3. Energy level diagrams of the fabricated device.

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Ultraviolet Emission from Gd³⁺ Doped NaSrBO₃ Orthoborate for Medical Applications

A. K. Bedyal¹, Vinay Kumar², and H. C. Swart³

¹ Department of Physics and Astronomical Sciences, Central University of Jammu, Rahya-Suchani, Samba-181143 ²Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein, ZA9300, South Africa

*Corresponding author: vinaykdhiman@yahoo.com, ankushbadiyal@gmail.com

Abstract

 Gd^{3+} doped sodium strontium borate phosphors were prepared at different concentrations of Gd^{3+} ions and examined for their luminescence properties. The material was synthesized by solid-state reaction using carbonates as initial materials. Powder X-ray diffraction (PXRD), Scanning Electron Microscopy (SEM) and photoluminescence studies were done to examine the structural, morphological and luminescence properties of the material. The PXRD results reveal that the NaSrBO₃ has a monoclinic phase with the space group. The luminescence spectra of the material show UV emission at 312 nm at different excitation wavelengths assigning to the Gd^{3+} emission.

Exploration of Polythiophene (PTh) Thin Films for Chemiresistive Gas Sensors

D. B. Sabale¹, N. S. Harale² and S. N. Kale^{*1}

¹Defence Institute of advanced technology, Pune-411 025, M.S., India ²Sadguru Gadge Maharaj College, Karad -415 124, M.S., India * Corresponding author: sangeetakale2004@gmail.com

Abstract

In the present investigation, the effect of the oxidant concentration of PTh thin films on gas sensing performance was studied and discussed. The deposited thin films were characterized for their structural, morphological, optical, compositional, and electrical properties. The increase in oxidant concentration leads to increased film porosity and thickness (94nm to 294nm) due to systematic development of organised polymeric structures (from agglomerated structure to nanobelts). The amorphous structure of PTh was confirmed by using the X Ray Diffraction technique. The surface morphology was observed in Scanning Electron Microscopy images specified the formation of nanobelts. The gas sensing measurement study indicated that the PTh thin film sensor is highly selective and sensitive to NO₂ gas. The maximum gas sensitivity of 55% for the PTh thin film sensor is observed for 1:2.5 monomer to oxidant ratio. The PTh thin film based sensor shows an excellent response to NO₂ gas at even low gas concentrations (10 ppm) along with flexibility, low cost, portable and wearable nature. The sensor exhibits not only high sensitivity but also good selectivity towards NO₂ gas.

Using metal Ion embedded nanocomposite glass materials - For Biosensing Application.

S. Rafi Ahamed^{1*}, P.Manikandan², S Mohamed Nizar³, N Maheswari¹

¹ Department of Physics, Academy of Maritime Education and Training,

Kanathur -603112, Chennai, Tamil Nadu India

² Department of Physics, Krishnasamy College of Engineering & Technology,

S Kumarapuram 607109 Cuddalore Tamil Nadu India

^{3.} Department of Electronics and Communication, IFET College of Engineering

Villupuram Tamil Nadu India

*Corresponding author: rafiahamed81@ametuniv.ac.in

Abstract

The physicochemical properties of metal embedded nano clusters are totally different from those of the bulk materials. The nanocomposite nanocluster depends on their size, shape and the chemical composition and they have more reactivity which is taken considerably larger than those of the bulk by orders of magnitude with size. Optical absorption spectroscopic analysis was done on the metal nanocluster composite glasses, and the spectra are well studied as a function of various post ion-exchange treatments and different sizes. The noble metal nanoclusters play an important role for nanobiomedical and modern optical devices. Raman scattering is a nondestructive tool for probing the composition and symmetry of nanocrystalline semiconductors and insulators. The present paper explored the single and bi-metallic nanoclusters embedded in soda–lime glass that is prepared by ion-exchange method. The ion-exchanged glasses are annealed by different methods. These samples exhibit surface plasmon and surface enhancement effect. As size effects are an essential aspect of nanomaterials, the effect of size on the optical absorption metal nanoclusters shall be studied through optical absorption, SERS. From this study, we find optimized SERS substrate for single and different molecule detection.

Antioxidant and cytotoxic potential of Diosgenin nanoparticles against Ehrlich ascites carcinoma (EAC) cells

Surya Kanta Dey¹ and Sujata Maiti Choudhury^{1*}

¹Department of Human Physiology, Vidyasagar University, Midnapore, West Bengal, India, Pin-721102.

*Corresponding author: <u>sujata_vu@mail.vidyasagar.ac.in</u>, <u>sujata.vu2009@gmail.com</u>

Abstract. Diosgenin (DG), a naturally occurring steroidal saponin from therapeutic herbs, is reported to be a potential natural antioxidant and anticancer agent. However, its clinical application was limited due to its high hydrophobicity and poor bioavailability. We developed a nanoparticle platform to increase its clinical efficiency by producing PLGA-DG nano-particles and have been characterized by DLS, FTIR and FE-SEM. We evaluated the cytotoxic and antioxidant activity of PLGA-DG NPs against Ehrlich Ascites Carcinoma (EAC) cells and in EAC- bearing mice. PLGA-DG NPs has shown potent cytotoxicity against EAC cells. Very significant antioxidant effects were seen in liver superoxide dismutase (SOD) and catalase (CAT) activity and in malondialdehyde (MDA) content of EAC- bearing mice compared to DG. These findings revealed the cytotoxic and antioxidant potential of PLGA-DG NPs which was significantly increased by the above said nano-formulation.

Green exfoliation-assisted evolution of g-C₃N₄ rods and their structure-modification induced photocatalytic activities

R. Vijayarangan¹, M. Sakar², and R. Ilangovan^{1,*}

¹National Centre for Nanoscience and Nanotechnology, University of Madras, Guindy Campus, Chennai 600025 ²Centre for Nano and Material Sciences, Jain University, Bangalore 562112

*Corresponding author: rajangamilangovan@gmail.com

Abstract

One dimensional rod-like structures of $g-C_3N_4$ (GCN) have been synthesized via the ultrasonic-assisted green treatment process using *Azadirachta indica A. Juss* (neem) extract as exfoliating-cum-shape directing agent. It is observed from various studies that the green-modified GCN is rich in amine groups that effectively bridge the heptazine and triazine networks, which eventually gives rise to the structural, morphological, optical and photocatalytic properties of GCN as compared to the conventional-GCN.

Introduction

Photocatalysis has gained significant interest and largely explored for several applications such as pollutant degradation, water splitting, CO₂ reduction, N_2 fixation, etc.¹ Accordingly, there is an increasing pursuit of materials to meet the required properties such as suitable band structure, low bandgap energy, high surface activity, improved charge separation, recombination resistance, etc. in order to achieve the desired photocatalytic efficiencies. In this direction, graphitic-carbon nitride $(g-C_3N_4/GCN)$ has grabbed considerable attention and demonstrated for the aforementioned applications. g-C₃N₄ is being a 2D material, their anisotropic structures are of great interest due to their interesting features such as tunable electrical and optical properties.² In this direction, herein, a green treatment using Azadirachta indica A. Juss (neem) extract as exfoliating-cum-shape directing agent has been used for the first time and developed the GCN rods via the ultra-sonic-assisted process. The treated-GCN demonstrated superior properties as compared to untreated-GCN.

Experiment

The conventional GCN was prepared using 4g of melamine and thermally condensed at 500 °C for 4 h using a tubular furnace. In parallel, the extract of the neem was prepared via refluxing process using water and methanol as a solvent at 120 °C for 6 h. Then, the as-prepared GCN was dispersed in the extract and ultra-sonicated for 30 min. Finally, the treated-GCN was dried at 80 °C overnight.

Results and Discussion

The obtained XRD pattern (Fig. 1) of green-GCN clearly showed the (i) broadening of peak at 2θ ~27.7° and (ii) suppression of peak at 2θ ~13.6° with respect

to the conventional-GCN. This indicated that greentreatment process might have altered the stacking and inter-planar structure of GCN. Notably, the observed peak- broadening and suppression could be attributed to the greater exfoliation of GCN layers and alteration in tri-s-triazine due to the surface-grafting of amine groups of extract onto the GCN.³



Fig. 1. XRD patterns of the untreated and treat GCN.

Rod-like and particle-like morphology (Fig. 2a-b) is observed for the green and conventional-GCN, respectively. It can be attributed to the functional group presence in the neem extract, which directed the growth of GCN into rod-like structure. The binding habit of molecules in the extract might have influenced the condensation polymerization of GCN network and directed to a rod like growth, while, their grafting in the inter-planar network led to a stronger exfoliation of GCN layers. Particle-like morphology of the conventional-GCN is typical due to the nature of thermal condensation process. Optical absorption and PL of green-GCN showed modifications toward visible light response of the system (Fig. 2(c)-(d)) with bandgap energy of 2.53 and 2.72 eV (insert

image) for untreated and green-GCN, respectively. This can be attributed to the observed rod-like morphology and alteration in the tri-s-triazine network as observed from their XRD patterns.³ The observed shift in PL could be attributed to the modified HOMO-LUMO structure in GCN due to these morphological and structural changes.



Fig. 2. (a)-(b) FESEM images, (c) UV-visible absorption and (d) PL spectrum of the obtained GCN.

In the photocatalytic studies, 20 mg of the prepared GCN was dispersed in 50 mL of 10 ppm rhodamine B (RhB) dye and stirred under dark to the adsorption-equilibrium and achieve then introduced into solar light. During the reaction, a small amount of dye solution was taken for every 30 min to record its degradation via UV-Vis absorption spectrometer. It is observed from the C/C_0 ratio plot (Fig. 3a) that the green and conventional-GCN degraded ~98 and 83% of the dve, respectively. The enhancement observed in the green-GCN could be attributed to the improved charge transfer in the GCN polymeric network.⁴ This can be possible due to the presence of amine-group, which bridges the heptazine and triazine network, and effectively helps in separating the excited charge carriers in GCN as depicted in Fig. 3b.

Further, the radicals responsible for the degradation was analysed via scavenger test using benzoquinone (BQ) and iso-propanol (IPA) to scavenge $O_2^{\bullet-}$ and \bullet OH radicals, respectively. The results demonstrated that the degradation is largely driven by $O_2^{\bullet-}$ radicals followed by the \bullet OH radicals (Fig. 3c). The obtained results can also be attributed that there could be a competing formation of both the radicals and their active participation in degrading the dye molecules.

Upon the incident photons, the electrons are excited to the conduction band of GCN, leaving the

holes in valence band. In typical GCN structure, the charge transfer happens between the heptazine and triazine networks, wherein the charge recombination occurs rapidly as depicted in Fig. 3b.



Fig. 3. (a) C/C_0 ratio plot, (b) charge transfer mechanism in GCN and (c) scavenger studies for key radical detection.

In contrast, the amine groups in green-GCN graft with heptazine-triazine networks and strongly bridge them. This network thereby acts as a carrier-sink and facilitates an effective carrier separation and rapid generation of radical ions for the effective redox degradation of the dye molecules as shown in Fig. 3b.

Conclusion

The treatment of $g-C_3N_4$ (GCN) with extract of neem yielded it with rod-like morphology, which showed improved structural and photo-catalytic properties. This observed improvement was attributed to amines that grafted onto the GCN, which bridged the heptazine-triazine network and facilitated the charge separation in GCN. As a result, green-GCN showed ~98% degradation of RhB dye in 2 h, while it was 82% in the case of conventional GCN.

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Influence Of Silver Doping On Structural And Optical Properties Of Tungsten Oxide (WO₃).

Surbhi Chalotra¹, Simranpreet Kaur¹, Puneet Kaur¹, Kriti Seth¹, D.P Singh^{1*}

¹Department of Physics, Guru Nanak Dev University, Amritsar, Punjab, India 143005

*Corresponding author: dpsingh.phy@gndu.ac.in

Abstract

Pure and Silver (Ag) doped WO₃ nanoparticles are synthesized by solid state reaction method. Powder X-ray diffraction results show that the Ag doped WO₃; Ag concentration from 0 to 3% crystallizes into monoclinic structure. There is increase in intensity of the XRD peaks with Ag doping which depicts that crystallinity has improved with Ag doping and crystallite size shows increment from 41.5 to 45.1 due to Ag doping. Considerable decrease in the band gap energy from 2.52 to 2.38 eV for Ag doped samples is observed by using UV–DRS spectra analysis. Oxygen vacancies and the defects in crystal are analyzed by photoluminescence spectra analysis. Commission International De I'Eclairage (CIE) chromaticity coordinates are used to characterize the overall emitted colours. The light emitted from the prepared samples show shift from violet to red region with the change of excitation wavelength which means the prepared samples can be used for various lighting applications.

Flow synthesis of ultra small gold nanoparticles in PTFE microchannel

Nirvik Sen¹, R. Chakravarty², K.K. Singh¹ and S. Chakraborty²

¹Chemical Engineering Division, ²Radiopharmaceuticals Division, Bhabha Atomic Research Center, Trombay, Mumbai, INDIA 400085

*Corresponding author: nirvik@barc.gov.in

Abstract

Flow synthesis of ultrafine colloidal gold nanoparticles (AuNP) below 5 nm in a microreactor is reported. The gold precursor (tetrachloroauric acid) along with trisodiumcitrate (reducing agent) are premixed and infused into a PTFE microbore tube kept immersed inside a hot oil bath using a syringe pump. The synthesized AuNP are less than 5 nm in size and are mostly spherical in shape. Systematic studies are conducted to investigate effect of residence time on particle size. A mechanistic picture of the synthesis process is proposed to justify the experimental trends.

Protein Coated Nanoparticles: Biodistribution Study in Dalton Ascites Lymphoma Bearing Mice

Tamanna Roy¹ and Sujata Maiti Choudhury^{1*}

¹Department of Human Physiology, Vidyasagar University, Midnapore, West Bengal, India, Pin-721102.

*Corresponding author: sujata_vu@mail.vidyasagar.ac.in, sujata.vu2009@gmail.com

Abstract. The field of bio-nanotechnology has opened up new avenues for various aspects. This study reports the synthesis, characterization and pharmacological properties of albumin coated biogenic silver nano-formulated chlorogenic acid (AgNPs-CGA-BSA). AgNPs-CGA-BSA was characterized by DLS, XRD and SEM. AgNPs-CGA was crystalline with a uniform distribution in shape and size. AgNPs-CGA-BSA was mostly crystalline with a uniform spherical shape. It may be considered as a stable new nano-drug against cancer in future.

Introduction

The advent of nanotechnology has accelerated development in drugs delivery system [1]. Biogenic silver nanoparticle (AgNPs) has gained increasing interest due to its unique properties and therapeutic potentiality. Phytochemicals or their derived compounds being increasingly recognized are as potent complementary treatments for various diseases. Chlorogenic acid (CGA) is a natural polyphenolic compound which is the ester of caffeic acid and (-)quinic acid. It is broadly distributed in fruits and vegetables [2]. Serum albumin is the most abundant protein in the circulatory system and is chiefly responsible for the maintenance of blood p^H. Bovine serum albumin (BSA) has the property of an efficient nanocarrier, because of its bioavailability and biodegradability. It has well-defined size and reactive functional groups (thiol, amino, and carboxyl) on its surface that can be used for biocompatible ligand binding and other surface modifications [3].

The aim of the present study was to synthesize and characterize albumin coated chlorogenic acid nanoformulation and to investigate its Biodistribution study in Dalton ascites lymphoma bearing mice.

Experimental details

Colloidal AgNPs was first prepared using the conventional method and then biogenic AgNPs-CGA was prepared using CGA. After that BSA was added to AgNPs-CGA under 440 rpm of magnetic stirring at room temperature and this freshly synthesized solution was centrifuged at 12000 rpm for 30 min [4]. Then the obtained supernatant was collected and the pellet was air dried by vacuum and used for experiments. Characterizations were done by

DLS,XRD and SEM studies. Stability study of AgNPs-CGA-BSA assessments was performed at different concentrations and time intervals and pH using UV-vis absorption spectra. The measurements were performed in triplicate manner [5]. For biodistribution study, Dalton ascites lymphoma (DLA) cell suspension $(1 \times 10^6 \text{ cells})$ was injected subcutaneously. After development of tumor at the volume of 100 mm³, mice were divided into three groups (6 mice each group) and AgNPs-CGA-BSA were injected at the various concentrations via the mouse tail vein. All mice were sacrificed at different time point and individual tissues and organs were collected. The tissues were washed immediately with PBS. To extract CGA, tissue was homogenized in 2 ml of methanol and was centrifuged at 5000 rpm for 10 min. After extraction, the clear supernatant was transmitted to a clean tube and CGA was quantified by spectrometric method at 324nm [6].

Results and Discussion



Fig.1. Morphological study of AgNPs-CGA-BSA: Hydrodynamic size distribution and zeta potential of AgNPs-CGA [(a) &(b)] and AgNPs-CGA-BSA[(A) &(B)].(i) XRD pattern showing peaks corresponding to the diffraction planes of AgNPs,AgNPs-CGA and AgNPs-CGA-BSA at 20 degree.(ii) SEM image of AgNPs-CGA and AgNPs-CGA-BSA.

In DLS study, fig.1[(a) &(b)] and [(A) &(B)]the hvdrodynamic of AgNPs-CGA and AgNPs-CGA-BSA was found to be 126.5±0.288nm and 96.33±0.333 nm, respectively. With a PDI and zetapotential measurement of AgNPs-CGA and AgNPs-CGA-BSA are 0.270 and 0.265 and -10.3 my, -17.5mv separately.In XRD study, fig.1(I) shows the sharp Bragg peaks due to capping and stabilizing of NPs. Bragg reflections can be seen with 2θ values of 38.04, 44.31 and 64.49° corresponding to the lattice planes, which may be indexed to (111), (200) and (220) facets of Ag, accordingly. In SEM study, fig.2 (II) shows that AgNPs-CGA was crystalline with a uniform shape and size distribution. AgNPs-CGA-BSA were crystalline with a uniform distribution of and size shape.



Fig.2. Stability study of AgNPs-CGA-BSA. Here (a) different concentration;(b) different PH and (c) different Time.

The results of stability study of AgNPs-CGA-BSA showed that the absorption wavelength and color of AgNPs-CGA-BSA solution hardly changed in 2 months shown in fig.2. This indicates that the synthesized AgNPs-CGA-BSA is quite stable.



Fig.3. Bio-distribution and Pharmacokinetics study of AgNPs-CGA-BSA in DLA induced tumor-bearing mice. The data are expressed as Mean \pm SEM (n = 3).

In biodistribution study fig.3, it was clearly indicated that a relatively high amount of CGA was accumulated in tumor in AgNPs-CGA-BSA injected mice. Whereas CGA distribution was decreased in the following order: Tumor > Liver > Spleen > Kidney > Lung > Heart, respectively. This observation indicating that the AgNPs-CGA-BSA was successfully delivered CGA into tumor while reducing its deposition in other vital organs.

Conclusion

The present study demonstrates the simple, ecofriendly and cost-effective synthesis of stable AgNPs-CGA-BSA. This study suggests that it may be considered as a stable new nano-drug against cancer in future.

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Role of Solvents on Exfoliation and Optical Properties of Hexagonal Boron Nitride

Vidyotma Yadav¹, Tanmay Mahanta¹, and Tanuja Mohanty^{1)*}

¹School of Physical Sciences, Jawaharlal Nehru University, New Delhi – 110067, INDIA.

*Corresponding author: tanujajnu@gmail.com

Abstract

2D materials like hexagonal boron nitride nanosheets (hBNNS) are remarkable nanostructured material that find a lot of technological applications thus demanding easier and faster ways for its synthesis. In this work, liquid phase exfoliation method is followed for the synthesis of a few-layers hBN. For this purpose, three different solvents were used. A suitable solvent activates the exfoliation of bulk hBN to mono or a few layered hBNNS and at the same time it offers stability of the suspension. UV-Vis spectroscopy was employed to quantify the optical band gap of synthesized hBNNS. Raman spectroscopic results were used for estimation of approximate number of layers. The Raman results support the UV-Vis findings. This study will help in selection of suitable chemical solvents for synthesis of hBNNS with higher yield and stability.

Introduction

In recent years various graphene like 2D materials such as hBN, MoS_2 , WS_2 have been proven to have quite exciting properties beneficial for device fabrication [1]. Among these, hBN has structural similarities with graphene with only a lattice mismatch of ~1.7%.

hBN having a wide optical energy band gap of about 5.97 eV behaves as an electrical insulator. Its high dielectric constant (~3-4), makes it suitable for application in memory capacitors or gate dielectric as substrates. hBN nanosheets have optical transparency because it shows no absorption in the visible region rather it is observed in the deep ultraviolet region.

There exists a variety of methods like mechanical exfoliation, sputtering, liquid-phase-exfoliation, ball milling method, pulsed laser deposition, chemical vapour deposition to synthesize hBNNS. Liquid phase exfoliation process is preferred over others for requirement of large-scale production [2]. Here in this paper liquid-phase-exfoliation method using three different organic solvents is followed to exfoliate a few layers stable hBNNS (Fig. 1).

Experimental Methods

Necessary chemicals such as bulk hBN powder (~1 μ m, 98%). Isopropyl alcohol (IPA~99.5%) and ethanol were purchased from Sigma Aldrich and SRL. Triple deionized (DI) water was bought from Organo Biotech Laboratories. All the chemicals were used asobtained.



Fig.1. hBN suspension in ethanol, DI and IPA.

For the liquid-phase-exfoliation of hBN, 50 mg bulk hBN powder in 100ml of 3 different suitable solvents (IPA, DI, ethanol) were used. Sonication of hBN solvent suspension for 24 hours was followed by centrifugation at 3000 rpm for 30 minutes [3]. The collected supernatant was drop-casted on Si substrates for preparing thin films. The exfoliated hBNNS were characterized by UV/Vis spectroscopy using Shimadzu and Raman spectroscopy using Witech alpha300 RA correlative Raman-AFM microscope having 532 nm laser.

Results and Discussion

The UV-Vis spectra of hBNNS in IPA and DI exhibit absorption peaks at 211.28 nm, 200.34 nm respectively and in ethanol it exhibits two peaks at 206.63 nm and 271.88 nm [4] (Fig. 2). The Tauc plot (Fig.2 inset) was plotted to quantify the band gaps of hBNNS. The corresponding bandgaps are given in Table.1.



Fig.2. UV-Vis Spectra of hBNNS in IPA, DI and ethanol.

The Raman spectra of hBNNs in IPA, DI and ethanol solvents shown in Fig.3 exhibit Raman peak at 1366.51cm⁻¹, 1365.96cm⁻¹ and 1365.83 cm⁻¹, respectively.



Fig. 3. Raman Spectra of hBNNS in IPA, DI and ethanol.

Number of layers of hBNNS are calculated using Raman FWHM of three different samples using equation (1) mentioned below [3].

$$< N >_{vf} = \frac{17.2}{[\Gamma_{\rm G} - 8.5 - 1.19*\log P]} - 1$$
 (1)

< N > is the mean number layer, $<N>_{vf}$ is the volume fraction weighted mean number layer and P is the power used (10 mW) for the laser during Raman measurement. Γ_{G} is the calculated FWHM for three solvents using Gaussian fit for each.

The number of layers present in hBNNS exfoliated using IPA, DI, and ethanol solvents are calculated to be ~ 7, 5 and 3, respectively and are given in Table.1. It is observed that ethanol exfoliated hBNNS having highest bandgap comprise of lowest number of layers thus synchronizing the effects of solvents on their exfoliation process as well as on optical properties. The band gap becomes progressively higher and Raman red shift progressively lower as N decreases [5].

hBN in Solvent	UV-Vis peak position (nm)	Band Gap (eV)	Raman Peak Position (Cm ⁻¹)	Number of Layers
IPA	210.60	5.54	1366.51	7
DI	200.34	5.70	1365.96	5
Ethanol	206.63	5.71	1365.83	3

Table .1. UV-Vis and Raman spectroscopic analysis

Conclusion

The optical properties of chemically exfoliated hBNNS are analyzed by spectroscopic techniques. UV-Vis spectrum shows that ethanol is best suitable solvent for exfoliation of hBNNS having band gap \sim 5.71 eV closer to the theoretical value. Raman spectroscopy confirmed the UV-Vis results where \sim 3-layer hBNNS are obtained using ethanol as a solvent in the exfoliation process.

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Mesoporous ZnS/NiS Nano-Composite for Multi-Functional Visible-Light-Driven Applications

Prayas C. Patel¹*, P. C. Srivastava² and Hem C. Kandpal¹

¹Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee -247667, India. ²Department of Physics, Institute of Science, Banaras Hindu University, Varanasi-221005, India.

*Corresponding author: prayasyogi@gmail.com

Abstract

Present study reports the facile synthesis of phase separated ZnS/NiS nanocomposite by two-step solvothermal approach. Structural analysis showed the formation of highly crystalline uniform-sized, sharp-edged hexagonal pyramidal particles. Transient photocurrent response and electrochemical impedance spectroscopy showed enhancement in the electron-hole separation and their mobility, which ultimately resulted in decreased charge-transfer distance, improved electrical conductivity and reduced charge-transfer resistance. Moreover, the synthesized nanocomposite also showed a significant improvement in the catalytic behavior which was attributed to the restructuring of surface properties and modification in the band structure of the constituent phases.

Introduction

With recent surge in the inter-disciplinary researches, quest for materials with multifunctional properties seems never-ending. In this context, nanostructured porous semiconductors have received considerable interests owing to their pore-structure type and large surface area, which makes them suitable for various applications, such as in optoelectronics, catalysis, sensing, energy storage etc.¹⁻³

Earlier, wide-band gap transition metal sulfides (such as ZnS and NiS) received great attention not only for fundamental physics, but also served other industries as well.⁴ Their low cost, rich redox valences, higher electrical conductivity than metal oxides made them a lucrative material for electrochemical and catalytic applications.^{5, 6} To further improve/tailor their versatility, it also becomes prudent to thoroughly investigate their nanocomposites for the possibility of various exotic properties. Nanocomposites are not unusual, and there are plenty of state-of-the art approaches available which are useful for the synthesis of nanocomposite.^{7, 8}

This report presents the study of ZnS and NiS based nanocomposite. Herein, three samples namely ZnS, NiS and ZnS/NiS were synthesized by two step solvothermal approach and studied for their photoelectric, electrochemical and catalytic performances.

Results and Discussion

Microphase analysis by X-ray diffraction (shown in Fig. 1 (a)) confirms the successful synthesis of highly crystalline phase separated ZnS/NiS nanocomposite. Electron microscopy also shows the formation of highly crystalline particle, where uniform-sized, sharp-edged hexagonal pyramidal particles are clearly visible. Such morphology is rarely seen in transition metal sulfides.

Fig. 2(a) shows the transient current response of all three samples under intermittent light illumination. When the sample was illuminated, majority of the photogenerated electron-hole pairs tend to recombine, however a significant number of electrons were still there which start moving to form a stable photocurrent. Notable enhancement in the photocurrent response of ZnS/NiS sample (shown in Fig. 2(a)) indicates the improvement in electron capture/release capacity due to reduced conduction path of photoelectrons, thus leading to more efficient separation of photo-excited carriers.

The electron transfer process was further studied by electrochemical impedance spectroscopy (EIS) performed on a three-electrode system. Figure 2(b) shows the EIS Nyquist plots of the samples in the frequency range of 1000 kHz to 0.1 Hz, which consist of a semicircle arc followed by a straight line. Here, smaller semicircle for ZnS/NiS sample indicates that the formation of nanocomposite decreases the charge-transfer path, thereby improving the electrical conductivity and mobility of the charge carriers.





Fig. 2. (a) Transient photocurrent responses; (b) Electrochemical impedance spectroscopy (EIS).

Surface properties of the samples determined by Brunauer-Emmett-Teller (BET) analysis (shown in Fig. 3) show that all the samples were mesoporous and have type-IV hysteresis loop. However, significant enhancements of N2 adsorption in ZnS/NiS sample along with reduced poresize distribution suggest the possibility of enhanced catalytic activity. Here, gain in mesoporosity could be attributed to the increase in number of grain boundaries due to the formation of phase separated nano-composite. The effect of improved surface properties in ZnS/NiS nanocomposite could be clearly seen in the rapid catalytic degradation of methylene blue dye. Fig. 4 shows the corresponding normalized degradation curve and pseudofirst order kinetics plot drawn from the analysis of UV-vis spectroscopy data. It is interesting to note that almost 90 % of the dye degrades within 30 min., which is significantly greater than many of the earlier reported values.

Conclusively, the study showed there is always a possibility of many multi-functional properties that may appear in an enhanced fashion which may/may-not be present in the constituent phases.



Fig.3. BET analysis; N₂ adsorption isotherm showing type-IV hysteresis loop; Pore size distribution (inset).



Fig.4. Degradation curve of methylene blue dye; Pseudofirst order kinetics plot (inset).

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Effect Of Temperature Variation On Structural Property Of NiFe2O4/ZnO Nanocomposite

Tripta¹, Pawan S. Rana^{1*}

¹Department of physics, Deenbandhu Chhotu Ram University of Science and Technology, Murthal, sonepat, Haryana India-131039

*Corresponding author: drpawansrana.phy@dcrustm.org

Abstract

Nanocomposites NiFe2O4/ZnO were synthesized by two-step methodology at different annealing temperatures (400°C, 500°C and 700°C). Zinc oxide (ZnO) nanoparticles having unique physical and chemical properties synthesized by co-precipitation method. X-ray diffraction (XRD) is used to confirm the formation of both NiFe2O4 (NFO) and ZnO phases in NiFe2O4/ZnO nanocomposites. FTIR is used to determine the functional groups present in the prepared sample in the range of 400-4000 cm-1. Crystallite size was calculated using Debye Scherrer formula and are found to be 36.28 nm, 36.27 nm for NFO and ZnO respectively.

Introduction

Magnetic spinel ferrite nanoparticles are widely used with the development of nanotechnology [1]. Spinel ferrites, with common formula of AB_2O_4 , where A is Zn^{2+} , Mn^{2+} , Co^{2+} , Mg^{2+} , Cu^{2+} etc, a divalent cation located in tetrahedral positions and B is Fe³⁺, a trivalent cation from octahedral position. Spinel ferrites are important class of ceramics and used in various device such as gas sensors, telecommunication equipment, high frequency devices, switching circuit, magnetic fluid, refrigerators, etc [2]. ZnO has secured awareness due to its pleasing properties such as nontoxic, photonic, high band gap. Nanocomposite of transition metals or their oxides remarkably enhanced the photocatalytic activity of ZnO [3].

Experimental

Materials

The chemicals used are: $(NiNO_3)_2.6H_2O$ (99%), $(Fe(NO_3)_3.9H_2O)$ (98%), $(Zn(NO_3)_2.6H_2O)$ (96%), ammonia and sodium hydroxide pellets (NaOH). All the chemicals were used without any supplementary rebirth and analytical grade.

Synthesis of NiFe₂O₄/ZnO nanocomposites

Nanomaterials of ZnO and NiFe₂O₄ were synthesized by chemical co-precipitation process. An optimum amount of precursors is dissolved separately in distilled water as a solvent. The solution was stirred to achieve the homogenous solution about 20 min at 30-40°C. Then pH is maintained at 9-12 by adding NaOH solution dropwise with continuous stirring at 70°C. This solution is dried on hot plate to get powder and then annealed at different annealing temperature.

Characterizations

X-Ray powder Diffraction (XRD)

The XRD measurement for ZnO, NiFe₂O₄ and NiFe₂O₄/ZnO nanocomposites is shown in the Figure 1. All peaks of ZnO and NiFe₂O₄ are well matched with the JCPDS card no.36-1451 and 01-087-2336 with structure wurtzite and spinel respectively [4]. XRD pattern of ZnO observed at (100), (002), (101), (102), (110), (103), (112) and (201). NiFe₂O₄ pattern observed at (220), (311), (400), (422), (511) and (440). No extra peak has been appeared in synthesized materials. The intensity of ferrite peaks increases gradually as we increase the annealing temperature of the materials.



Fig.1 XRD pattern of ZnO, NiFe₂O₄ and their composite at different annealing temperatures.

Formula used for calculating the Crystallite size is Debye-Scherrer equation.

$$\mathbf{D} = \frac{k.\lambda}{\beta. \cos\theta} \tag{1}$$

Here D is crystallite size, k is here constant, λ is wavelength of incident ray (1.5406 Å), β is FWHM (full width at half maxima), θ is Bragg's angle.

Fourier transform infrared spectroscopy (FTIR)

To consider the molecular structure of ZnO. NiFe₂O₄ and their composites at different annealing temperature, infrared spectroscopy is used. In ZnO, a broad peak is appeared at 3676-3082cm⁻¹ region because of hydroxyl groups (O-H), absorbance peak at 2920cm⁻¹ is attributed to the presence of C-H group. The climax at 1594cm⁻¹ is due to the splitting of hydrogen bond and OH stretching bond is appeared at 1417cm⁻¹. The sharp peak appeared at 510 cm⁻¹ is ascribed to the vibrational phonon of ZnO [5]. In NiFe₂O₄ spectra, peaks near 3450 and 1650 cm⁻¹ are due to the stretching bands and H-O-H bending vibration. The spectra between 2800-3000cm⁻¹ is due to the presence of C-H groups. The spectra near 1450 cm⁻¹ appeared because of the antisymmetric N=O stretching vibration. The spectra appeared in the range of 600-550cm⁻¹ indicates the presence of metaloxygen (M-O) bond[6]. These results indicate the production of nanomaterials successfully.



Fig. 1 FTIR pattern of ZnO, NiFe₂O₄ and their composite at different annealing temperatures

Conclusion

ZnO, NiFe2O4 and their composites are prepared through chemical co-precipitation route. Synthesis of ferrites and oxides by co-precipitation process is suitable for small size. Ferrites have single phase cubic spinel structure and oxide have hexagonal wurtzite structure.

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Annealing Effects on 100 keV Silicon Negative Ions Implanted SiO₂ Thin Films

S. B. Vishwakarma¹, S. K. Dubey², and R. L. Dubey³

^{1, 2}Department of Physics, University of Mumbai, Vidyanagari, Mumbai-400 098, India ³Department of Physics, St. Xavier's College, 5 Mahapalika Marg, Mumbai-400 001, India

*Corresponding author: svphysics1983@gmail.com

Abstract

SiO₂ thin film of thickness 300 nm grown on p-type silicon substrate was implanted with 100 keV silicon negative ions for the fluences of 1 x 10^{16} , 5 x 10^{16} and 1 x 10^{17} ions cm⁻². The implanted samples were annealed at the temperature of 900 °C. Ultraviolet visible near-infrared spectroscopy technique has been used to investigate the implanted SiO₂ thin film samples before and after thermal annealing. Thermally annealed samples showed higher transmittance as compared to non-annealed samples. This may be attributed to the creation of new SiO_x phase in the SiO₂ matrix at higher temperature. The energy band gap value was found to increase after thermal annealing. This effect may be related to the formation of silicon nanoclusters.

Fe₃O₄ loaded g-C₃N₄ layered composites for photoreduction-driven degradation of organic dye molecules under sunlight

R. Mithun Prakash, C. Ningaraju, K. Gayathri, M. Kanmani, and M. Sakar*

Centre for Nano and Material Sciences, Jain University, Bangalore 562112, Karnataka, India.

*Corresponding author: <u>m.sakar@janiuniversity.ac.in</u>

Abstract

Magnetite (Fe₃O₄) particles loaded g-C₃N₄ (GCN) layered composites have been synthesized via melamine condensation-cumprecipitation method. The characteristic presence of Fe₃O₄ in g-C₃N₄ is confirmed from the XRD patterns and a reduced bandgap energy of 2.38 eV is observed for Fe₃O₄/GCN composite, while it is 2.51 eV for bare-GCN. It is proposed based on the relative band edge potential of Fe₃O₄ and GCN that the photocatalytic process could have largely driven by reduction-mediated degradation process rather than oxidation-mediated process towards degradation of rhodamine B under sunlight irradiation.

Introduction

Enhancing the photocatalytic efficiency under sunlight has become a hot topic in photocatalysis research. In this direction, graphitic-carbon nitride (g-C₃N₄) has gained a significant importance in the visible light driven photocatalytic applications owing to their narrow bandgap energy of around 2-3 eV.¹ To further enhance its photocatalytic properties, g-C₃N₄ has been modified in their physical and chemical structures.1 In the chemical modification of g-C₃N₄, the integrating material often determines its overall properties. For instance, the integration of magnetic materials such as iron oxide introduces the magnetic properties in the composite and considerably improves the photocatalytic properties. Among various iron oxide phases, the Fe₃O₄ phase shows high magnetic and electrical conductivity properties due to the rich electron-exchange process in Fe^{2+} and Fe^{3+} centres in Fe₃O₄.² Therefore, herein, we have integrated Fe₃O₄ nanoparticles in the layers of GCN and studied their photocatalytic efficiency towards the degradation of RhB molecules under sunlight.

Experimental

5 g of melamine was thermally condensed at 550 °C (3 h) using a muffle furnace to obtain the bare g- C_3N_4 . To obtain Fe₃O₄/g- C_3N_4 composites, Fe(NO₃)₃ 9H₂O (5 wt%) was dissolved in water along with 2 mL of NH₃(aq). To this, 5 g of melamine was dissolved and stirred under heating to obtain the powder and annealed at 550 °C for 3 h. Bare-Fe₃O₄ was obtained as above without adding melamine.

Results and discussion

Graphitic-carbon nitride $(g-C_3N_4)$ and iron oxide (Fe_3O_4) phase is confirmed from the XRD pattern, while the major peaks of the respective components

are found in the XRD data of Fe₃O₄/GCN (Fig. 1a). The low-intensity peak corresponding to Fe₃O₄ could be due to its low amount (5 wt%) in the composites. Notably, the major-peak of GCN (~27.6°) is shifted to $\sim 27.9^{\circ}$ in the composites, and the peak at $\sim 12.9^{\circ}$ is also largely suppressed and shifted to ~13.1°. This indicates that Fe₃O₄ is well integrated in the GCN polymeric network, and especially, the suppression of peak at ~13.1° could be attributed to the improved exfoliation of GCN layers due to Fe₃O₄ integration.³ Further, the crystallite size estimated using Scherrer's formula showed that the crystallite size of GCN (5.4 nm) is increased in the composite (12.2 nm). This could be attributed to the interaction of Fe₃O₄ over the growing polymeric network that facilitated the growth as they occupy in the inter-layers of GCN.



Fig. 1. (a) XRD pattern and (b) N_2 adsorption-desorption hysteresis of bare and Fe₃O₄ integrated g-C₃N₄ layers.

The BET N₂ adsorption-desorption curves showed that the Fe₃O₄ integration improved the surface area of the composite to 29.7 m²/g as compared to bare GCN (21.7 m²/g). This smaller enhancement could be attributed to the modifications induced in the GCN layer, rather than the contribution from Fe₃O₄. This is because the hysteresis in the pressure (*P*/*P*₀) range of 0.4-0.9 is relatively larger for the composites (Fig. 1b),² which indicates that the Fe₃O₄ may be blocking the pores and limits the desorption of the adsorbed N₂ gases, which may be favorable for strong interactions. The FESEM image (Fig. 2a) showed aggregated morphology of Fe_3O_4 with a size range from 100-200 nm, while a well-integrated structure of Fe_3O_4 in the layers of GCN is observed in composites (Fig. 2b). This revealed that the adopted synthesis method could be suitable for the specific site introduction of Fe_3O_4 particles in between the layers of GCN. It was possibly due to the iron (Fe^{3+}) precursors that mixed along with melamine, which are anchored on the surface, and the addition of $NH_3(aq)$ led to the nucleation of Fe particles and crystallized into Fe_3O_4 upon annealing. Notably, both Fe_3O_4 and GCN were crystallized concurrently, which facilitated the integration of Fe_3O_4 in between the layers of GCN as these particles are nucleated and grown in between the GCN layers.



Fig. 2. FESEM image of (a) Fe₃O₄ and (b) Fe₃O₄/g-C₃N₄.

UV-Visible absorption of materials indicated that the integration of Fe₃O₄ inherits the properties of g-C₃N₄ in Fe₃O₄/GCN composite (Fig. 3a). It shows that the Fe₃O₄ energy levels may not be interacting with the band structure of GCN; rather, it facilitates to receive the electrons from the CB of GCN. Therefore, Fe₃O₄ helps only in an optical transition involving the interband transition rather than the intra-band transition in the composites.⁴ Accordingly, the Tauc's plot indicated only a decrement in the bandgap energy for Fe₃O₄/GCN (2.38 eV) as compared to bare-GCN (2.51 eV), as shown in Fig. 3b.



Fig. 3. (a) UV-Visible spectra and (b) Tauc's plot for the estimation bandgap energy of bare and $Fe_3O_4/g-C_3N_4$.

In the typical photocatalytic studies, 10 mg of photocatalyst and 50 mL of 10 ppm rhodamine B (RhB) dye was taken and irradiated under solar light. The obtained C/C_0 ratio plot showed that the bare and Fe₃O₄-integrated GCN degraded ~73 and 97% of dye at the end of 2 h as shown in Fig. 4a. It can be proposed

that upon irradiation, the electrons get excited to CB of $g-C_3N_4$, which is further transferred to the Fe₃O₄ as their energy levels are favourable to receive electrons from GCN (Fig. 4b).⁵ This process sufficiently inhibits the charge recombination in the system and lets more electrons available for the photo-reduction mediated degradation. This is because the holes in the VBs of GCN and Fe₃O₄ are in pursuit of recombining with the electrons rather than effectively involving in the oxidation of surrounding molecules.



Fig. 4. (a) C/C_0 ratio plot and (b) Photocatalytic mechanism in Fe₃O₄/g-C₃N₄ composites.

Conclusion

The integration of Fe_3O_4 in the layers of $g-C_3N_4$ was performed and explored their photocatalytic efficiency towards the degradation of rhodamine B under sunlight. From the performed characterizations, it can be proposed that the developed method can be suitable to grow the Fe_3O_4 particles in the inter-layers of $g-C_3N_4$. This structure largely facilitated the photocatalytic process through reduction reactions rather than oxidation as the rich availability of electrons compared to holes due to their inter-band structures.

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Quantifying Pattern Formation During Evaporative Assembly of Colloids in a Drying Droplet on Porous Substrate

Ashwani Kumar^{1*}, Debasis Sen^{1,2*}, Avik Das^{1,2}, Jitendra Bahadur^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094

*Corresponding author: ashwanikumar@rrcat.gov.in, debasis@barc.gov.in

Abstract

Evaporative-drying of a colloidal droplet leads to the formation of various patterns on a porous substrate. Such pattern formations on porous membranes have been investigated using scanning SAXS to understand the structural correlation of the self-assembly process of colloidal nanoparticles. Parameter space diagram, revealing the relationship between three competitive processes of flow, evaporation, and coagulation, which determines the colloidal assembly, have been generated by feasible computation model corroborating the experimental SAXS data. The phase diagram demarcates different domains of evaporative assembly processes on porous substrate leading to various forms of dried patterns of correlated nanoparticles.

Structural Investigation of NdFeO₃-PbTiO₃ Solid Solution by Rietveld Refinement and Raman Spectroscopy

Ateed Ahmad¹, Anand Somvanshi¹, Shahid Husain^{1*}

¹Department of Physics, Aligarh Muslim University, Aligarh (INDIA), 202002

*Corresponding author: <u>s.husaincmp@gmail.com</u>

Abstract

The preparation of NdFeO₃-PbTiO₃ nano composite was carried out by mixing of both the samples in proposed proportions. The presence of tetragonal phase of PbTiO₃ in the orthorhombic crystal structure of NdFeO₃ is established by Rietveld refinement of XRD data. W-H plot confirms the nanocrystalline behaviour of the sample. The room temperature Raman analysis of the composite sample indicates the presence of *Pbnm* and *P4mm* symmetry in the system and show blueshift in the spectra.

Structural Properties of Sm and Co co-doped BiFeO₃

Prabhav Joshi¹, Shivendra Tiwari², Jyoti Shukla³ and Ahutosh Mishra⁴

School of Physics, Devi Ahilya Vishwavidyalaya, Taxshila Parisar, Khandwa road Indore, 452001

*Corresponding author: prabhavjoshi31@gmail.com

Abstract

The 5% Sm & Co co-doped $BiFeO_3$ sample are processed by solid state reaction route, in order to study structural properties of the sample, The Reitveld Refinement has been performed using rhombohedral (R3c) symmetry. The change in lattice parameter confirms the substituion of Sm at Bi site and Co at Fe site respectively. The particle size using debye scherrer equation and W-H plot confirms the nanometer scale particle size. Secondary phase of $Bi_2Fe_4O_9$ and sillenite is also confirmed.

Introduction

Multiferroics are the materials exhibits ferroelectric and ferromagnetic properties in same phase. Among the well-studied multiferroic only a few show both ferroelectricity and ferromagnetism at room temperature. BiFeO₃ (BFO) is one such multiferroic with ferroelectricity at ($T_c \sim 1103$ K) and G type antiferromagnetism at $(T_N \sim 643)$ [1]..Prestine BFO has distorted rhombohedral structure with space group R3c. However, bulk BFO has some inherent properties that limit its application in practical applications. Large leakage current, weak ferromagnetism, poor magnetoelectric coupling and volatility of bismuth and the formation of impurity[2] phases have made its usability a challenge to the material scientists.

To overcome such shortcomings various methods have been employed either the synthesis process or with the help of doping. The ferroelectric properties of BFO are attributed to 6s lone pair electrons of Bi^{3+} and magnetic properties to Fe^{3+} [3]. A site doping with a rare earth has been found suitable as its valancy and and ionic radius matches with Bismuth. Samarium(Sm) have shown to improve the ferroelectric properties due to reduction of oxygen ion vacancies and saturation polarization. At the B site Co has also shown to disrupt the spiral chain of magnetic moment that improve the macroscopic magnetization of the overall sample. [4]. The charge imbalance between Fe^{3+} and Co^{4+} leads to modification on both internal structure and the morphology. Also high dielectric and low loss along with improved ferromagnetism makes Co doping a preferred choice.

Sm and Co Codoped BFO has shown a substantial improvement in Magnetoelectric effect. In this paper

we report detailed structural and vibrational study of $Bi_{0.95}Sm_{0.05}Fe_{0.95}Co_{0.05}O_3$. And the effect of ion substitution on the particle size, phase and structure of the sample.

Experimental Technique

 $Bi_{0.95}Sm_{0.05}Fe_{0.95}Co_{0.05}O_3$ was prepared via solid state reaction route. The starting materials $Bi_2 O_3$, $Fe_2 O_3$, $Sm_3 O_3$ and $Co_3 O_4$ were weighed, mixed in stoichiometric ratio. Grinded thoroughly in an agate mortar for 8 h and calcinated at 800 ° C , then regrind and sintered at 850° C.. The powder were pressed into pallets of size 10 x 2 mm. The X ray diffraction was carried out with Cu K α_1 (1.5405 Å) radiation using Bruker D8 Advanced X-Ray diffractometer over the angular range of 10°-90° at room temperature. Raman measurement were carried out using Labram HR800 micro-Raman spectrometer equipped with 50 x objective, edge filter and a Peilter-cooled charge coupled device(1024 x 256 x 26 microns). The spectra were excited with 488 nm radiation(2.53 eV) from an air cooled Argon Laser.

Results and Discussion

XRD pattern of $Bi_{0.95}Sm_{0.05}Fe_{0.95}Co_{0.05}O_3$ sample are shown in Figure 1. From the X-Ray diffraction pattern, it is observed that the doped sample has distorted rhombohedral structure with R3c space group. The peak postions are in accordance with the JCPDS file No.71-2494. Reitvield refinement was performed which confirm rhombohedral phase formation, along with some impurity phases of $Bi_2Fe_4O_9$ and sillenite. The calculated value of lattice parameters are a=5.5769 Å and c=13.8630 Å. These

Fig. 1. X-Ray pattern of 5% Sm and Co co-doped BFO j



are slightly smaller than what is observed in perstine BFO.Also the cell volume decrese from 374.57 Å³ to 373.39 Å³ indicating the substitution of Sm and Co in the phase of BFO[-]. The particle size calculated by debye-Scherrer equation is 97.67 Å for BFO phase.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad \dots (a)$$

The particle size when calculate using Williamson-Hall plot appears to be 154.11 Å. This confirms the average particle size to be in this range only. The major secondary phase that appears in the sample primarily due to overheating of the sample is $Bi_2Fe_4O_9$ have orthorhombic structure with space group Pbam .with cell parameters a=7.9649 Å, b=8.4385 Å and c=5.9987 Å. And the cell volume of 403.1869 Å³. Another minor phase of sillenite having cubic structure with space group I23 has also been identified, with lattice parameters a=b=c=10.13 Å 1039.81 Å³ and cell volume of



Fig. 2. Rietveld refinement of 5% Sm & Co co-doped BFO

Table 1. Index refinement of co-doped BFO				
Parameter	BSFCO			
Chi2	2.60			
Lattice parameter				
a (Å)	5.5			
c (Å)	13.86			
V (Å ³⁾	373.39			
Mol%	82.48			
$\mathbf{S}_{\mathbf{occ}}$				
Bi	0.31643			
Sm	0.01805			
Fe	0.31655			
Со	0.00276			
0	1.04836			
R _{Bragg}	6.02			
$R_{\rm f}$	3.79			



Fig. 3. Williamson-Hall plot of 5% Sm and Co co-doped BFO

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Evaluation of Ni Doped SnO₂ Nanocomposites for Selective Cadmium Detection in Wastewater

Upasana Choudhari¹, Shweta Jagtap^{1*}, Niranjan Ramgir^{2**}, A. K. Debnath², K. P. Muthe²

¹ Department of Electronic and Instrumentation Science, Savitribai Phule Pune University, Pune 411007.

² Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085. *Email: *shweta.jagtap@gmail.com/**niranjanpr@yahoo.com*

Abstract

An electrochemical sensor based on Ni/SnO₂ nanocomposites prepared by co-precipitation method has been reported for the detection of Cd^{2+} . Cyclic voltammetry (CV) studies indicated that the developed sensor has superior selectivity towards Cd^{2+} in comparison to its response towards other toxic metal ions. The sensor could detect Cd^{2+} in a wider linear range from 1 to 200 ppb with a detection limit of 0.4 ppb. These superior sensor responses are attributed to the synergetic effect of nickel doping and SnO₂. In particular, the enhancement of the charge transfer ability of the synthesized nanocomposites leads to an improved response characteristic.

Synthesis and Characterization of Cost-Effective Calcium Titanate Nanostructured Powder and Fibers for Display Applications

Pooja Yadav, M Krishnam Raju, and P Abdul Azeem*

Department of Physics, National Institute of Technology Warangal, Warangal 506004, India

*Corresponding author: <u>drazeem2002@nitw.ac.in</u>

Abstract

Calcium titanate (CaTiO₃) nanostructured powder has been synthesized by modified sol-gel method using eggshell (ES) as the precursors for CaO and titanium (IV) isopropoxide as a source of titanium oxide. The powder X-ray diffraction peaks demonstrate pure phasic structure of calcinated sample as orthorhombic. The average crystallite sizes were calculated by Debye scherrer's formula and are in the range of 25–30 nm. FTIR results confirmed the characteristic functional groups of CaTiO₃. Furthermore, calcium titanate nanofibers with controlled microstructure were fabricated by electrospinning method. Finally, from the present study it can be concluded that the presented sol-gel synthesis could be novel way for producing nano CaTiO₃. This new nanostructured material and nanofibers could be low-cost potential candidates for the display and lighting applications.

Synthesis and Photocatalysis of ZnO Nano/Micropeony

Sambhaji Subhash Warule^{1, 2}

¹Department of Physics, Modern Education Society Nowrosjee Wadia College, Pune, Maharashtra, India-411 001. ²Department of Chemistry, Indian Institute of Science Education and Research, Pune, Maharashtra, India-411 008.

*Corresponding author: <u>warulesam@gmail.com</u>

Abstract

Large scale, low temperature and template free synthesis of hierarchical ZnO nano/micropeony using simple hydrothermal method. The morphological, structural and optical properties of the as-synthesized ZnO products were studied using various physico-chemical characterizations. The ZnO morphologies reveal well defined and self-assembled interconnected sheet-like structures and which is observed to be sensitive to the hydrothermal temperature. The possible growth mechanism is discussed briefly. Furthermore, the photocatalytic activities of ZnO nanostructures toward methylene blue dye under ultraviolet light showed enhanced activity over commercial Degussa P25. Larger surface area, high adsorption rate, large charge separation and the slow recombination of electrons/holes in ZnO establish nano/micropeony as favourable morphology for good photocatalysis. Being wide band gap semiconductors, these unique nanostructures will have prospective application in ZnO based dye sensitized solar cells.

Low temperature synthesis and optical properties of ZnO nanoparticles

Yogesh Kumar¹, Harish Sinhmar², Mahaveer Genwa³ and P. L. Meena^{2,*}

¹Department of Physics, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand-826004, India.

²Department of Physics, Deen Dayal Upadhyaya College (University of Delhi), Sector – 3, Dwarka, New Delhi-110078, India.

³Department of Chemistry, Deen Dayal Upadhyaya College (University of Delhi), Sector – 3, Dwarka, New Delhi-110078, India.

*Corresponding author: plmeena@ddu.du.ac.in plmeena@gmail.com

Abstract

ZnO nanoparticles were synthesized through the thermal decomposition method and were characterized by using X-ray diffraction (XRD) and UV-Visible (UV-Vis.) spectroscopy. XRD study confirmed the synthesis of ZnO nanoparticles at 250 °C with a crystallite size of 19.4 nm. UV-Vis. spectra showed a characteristic peak at 362 nm. Energy bandgap was calculated using the numerical derivative method and the Tauc plot method. The concentration of ZnO nanoparticles was also computed using Beer-Lambert law.

Introduction

Zinc oxide is considered the most appropriate material for electronic-based applications based on its various morphologies and low-cost processing. It is a wide bandgap (3.3 eV) semiconductor and possesses high exciton binding energy¹. In addition to the above properties, ZnO has excellent adsorption, high photon absorption efficiency, is non-toxic, etc.², thus making it a potent material of interest for optoelectronic applications. According to the literature³, ZnO nanoparticles are synthesized at higher temperatures using the thermal decomposition method, i.e., 600 °C.

In this paper, we have synthesized ZnO nanoparticles through the thermal decomposition method at low temperatures and characterized them using XRD and UV-Vis. spectroscopy. Energy bandgap was also computed using the numerical derivative method and Tauc plot method for comparative analysis.

Experimental and Characterization

ZnO nanoparticles were synthesized through the thermal decomposition method with ZnCO₃ (Qualigens Fine Chemicals with 97 % purity), C₂H₅OH (Analytical reagent 99.9%), and KOH (Fisher Scientific with \geq 85 % purity) as starting materials. The synthesis method is being reported in the literature⁴.

XRD measurements were done by using XtaLAB Synergy-I Diffraction System (Rigaku) in the 2θ range of 25-80° with Cu-K_a radiation source with a wavelength of $\lambda = 1.5406$ Å. UV-Vis. spectroscopy

was done in the wavelength range of 300-500 nm by using UV-1800 SHIMADZU spectrophotometer.

Results and Discussion

Room temperature XRD measurements have been performed on the ZnO nanoparticles synthesized at different temperatures, i.e., 100 °C, 150 °C, 200 °C, and 250 °C, as shown in Fig. 1. The observed XRD data is in good agreement with the crystallographic data in the JCPDS Card No. 79-2205 for the prepared ZnO at 250 °C, and Bragg positions are also indexed. In the XRD data, impurities⁵⁻⁶ were observed for the sample up to 200 °C, at angle $2\theta = 53.84^{\circ}$ corresponds to ZnO_2 , $2\theta = 28.54^{\circ}$ (ZnCl₂) and $2\theta =$ 32.37°, 59.39° [Zn(OH)₂] as shown in Fig. 1. However, impurity was not observed in the samples prepared at 250 °C. Thus, the XRD measurements confirmed the synthesis of the ZnO sample at 250 °C in the hexagonal wurtzite structure without the presence of any external phase.



Fig. 1. XRD data of ZnO nanoparticles synthesized at four temperatures.
The crystallite size of these nanoparticles was also computed by using Deby Scherrer formula⁷ as shown in Table 1, along with lattice parameters.

Table 1. Crystallite size of ZnO nanoparticlessynthesized at 250 °C.

Crystallite Size D (nm)	Lattice Parameters	
	a = b (nm)	<i>c</i> (nm)
19.4	0.3250	0.5209

UV-Vis. spectra of the prepared ZnO sample at 250 °C have been shown in Fig. 2 with the absorbance peak at 362 nm. The bulk bandgap was computed using $E_g = (hc)/\lambda$ as 3.42 eV. The numerical derivative of absorbance with respect to energy has also been shown in the inset of Fig. 2 and indicating a bandgap value at 3.28 eV. In addition, peak broadening is also observed under the influence of temperature that may be due to the quantum confinement effect⁸.

The Tauc plot for ZnO nanoparticles with the computed value of bandgap as 3.1 eV, shown in Fig. 3. Energy bandgap (E_g) was computed using Tauc equation⁹ for n = 1/2 (direct bandgap with allowed transitions)

$$(\alpha hv)^{1/2} = A(hv - E_g) \tag{1}$$

where α , h, v and A represent the absorption coefficient, Planck constant, photon's frequency and slope of Tauc plot in the linear energy region (3.24-3.35 eV), respectively.

Tauc plot has two regions, i.e., linear and nonlinear/curved. Among these two methods, as mentioned above for calculating the bandgap energy, the numerical derivative method is more accurate and feasible than the Tauc plot method, may be due to its identification of peaks in a small wavelength range.



Fig. 2. UV-Vis. spectra for ZnO nanoparticles synthesized at 250 °Cand the inset shows dA/dE.

The particle size was also computed using an effective mass model¹⁰ and was found 4.74 nm.

1/2

$$r(nm) = \frac{-0.3409 + \left(-26.23012 + \frac{10240.72}{\lambda_p}\right)^{1/2}}{-6.3829 + 2483.2/\lambda_p}$$
(2)

where r represents the size of the particle, and λ_p (in nm) represents the peak absorption wavelength which is 362 nm.

The concentration of these nanoparticles was also calculated using Beer-Lambert law as 79.1 mol/L, which indicates the interaction between the ZnO nanoparticles and UV radiation for optoelectronic applications.



Fig. 3. Tauc plot for ZnO nanoparticles.

The energy bandgap (direct bandgap), size, and concentration of these synthesized ZnO nanoparticles indicate their optical nature and scope for various device applications.

Conclusion

ZnO nanoparticles were successfully synthesized at 250°C with hexagonal wurtzite structure in singlephase, the crystallite size of 19.4 nm as confirmed from XRD. UV-Vis. Spectroscopy confirmed the characteristic peak at 362 nm with a bandgap of 3.28 eV. Numerical derivative (dA/dE) has been proven to be a better approach for computing energy bandgap.

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Zirconium incorporated 1-D titanate nanostructures and its application in defluoridation of water

Anjana Biswas, C Prathibha^{*}

Department of Physics, Sri Sathya Sai Institute of Higher Learning, Anantapur Campus, Andhra Pradesh - 515001

*Corresponding author: cprathibha@sssihl.edu.in

Abstract

In this work, the authors present an efficient method of inclusion of Zr(IV) ions in the interlayer region of 1D titanate nanostructures, resulting in the formation of zirconium intercalated titanate nanostructure (ZTNS). The phase, tubular morphology and elemental analysis of the material was confirmed by XRD, TEM and EDS respectively. The developed material proved to be a promising adsorbent for defluoridation of water. Fluoride contamination of water is a problem that is affecting people worldwide. There is an emerging need for efficient defluoridating adsorbents. The successful inclusion of the Zr into the titanate nanostructure leads to enhanced fluoride adsorption, with 95% fluoride adsorption efficiency. The high defluoridation capacity of the material was obtained using low adsorbent dosage and short contact time period.

Cobalt Doped Hydroxyapatite as Efficient Adsorbent for the Removal Congo Red Dye

Kurinjinathan Panneerselvam, Lin Sunil, Anita R Warrier*

Nanophotonics Research Laboratory, Department of Physics, Academy of Maritime Education and Training Kanathur, Chennai- 603 112, Tamil Nadu, India

*Corresponding author: anitawarrier2@gmail.com.

Abstract

Removal of carcinogenic industrial effluents is a great challenge in water treatment. In this work we synthesized nano structured Hydroxyapatite (HAp) and Cobalt (Co) Doped Hydroxyapatite via facile wet chemical precipitation technique. The dye removal efficiency and adsorbent - adsorbate interaction kinetic study were conducted against the aqueous solution of Congo Red (CR) dye. The reduced crystallite size (0.49 nm for 10CH) and high surface area ~ 193.97 m²/g is responsible for the high dye removal efficiency (84.78%). The pseudo second order kinetic reaction shows better fit for this mechanism in which electrostatic interaction and chemisorption process are involved. HAp and Co-HAp could be used as a potential adsorbent for the removal of dye molecules from contaminated water.

Surface Potential Alternation of Graphene Using hBN Substrate

Tanmay Mahanta¹, Vidyotma Yadav¹, Sanjeev Kumar¹ and Tanuja Mohanty^{1)*}

¹School of Physical Sciences, JNU, New Delhi, INDIA - 110067

*Corresponding author: tanujajnu@gmail.com

Abstract

Hexagonal boron nitride (hBN) as a substrate relaxes graphene surface; the conventional SiO_2 imposes microstrain on pristine graphene whereas a little lattice mismatch with graphene makes hBN a perfect substrate of graphene. Raman spectroscopic studies show the relaxation in the lattice structure of graphene. AFM image-derived surface roughness shows a decrease in surface roughness of graphene when hBN is used as a substrate in the place of SiO_2 . The work function enhancement as mapped from scanning Kelvin probe microscopy supports the morphology of graphene where surface roughness and work function are inversely proportional.

Introduction

Hexagonal boron nitride popularly known as hBN or white graphene due to its structural similarities with graphene has emerged as a very useful nanomaterial in the lubricating industry, photonics, and as a substrate or template[1]. A little mismatch between hBN and graphene makes it a suitable substrate for graphene. The conventional SiO₂ as a substrate falls behind hBN when it comes to device performance, preservation of generality, etc.

The bandgap of hBN is very high, making it an insulator, as well as the work function too, is comparatively high [2]. As there is inversion symmetry breaking in hBN, graphene on hBN could be made showing piezoelectric response, which inherently graphene does not possess. Graphene's non-zero bandgap makes the on-off ratio infinite which excludes it from being used in the area of nano-electronic technology. All these limitations drawbacks could be improved using hBN as a substrate.

Experimental Method

The graphene samples grown on SiO_2 and hBN substrate were bought from Graphene Supermarket (1cm×1cm in size). Before the experiment, to avoid any contaminants on the samples, these were gently cleaned with acetone. AFM images were taken using the Park Systems XE series; Raman spectra were taken using WiTec Alpha 300 (wavelength 532 nm). Scanning Kelvin probe microscope of KP Technology was employed to map the contact potential difference (CPD). The work function was calculated using the following equation.

$$eV_{CPD} = \varphi_{tip} - \varphi_{sample} \tag{1}$$

Where V_{CPD} represents contact potential difference and $\varphi_{tip, sample}$ stands for work function of gold tip and sample. Analyzing the contact potential difference one can measure the value of the work function [3].

Results & Discussions

The AFM images of graphene on SiO_2 and graphene on hBN are given in figure-1(a,b). It is visible that the surface of graphene is more relaxed and experiencing less external stress due to a little lattice mismatch when deposited on hBN. To get insight into the actual effect, the roughness of both films is calculated from AFM images. It comes out that graphene/SiO₂ has r.m.s roughness (S_q) 219.9 pm; average roughness (S_a) 192.1 pm.



Fig.1. AFM image of (a) graphene/SiO₂ (b) graphene/BN..

Whereas S_a and S_q values of graphene/hBN are 105.4 pm and 138 pm. The roughness is less in graphene/hBN than in graphene/SiO₂. This is due to the structure being more relaxed on hBN. The roughness has an impact on several graphene properties.

The Raman spectrum of graphene/SiO₂ and graphene/hBN is given in figure-2. The characteristic peak positions (G and 2D) are slightly blueshifted in

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graphene/hBN. The relaxed graphene/hBN structure effectively experiences compression than in graphene/SiO₂. The effect of charge impurities was also considered, but the effect is negligible as the FWHM does not get reduced [4,5]. The G peak is highly affected by charge impurities than the 2D peak but here the shift is higher in the 2D peak than in the G peak.



Fig.2. Raman spectrum of graphene/SiO2 and graphene/hBN.

The work function of the samples as computed from SKPM is given in figure-3. The average work function value of graphene/SiO₂ is ~4.73 eV; for graphene/hBN it is ~5.08 eV. The work function has been increased when graphene is deposited on hBN compared to when deposited on SiO₂.

The electronic work function of materials depends upon several factors like doping, adatoms present on the surface, strain, roughness, etc. Depending upon the electronegativity of the adatoms, it might increase or decrease [6].



Fig.3. The work function mapping of graphene/SiO₂ and graphene/hBN.

As it was observed from the roughness calculation that the surface roughness decreases in the case of graphene/hBN sample compared to graphene/SiO₂, the impact of surface roughness would be dominating for the work function modification. The effect of charge impurity can be ruled out as evident from the Raman spectrum. It is reported that the surface roughness is inversely proportional[7] to the electronic work function hence reduction of roughness will lead to enhancement of work function as observed in this case.

0 1.00

Quantity	Graphene/SiO ₂	Graphene/hBN
Average roughness (pm	n) 192 .1	105.4
Raman 2D position(cm	-1) 2683	2690.5
Raman G position(cm ⁻¹ Work function (eV)) 1584 4.73	1588 5.08

The substrate's playing a major role for application of graphene where efficiency and stability are more important criteria. hBN as a substrate relaxes graphene structure, as well as the charge transfer, is negligible which makes it a suitable candidate for graphene. The work function which is an important parameter considered in optoelectronic devices could also be tuned using hBN as a substrate.

To conclude we have studied that hBN as a substrate alters graphenes' work function, as well as graphene's lattice structure is relaxed. This roughness-dependent work function modulation of graphene could be a metric for substrate selection at the industrial level.

Acknowledgment

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Synthesis of Boron Carbon Nitride (BCN) by Thermal Annealing of hBN in Graphitic Environment

M K Kumawat¹, Tanmay Mahanta¹, Sanjeev Kumar¹, T Mohanty^{1)*}

¹School of Physical Sciences, Jawaharlal Nehru University, New Delhi, India - 110067

*Corresponding author: tanujajnu@gmail.com

Abstract

A novel synthesis method of boron carbon nitride is presented here. For this purpose, thin film of hBN on SiO₂/Si was annealed at ~1000°C in presence of graphite powder. The whole process was performed in a vacuum-sealed quartz tube. Confirmation of presence of carbon atom in synthesized BCN was ascertained by Raman spectroscopy. Carbon bonding with boron and nitrogen atoms was confirmed by FTIR spectroscopy. This work has opened up a sustainable, fast and reliable method of synthesizing boron carbon nitride which finds excellent applications in optoelectronic devices.

Introduction

Boron carbon nitride (BCN) with varying contents of boron, carbon and nitrogen imitates the hybrid structure of boron nitride and graphene with different phases. These new form of material offers excellent features which outweigh the conventional parent materials. The BCN structures show tunable electrical properties, high thermal stability, remarkable mechanical behavior and low dielectric constant. The synthesis methods have impact on such hybrid material's properties hence on device performance. A suitable, less time taking and efficient method of synthesis is necessary for bulk production of such kind of hybrid materials.

Here, in this work synthesis of BCN is presented using graphite and hBN thin films as precursor. Thermal annealing of the aforementioned at ~1000°C at low pressure (~10⁻⁴ mbar) has been done. The hBN nanosheets were synthesized following chemical route (sonication of bulk hBN powder using NMP as solvent followed by centrifugation at 3000 rpm for 30 minutes). The thin film of hBN on SiO₂/Si nanosheets was produced by spin-coating method. For production of BCN thermal annealing in graphite environment has been done. The resultant material has been characterized by Raman and FTIR spectroscopy.

Experimental Methods

Hexagonal boron nitride (hBN) nano-sheets were synthesized by 24 hours bath sonication in NMP (1-Methyl-2-pyrrolidone) solvent[1]. Sonicated solution was centrifuged at 3500 rpm for 30 minutes and supernatant was collected and preserved for further experiments. hBN nano-sheets were transferred on SiO₂/Si substrate by spin coating technique and presence of sheets was confirmed by Raman spectroscopy (532nm laser).

hBN nanosheets grown on SiO₂/Si substrate was placed in quartz tube in presence of graphite powder. It was sealed at low pressure ($\sim 10^{-4}$ mbar). This sealed tube was placed in furnace and annealed at 1000°C for 24 hours. After that, temperature was lowered down to room temperature and sample was collected for further characterization.



Fig. 1. Schematic diagram showing carbon doping of hBN in the presence of graphite powder.

Results and Discussion

The Raman spectrum[1,2] of annealed hBN nanosheets on SiO₂/Si in the presence of graphite powder is depicted in Fig-2. The presences of D and G peaks (~1347 and ~1599 cm⁻¹) confirm the presence of carbon atoms in hBN. Since, the peak intensity of hBN (~1372 cm⁻¹) is comparatively lower than graphite; its presence is observed as a tangle adjacent to D peak (~1350 cm⁻¹). The defects in hBN during its synthesis are expected to be replaced by carbon atoms from graphite powder during annealing. The possibility of nucleation and production of graphene sheets separately on SiO₂ substrate could be ruled out as Raman spectrum has shown no significant 2D peak. For further confirmation of doping in hBN by carbon atoms, FTIR spectrum[2] was taken (Fig-3). The most prominent peak found is out-of-plane sp² bonded B-N-B bending modes at \sim 780 cm⁻¹[2]. This Peak may denote the Presence of hexagonal boron nitride or hexagonal carbon boron nitride. Another peak is near ~1020 cm⁻¹ which denote to the infrared vibration of boron carbon bond (B-C)[3.5]. Peak around ~1515 cm⁻¹ define the vibration of carboncarbon vibration mode (>C=C<)[4]. Peak around ~1730 cm⁻¹ confirm carbon nitrogen bonding[4]. A broad peak between ~1100-1250 is a combination of some peaks like, ~1100 cm⁻¹ for sp³C-B bonding, ~1200 cm⁻¹ for sp²C-B bonding and also for hBN. ~1120 cm⁻¹ define C-N bonding[2,3].



Fig.2. spectra of pristine hBN nanosheets (Upper right side) and graphite mediated annealed hBN (BCN). Left side box is showing tangle adjacent of D peak (~1350 cm⁻¹) and hBN peak (~1365 cm⁻¹).



Fig.3. FTIR spectra of pristine hBN nanosheets and graphite mediated annealed hBN (BCN).

Conclusion

hBN nanosheets were synthesized by bath sonication method and deposited on SiO_2/Si substrate by spin coating method. hBN sheets were annealed at 1000°C in the presence of graphite powder. Confirmation of doping was done by Raman and FTIR spectroscopy. D and G peak of Raman indicate the presence of carbon in hBN while FTIR peaks indicate the bonding of carbon with boron and nitrogen.

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Facile synthesis and characterization of ZnO/NiO composites for antibacterial applications

N. Dineshbabu^{1,*}, **P. Karuppasamy**¹, **Muthu Senthil Pandian**¹, **P. Ramasamy**¹, **T.Arun**² ¹SSN Research Centre, SSN College of Engineering, kalavakkam-603 110, Chennai, India.

²Instituto de Investigaciones Científicas y Technologicas (IDICTEC), Universidad de Atacama, Copayapu, 485,

Copiapo, Chile.

*Corresponding author: dineshharish87@gmail.com

Abstract

Semiconducting oxide based nanocomposites have gained more attention in environmental applications. Present investigation is devoted to prepare ZnO/NiO nanocomposites (1:1 ratio) using a facile co-precipitation method. XRD patterns exhibited diffraction peaks corresponding to hexagonal wurtzite structure of ZnO and face centered cubic structure of NiO. UV-vis spectrum shows the optical property of the prepared samples. Band gap energy of ZnO/NiO samples is 2.93 eV. HRTEM image shows the morphology of ZnO/NiO composites, containing randomly oriented spherical and pebble shaped particles. From antibacterial study, ZnO/NiO composites show a good antibacterial activity against E. coli bacteria.

Possible Origin of Local Symmetry Breaking in Transition Metal Doped SnO₂ Nanocrystals

S. Roy^{1,*}, Anup K. Ghosh², S.K. Sharma¹, Sreerupa Roy³, Amish G. Joshi^{4,#}, Ranjan K. Singh² and S. Chatterjee⁵

¹Department of Physics, Indian Institute of Technology (Indian School of Mines), Dhanbad, Dhanbad – 826004, India ²Department of Physics, Institute of Science, Banaras Hindu University, Varanasi – 221005, India ³Department of Chemistry, Nirmala College, Ranchi – 834002, India

⁴CSIR-National Physical Laboratory, Dr. K. S. Krishnan Road, New Delhi – 110012, India
 ⁵Department of Physics, Indian Institute of Technology (BHU), Varanasi – 221005, India
 [#]Presently at: CSIR - CGCRI, Naroda Centre, 168-169, Naroda Industrial Estate, Ahmedabad – 382330, India

*Corresponding author: som.2108leo@gmail.com

Abstract

INTRODUCTION

SnO₂, a IV-VI wide band gap semiconductor, has attracted immense interest for device applications^{1,2,4}. However, due to the presence of inversion centre symmetry in the crystal lattice of SnO₂ (P4₂/ mnm space group), conduction-band minimum and valence-band maximum occur at the $\Gamma(0,0,0)$ point of the Brillouin zone with an even parity symmetry, hence forbidding the band edge transitions - which eventually means either complete absence or very low intensity of any resulting UV emission^{1,2}. This limits the potential use of SnO₂ in optical applications. Moreover, SnO₂, being diamagnetic in its bulk state, is also rendered unsuitable for next generation spintronics applications. Thus, it becomes a task of paramount importance to simultaneously break the local inversion symmetry and to induce magnetic properties in SnO₂ crystals. Nanostructuring of SnO₂ have been known to be an effective method for enhancing its UV emission properties¹. Doping SnO₂ with transition metals has been effective in inducing the magnetic properties through an interaction of the itinerant host electrons with localised d-electrons of dopant - a mechanism also known to cause lowering of symmetry³. Hence, an understanding of the origin of inversion symmetry breaking on doping SnO₂ nanocrystals with transition metals becomes very important.

Localised breaking of inversion centre symmetry has been observed on doping SnO₂ nanocrystals with cobalt². The long range tetragonal SnO₂ crystal structure is preserved in these nanocrystals as well as on codoping them with nickel, throughout the doping concentration^{2.4}. Mn can also exist in multiple stable oxidation states, leading to possible interaction between the localized *d*-electrons of Mn with the delocalized *s* and *p*-electrons of host. Thus, in the present study, three prototype systems of transition metal doped SnO₂ nanocrystals – Sn_{1-x}Co_xO₂, Sn_{0.97y}Co_{0.03}Ni_yO₂ and Sn_{1-z}Mn_zO₂ have been chosen to understand a possible origin of the local modulation of inversion symmetry in these nanocrystals.

EXPERIMENTAL DETAILS

The Sn_{1-x}Co_xO₂ (x = 0.00, 0.02, 0.03 and 0.04), Sn_{0.97-y}Co_{0.03}Ni_yO₂ (y = 0.02 and 0.04) and Sn_{1-z}Mn_zO₂ (z = 0.02 and 0.04) have been synthesized using chemical coprecipitation technique, as reported earlier^{2,4}. MnCl₂.4H₂O has been used as the precursor for Mn in Sn_{1-z}Mn_zO₂ nanocrystals. The experimental details for X-ray diffractograms (to study long range crystal symmetry), micro-Raman spectroscopy (to study lattice dynamics) and X-ray photoelectron spectroscopy (to study electronic structure) are also same as reported earlier^{2,4}.

RESULTS

1. X-ray diffraction (XRD)



Fig. 1. XRD profiles along with Rietveld refinement for Sn_{1-z}Mn_zO₂ nanocrystals. Average crystallite size is \approx 7.6 nm for z = 0.02 and \approx 6.7 nm for z = 0.04.

Fig. 1 shows the XRD profile of $Sn_{1-z}Mn_zO_2$ (z = 0.02 and 0.04) nanocrystals. All the peaks have been indexed following JCPDS file no.# 41-1445. Hence, all the three systems of transition metal doped SnO_2 nanocrystals^{2,4} retain the tetragonal SnO_2 crystal structure throughout the doping concentrations.

2. Raman Spectroscopy

The Raman spectra of $Sn_{1-x}Co_xO_2$ nanocrystals, along with the interpretation of observed vibrational modes have been reported earlier². The Raman spectra of $Sn_{0.97-y}Co_{0.03}Ni_yO_2$ and $Sn_{1-z}Mn_zO_2$ nanocrystals are shown in Fig. 2a and 2b resp. The intensity of S6 and S7 increases on increasing the Co and Mn concentration, whereas on increasing the Ni codoping concentration, their intensity decreases.

3. X-ray Photoelectron Spectroscopy (XPS)

Fig. 3 shows the Sn 3d core level XPS spectra of $Sn_{1-z}Mn_zO_2$ nanocrystals, and those for $Sn_{1-x}Co_xO_2$ and $Sn_{0.97-y}Co_{0.03}Ni_yO_2$ have been reported earlier^{2,4}. The relative concentration of Sn_i^{-w} w.r.t. host Sn_{Sn}^{x} increases for increase in Co and Mn doping whereas decreases with increase in Ni codoping concentration.

DISCUSSION

The irreducible representation for normal lattice vibrational modes at $\Gamma(0,0,0)$ point of the Brillouin zone for SnO₂ dictates that three optical modes $- {}^{1}\Gamma_{1}^{+}$ (A_{1g}) , ${}^{1}\Gamma_{4}$ (B_{2g}) and ${}^{1}\Gamma_{5}$ (E_{g}) are to be Raman active². However, it can be observed from ref. 2 and Fig. 2a and 2b that on Co and Mn doping, there exists two prominent IR active modes $-{}^{2}\Gamma_{5}^{+}(3)$ TO (S6) and ${}^{1}\Gamma_{1}^{-}$ (2) LO (S7), the intensity of which increases with increase in Co and Mn concentration and gradually decreases on codoping with Ni. However, the long range SnO₂ tetragonal crystal structure is well maintained for all the three systems^{2,4, Fig.1}. Thus, it can be concluded that Co and Mn doping leads to an enhancement of localized inversion symmetry breaking whereas codoping the cobalt doped SnO₂ nanocrystals with Ni, leads to a partial restoration of the inversion symmetry. This synchronicity of the variation in intensity of S6 and S7 modes with systematic increment in concentration of Sn;" w.r.t. Sn_{Sn}^{x} for Co² and Mn doped nanocrystals (Fig. 3) and that decrement for Ni codoped nanocrystals⁴,

indicates that evolution of Sn_i^{\dots} might be the possible defect responsible for the observed local inversion symmetry breaking in transition metal doped SnO_2 nanocrystals.



Fig. 2a. Raman spectra of $Sn_{0.97-y}Co_{0.03}Ni_yO_2$ nanocrystals.



Fig. 3. Sn 3*d* core level spectra of $Sn_{1-z}Mn_zO_2$ nanocrystals.

SUMMARY AND CONCLUSIONS

The local breaking and restoration of inversion symmetry in transition metal doped SnO_2 nanocrystals have been found to be an origin of enhancement and decrement respectively of $Sn_i^{...}$ defects in the lattice of these nanocrystals. However, it merits further investigations.

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Synthesis and Characterization of Yttrium doped Carbon Nitride

C. Stella¹, Priyanga. R^{2,*}V. S. Manikandan³

^{1,2}Department of Physics, Stella Maris College (Autonomous), Chennai, India ³Department of Physics, SRM University, Chennai, India

*E-mail: stellachandran89@gmail.com

Abstract

Undoped and yttrium-doped Carbon nitride (Y/ C_3N_4) was synthesized by using melamine as a precursor and yttrium as a dopant material. The prepared samples were characterized by X-ray diffraction pattern, UV-Vis absorption and FTIR analysis. The results confirm the formation of Y-doped C_3N_4 . Introduction of Y species effectively extends the spectral response of C_3N_4 from ultra-violet to visible region and it does not modify the crystalline structure of C_3N_4 . The results suggest that Y-doped C_3N_4 may use as photo catalytic material because of its enhanced absorption property.

Keywords: Carbon nitride, Yitrium, Y-doped C₃N₄, Photocatalysis.

1. Introduction

Carbon Nitride (C₃N₄)is a polymeric material and is composed of C. N. and a small amount of impurity H elements has an excellent physicochemical property including a unique electronic structure and suitable band gap. Once bulk C₃N₄ is transformed into nano sheets it can be transformed into different morphologies, such as nano rods/nano tubes and quantum dots. Carbon nitride has a variety of emerging applications, including sensing, biomedical applications, wastewater and environmental treatment, solar energy utilization, and system manufacturing. Yttrium (Y) is a rare-earth metal belonging to group 3 of the periodic table. The metal is formed by metallothermic reduction of anhydrous fluoride with calcium, and it is separated from the other rare earths by liquid-liquid or ion-exchange extraction. Photo catalysis occurs when a light source interacts with the surface of semiconductor materials, which is referred to as photo catalysts, at least two simultaneous processes, oxidation from photo generated holes and reduction from photo generated electrons, must occur throughout this process. The acceleration of a photoreaction in the presence of a catalyst is known as photo catalysis. Light is absorbed by an adsorption substrate in catalysed photolysis. A photo catalyst is a substance that absorbs light to raise its energy level and then transfers that energy to a reacting substance to cause a chemical reaction. [1]. Recently, multiple methods have been developed to synthesis yttrium-doped Carbon nitride nanomaterial, including thermal condensation, solvothermal, chemical vapor deposition, microwave-assisted, polymerization and hydrothermal method. Among various methods for synthesis, Calcination technique was used here to synthesis yttrium-doped Carbon nitride nanoparticles[2].

2. Prepration of undoped and Y-doped C_3N_4

The Yttrium-doped Carbon nitride (Y/C_3N_4) is prepared by the Calcination method[3]. Melamine is placed in the muffle furnace at 550°C for 2 hours. The appropriate amount of Yttrium(1% and 3%) is mixed with Melamine and the chemical compositions is dissolved in ethanol. The resultant solution is placed in a magnetic stirrer and stirred well until ethanol gets completely evaporated. Then all the three mixtures were transferred to 3 different quartz crucibles with a cover and placed in the hot air oven and dried at 80°C for 2 hours. The obtained product were at calcinated at 550°C for 2 hours. The products as-synthesized were labelled as Y1%, Y3%, and Y0. Hence, Y1%, Y3% are Yttrium doped carbon nitride and Y0 is pure carbon nitride respectively.

3. Results and discussion

3.1. XRD analysis

The texture properties of C_3N_4 and Y-doped C_3N_4 examined from x-ray diffraction (XRD) patterns. Carbon Nitride, Y-1% and Y-3% doped Carbon nitride samples shows the diffraction peaks at (100) and (002) plane, which confirms the initial texture of Carbon Nitride is mainly retained even after doping yttrium. Besides, the (002) diffraction peak was showing a slight shift from $2\theta = 27.75^\circ$ to 27.65° for Y-doped C_3N_4 as compared to the pure C_3N_4 , which is clearly shown in Fig.1. The XRD pattern shows the broad humps instead of sharp peaks this is because of the increased reaction time and the crystallite size slightly increases and the sharpness increases.



Fig. 1.XRD pattern of the Carbon Nitride and Yttrium-doped Carbon Nitride.

3.2. FT-IR analysis

The presence of vibration modes in the prepared samples were characterized by FTIR analysis. The absorption peaks are recorded in the range of 500 to 4000 cm⁻¹.



Fig. 2.FT-IR spectra of the Carbon Nitride and Yttrium-doped Carbon Nitride.

From Fig.2, it is clear that pure carbon nitride and 1% yttrium doped carbon nitride is quite similar when compared to 3% Yttrium doped carbon nitride. This means that, only a slight change occurs when 1% of yttrium is added to pure carbon nitride. The first peak for all the three samples takes place around the wave number of 3500 cm^{-1} . The highest trough takes place at the wave number 1500 cm^{-1} for all the three samples. This variation in the observed wavelength may be due to the difference in the particle size for the synthesized yttrium doped carbon nitride samples[4].

3.3. UV-Vis analysis

UV-Vis absorption spectra of undoped and Y-doped C_3N_4 are shown in Fig.3. The UV-Vis spectra of each Y-doped sample show an extended red shift and a significant absorption within 350-450 nm. The red shift of the adsorption edge in Y/C₃N₄ catalysts is attributed to the charge-transfer transition between the d-electrons of yttrium ion and the conduction or valence band of C_3N_4 . Using the Kubelka–Munk equation, the band gap (Eg) is evaluated and the

estimated E g values are 2.86 e V, 3.04 e V, 3.06 e V for Y0, Y1 and 3% doped C_3N_4 , respectively. From Fig.3, The absorption edge of C_3N_4 is higher compared to the Y-doped C_3N_4 , which ranges between the wavelengths 350-400 nm. And the absorption edge of Y-doped CN, ranges between the wavelength 400-450nm



Fig. 3.UV-Vis DRS of pure carbon nitride and Yttrium doped carbon nitride.

4. Conclusion

The Carbon nitride nano particles have been successfully synthesized and characterized by X-ray Diffraction, UV-Vis absorption spectroscopy, Fourier Transform Infrared Spectroscopy. The UV-Vis spectra of each Y-doped sample show an extended red shift and a significant absorption within 350-450 nm. The absorption edge of C_3N_4 is higher compared to the Y-doped CN. The small crystallites in the XRD show humps not sharp peaks, so when the reaction time increases, the crystallite size slightly increases and the sharpness increases. In future the as prepared samples can be used for for energy-storage applications.

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Uncapped SnO₂ QDs for Efficient Photocatalytic Degradation of Dye Reshma.T.S¹, Binaya Kumar Sahu^{1,2}, Arindam Das¹

¹Surface and Nanoscience Division, Indira Gandhi Centre for Atomic Research,

HBNI Kalpakkam, Tamil Nadu-603102

²School of Physical Sciences, National Institute of Science Education and Research, Bhubaneswar

Odisha-752050, India

tsreshma171@gmail.com

Abstract

 SnO_2 nanoparticles in size less than the Bohr exciton radius (QDs) were synthesized by a simple chemical method without capping agent. It is characterized by various techniques such as XRD,UV–Vis, Photoluminiscence (PL) and BET. The photocatalytic degradation of Methylene blue (MB) dye was investigated by synthesized SnO_2 and commercial TiO₂. Only complete degradation of MB is achieved by SnO_2 within 16 min with a rate constant of 0.13 min⁻¹. Such exceptional catalytic performance compared to TiO₂ is attributed to the crucial role of high defects density that delays the recombination process.

Structural and Thermal Properties of Bare Polypyrrole (PPy) and TiO₂/PPy Composite

Neha Luhakhra and Sanjiv Kumar Tiwari

Department of Physics and Materials Science, Jaypee University of Information Technology, Waknaghat, Solan (H.P.), 173234

*Corresponding author: neha1996luhakhra@gmail.com

Abstract

Current research article emphasize on structural and thermal properties of the polypyrrole and it's composite with TiO_2 . The composites were characterised using FTIR and TGA. FTIR revealed the presence of TiO_2 in polypyrrole matrix. The shift in N-H peak may be attributed by TiO_2 doping in the polypyrrole. The interactions between TiO_2 and polypyrrole enhanced its thermal stability as confirmed by TGA analysis of PPy and TiO_2 /PPy composite.

Introduction

Conducting polymers (CPs) are alternate arrangement of single and double bond throughout its structure. These alternate single and double bond arrangements are intrinsic property of CPs that defines its applications in various fields. CPs are the new class of materials and has been successfully utilizing for applications in electrical, optical and catalytic technologies [1, 2]. Although, bare conducting polymers have been utilizing in various applications, but its combination with metal oxides semiconductors can enhance their efficiency remarkably.

Composite of polypyrrole (PPy) with TiO_2 had many advantage over bare PPy for diverse range of applications [3, 4]. The structural and thermal properties are the basic properties of the material before applying for the any of the above mentioned applications. In the current study, FTIR was done to confirm the formation of PPy and its composite with TiO_2 in the PPy matrix. Thermal stability of the resultant materials was explored by using TGA.

Materials and Methods

Deionized water was used as solvent for the reaction. Pyrrole monomer, Titanium dioxide (40-50nm) and Iron(III) chloride anhydrous and sodium dodecyl sulphate were purchased from Alfa Aesar, SRL and Merk, India respectively. All the procured chemicals used in this study were of analytical grade and used without further purification.

The synthesis of PPy and its composite with TiO_2 doping was achieved using chemical oxidative polymerization [5]. Fig. 1 shows flow chart of synthesis steps of PPy and PPy/TiO₂ composite.



Fig. 1. Flow chart representing the synthesis of PPy and TiO₂/PPy.

Result and Discussion

Fourier transformation infrared spectroscopy (FTIR):

Fig. 2(a) represents the FTIR transmittance spectra of bare polypyrole (PPy) and TiO₂ composite with PPy. Fig. 2(b) shows the prominent peak at 1538 cm⁻¹ and a diminished peak at 1449 cm⁻¹ which corresponds to stretching vibration of C=C and aromatic C–N in the pyrrole respectively.





Fig. 2. FTIR Spectra of (a) Polypyrrole(PPy) and TiO₂/PPy, (b) extended scale spectra from 1800 cm^{-1} to 500 cm^{-1}

The small peaks at 1166 cm⁻¹, 1033 cm⁻¹ 896 cm⁻¹, 962 cm⁻¹ and 775 cm⁻¹ corresponds to =C-C stretching, C-H deformation, C-H out of plane stretching, C-H stretching and C-C bending (interring) respectively [4]. There was no shifting in these peaks of TiO₂ doped polypyrrole and bare polypyrrole as it can be seen in Fig. 2(b). Furthermore, there were peaks at 1348 cm⁻¹, 665 cm⁻¹ and 600 cm⁻¹ representing Ti-O, Ti-O-Ti bending (inplane and out-plane) and scratching in TiO₂/PPy [6].

Fig. 2(a) shows that the band at 3430 cm⁻¹ corresponding N-H stretching got adjusted to 3415 cm⁻¹ by doping of TiO₂ into the polymer matrix. The reason for this shifting could be the presence of TiO₂ nanoparticles near to the N-H bond of the polypyrrole and hence influenced its vibrational frequency. The N-H peak position ratio of PPy and TiO₂/PPy was 1.0044. The calculated ratio of N-H vibration of PPy to TiO₂/PPy was 1.0245. These experimental and calculated values of PPy and TiO₂/PPy were in close vicinity. This indicated that TiO₂ nanoparticle doped near to the nitrogen of PPy and effects its vibrational frequency.

TGA (Thermo gravimetric Analysis)

Thermal characteristics of the synthesized samples (PPy and TiO₂/PPy) were studied by TGA in the inert atmosphere of N₂. Fig. 3 shows that there was approximately 9% weight loss at 100°C temperature is observed because of presence of volatile and water content in the sample. However, this weight loss was same for TiO₂/PPy and PPy.

There was a weight loss of 17% from the 100°C to 300°C. However, this weight loss can be due to degradation of un-polymerised pyrrole (monomers), small length polymers (dimmer, trimmer etc.), breakdown of long chain of polypyrrole and impurities. Interestingly TiO_2/PPy composite degraded only 8% from 100°C to 300°C. The reason

for this may be the interaction between TiO_2 and polypyrrole which eventually increased its thermal stability. Furthermore, there was huge weight loss of 74% of PPy beyond 300°C and can be attributed by burning of long length or heavy molecular weight fragments of PPy whereas there was only 55% weight loss in TiO₂/PPy composite up to temperature 600°C. Additionally, there was 100% weight loss of PPy at 600°C whereas in case of TiO₂/PPy it was about 74% [7]. Hence, it can be conclude that conjugation of TiO₂ in polypyrrole increased the thermal stability of polypyrrole.



Fig. 3. TGA of PPy and TiO₂/PPy

Conclusion:

In summarized way it can be concluded that there was successful conjugation of TiO_2 in polypyrrole matrix. FTIR data reveal that N-H shifting was due to the interaction between TiO_2 and polypyrrole. Further, the doping of TiO_2 increased thermal stability of polypyrrole as reveal by TGA analysis.

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Structural and Optical properties of $M_{0.01}Ni_{0.99}O$ (M = Li, Na and K)

Anupama, Monika Saini, Swati, Rajni Shukla*

Dept. of Physics, Deenbandhu Chhotu Ram University of Science and Technology, Murthal, Sonepat, 131039

*Corresponding author- rajnishukla3871@gmail.com

Abstract:

 $M_{0.01}Ni_{0.99}O$ (M = Li, Na and K) samples were synthesized via sol-gel process. X-ray diffraction (XRD) spectrum of synthesized material confirmed the formation of metal oxide nanoparticles. WH-UDM (Williamson Hall Plot Uniform Deformation Model) has been used to calculate the crystallite size of the synthesized materials. The optical properties of Lithium, Sodium and potassium doped Nickel Oxide, have been done using UV-Vis and Photoluminescence (PL) study.

Introduction

Metal oxide exhibit diverse properties resulting in wide range of applications. Nickel oxide is a p-type semiconductor which is chemically stable with dynamic optical, electrical, and magnetic properties [1]. Doping of nanomaterials with Li, Na and K etc. have been reported to improve properties of these material to a considerable extent. The doping of group-I monovalent atoms, such as Li, Na and K increases Ni vacancies in NiO and making them suitable for application in electrochromic device, electrode, sensor, electromagnetic shielding, catalyst and supercapacitor [1-3]. Thereby to design a new smart composite material doping of NiO with Li, Na and K has been done with conducting polymers like aniline, pyrrole, thiophene etc [3].

Experimental

 $M_{0.01}Ni_{0.99}O$ (M = Li, Na and K) has been synthesized using sol-gel method [4]. Chemical reagents utilized for synthesis of material are extra pure analytical grade (AR). The synthesized samples were calcinated at 400°C temperature for 2 hours.

Results and Discussion

The structural study of synthesized materials has been done using X-Ray diffraction (XRD). The Rigaku Ultimate-IV, Japan instrument, at the rate of 4°/min in the range of 10° to 80° diffractometer was used. The XRD peaks of Li_{0.01}Ni_{0.99}O are at angles (2θ) 37.24°, 43.28°, 62.88°, 75.44°, 79.43°; Na_{0.01}Ni_{0.99}O are at angles (2θ) 37.24°, 43.29°, 62.89°, 75.44°, 79.41° and; K_{0.01}Ni_{0.99}O are at angles (2θ) 37.26°, 43.30°, 62.90°, 75.45°, 79.43°. The XRD peaks match with the JCPDS card no. 73-1523 shows cubic lattice structure of M_{0.01}Ni_{0.99}O (M = Li, Na and K). It has been reported that size confinement and intrinsic strain, broaden the XRD peaks. WH method considers the effectiveness of induced strain on XRD peak. The crystallite size and microstrain of the sample both are taken into consideration in WH Plot [5]. The crystalline size broadening is represented by:

$$\beta_{size} = \frac{k \cdot \lambda}{D \cdot \cos \theta} \qquad \qquad a)$$

The microstrain (β_{strain}) induced broadening is because of size confinement, distortion and crystal imperfection and is mathematically given as:

$$\beta_{strain} = 4\varepsilon. \tan \theta$$
 b)

where ε is the induced strain. Considering the crystallite size and microstrain to be independent and additives, it can be written as:

 $\beta_{hkl} = \beta_{total} = \beta_{size} + \beta_{strain} c$) where, β_{hkl} is FWHM intensity of *hkl* planes.



WH-UDM (Williamson Hall Plot Uniform Deformation Model) supposed crystal as isotropic in nature [5]. WH-UDM had taken into consideration the uniform nature of microstrain and from equation a) and b) the total broadening is given as:

$$\beta_{hkl} = \frac{k \lambda}{D.\cos\theta} + 4\varepsilon \tan\theta \qquad d)$$
or
$$\beta_{hkl} = \frac{k \lambda}{D.\cos\theta} + 4\varepsilon \sin\theta \qquad d$$

$$\cos\theta \cdot \beta_{hkl} = \frac{\kappa \cdot \lambda}{D} + 4\varepsilon \cdot \sin\theta \qquad e)$$

Equation e) represents the WH-UDM. The $(4 \sin \theta)$ Vs $(\cos \theta . \beta_{hkl})$ plot corresponding to each (hkl)peak is linear. Intercept and slope of corresponding axis gives induced crystallite size and microstrain respectively [5].

Table 1. Crystallite Size and Strain of Li_{0.01}Ni_{0.99}O, Na_{0.01}Ni_{0.99}O and K_{0.01}Ni_{0.99}O evaluated by WH-UDM

Material Name	Crystallite Size [D (nm)]	Strain [ɛ]
Li _{0.01} Ni _{0.99} O	37.73	1.96 x 10 ⁻³
Na _{0.01} Ni _{0.99} O	31.79	2.14 x 10 ⁻³
K _{0.01} Ni _{0.99} O	29.25	2.28 x 10 ⁻³

UV-Vis absorption spectra reveal the optical properties of the synthesized materials [6, 7]. The optical absorption peaks found at ~334.5 nm, \sim 335.5nm and \sim 336.5 nm for M_{0.01}Ni_{0.99}O (M = Li, Na and K) samples respectively are shown in Fig. 3. The energy band gap of nanoparticles has been calculated using Tauc relation:

 $(\alpha(h\nu))^n = A (h\nu - E_g)$

f) Where, α is absorption coefficient, hv is photon energy, A is constant, Eg is optical band gap, n is the number characterizing the nature of the transition process; n = 2 for the direct transition and n = 1/2 for indirect transition [6, 7]. From the curve the band gap of the $M_{0.01}Ni_{0.99}O$ (M = Li, Na and K) samples has been found to be ~2.95 eV, ~3.18 eV and ~3.44 eV respectively shown in Fig. 4. The samples having higher crystallite size were found to have low optical energy band gap, which means blue shift of band energy from Li_{0.01}Ni_{0.99}O to K_{0.01}Ni_{0.99}O.



Room temperature photoluminescence (PL) emission spectrum of $M_{0.01}Ni_{0.99}O$ (M = Li, Na and K) nanoparticles have broad and intense peak at 466 nm, 467 nm and 468 nm respectively with an excitation wavelength of 300 nm. These peaks arise because of transitions involving 3d⁸ electrons of Ni²⁺ ions [5-7]. Occurrence of these intense and broad peaks indicates the direct and higher recombination rate of electrons and holes. These peaks show blue emission in PL Spectra (Fig. 5), confirm the presence of defects (Li ion, Na ion and K ion) in NiO lattice.



Conclusion

XRD shows cubic lattice structure of synthesized materials. Crystallite size decreases (37.73nm> 31.79nm>29.25nm) while the strain increases from Li_{0.01}Ni_{0.99}O to K_{0.01}Ni_{0.99}O. UV-Vis shows direct band gap that increases from Li_{0.01}Ni_{0.99}O to K_{0.01}Ni_{0.99}O (~2.95eV<~3.18eV<~3.44eV) with shift in absorption peaks Li_{0.01}Ni_{0.99}O to K_{0.01}Ni_{0.99}O (~334.5nm<~335.5nm<~336.5nm) which is because of decrease in crystallite size due to electron confinement. PL showing blue emission in spectra confirms the presence of defect in the crystal lattice. Thus makes these materials suitable for applications like solar cell, LEDs and photocatalysis etc.

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Enhancement in Field Emission behavior of RGO emitter in N₂ ambience under high vacuum conditions

Sanjeewani R. Bansode¹, Mahendra A. More¹, Rishi B. Sharma^{1*}

¹Centre for Advanced Studies in Materials Science and Condensed Matter Physics, Department of Physics, Savitribai Phule Pune University, Pune 411007, India.

*Corresponding author: rbsharma111@gmail.com, rbs@physics.unipune.ac.in

Abstract

A facile approach to synthesize Reduced graphene oxide (RGO) nanosheets in large scale through thermal evaporation of exfoliated graphite oxide precursor is reported. We have investigated the gas dependent field emission (FE) behavior of the RGO emitter under ultra high vacuum (UHV, $\sim 1 \times 10^{-8}$ mbar), and N₂ base pressure of $\sim 1 \times 10^{-6}$ mbar. Interestingly, the RGO emitter exhibits relatively lower values of turn-on and threshold fields in N₂ ambience. The observed enhanced electron emission behavior in N₂ ambience is attributed to modulation of the work function of RGO emitter.

The Electronic properties of Germanene nanoribbon doped with boron and nitrogen : Ab initio study

Premlata Narwaria¹, Satyendra Singh Chauhan², A.K.Shrivastava³

¹Jiwaji University, Gwalior, MP, 474001, India, ²Institute of Technology & Management, Gwalior, MP, 474001, India ³Jiwaji University, Gwalior, MP, 474001, India

*Premlata Narwaria : <u>narwaria.premlata@gmail.com</u>

Abstract

Germanene nanoribbons (GeNRs) possess electronic properties similar to carbon based materials like graphene. The effective boron and nitrogen substitutional doping at edge and centre site alters electronic properties of zigzag germanene nanoribbons (ZGeNRs). The study conducted using spin unpolarized density functional theory (DFT) calculations. We have calculated the total energy, fermi energy and band gap. The substitutional boron and nitrogen atoms changes property of material from semi-metal to metallic in ZGeNR. These materials have potential application in spintronic devices.

Introduction

Last three decades have seen many advancements in nano-materials research. Initially the carbon based materials like fullerenes and graphenes, were the focus of nano-materials research. The research was centered on carbon based materials due to their unique honeycomb structures. Last one decade witnessed shift of nano-materials research from carbon based materials to other single atom sheets having graphene like characteristics such as silicon carbide and germanane etc. Germanium is a IVth group element and it is two dimensional honey comb structure[1]. Germanene (Ge) is a one-atom thick sheet of H terminated germanium atoms structured similar to graphene. The single layer of fully hydrogenated germanium was also made up which is known as Ge [2]. Ge possess the extra oridinary characteristics like massless fermion behaviour, high mobility and spin-orbit coupling which draw attention of researchers for investigating use of Ge in high performance nano-devices [3]. Ge has excellent physical properties of quantum spin Hall effect and massless Dirac fermions which attracted attention of research fraternity for finding new avenues of material science [4]. Study of geometries, electronic and magnetic properties and stabilities of fully and partially hydrogenated GeNRs of both type of edge terminations zigzag and armchair by applying DFT calculations, it was observed that irrespective of edge chirality, fully hydrogenation can efficiently widen the band gap of GeNRs and band gap decreases with increase in ribbon width [5]. Band structure, density of states, geometrical stability and quantum transport properties of armchair GeNR (AGeNR) doped with various elements like As, Bi, Sb was studied by applying DFT and NEGF which revealed that p-type dopants make the Fermi level to shift towards valence band (VB) and n-type dopants like Ga, In and Tl make the Fermi level shift towards conduction band (CB). Negative Differential Resistance observed for each doped AGeNR [6]. Band structure analysis of Al doped zigzag GeNR suggest that unlike semimetallic behaviour of pristine ZGeNR, Al doped ZGeNR behave metallic which makes it useful in nano-scale interconnects [7]. Band gap of 7AGeNR was found to be 0.48eV which presents its semiconducting behaviour. Band gap of 8AGeNR was found to be 0.02eV which reflects its semimetallic behaviour. Doping of 7AGeNR by elements like Pt and Sn makes no effect on its semiconducting behaviour. However, doping by elements like In, Ag and Au result in transition from semiconducting to metallic. Doping in 6AGeNR transform its behaviour from metallic to semiconducting [8]. In the present work we intend to study the structural and electronic properties of boron and nitrogen doped ZGeNR at different two positions as shown in Fig. 1.

Computational Methodology

Based on first principles methods spin unpolarized DFT calculations are performed using ab initio code package ATK VNL. Brillouin zone integration is performed using Monkhorst pack parameters with a regular k-point grid 1*1*100 for electronic relaxation for Single layer of zigzag GeNRs. Double zeta polarization (DZP) basis orbitals were used for 6ZGeNR and energy cut off of 2500 Ry. To balance between calculation efficiency and accuracy the mesh cut off of germanene atom is 150Ry. The exchange correlation functional is the spin unpolarized with local density approximation (LDA).The Ge-Ge, Ge-H, B-Ge, B-H, N-Ge and N-H bond lengths are set to be 2.47Å,1.51Å, 2.19Å,1.40Å,2.10Å and 1.30Å.



Fig. 1. Geometry optimization of 6GeNR pristine with edge and center doped boron and nitrogen atoms



Fig. 2. Band structure of 6GeNR (a) Pristine (b) edge doped B (c) edge doped N (d) centre doped B (e) centre doped N

Result and Discussion

Electronic properties of pristine as well as doped B and N in ZGeNRs were investigated as shown in Fig.1. We have also calculated the Fermi energy, Total energy and Band gap as shown in table 1. When boron and nitrogen atom doped at edge site and centre site, the total energy value is same for both sites. Fig. 2 shows nearly semiconducting behaviour of pristine 6ZGeNR and nitrogen doped ZGeNR at center site and edge site. With doping of boron atom at edge site the electronic behaviour transforms from semiconducting to metallic while boron doping at center site makes no change in its semiconducting behaviour. The electronic structures closely matches with that of previously reported literatures.

 Table 1. The value of Total energy, Fermi energy and Band
 gap

Element	Fermi	Total	Band
	Energy	Energy	Gap
	(eV)	(eV)	(eV)
6GeNR_Pristine	-3.81	-1706.60	0.67
6GeNR_Edge doped B	-4.29	-1505.70	0.27
6GeNR_Edge doped N	-4.01	-1697.47	0.49
6GeNR_Centre doped B	-4.10	-1505.63	0.50
6GeNR_Centre doped N	-3.75	-1697.00	0.68

Conclusion

It was observed in the study that pristine ZGeNR has nearly semiconducting behaviour. Doping of boron at edge sites changes the behaviour from semiconducting to metallic. Doping of nitrogen at edge sites and center sites makes no changes in its semiconducting behaviour. Doping of boron at center too makes change in behaviour. We further observed that boron and nitrogen doping reduce the band gap except nitrogen doping at center site. These materials have application in spintronic devices.

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Synthesis and Characterization of Monodispersed Polystyrene Spheres and Hydrophilic Sulfonated Polystyrene spheres.

Sree Sanker S S*, Subin Thomas and K N Madhusoodanan

Department of Instrumentation, Cochin University of Science and Technology, Kalamassery, Kerala, India, *Corresponding author: sreesanker@cusat.ac.in

Abstract

The synthesis of monodispersed polystyrene spheres has got plenty of attention nowadays. Controlling the particle size is the most crucial task in the synthesis route. This study aims to synthesize monodispersed cationic polystyrene spheres using the single-step facile method. We could control the size of the particles by varying the amount of monomer used. We found that the amount of monomer got proportional dependence on the size of spheres. It was found that the synthesized PS spheres to be highly hydrophobic. This hydrophobicity may be a limitation in many cases when sensing applications come into play. We can overcome this limitation by modifying the polystyrene spheres by a method called sulfonation reaction. After sulfonation, polystyrene spheres are hydrophilic and can be used as templates for sensing applications.

Introduction

Polystyrene is an aromatic polymer with benzene polymeric backbone. Monodispersed the as polystyrene spheres have gained remarkable attention because of their excellent properties, making them a good candidate for many applications[1]. Many approaches of synthesis have been reported Polystyrene is found to be highly [2],[3],[4]. hydrophobic. The hydrophobicity may be a limitation on the sensing applications of polystyrene spheres are concerned. By modifying the benzene ring backbone of polystyrene with sulfonate groups will make them hydrophilic. The addition of the sulfonate functional group to the organic compound is the sulfonation reaction. Different approaches to sulfonation reactions have been reported so far[5],[6],[7],[8].

This study reports the synthesis of monodispersed polystyrene spheres using a single-step approach and hydrophilic sulfonated polystyrene spheres using sulfonation reaction. The sulfonation reaction is performed by heating the PS spheres in Con. H_2SO_4 at an elevated temperature. We have investigated the effect of monomer concentration on the particle size of synthesized PS spheres. Several characterizations were performed to study morphology, size distribution and chemical composition of spheres.

Experimental Method

A. Materials Required

Several chemicals were used for the study. Styrene monomer (C_8H_8), Potassium peroxodisulfate (KPS), Sulfuric acid (H_2SO_4), Sodium hydroxide (NaOH) were purchased from Sigma Aldrich, USA. Double distilled water was used for the total synthesis. The monomer was cleaned using a ten molar NaOH solution and an equal amount of water before use.

B. Synthesis of monodispersed polystyrene spheres

The present study involves the synthesis of monodispersed polystyrene spheres using emulsifier-

free emulsion polymerization. The entire synthesis was conducted on a three-neck flask equipped with a reflux condenser in an inert atmosphere. In a typical synthesis, 50 ml distilled water was taken in the flask and stirred at 400 RPM for 30 minutes at an elevated temperature of 80°C. Subsequently, inhibitor removed styrene (0.5 ml - 3.0 ml) is added to the system and kept for another 30 minutes. After ensuring homogeneous monomer mixing with the aqueous solution, previously mixed initiator solution (KPS) is added to initiate the polymerization reaction. The reaction system was maintained for 20 hours to complete the polymerization reaction [9]. Figure 1 shows the schematic representation of the experiment setup. The system was brought to room temperature to terminate the reaction[10]. The colloidal suspension was filtered to remove the unreacted byproducts and centrifuged several times before use.



Fig. 1. Schematic representation of apparatus used for the synthesis of PS spheres.

A. Synthesis of sulfonated polystyrene spheres

Hydrophilic sulfonated polystyrene spheres were synthesized by performing sulfonation reaction on the synthesized PS spheres[6]. The centrifuged PS colloidal suspension (3wt%) was taken and mixed with Con in a typical reaction. H₂SO₄. Ultrasound sonication was performed for 5 minutes to ensure proper mixing. Subsequently, the solution was heated at 40^oC for 1-5 hours. After completion of the reaction, the suspension was centrifuged. Since H₂SO₄ is denser, it will remain at the bottom of the tube. It can be easily separated using a pipette. The residue was taken and cleaned with ethanol[6], [11].

A. Characterization of polystyrene spheres

The particle size and morphological behaviour were characterized using a field-effect scanning electron microscope (CARL ZEISS FESEM). To ensure the particle size, dynamic light scattering (Horiba SZ100) was also performed. For studying the chemical compositions of PS spheres, the samples were evaluated with Fourier transform infrared spectroscopy analysis (FTIR). To investigate the hydrophilicity of the samples, contact angle measurement (RAME-HART standard goniometer) was also done.

Result and discussion

A. Synthesis of monodispersed polystyrene spheres

The effect of monomer amount on particle size was studied. Table 1 gives data on the effect of the amount of monomer on particle size. It was found that, as the amount of monomer increases, mean particle size also increases. Figure 2 shows the FESEM images and DLS results of synthesized polystyrene spheres. Good monodispersity of particles and spherical shape of spheres were observed in all the cases. When the morphology of spheres was concerned, the surface of the spheres was smooth, and the particle boundaries were well defined. The contact angle measurement image shows that the PS spheres are highly hydrophobic. Table 1 Amount of mor

. 1 .

Table 1. Amount of monomer and particle size	
Amount of styrene	Mean particle size
(ml)	(nm)
0.50	215
1.50	240
2.75	280



Fig. 2. FESEM and contact angle images of Polystyrene spheres with different sizes.

B. Synthesis of sulfonated polystyrene spheres

FESEM and contact angle images of the sulfonated PS (SPS) spheres are given in figure 3. The morphological study shows that the surface of the spheres got rough compared to the pristine PS spheres. Also, the particle boundaries got less defined as the sulfonation was carried out. From the contact

angle image, it is evident that after performing sulfonation reaction, PS spheres got hydrophilic. FTIR results of the samples show the presence of sulfonate functional groups in the sulfonated PS sample compared to the PS sample. Figure 4 shows the FTIR spectra of synthesized PS and SPS samples.



Fig. 3. FESEM and contact angle images of sulfonated Polystyrene spheres



Fig. 4. FTIR results of (a) PS and (b) SPS samples Conclusion

This paper has reported a facile approach to synthesize monodispersed polystyrene spheres the emulsifier-free emulsion polymerization technique. Precise control on particle size can achieve by varying the monomer amount. Synthesized particles show good monodispersity, spherical appearance and high hydrophobicity. To make the particles hydrophilic, a sulfonation reaction was done on the synthesized PS spheres. Characterization of SPS spheres shows the evidence of sulfonation reaction and subsequent hydrophilicity of spheres.

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Influence of Ni doping on the structural and ferroelectric properties of BaTiO₃ solid solution

M. Arshad^{1*}, Wasi khan¹, M. Abushad¹, M. Nadeem² and Shahid Husain¹

¹Department of Physics, Aligarh Muslim University, Aligarh-202002, India

²Department of Applied Physics, Z.H. College of Engineering & Technology, Aligarh Muslim University, Aligarh-202002, India

*Corresponding author: arshadsheikh271@gmail.com

Abstract

In the present study, we have synthesized undoped and Nickel doped BaTiO₃ ceramics with their compositional formula BaTi_{1-x}Ni_xO₃ (x=0 and 0.08) using sol-gel auto combustion process. X-ray diffraction technique were used for the phase purity confirmation. Rietveld refinement analysis ensures that undoped sample are in tetragonal phase within *P4mm* space group while doped sample have both tetragonal and hexagonal phase within *P4mm* and *P6₃/mmc* space group. It means that the transformation of phase from tetragonal to hexagonal is strongly depend upon the Nickel doping. The average crystallite found to be in the range of 37-51 nm using Scherrer's equation. Various unit cell parameters were determined through Rietveld refinement studies. Ferroelectric measurements demonstrate that the pristine sample has maximum values of remnant polarization (*P_n*) and maximum polarization (*P_m*) which decrease linearly with the increase in Ni doping suggesting doped samples suggesting system is going towards centrosymmetric phase.

Unraveling the Enriched Photoluminescent Tunability in Heteroatom Doped Cdots Derived from Folic Acid

Akhila Murali J¹, Sibi K S^{*}, Subodh G^{*}, and V Biju^{*}

^{1,*} Department of Physics, University of Kerala, Kariavattom, Thiruvananthapuram - 695581

*Corresponding author: sibi@keralauniversity.ac.in, gsubodh@gmail.com, and bijunano@gmail.com

Abstract

Broad emission spectrum of Cdots is indispensable in detection applications, since the entire spectrum of Cdots can be detected. We synthesized N, F- heteroatom doped Cdots derived from folic acid through a simple hydrothermal treatment. They exhibited a broad emission spectrum with a FWHM of \sim 70 nm. FTIR spectrum confirms the presence of oxygen functional groups in the as synthesized CDs. Considering the fluorescence origin, it was understood that the blue emission is from single emission center and the multi-exponential decay fitting further confirms the presence of several emission bands within a single center. The NH₄OH doped Cdots exhibited a redshifted emission from bare Cdots.

Introduction

Carbon dots (Cdots) with tunable photoluminescence are promising candidates for biosensing and bioimaging applications which require long wavelength region of visible spectrum¹. The fascinating property of carbon dot is that they can light up our invisible biological processes since being biocompatible and non-toxic. The tunable fluorescence emission of Cdots find applications in the field of sensors, catalysis, optronics etc. It is relatively easier to modify the surface of cdots and thereby tune its emission color. This means they can be doped with heteroatoms or other passivating agents which in turn affect the electronic levels and thereby cause changes in luminescence mechanism.

The unique property of carbon dot is the 'structural memory' of the carbonaceous precursor. Recently, Liu *et al.* synthesized Cdots from folic acid with a high quantum efficiency of 94.5% ². Folic acid is one of the B vitamins, which consists of rich oxygen and nitrogen functional groups. Since it helps in regenerating healthy cells, folic acid is one way to track the cancer cells in human body. From this background, we synthesized folic acid derived carbon dots and tried to manipulate their surface by incorporating heteroatoms, fluorine (F) which is seldom reported to the best of our knowledge and the commonly doped nitrogen (N).

Experimental Section

Materials: Folic Acid (FA), Ammonium fluoride (NH₄F), Ammonium hydroxide solution (NH₄OH), Lithium fluoride (LiF), Tin fluoride (SnF₂), and deionized water were purchased from Sigma-Aldrich.

Synthesis: The folic acid derived carbon nanodots (FCNDs) were synthesized via hydrothermal process.

Folic acid was dissolved in 10 mL deionized water and it is sonicated for 10 minutes for obtaining a homogenous solution. The solution was transferred into a Teflon lined stainless autoclave. The sealed autoclave was heated for 6 hours at 180 °C in a hydrothermal furnace. A dark golden yellow color solution was obtained cooled naturally and centrifuged at 5000 rpm for 20 minutes. Finally, the obtained solution was filtered to remove aggregates. NH₄F, NH₄OH solution. LiF and SnF_2 were stoichiometrically weighed and added with folic acid to prepare FFCND, NFCND, LFCND, and SFCND respectively.

Characterization: UV-Vis Absorption Spectroscopy UV-Vis Spectrophotometer), (JASCO V-750 Photoluminescence Spectroscopy (Fluorolog TCSPC Horiba Scientific), X-ray diffraction analysis (Bruker D8 Advance diffractometer), Raman Spectroscopy (Horiba Lab RAM HR Evolution), FTIR spectroscopy (JASCO FT/IR 6800 Interferometer), X-rav Photoelectron Spectroscopy (ESCALAB XI+A1528), Fluorescence Life time analysis, Quantum Yield Measurement, and Scanning Electron Microscopy technique were used for the characterization of the prepared samples.

Results and Discussions

The optical properties of the as-prepared CDs were shown in Fig.1 and Fig. 2. The absorption spectrum of FCND and FFCND showed three distinct peaks at ~ 230, ~280, and ~ 330 nm arising from the 1Π - Π ^{*} transition of sp² domains of C=O, absorption of aromatic Π system of C=O bond, and n- Π ^{*} transition respectively³. The peak at ~ 230 nm disappears for other three Cdots. For NFCND, there is a long wavelength absorption band at ~540 nm which may be

a low energy state that originates from the surface functional groups. The photoluminescence (PL) spectrum of CDs was located in the blue-cyan region of visible spectrum. By varying the amount of folic acid, a progressive redshift was observed for emission peaks of bare Cdots with an increase in the concentration of FA, by an amount ~ 80 nm. NH₄F, and NH₄OH doped Cdots produce longer wavelength emission (green emission) on higher wavelength excitation. It can be attributed to the increase of sp^2 domains and the delocalization of valence electrons. But due to the electro positivity of Li and Sn, LFCND and SFCND samples does not show any observable greenish emission. For 380 nm excitation, NH4OH doped sample show a redshifted emission (~30 nm) compared to bare Cdots. Being an immediate neighbor of carbon and an electronegative element, N-doping may substitute the core state carbon which induces an upward shift in the fermi level and electrons in the conduction band. This will further enhance PL emission. The introduction of nitrogen produces new states that will trap electrons and enhances radiative recombination⁴. The large stokes shift ~140 nm (8.8 eV) was observed for its broad emission spectra. It improves the detection sensitivity as the complete spectra of Cdots can be detected⁵.





Fig. 3. SEM image of FCND.

According to previous reports, surface groups are the main contributors of optical properties. FTIR spectra unveil the N, F-doping and functional groups present in the carbon dots. The stretching vibrations of -OH and NH₂ are observed in the range 3100-3500 cm⁻¹.

The semi-ionic C-F and covalent C-F bond in the range 1000-1300 cm⁻¹ indicates that the fluorine get bonded with carbon. The Raman spectra of the samples excited at 735 nm is recorded for the structural analysis. The deconvolution of main peak using Lorentzian function shows a high intensity D band which indicates the presence of sp³ defects within sp² cluster. The other one around 1897 cm⁻¹ is associated with folic acid residue. The Scanning Electron Microscopic image of Cdots shows a reasonable size distribution about 3-7 nm range (Fig. 3). The XPS analysis shows that all these samples were mainly composed of C, O, H, and N. The difference in the PL properties may be related to the oxidized functional groups. The variation in the green luminescence is consistent with the percentage of the oxidized groups from the XPS analysis. It is generally believed that green luminescence from carbon dots originates from the defect states with oxygen containing functional groups. The small shift in the blue emission of Cdots means that they possess a similar emission center, but with different intensities or these dots consists of several emission states from specific emission center. It was supported by the TCSPC result, wherein multi-exponential decay was observed.

Conclusions

We have synthesized hetero-atom doped carbon dots derived from folic acid. N, and F doped Cdots emitted green fluorescence light under the excitation of blue light. N-doping induces redshift in the PL emission of Cdots. The broad emission spectra of NFCNDs demonstrate the great potential of Cdots in detection sensitivity.

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Tuning Specific Absorption Rate Of Fe₃O₄ By Forming An Inverted Core/shell NiO@ Fe₃O₄ For Effective Magnetic Hyperthermia.

S P Tsopoe¹, C Borgohain², J P Borah^{1,*}

¹Department of Physics, National Institute of Technology Nagaland, Dimapur, Nagaland-797103, India ²Central Instrumentation Facility (CIF), Indian Institute of Technology Guwahati, Guwahati 781039, India

*Corresponding author: jpborah@rediffmail.com

Abstract

One of the leading causes of death in today's world is cancer and it has become a major problem worldwide. Hyperthermia is one of the emerging cancer therapies that can effectively kill the tumour cells. In this work, we have tuned the magnetic properties of Fe_3O_4 (F) magnetic nanoparticles (MNPs) to enhance the heating efficiency through magnetically exchange coupling at the interface of the two materials by forming an inverted core@shell (CS) nanostructure NiO@ Fe_3O_4 (Ni@F) and we have reported higher specific absorption rate (SAR) for the CS over the single material F attributing to the interface exchange coupling. The formation of CS nanostructure is confirmed through TEM image and the magnetic study reveals an exchange bias effect (EBE) phenomenon which is an evident of strong magnetically exchange coupling at the interface of the CS nanostructure.

Photocatalytic performance of visible light irradiated Tin disulfide (SnS₂) nanoparticles prepared with different aged times

R. Vidhya^{1*}, R. Karthikeyan², R. Gandhimathi³, K. Neyvasagam⁴ ¹Department of Physics, V.V.Vanniaperumal College for Women, Virudhunagar, India. ²Department of Physics, Anna University Regional Campus, Tirunelveli, India ³<u>https://orcid.org/0000-0003-0013-962X</u>

⁴ Department of Physics, The Madura College, Madurai, India * Corresponding author: E-mail: vidhya3vc@gmail.com

Abstract: It is proposed to enhance the photocatalytic performance of Tin disulfide nanoparticles by changing the aging time for the preparation of the samples. The effect of aging time on the structural, optical, and photo catalytic properties of the SnS_2 nanoparticles were investigated. The powder X-ray diffraction analysis study reveals that the prepared samples belong to the hexagonal crystal system and displays that with the increased synthesis time, the crystallinity of the prepared samples have been improved greatly. Likewise, the UV-Visible study reports that with the increased aging time, the absorption edge of SnS_2 nanoparticles has been extended to visible region with the absorption cut off around ~570nm (band gap 2.17eV). The extension in the absorption edge promotes the photo catalytic performance of the SnS_2 nanoparticles significantly with the utilization of less energy for electronic transitions. Thus, the SnS_2 samples obtained with different aging periods demonstrate the nanospheres with bigger crystallite size, narrower bandgap and enhanced catalytic efficiency and these qualities make them as an efficient material for environmental air and water filtration and purifications.

Rough Bimetallic Substrate for Surface -Enhanced Raman Spectroscopy Application

Savita Rani¹, A.K.Shukla²

Laser-Assisted Material Processing and Raman Spectroscopy Laboratory, Department of Physics, Indian Institute of Technology, Hauz Khas, Delhi 110016, India *Corresponding author: phz188348@physics.iitd.ac.in

Abstract

For analytical application in the field of sensors to be used in the point of need, low-cost Surface-enhanced Raman spectroscopy (SERS) substrate using rough copper as a base, are an alternative. Bimetallic nanostructures are getting more attention due to high sensitivity, high density of hot spots and high enhancement factor. Our novel approach is based on the deposition of silver nanorods (AgNRs) on rough copper that allowed for the determination of trace levels of Rhodamine 6 g with a limit of detection of 10^{-4} M. These results show the promise of a solid substrate decorated with AgNRs for SERS applications.

Optical And Structural Properties Of Tb:CePO₄ Nanowires S. Tripathi^{1,a)}, Y. Kumar^{1,2}, Mangla Nand^{1,2}, R. Jangir³, U. Deshpande⁴, A. Roy⁵ and S. N. Jha^{1,2}

¹Beamline Development and Application Section, Bhabha Atomic Research Centre, Mumbai, India
²Homi Bhabha National Institute, BARC Training School Complex, Anushaktinagar, Mumbai, India
³Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore, India
⁴UGC-DAE Consortium for Scientific Research, Indore Centre, Indore, India

⁵ High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai, India

^{a)} Corresponding author: shilpatripathi75@gmail.com

Abstract

Pure and 5 wt% Tb doped CePO₄ nanomaterials (nanowires) were synthesized using chemical route and were characterized for their optical and structural properties. Thesenanomaterials wereprepared using of Ce and Tb nitrates as starting materials. FromFTIR data, it was confirmed that pure CePO₄ has formed without any FTIR sensitive chemical impurity and contains the desired PO_4^{3-} tetrahedrons which are characteristics of the phosphate group.UV-Visible spectrum also shows characteristic peaks from monoclinic CePO₄ structure and corresponding absorption versus energy plot provided the values of bandgaps to be ~3.6 eV (pure) and ~3.9 eV (doped) confirming the modifications upon doping. The experimental work presented here would be helpful in understanding the photoluminescence behaviour and its dependence on doping amount in future.

Introduction

For luminescence applications of CePO₄ phosphor, we require Tb³⁺ ions as the dopant material because it acts as an activator in this host material (CePO₄) and shows emission in the wavelength band ranging from visible to NIR depending upon the amount of doping. The origin of this luminescence in Tb: CePO₄ material has been of interest ever since its application as fluorescent material has been realized. In pure CePO₄, the luminescence is known to occur due to transitions from 4f-5d, while in Tb doped CePO₄, the luminescence in Tb³⁺ ions is excited by Ce³⁺ ions [1].

Nanomaterials, in particular nanowires (NWs) present a novel way to produce tunable luminescence material as the emission intensity depends on the size of nanomaterial and doping [2,3]. Therefore, keeping these points in view, an attempt has been made to prepare Tb: CePO₄ NWs with desired optical and structural properties. Here we present the synthesis of nanowires via instantaneous mixing of ingredients as against the slow mixing used in past to produce such NWs [4]. The optical and bonding properties were studied using UV-Visible and FTIR spectroscopy.

Experiments

Nanowires (NWs) were synthesized by chemical route using Ce (NO₃)₃.6H₂O, Tb (NO₃)₃.5H₂O and H₃PO₄ mixed in 50 ml DI water followed by repeated washing using ethanol and DI water. They were then annealed at 900° C for 8 hrs in N₂ environment to enable complete phase transformation from hexagonal to stable monoclinic phase (confirmed from X-ray diffraction, not shown here).

UV-Visible spectroscopy measurements were done on Perkin Elmer Lambda 950 dual beam photospectrometer (wavelength range of 200-800 nm). FTIR measurements were carried out onBruker Vertex 80V spectrometer equipped with Globar source in the mid IR region (400-4000 cm⁻¹).

Results and Discussion

The FTIR spectra of nanowires of pure and Tb doped $CePO_4$ (figure 1) show similar characteristic absorption bands formation with slight differences in absorption intensity.



Fig. 1. FTIR spectra of pure and Tb:CePO₄ NWs.

Apart from the CePO₄ bonds and absorbed moisture, no additional impurity peaks/bands are observed confirming high purity of the synthesized material. The modes of vibration appearing in the range of 500-3000 cm⁻¹ are depicted here. In the range from $400-1200 \text{ cm}^{-1}$, one can observe the appearance of a broad band due to PO₄³⁻ tetrahedrons of phosphate group of the studied sample in the nine fold coordination of monoclinic CePO4:Tb nanowires.The samples have absorbed a large amount of moisture before introducing into the FTIR experimental chamber, which has resulted in the appearance of C-H stretching vibrational modes in the range of 2800-3000 cm⁻¹. In addition, O-H bending mode also appeared at ~1635.6 cm⁻¹, which was subtracted from the standard KBr data. However, from XRD measurements, we could conclude that moisture has not entered inside the crystal structure and is only absorbed due to porous nature of nanowire samples.



Fig. 2. UV-Visible spectra of pure and Tb:CePO₄ NWs.

The major absorption peaks in the UV–Visible absorption spectra (figure 2) correspond to the monoclinic crystalline phase of the nanowires as per the literature [5]. These features appearing at 215, 238, 257 and 273 nm (main peak) with a shoulder at 338 nm arise due to the 4f-5d transitions of Ce^{3+} and are seen as a broad band. After doping, some changes are observed. The broad band peaks smear out and a bit stronger absorption takes place in the visible wavelength region. These may be attributed to the energy transfer from Ce^{3+} to Tb^{3+} in agreement with the reported photoluminescence on this sample.

The diffuse reflectance data (%R vs wavelength) was converted into absorbance, which is proportional to a function of R, namely, F(R) via Kubelka Munk transformation given as [6]:

absorption coefficient(
$$\alpha$$
) $\approx F(R) = \frac{(1-R)^2}{2R}$

The energy bandgaps were then determined from α versus incident photon energy plot and were obtained to be ~3.6 eV and 3.9 eV for pure and doped samples respectively confirming the formation of nanostructures with large bandgaps (figure 3).



Fig. 3. Absorption spectra of pure and Tb:CePO₄ NWs.

Conclusions

Optical and structural properties of pure and Tb doped CePO₄ NP were characterized. The samples were prepared using chemical route. The presence of PO_4^{3-} tetrahedrons of phosphate group was confirmed from FTIR measurements on both samples and the major bands are well matching with each other. The bandgap as calculated from diffuse reflectance measurement was ~3.6 eV in pure NWs, which increase to ~3.9 eV in doped sample.

These measurements are useful for further investigations of the electronic properties of the samples using photoelectron spectroscopy technique and also for gaining a better understanding of doping dependent properties.

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Fabrication of high-resistivity silicon nanowires for infrared sensing application

Rangeeta^{1,*}, Akhilesh Pandey², A. K. Shukla¹, and Shankar Dutta²

¹Laser Assisted Material Processing and Raman Spectroscopy Laboratory, Department of Physics, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India ²Solid State Physics Laboratory, DRDO, Lucknow Road, Timarpur, Delhi 110054, India

*Corresponding author: rangeeta23dhaka@gmail.com

Abstract

This paper presents fabrication of high-resistivity (ρ > 1000 Ω -cm) silicon nanowires (SiNWs) for infrared sensing application. The SiNWs structures are fabricated by using cost effective Metal Assisted Chemical Etching (MACE) process. After the synthesis the morphological, structural and reflectance of SiNWs were analyzed by using SEM, XRD and FTIR respectively. The fabricated SiNWs having length ~7.8-20 µm with diameter tens of nanometer, found to be (111) oriented. The FTIR study of the SiNWs showed drastically decreased transmittance (<1%) and reflectance (0.1-6%) characteristics in comparison to the bare Si (transmittance: 20-30%; reflectance: 35-40%). It infers an excellent IR absorption material for futuristic infrared sensing applications. The reduced transmittance and reflectance characteristics are appearing due to the plasmonic effect of the SiNWs.

Morphological, Optical and Electrical analysis of ZnO nanorods grown by hydrothermal method for vibration sensor application

G.Iyappan¹, R.Govindaraj², P.Ramasamy³, R.Kiruthika⁴ and S.Radha⁵

1.2.3 Department of Physics, SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai-

603110

^{4,5}Department of Electronics and Communication Engineering, Sri Sivasubramaniya Nadar College of Engineering, Chennai-603110

*Corresponding author: iyappan.gyuva@gmail.com

Abstract

Zinc Oxide (ZnO) nanorods were grown on Fluorine doped Tin Oxide (FTO) substrate using hydrothermal method. Morphological analysis shows growth of nanorod with more defects. The optical properties (UV-Vis spectroscopic and fluorescence spectrum) reviled the bandgap and quality of the grown nanorods. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) is used to provide p-type contact over n-type ZnO nanorods to form p-n junction. The photoconductivity study confirms the formation of a p-n junction with turn-on voltage of 0.3 V.

Introduction

Piezoelectric based vibration sensor is gaining attention for past few years due to its self-powered application. Zinc Oxide (ZnO) and Barium titanate (BaTiO₃) being a piezoelectric material can be used as a self-powered nanogenerator using piezoelectric property (Conversion of mechanical vibration in to electrical energy) and has attained wide interests in the application of piezoelectric vibration sensor of all the available piezoelectric materials like Lead Zirconate Titanate(PZT), Aluminum Nitride (AlN), Lithium Niobate (LiNbO₃), Gallium Arsenide (GaAs) due to biocompatibility, eco-friendly, easily synthesizable characteristics [1]. Piezoelectric cantilevers can be used as actuators or sensors. As actuators, they exploit the converse piezoelectric effect to convert electrical energy into mechanical energy, i.e. displacement and force. Typical piezoelectric cantilever actuators include ultrasonic motors. One area of increasing interest is the use of the piezoelectric effect in ZnO nanostructures to convert the stray kinetic energy in the form of vibrations or movements into electrical energy. Accordingly, different piezoelectric nanogenerators (NGs) based on ZnO nanostructures have been realized as sustainable energy sources due to their unique physical and chemical properties [2]. Furthermore, ZnO nanostructures can be formed using either low or high temperature methods. The low-temperature growth possibility is of interest to NG since it can be used to obtain piezoelectric ZnO nanorods on flexible substrates [3]. In this work, ZnO nanorods are to be synthesized on rigid substrates using hydrothermal method. Their morphological,

optical and electrical properties are analyzed to find possible application in vibration sensor in future.

Experimental Procedure

The FTO glass substrates were pre-cleaned to achieve contaminant free device for the fabrication process. Next is the deposition of seed layer which comprises of Ethanol, Zinc Acetate and Potassium Hydroxide. The prepared ZnO seed layer solution was deposited on the FTO substrate using spin coating technique at 2000 rpm for 30 seconds and annealed at 360 °C for 1 hour. The growth solution of ZnO nanostructure was prepared using HMTA and Zinc Nitrate at equimolar ratio in DI Water. The prepared solution is stirred for 1 hour continuously. After that, the solution is poured inside the autoclave with the substrate dipped inside it. Then the autoclave is kept inside the hot air oven at 90 °C for 6 hours. After slow cooling, the substrate is taken out from the autoclave and annealed at 360 °C for 1 hour. Then, PEDOT: PSS is spun coated on the grown ZnO nanorods. The schematic representation of device



structure is shown in Fig.1.

Fig. 1. The schematic representation of device architecture

Morphological Analysis

The morphological analysis is done using SEM analysis. The SEM images reveals (Fig.2.), the growth of nanorod morphology. This also shows, the defects with lot of distorted nanorods morphologies.



Fig. 2. The SEM image of grown ZnO nanorods **Optical Analysis**

Using UV-visible spectroscopy, the ZnO sample absorption spectrum in the wavelength range of 300 to 700 nm at room temperature was analyzed. The absorption spectrum of ZnO sample is shown using Fig. 3 a. The bandgap was found using the Tauc plot (1), the optical band gap Eg was calculated $\alpha hy = B(hy-Eg)1/2$ (1)

where α is the absorption coefficient, B is a constant and hv is the photon energy. The optical band gap calculated is 3.12 eV which is shown using Fig.3 b.



Fig.3 a. Absorption Spectrum, b. Tauc plot

The Photoluminescence (PL) spectrum obtained using a xenon lamp at 325 nm excitation wavelength. There are usually two main peaks called ultraviolet emission and blue green band emission peaks. A green emission peak at 466 nm and UV emission peak at 382 nm is inferred from Fig. 4.



Fig. 4. The Photoluminescence (PL) spectrum **Electrical Analysis**

J-V analysis of the fabricated device is studied using photoconductivity study. The Fig.5. confirms the formation p-n junction. The obtained turn-on voltage is 0.3 V.



Fig.5. J-V analysis of the fabricated device

Conclusion

Zinc Oxide nanorods is successfully grown using low-cost hydrothermal method. The fabricated device is spin coated with PEDOT: PSS to form a p-n junction. The respective optical characteristics like UV-Vis spectroscopy and Photoluminescence spectroscopy were performed on grown nanorods. The electrical properties of fabricated device are studied through J-V analysis which confirms the formation of p-n junction contact. The fabricated device when subjected to mechanical vibration is expected to a stress causing electrical output signal. Hence, this work reports the possible application in self-powered vibration sensor.

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PHOTOCATALYTIC CLEANING OF OIL SPILL IN SEA WATER USING INDIUM SULFIDE NANOPARTICLES

Amirthavalli.V¹ and Anita R Warrier^{2, a}

¹Department of Petroleum Engineering, ²Nanophotonics Research Laboratory, Department of Physics Academy of Maritime Education and Training, 135, ECR Road, Kanathur, Chennai-603112.

^{a)}Corresponding author:anitawarrier2@gmail.com

Abstract. An oil spill is the release of petroleum hydrocarbons into the marine environment. We report on the decomposition of oil spill using In_2S_3 photocatalyst. The In_2S_3 nanoparticles with In to S stoichiometry 1:1 were synthesized by homogenous precipitation method. The structural and optical properties of synthesized particles were studied using FTIR, BET and UV-Vis spectroscopy. The decomposition of oil spilled in sea water was achieved using 10 mg of In_2S_3 nanoparticles uniformly dispersed in the oil spill solution under the irradiation of visible light from 500 W Halogen lamp. Gas chromatography studies of the treated and untreated oil spill water confirms the decomposition of the crude oil compounds after 20 hrs of exposure to visible light.

Structural, Optical And Luminescent Studies In Calcium Silicate Doped With Ce

Parvathy M¹, Elina Prakash², and Sabeena M³*

^{1,2,3}Department of Physics, Cochin University of Science and Technology, Kochi, 682022

*Sabeena M: Sabeena@cusat.ac.in

Abstract

Present work focuses on the modification of structural, morphological, luminescence, and optical properties of calcium silicate (CS) phosphor doped with 0.1% and 1% of Ce. The phase analysis confirms the formation of CaSiO₃ in the Wollastonite form with monoclinic crystal structure in CS and absence of variations in the crystal structure and the lattice parameter due to Ce doping. The agglomerated morphology, along with the absence of impurity atoms, are confirmed via Field Emission Scanning Electron Microscopy (FESEM) analysis along with Energy Dispersive X-ray spectroscopy (EDX). The photoluminescence studies confirm the predominant green colour in the emission spectrum of CS: Ce. Due to spin-orbit coupling, 5d-²F_{5/2} and 5d-²F_{7/2} transitions are noticed at 480nm and 502nm in CS: Ce. The bandgap measurement using UV-Visible spectroscopy confirms a bandgap of 4.92 eV in the CS host lattice. A concentration dependent reduction in the bandgap is identified with the Ce addition.

Introduction

Luminescent materials, phosphors have become a vibrant topic in the scientific fields and research industry in the last century due to their potential application as a lighting source. The host materials of phosphors can be oxides, phosphates, silicates, etc. Among these, silicates have advantages over other host materials due to its high chemical and thermal stability and easy method of preparation. Additionally, the dopant, Ce has two different oxidation states, +3 and +4, broad emission band (350-550nm), better sensitization, larger stokes shift, and an efficient energy transfer process. Ce³⁺ shows characteristic bands corresponding to the 5d- ${}^{2}F_{5/2}$ and 5d- ${}^{2}F_{7/2}$ transitions (1,2).

Most of the studies in calcium silicates doped with Ce^{3+} focusses on identifying the crystal structure, morphology, and PL emission region (1). So, the present work is analyzing the influence of Ce concentration (0.1% and 1%) on deciding the crystal structure, morphology, photoluminescence, and bandgap of CS: Ce.

Experimental

The CS: Ce phosphor is prepared via sol-gel method using the precursors, $Ca(NO_3)_2.4H_2O$ and $SiC_8H_{20}O_4$ (TEOS) in the stoichiometric ratio of 1:1 at a pH of 2.5. For dopant, 1 and 0.1 mol% of Ce(NO₃)₂.6H₂O is used. The addition of TEOS after 30 minutes of stirring initiates the sol formation. The sol is allowed to stir at a temperature of 70°C for about 2 hrs to obtain the gel phase and then, dried at 110°C-120°C for 12 hrs. This is followed by an annealing at 1000°C for 3hrs, and then ground into fine powders for various characterization.

The phase identification is carried out using XRD (Miniflex Rigaku benchtop diffractometer) with Cu K_a radiation source (0.15418 nm) for a 20 varying from 15° to 80° , and step size of 0.05° at a scan speed of 1° per minute. The phase analysis is carried out by comparing the peak position with the standard ICDD database of card no.:00-043-1460 for CaSiO₃. Morphological studies and chemical analysis are carried out using Carl Zeiss Sigma Supra 40VP FESEM and Bruker X-flash 6100 EDX detector. The Photoluminescence studies are carried out using Horiba scientific spectrofluorometer and bandgap measurement with JASCOV570 spectrophotometer.

Results&Discussions

1. Phase identification using XRD

Fig.1 shows monoclinic structure with wollastonite form in Cs: Ce (1%). The host material, i.e., CS and Cs: Ce (0.1%) also show the formation of 100% monoclinic structure, without a variation in the 20 position. So, the crystal structure and lattice parameter of host lattice are invariant due to Ce addition. Ce³⁺ replaces some of the Ca²⁺ ions (2) during doping. So, the matching ionic radii of Ce (0.101nm) and Ca (0.1nm) (2) do not modify the crystal structure.

2. Morphological and chemical analysis using FESEM&EDX

The particle size and shape can influence the luminescent characteristics of phosphors. Hence, the FESEM analysis has been carried out in CS, CS: Ce (1%), and CS: Ce (0.1%).

Fig.2 shows the FESEM images of CS: Ce 1%. The morphological analysis confirms the formation of agglomerated and porous structures irrespective of the dopant concentration. This indicates that homogenization at 1000°C for 3 hours is not sufficient for the evolution of grains in CS. Also, the present heat



Fig. 1. XRD profile of CS: Ce 1% with monoclinic structure

treatment does not make any variations in the morphology of the material. The EDX analysis shows the presence of constituent elements and absence of any impurity elements in all the phosphors. This confirms the purity of the prepared material.



Fig. 2. FESEM image of CS: Ce 1% showing agglomerated morphology and absence of clear grain formation.

3. Photoluminescence Study (PL)

The photoluminescence emission and excitation studies are carried out in CS doped with 1% Ce. The excitation wavelength of CS: Ce is 284nm. The PL emission spectra shows the characteristic $5d^{-2}F_{5/2}$ and $5d^{-2}F_{7/2}$ transitions. The emission wavelengths are at 480nm and 502nm for CS: Ce. The emission peaks are the characteristic 4f-5d transitions. The electronic configuration of Ce³⁺ is [Xe]4f¹. Due to the spin-orbit coupling, the 4f subshell split into ${}^{2}F_{5/2}$ and ${}^{2}F_{7/2}$, which

are separated among each other by 2253cm⁻¹ and 50,000cm⁻¹ from the higher 5D orbital (3). The PL studies confirmed that when CS doped with the rare earth element, Ce³⁺ exhibits luminescent properties predominantly in the green region. This is in agreement with the reported literature (2).

4. Bandgap Analysis

In order to study the influence of dopant and its concentration on deciding the bandgap of calcium silicate, Diffuse Reflectance Spectroscopy (DRS) is carried out. From the reflectance spectra, the bandgap is calculated using Tauc plot (4).

The measured band gap of CS and CS: Ce are given in table 1. The measured bandgap of 4.92 eV of CS is in agreement with the reported value of 4.93 eV of CS. 0.1% and 1% Ce in the CS lattice reduces its bandgap to 4.904 eV and 3.41 eV respectively. This shows a concentration dependant reduction in the band gap of CS with Ce (4). The bandgap modification in CS: Ce confirms the dependence of dopant concentration on deciding the conducting and insulating nature of the material. So, by tuning the concentration of the dopant, the bandgap can be modified. This is favourable for tuning the optical frequency of the devices such as laser, LED, etc.

Table 1. Bandgap a	nalysis using	DRS s	pectrum.
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Sample	Bandgap(eV)
CS	4.92
CS: Ce (0.1%)	4.904
CS: Ce (1%)	3.41

Conclusions

The structure-property correlation studies in CS, CS: Ce confirms the formation of wollastonite, $CaSiO_3$ with agglomerated porous morphology. The PL emission spectra shows characteristic green emission at a wavelength of 480nm and 502nm corresponding to $5d^{-2}F_{5/2}$ and $5d^{-2}F_{7/2}$ transition of Ce³⁺. Bandgap analysis shows a reduction in the bandgap of CS due to the addition of Ce, and the reduction is maximum for the highest concentration of dopant.

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Effective and Environmental Friendly Lead-Free Tin Oxide Nanocomposite for X-Ray Shielding

^aSanjeevi.P.,^bPuviarasu.P.,^cElango.M*.

^{a, c}PG& Research Department of Physics, PSG College of Arts & Science, Coimbatore-14, ^bDepartment of physics, PSG college of Technology, Coimbatore-04,

*Corresponding author: elango@psgcas.ac.in

Abstract

The present study is focused on the development of a lightweight, lead-free apron that can be used to shield low intensity radiation in medical imaging room. Sol-gel technique was used to produce SnO₂ nanoparticles (Nps). The synthesized Nps were coated on Rexine cloth with the help of Epoxy Resin. Similarly another sample was prepared using lead oxide micro particles and this sample was taken as the reference to study the shielding effect of SnO₂ Nps. The X-ray diffraction (XRD) data was used to analyze the structure of the Nps. The crystallite size for prominent peak of the Nps was calculated around 31nm and found the crystal system was found to be tetragonal. The attenuation results of NC are compared with properties of lead oxide sample. The NC gives better attenuation results in low X-ray tube voltage.

Introduction

High atomic number (Z) materials can effectively resist X-ray exposure through photo electric effect. In this way lead (Z=82) is the most advantageous material for protecting against X-ray exposure(1). Lead aprons is commonly used to protective healthcare workers and patients during medical procedures from radiation exposure. But Lead is heavy metal it can cause back pain and fatigue.Long term exposure to lead can cause various health problems. The accumulation of lead-heavy metal within the body can lead to various health issues,like kidney failure, neuronal disorders and reduced levels of red blood cells etc. So, we have to replace lead and develop the lead equivalent, environmental and human friendly material (2).

Nowday's nanomaterials are used in many applications. Because of its size and high surface area coverage. Nps has novel physical and chemical properties relative to the same macro sized material. As the result, it's widely employed in X-ray blocking materials. Furthermore, when combined with the right polymer such as semiconductors, it can be used as a wearable material. Because polymers have great potential in many important applications due to their unique properties, such as low the ability to form intricate shapes, optical transparency, low manufacturing cost and toughness. Filler reinforced polymers have gained increasing X-ray attenuation(2). Tungsten tri oxide, titanium oxide, copper oxide and antimony tin oxide have all recently been studied for their X-ray shielding capabilities (3). In this paper SnO₂Nps prepared by Sol-gel method. The prepared Nps blended with epoxy resin and drop casted on rexine. The drop casted film used for X-ray attenuation study.

Experimental Methods

SnO₂Nps were prepared by sol-gel method using Sn precursors in the form of chloride. In detail 20gm of SnCl4.2H₂O was dissolved in 200ml of ethanol and agitated

for 30mins until a translucent sol was obtained. To attain 10 pH level aqueous ammonia solution added drop by drop, ring The resultant opal gel was centrifuged followed by washed with ethanol and distilled water more than 5 times to eliminate ammonia and chloride impurities. After 24hrs of aging in the air. The collected gel was dried in an oven at 80°C for 5hrs to remove moisture then the sample was crushed and sintered at 500°C for 5hrs in muffle furnace. Finally, a colored SnO₂Nps was discovered (5). Epoxy Resin (ER) (Bisphenol-Adiglycidyl ether polymer) and FR251hardener (isophoronediamine) was mixed with the prepared nanopowder and then it was stirred for 20mins at a steady speed in a beaker to achieve equal dispersion of the powder in epoxy matrix (1:2 ratio). The well-stirred liquid was then poured onto a 4x4 cm² square of rexine fabric and allowed to sit for up to 24hrs at room temperature (2).

Characterization techniques

X-ray diffraction (XRD) studies were performed on the prepared SnO₂ Nps using Malvern Panalytical XRD equipment, the energy source CuK_a radiation($\lambda = 1.5406$ Å) and tube voltage, current of 40kV, 30mA used respectively. The coated NC sample (fig 1) was investigated by X-attenuation studies by using Radiography (Model number HF advantage and manufacturer by Wipro GE healthcare Private Limited, India).



Fig. 1: coated samples a) SnO₂ nanocomposite b) Lead Oxide and epoxy resin composite

Results and Discussion

XRD Analysis

XRD analysis was performed to examine the crystal structure, crystallite size and lattice parameters of SnO₂ Nps. The XRD patterns sintered at 500°C are exhibited in fig 2.



Fig. 2: XRD of SnO₂ Nps at 500°C

Origin software was used to index the peaks. The crystal structure of Tetragonal found for SnO2 by standard card (JCPDS 077-0448) with a maximum intensity matching to the (110) plane. Additionally, the lattice parameters a and c are computed using software program of unit cell and given in table 1. The computed values all match with JCPDS 077-0448.

Debye-Scherer's was used to estimate the sample's average crystallite grain size (Dhkl nm), dislocation density (δ lines/m²), inter planar distance, d (Å) and Macrostrain (E) formulas is given by (5),

$$D_{hkl} = \frac{0.9\lambda}{\beta \cos \theta} \quad (1) \qquad \delta = \frac{1}{D^2} \quad (2)$$
$$d = \frac{n\lambda}{2\sin \theta} \quad (3) \qquad \xi = \frac{\beta}{4\tan \theta} \quad (4)$$

Table 1: The calculated values of the grain size, lattice parameter, microstrain, dislocation density

20	D (nm)	a (Å)	b (Å)	d (Å)	δ (x10 ⁻ ³ line/m ²)	E (x10 ⁻ ³)
26.5	31			3.35	1.05	5.11
33.9	27	4.74	3.18	2.64	1.42	4.68

Measurement of X-ray attenuation

Fig. 3 shows that nano-structured SnO₂ sample isbetter in attenuating low energy X-ray photons than Microstructured Lead Oxide sample (1, 2). The overall attenuation of a material is determined through photoelectric and Compton interactions in the diagnostic

energy range. Photons interact with materials mostly via the photoelectric effect in the low energy range, whereas Compton scattering predominates at high energies. Due to the photoelectric effect's energy dependency, attenuation reduces as photon energy increases. The number of SnO₂ particle/gram in nano structured plates is higher than the micro sized material due to particle size. Therefore, it is possible that the interaction and absorption probability of the low energy X-ray photon is higher in the nanocomposite than in the micro structured material (4).



attenuation electrometer reading without sample – electrometer reading with sample X 100electrometer reading without sample



Fig. 3: Percentage attenuation for Nanocomposite using primary X-ray beam.

Conclusion

This paper deals with structural and X-ray attenuation characterization of obtained coated nanocomposite by drop cast method. The XRD study shows that the obtained Nps have Tetragonal structure. Finally, percentage of attenuation has been successfully investigated by SnO₂ NC. The experimental result indicates that SnO₂ NC better in attenuating low energy X-ray photons than Microstructured Lead Oxide sample.

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Synthesis of Polyaniline-Crystalline Rubrene nanosystem by Onestep Plasma Process: Exploring its Applicability in Broadband Optoelectronics by Plasmonic Functionalization

Deepshikha Gogoi¹ and Arup R Pal^{1*}

¹Plasma Nanotech Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Garchuk, Guwahati-781035, India.

*Corresponding author: arpal@iasst.gov.in

Abstract

In this report, the crystalline Rubrene and polymer material synthesis as well as the thin film deposition have been performed simultaneously in a unique plasma based single-step process. The applicability of the as-prepared thin film for development of a light responsive device in sandwich structure has been studied. We also demonstrate the plasmonic effect that occurs due to the incorporation of gold nanoparticles (Au NPs) in the prepared system. Significant enhancement in the spectral responsivity and specific detectivity of the device is observed after incorporating Au NPs in the organic semiconductor matrix.

Introduction

Noble metal nanoparticles of different shape, size and distributions are employed as the plasmonic absorbers in several optoelectronic device geometry¹ because fine tuning of the size, shape as well as the distribution of such metal nanoparticles can be done in order to vary the LSPR band. Some extensively used metals are gold (Au), silver (Ag), copper (Cu) etc. Enormous research works have been done in plasmon enhanced organic photovoltaic (OPV) devices by many research groups.²

Here we report the synthesis of crystalline Rubrene by a conceptually new plasma based process and its application in optoelectronic device geometry with the incorporation of plasmonic Au NPs. The fabricated device shows broadband enhancement covering the entire UV-NIR region of the electromagnetic spectrum due to plasmonicfunctionalization. Gold nanoparticles (Au NPs) are taken as model plasmonic absorbers and are prepared by magnetron sputtering. The crystalline Rubrene film along with plasma polymerized aniline (PPA) acts as the charge transport matrix. The material property analysis of this study reveals that the plasmon absorption band of Au can be extended up to the near IR region since the position of LSPR band depends on the particle size and distribution. Thus, integrating such optimized Au NPs in the device geometry leads to enhanced IR sensitivity of the device without the use of any electron or hole transporting layer which is usually essential for efficient charge transport.

Due to the strong plasmonic coupling between the Au NPs and PPA-Rubrene system, an efficient amount of free carriers are generated in the photoactive film and consequently broadband enhancement of spectral responsivity and detectivity of the fabricated device is achieved. The highlighted aspects of this work are- (i) synthesis of PPAcrystalline Rubrene film in order to have a semiconductor matrix with enhanced conductivity and (ii) Application of this PPA-crystalline Rubrene film in broadband optoelectronic device fabrication by incorporating spectrally tunable plasmonic Au NPs into the organic semiconductor matrix.

Results and discussions



Fig. 1. XRD patterns of (a) PPA-CRB and (b) PPA-CRB/Au. The broad peak comes due to the amorphous form of Rubrene present in the samples.

In this work, because of the utilization of plasma based process, it is possible to get the crystalline phase of Rubrene without undergoing any high temperature methods simply by controlling the RF power. Further, the XRD pattern of the PPA-CRB/Au thin film presents sharp crystalline peaks of gold (Au) at 38.2° and 44.5° corresponding to the (111) and (200) crystal planes³ respectively along with the crystalline peak of Rubrene at 6.7°.as shown in Fig. 1(b) The presence of crystallinity along two different crystal planes shows the polycrystalline nature of the deposited Au NPs.



Fig. 2. The reproducible On-Off I-t curve of (a) PPA-CRB and (b) PPA-CRB/Au based device at 0 applied bias.

Both the devices show clear and reproducible on-off cycles at zero bias, which indicates that the devices can work well in the self-powered mode. Compared to the PPA-CRB (Fig. 2(a)) device, the plasmon-mediated device, PPA-CRB/Au (Fig. 2(b)) has highly improved photocurrent enhancement.



Fig. 2. Responsivity (R_{λ}) of PPA-CRB and PPA-CRB/Au devices at zero bias as a function of wavelength, (b) Detectivity (D*) of PPA-CRB and PPA-CRB/Au devices at zero bias as a function of wavelength, (c) Responsivity (R_{λ}) enhancement factor and (d) detectivity (D*) enhancement

factor of PPA-CRB/Au device at zero bias as a function of wavelength.

The PPA-CRB device shows a maximum responsivity of $R_{\lambda} = 0.00739 \text{ mAW}^{-1}$ and for PPA-CRB/Au device it is calculated to be $R_{\lambda} = 0.10337 \text{ mAW}^{-1}$. For PPA-CRB device, maximum detectivity is calculated to be 6.095×10^8 Jones (1 Jones = 1 cm Hz^{1/2}W⁻¹) while that for PPA-CRB/Au device it is found to be 2.011×10^9 . Thus, significant increase in responsivity and detectivity of PPA-CRB/Au device over the specified spectral range as compared to the PPA-CRB device. The enhanced responsivity and detectivity directly evidences the plasmonic functionalization of the PPA-CRB/Au device due to the incorporation of the Au NPs.

Conclusion

Prominent plasmonic enhancement in the responsivity (R_{λ}) and detectivity (D^*) of the control device PPA-CRB is observed after the incorporation of Au NPs in the device geometry. Due to the promising optical absorption of Rubrene in the visible region and tunable plasmon absorption band of Au NPs, broadband enhancement in R_{λ} and D^* is obtained.

Acknowledgement

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Structural Attributes of High Capacity Resin by SEM

Sangita Pal^{1, 2, 6*}, Sher Singh Meena³, Lata Panicker⁴, Supratik Roy Chowdhury⁵, K.P. Bhattacharyya², A. K. Adak²,

¹Board of Research in Nuclear Sciences (BRNS), ²Desalination and Membrane Technology Division, ³Solid State Physics Division, ⁴Radiation Biology & Health Sciences Division, ⁵Material Processing and Corrosion Engineering Division, Bhabha Atomic Research Centre, Mumbai - 400085, India, ⁶Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 094 India

*Corresponding author: sangpal@barc.gov.in

Abstract

Architectural and recurrence structure, spatial disposition of the resin and its accessibility w.r.t. metal ions and the related morphological attributes are investigated by SEM studies, where the fine channels, trammels, glimpses of ups and downs, corrugated structure have been found out by diagnosis of the spectroscopic view by microscopy such as optical microscopy (OM), scanning electron microscopy (SEM), etc.

Introduction

Uranium is found in the environment, in very small concentrations, mainly in rocks, soil, and water. Uranium is of great importance [1-3] as a nuclear fuel. Uranium metal is also used in X-ray targets for generation of high energy X-rays. At the same time, uranium and its compounds are extremely toxic, from the chemical, biological, and the radiological points. So, pre-concentration and immobilization for these radio-active waste samples [4,5] are necessary. One of the important methods besides solvent extraction, precipitation, foam based separation, electrodeposition, membrane based separation, adsorption, ion exchange, bio-sorption is sequestering macromolecules with specially fabricated [6, 7] stack layer structure. The latter has proved to be the most effective before final effluent disposal. In this paper, structural analysis of high selectivity (due to functional moieties) and high capacity (i) due to structural/architectural arrangement (SEM), ii) introduction of pores and channels in the bulk and iii) incorporation of innumerous track layers [SEM]) of a sorbent with sorption kinetics (OM) are the most effective aspects for radio-nuclides (e.g. U, Pu etc.).

Experimental

Sorbent synthesis

In the present work, PHOA (poly-acrylamide hydroxamic acid), a cross linked polymeric absorbent was used for radiotoxic metal removal from wastewater. The resin prepared by free radical polymerization method (from acrylamide to Polyacrylamide (PAM) in presence of cross-linker, initiator and aqueous solvent) followed by conversion reaction (i.e., conversion of PAM to PHOA resin when reacted with hydroxylamine hydrochloride and NaOH at 70°C for 4 hrs.).

Instrumental analysis

Optical Microscopy (OM) and Scanning Electron Microscopy (SEM) have been used for structural and performance analysis.

Optical microscopy analysis

One of the essential characteristics of OM is the i) instant analysis, ii) no coating or pre-diagnosis preparation is required. The dry resin (Fig. 1 "0 sec") was placed under the microscope which in contact with water droplet responded. A recording of structural changes w.r.t time in seconds (Fig. 1 "2 secs" and "8 secs") provided an authentic response of fast kinetics of PHOA. There was insignificant change w.r.t. its size even after 2 minutes (Fig. 1 "2 mins") indicates extremely high swelling kinetics.



FIGURE 1. Optical microscopy for swelling kinetics analysis.

Scanning Electron Microscopy (SEM)

SEM is a powerful microscope whose image is made by scanning a beam of electrons can be used for the study morphology i.e., investigation of the characteristics and configuration of the matrix. Morphology of the resin in different condition such as 1) fresh, 2) loaded, 3) unloaded/regenerated; 4) in acidic 3N HCl and 5) basic 1 N NaOH solution were examined by SEM. SEM images of the surface and the cross section of dry fresh beads are shown in Figure 2(a), which is rough and has macro pores of different diameter from 2-50 nm. The topographical picture in Fig. 2a of PHOA resin in comparison to Fig. 2b (commercial resin) also shows the presence of much larger bulk pores. Fig. 3 indicated corrugated structure, later width 12µ, thickness 20nm, and channel diameter 3µ to 0.2µ.



FIGURE 2. SEM for structural analysis of (a) fresh Resin w.r.t (b) commercial resin.

The structural criteria like corrugated folded part which ultimately creates a fine tunnels/channels/ or passageway for the incoming water enriched with metal ions also percolates through micro-cavities and further channeling revives the intricate pores.



FIGURE 3. SEM analysis of fresh resin, envisaged corrugated layer with ridges-groves distances

Conclusion

Method of free radial polymerization preparation i.e., initiation, propagation and termination steps as well as functionalization has effect on matrix, surface, pores, pore volumes etc A further comparison with commercial resin beads indicates that this PHOA gel resins comprises innumerous stack layers which contains innumerous functional moieties and each layer contributes to sorption capacity enhancement compared to commercial one. All above spectra's, microscopic views (SEM), indicate high performance resin should be complied with numerous functional groups throughout the bulk, tips and dips of corrugated recurrence as well as architectural arrangements which distinct as super-comparison w.r.t commercial one. Swelling kinetics (2.5 times in 8 seconds) data of OM is also supportive fact of accessibility of intrinsic micro-cavities (2 Å -2.5 Å) for participation towards sequestration of radio-toxic metals such as uranyl carbonate ions (8.3 Å).

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Optical and Electrical Properties of Sn Doped TiO₂ Nanoparticles

Avinash B S¹, Ashok R Lamani², Jayanna H S³, Chaturmukha V S⁴, and Suresha S⁵

¹D.V.S. College of Arts, Science and Commerce, Shimoga, Karnataka, 577201 ^{2, 3}Department of Studies and research in Physics, Kuvempu University, Shankaraghatta, Karnataka, 577451 ⁴Department of Forensic Science, Bnagalore, Karnataka, 560034 ⁵Government First grade College, Holalkere, Karnataka, 577526

*Corresponding author: ashok1571972@gmail.com

Abstract

In this work we successfully doped Sn in the place of Ti in an anatase and rutile structure From 0.1% to 0.5%. Scherrer formula confirms the average crystallite size from 92-40nm. SEM images shows the reduction in the size and tending towards spherical in nature with average particle size from 110-40nm. Pellet form of these samples were studied in the frequency range from 1MHz – 10MHz, which shows the ε' more in the lower frequency range for the particle size of 67nm at 1MHz it decreases instantly then saturates with increase in frequency due to charge carriers, with hopping conduction is prominent at this region. σ_{ac} increases with increase in frequency, at 1MHz σ_{ac} maximum for average particle size and it decreases with decrease in particle size due to hopping conduction become more prominent.

Synthesis of SnS Nanoparticles by Homogeneous Precipitation Technique by Varying Temperature

Lin Sunil¹, Anita R Warrier²

^{1,2}Nanophotonics Research Laboratory, Department of Physics, Academy of Maritime Education and Training, Chennai, Tamilnadu 603112, India

*Corresponding author: anitawarrier@ametuniv.ac.in

Abstract

This work investigates the formation of tin sulphide nanoparticles using homogeneous precipitation technique by varying the initial reaction temperature from 50 $^{\circ}$ C to 300 $^{\circ}$ C. The molarities of reactants (0.6M of SnCl₂ and 0.1 M of TAA) and time for heat treatment (2hrs) kept fixed throughout in the reaction. The prepared samples were characterized using UV-Visible absorption spectroscopy and X-Ray diffraction (XRD). Samples, synthesized under temperatures 100 $^{\circ}$ C -200 $^{\circ}$ C shows an increase in their band gap (from 1.88 eV to 3.19 eV) due to decrease in particle size. For 250 $^{\circ}$ C and 300 $^{\circ}$ C band gap decreases, this attributed to formation of the secondary phases. The structural properties and composition of samples were studied using XRD pattern and shows a prominent orientation along (111) plane which matches with orthorhombic phase of SnS. The formation of secondary phases, when treated at higher temperatures is in confirmed from the peaks corresponding to SnS₂ and Sn₂S₃particles.

Effect of Temperature on the Synthesis of β-In₂S₃ Quantum Dots in Perfluorinated Ion Exchange Membrane

Anju Subhash¹, Anita R. Warrier^{1*}

¹Nanophotonics Research Laboratory, Department of Physics, Academy of Maritime Education and Training, 135 East Coast Road, Kanathur, Chennai, Tamil Nadu, 603112

*Corresponding author: anitawarrier@ametuniv.ac.in

Abstract

Semiconductor quantum dots have found extensive industrial application due to their unique physical and chemical properties. In this study, β -In₂S₃ quantum dots were synthesized in perfluorinated ion exchange membrane (Nafion 117) through a simple wet chemical method at different temperatures from 50^oC to 90^oC and the effect of temperature in the process was studied. The band gap energy calculated from the UV-Vis absorbance shows a blue shift which confirms quantum confinement. The photocatalytic activity of this membrane under visible-light irradiation was investigated considering the degradation of organic matter in seawater. The results show reduction of organic matter and also the effective removal of micro-organisms like *e-coli* and *coliform bacteria* from sea water. The band gap energy of the membrane is found to reduce after each use as a photocatalyst.

Spin Coating Induced β-Phase in Ultrathin PVDF film for MEMS Based Devices

Pinki Malik and DipankarMandal*

Quantum Materials and Device Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali, 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

Poly(vinylidene fluoride) (PVDF) thin films with controllable thickness and surface roughness are prepared by heat controlled spin-coating technique. It has been realized that roughness down to 6 nm with 76% yield of ferroelectric β -phase is possible to achieve that exhibits superior nanoscale piezoelectric coefficient (d₃₃) -24 pC/N. In addition, long retention of ferroelectric phase switching behaviour is also observed. Ferroelectric switching associated to phase and generated strain vs. applied voltage hysteresis curves indicate the potential application of PVDF ultrathin film in MEMS based electromechanicalsensors, actuators, non-volatile memories.

Introduction

PVDF is one of the most suitable materials for ferroelectric and piezoelectric applications due to its good electro active properties among the polymers. It can exist in primarily four crystalline phases (α , β , γ and δ). Among them, β – phase exhibits the good ferroelectric and piezoelectric properties [1]. In the MEMS based device fabrication, ultra-thin film with good quality surface roughness is desirable. Noteworthy that lower thickness is prerequisite to reduce the device operating voltage. On the other hand, surface roughness plays a significant role to improve the adhesion between organic to organic and also organic to inorganic interfaces. In this context, the spin-coating is adopted as one of the best suitable techniques for obtaining good quality thin films of β PVDF. However, more often very high surface roughness (comparable to film thickness) and porosity are observed in PVDF thin film due to high boiling point of the selective solvent of PVDF [2]. So in this work, we have established a way of optimization of parameters involved in the fabrication of PVDF films by spin coating influence the properties, e.g. morphology, surface roughness and thickness.

Experimental Section

PVDF in pellet form was dissolved in N, Ndimethylformamide (DMF) using a magnetic stirrer. Then PVDF films were spin coated (at 4000 rpm, 30s) on clean ITO coated glass substrates in the presence of N₂ at 80 °C. In this work, we have prepared thin films with different wt% (w/v) of PVDF/DMF proportions, e.g., 2, 4 and 6 wt% in presence of N_2 with 4000 rpm followed by thermal annealing at 120 °C for 2h. Further, 4wt% related thin film sample (thickness of 350 nm) has been selected for the study of piezoelectric coefficient (d₃₃) and ferroelectric switching capability.

Results and discussion

The influence of the different concentration of PVDF-DMF solution on the morphology and surface quality of the PVDF films was studied. It is clear that the surfaces of all samples are appeared smooth and flat but the major changes in size of the spherulites are observed. Figure 1 (a, b and c) shows surface topography images of different PVDF films prepared with 2, 4 and 6 wt% of PVDF-DMF solutions respectively. In all cases, the predominant β -phase is observed as evident from the circular like spherulitic structures [3]. Gregorio and Borges mentioned that the spherical structure with small diameter refer to the formation of the B-phase whereas the radial lamella refer to the formation of the α -phase [4]. So in this way we can conclude that film spin coated from the 6 wt% (larger diameter of the spherulitic structures in case of 6 wt% as compared to 2 wt% and 4 wt%) more α -phase as compared to 2 wt% and 4 wt% which is supported by FTIR spectra also. The surface roughness and thickness of each films are enlisted in table 1. Due to absence of unexpected porosity, the overall improved film quality is achieved since heat control spin coating and N2 environment is improved the solvent evaporation rate

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and reduce the moisture content during spin coating.. It is noted 4 wt% film show more beta content (\sim 76%) as compared to 6 wt% (\sim 25%) because higher elongation force is generated during spin coating when lower concentration solution is employed.

TABLE 1.Surface roughness and thickness in thin film when 2, 4 and 6wt% PVDF-DMF solution is used.

Conc. (wt %)	2	4	6	
Surface Roughness (nm)	7	10	55	
Thickness (nm)	120	350	550	



Fig. 1.(1) Surface topographic images of different concentration of PVDF solution (a) 2 wt%, (b) 4 wt% and (c) 6 wt%. (2) FTIR-GIRAS of different concentration of PVDF solution (d) 2 wt%, (e) 4 wt% and (f) 6 wt%.

Piezo-response force microscopy (PFM) Ferroelectric domain switching characteristic investigated using piezoresponse force microscopy (PFM) mode. In fig 2(a), amplitude and phase response with DC bias has been shown. It has been found that d₃₃ coefficient value in case of 4 wt% PVDF film nearly -24pC/N. Further we have performed electrical lithography to write electrical domains on the PVDF film using a conducting tip by applying +18V in 1.5×1.5 μ m² area as shown in fig 2(b). It has been found that there is almost no phase change after 30 minutes as shown in fig 2(c).



Fig. 2.(a) PFM amplitude and phase hystersis loop of 4wt% PVDF-DMF solution comprised thin film. (b) PFM phase image after poling with +18 V(c) After 30 minutes of poling.

Conclusion

In summary, we have analysed the topography and surface roughness of the PVDF thin films with different weight% PVDF solution. Thin film of good beta phase (76%) and d_{33} coefficient (-24 pm/V) were directly prepared by heat controlled spin coating technique. Shear and elongation forces on the PVDF fims during spin coating was responsible for the formation of β -film. PFM analysis demonstrated the switching mechanism in the PVDF film that lead to the conclusion that this material is a good candidates for non-volatile memory applicaton.

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Morphology and Molecular Orientation of Nanofibers in Electrospinning and it's Piezoelectric Nanogenerator

Varun Gupta and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

The electrospinning parameters play a critical role to obtain a particular morphology and prominent electroactive phase of the PVDF in nanofibers, majorly governed by Taylor cone formation, viscosity of the polymer, flow rate and relative humidity. Polarization dependent vibrational spectroscopy technique is one of conclusive way to study the dynamics of the molecular dipoles nanofibers upon altering the polarization of IR light at particular angle. The fabricated Piezoelectric nanogenerator showed max open circuit voltage (Voc) of ~2.8 V and max short-circuit current (Isc) of ~ 48 nA.

Introduction

Polyvinylidene fluoride (PVDF) has been well known for years due to its excellent ferro-, pyro- and piezo-electric properties along with its non-linear susceptivity and electroactive nature. It is a semicrystalline polymorph with four distinct phases based on the different molecular conformations of the polymer. In which, a-phase is non-polar and nonelectroactive in nature. The β , γ , δ -phases are polar and electroactive in nature¹. Hence, they can used for fabricating piezoelectric energy harvesters and sensor as their potential application. The particular phase formation depends on different processing techniques like solvent casting, spin coating, mechanical stretching, and electrical poling etc. Among all the phases, β -phase is the most electroactive phase and can be also induced by electrospinning technique as it consists of in-situ poling and stretching mechanism simultaneously. Electrospinning technique was used by Reneher et al. to fabricate the PVDF nanofibers. As per reported literature, different morphologies can be obtained in electrospinning system by changing the polymer viscosity, solvent, electric field, temperature and humidity etc. These critical factors determine and improve the probability of inducing a particular phase in PVDF in electrospinning process^{2,3}. Electrospun fibers can be used for various applications such as tissue engineering, membrane formation, e-textile, flexible energy harvester and sensors etc.

In the electrospun, the understanding of molecular dipole orientation in the polymer chain of PVDF, in the different kinds of morphologies are yet to be explored and how the electrical, optical and dielectric properties are changing at nanoscale confinement. These molecular dipole orientations can be significantly observed and studied based on vibrational spectroscopy techniques as reported by Mandal et al. for electrospun nanofibers⁴.

Here we are reporting the formation of various morphologies of PVDF in electrospinning (ES) system and how the various ES parameters are affecting the formation of beads/ fiber formation. In later part this work, we have also tried to analyze the molecular dipolar orientation of PVDF chain in the fabricated random and aligned fibers.

Experimental Section

In this experiment, PVDF pallets (Avg. mol. wt. – 180,000 by GPC, Aldrich) was dissolved in in DMF/Acetone at 6:4 ratio to get PVDF solution. The solution was used for electrospinning where flow rates between $0.2 - 0.5 \,\mu$ l/ hr and Voltage range from 10-15 kV were employed, with different flow rates (0.3 μ l/hr, 0.41 μ l/hr and 0.6 μ l/hr) at constant voltage. We have fabricated the nanofibers with beads, nanofiber without beads, random nanofibers and aligned nanofibers from changing the different electrospinning parameters such as voltage, tip to collector distance and flowrates.

Results and Discussion

In the ES system initially, we obtained the fibers with beads (Fig. 1a) at higher flowrates and with discontinues flow of the polymer solution. As the solutions viscosity was increased at an optimum flow rate, and by controlling the humidity of the ES chamber, the fibers were obtained without beads (Fig. 1b) as shown in SEM images. This fact reveals that the ES parameters like viscosity, temperature and proper Taylor cone formation plays a crucial role to obtain the particular type of morphology in ES. Further analysis of these bead free random nanofibers as histogram (Fig. 1c) shows that the average diameter of fibers is between $\sim 180-220$ nm. In the next step of this experiment, to improve the alignment of these random nanofibers, the rotation



Fig. 1. SEM image of electrospun PVDF fibers (a) with beads (b) without beads (scale bar 5 μ m) (c) The histogram of SEM image of electrospun fibers (inset) of an average size of diameter ~180-220 nm. (d) The AFM topographic image of electrospun nanofibers of an average diameter ~ 200 nm (scale bar 10 μ m).



Fig. 2. (a) FTIR spectra of aligned (b) random PVDF nanofibers, measured at different polarizer angle. (c) Open circuit voltage and (d) Short circuit current of PNG fabricated from PVDF fibers.

speeds of the drum were optimized. As a result, at higher drum speeds, we have obtained the more aligned PVDF nano fibers as shown in Fig. 1(d) in AFM image. The AFM images show the average diameter of the nanofibers ~ 200 nm. To study further the effect of alignment of the PVDF nanofibers, the FTIR spectroscopy of the nanofibers

was performed in transmission mode. In case of aligned nanofibers (Fig. 2a), the IR absorption intensity at 1276 cm⁻¹ is higher as compared to the random nanofibers (Fig. 2b), in case of 0° polarization. This observation shows that aligned nanofibers has much higher electroactive β -phase as compared to random PVDF nanofibers, which could be due to result of dipoles alignment in the nanofibers. To get a proper understanding of this phenomenon, we have performed the FTIR study at different polarizer angle. As the polarizer angle was changed from 0° to 90°, the prominent changes in the IR bands were overserved between 1200- 1276 cm⁻¹. These changes are due to alteration in the polarization direction of electromagnetic field, which results the changes in the vibration of in-plane molecular dipoles in the nanofiber chain. Since most of the dipoles are oriented in a particular direction in case of aligned nanofibers (Fig. 2a), so it shows the effective change in the IR vibration as the polarizer angle changes. While the random nanofibers have dipoles oriented in random directions, hence the effective change is not prominent (Fig. 2b) after changing the polarizer direction.

Further to demonstrate the energy harvesting application of these aligned PVDF nanofibers with higher electroactive phase content than random nanofibers, we have fabricated the piezoelectric nanogenerator (PNG). The piezoelectric performance of the PNG was recorded in terms of open circuit output voltage and closed-circuit current, using repetitive finger imparting motion over the PNG with a constant frequency. The max open circuit voltage of ~2.8 V (peak to peak) was measured (Fig. 2c) along with the short-circuit current (Fig. 2d) of the PNG was observed max 48 nA (peak to peak). This voltage and current response shows that the fabricated PNG can be used as very efficient piezoelectric energy harvester and sensor.

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Synthesis and Magnetic Properties of Unusual Hexagonal Nickel Nanostructures

Ankit Kashyap, Nikita Kunwar, Divya Rawat and Ajay Soni*

School of Basic Sciences, Indian Institute of Technology Mandi, Mandi 175075, Himachal Pradesh, India

*Corresponding author: ajay@iitmandi.ac.in

Abstract

In this study, we report the synthesis and processing of hexagonal closed packed nickel (HCP-Ni) via the cost-effective and scalable polyol method. The reaction is carried out with stoichiometric amount of Nickel acetate, Polyvinylpyrrolidone, which have been refluxed in Ethylene glycol (EG-Ni) and Di-ethylene glycol (DEG-Ni), for 3hrs. DEG was chosen as an appropriate solvent that yields larger percentages of HCP-Ni in addition to FCC-Ni. Further processing of colloids improved the yield of HCP-Ni in the mixed powder made from DEG. The magnetic studies of synthesized nanostructures are also investigated.

Introduction

Transition metal nanoparticles such as Fe, Ni and Co are widely studied because of the plethora of applications.[1, 2] In general, the transition metals can exist in more than one crystal lattice structures, which is a unique property making them important for various applications. The interest is largely towards Ni due to the combination of characteristics it possesses, such as it shows slower oxidation rate, exceptional biocompatibility and capability in utility for magnetic hyperthermia.[1]

Nickel is found in two crystal structures, namely, Face centered cubic (FCC) and Hexagonal close packed (HCP). Under normal conditions Ni is found in FCC crystal structure and exhibit ferromagnetic behavior while HCP is rare. HCP-Ni is usually formed under certain special conditions of temperatures (200 - 360 °C), pressure and growth time.[3] Interestingly, the solution growth of nanocrystalline Ni using Di-ethylene glycol will always have a small fraction of HCP Ni,[4] however if processed, the ratio may increase for HCP Ni. Here, we report facile synthesis and processing of solution grown nanocrystalline Ni powder to obtain a better ratio of HCP-Ni in FCC-Ni and studied their magnetic properties.

Experimental Section

Synthesis of FCC-Ni was carried out by taking 0.75 g of Nickel acetate (Ni(CH₃CO₂)₂·4H₂O) in 50 ml ethylene glycol (EG) and kept in a round bottom flask. The mixture was stirred for well mixing of the precursor in the solvent and later transferred to heating-mantle followed by refluxing at ~ 197 °C for ~ 3 hrs. The black-colored solution was obtained indicating the formation of nanocrystalline Ni powder.[5] The solution was washed 2-3 times with acetone to remove organic by-products and was dried to get a nanocrystalline powder (EG-Ni). For synthesis of HCP-Ni same procedure was followed by taking 50 ml diethylene glycol (DEG) instead of EG and using polyvinylpyrrolidone

(PVP) as a shape guiding agent. The solution was refluxed for ~ 3 hrs at ~ 245 °C and obtained product was washed with acetone and dried to get powder (DEG-Ni). For obtaining a higher ratio of HCP-Ni, the magnet was used to isolate FFC-Ni from HCP-Ni and the process was repeated 2-3 times. The powders (EG-Ni and DEG-Ni) were then characterized using XRD and used for further measurements. The crystal structure study of the synthesized material was carried out by using *Rigaku SmartLab powder X-Ray Diffractometer* equipped with a monochromatic Cu Ka radiation source. Morphological analysis of the material was done by using *FEI- NanoSEM 450 scanning electron microscope.* Low temperature magnetic measurements were performed by using *SQUID magnetometer (MPMS-3).*

Results and Discussion



Fig. 1. (a) XRD pattern showing the presence of HCP-Ni and FCC-Ni and (b) FESEM image showing the self-assembled Ni nanoparticles synthesized in DEG.

The XRD pattern of the EG-Ni shows three peaks at $2\theta = 44.6^{\circ}$, 51.9° and 76.5° which corresponds to the FCC phase and matches well with the literature.[4] In DEG, the characteristic peaks of FCC at $2\theta = 51.9^{\circ}$ and 76.5° are present along with the less intensive peaks of HCP phase, showing the dominating phase is FCC (Fig.1(a)). Because of higher refluxing temperature of DEG ~ 245°C favours the formation of HCP over FCC, but with very less amount. [4] Our strategy of processing the solution favours the high yield of HCP phase, which is evident from the presence of intense XRD peaks corresponding to (010), (002), (012) and (110) planes, while the other peaks corresponding to (200) and (220) planes represent the FCC phase. The morphology of the synthesized DEG-Ni is shown in FESEM image, where a self-assembly of nanoparticles having particles size in range of 70 - 300 nm, is presented in Fig. 1(b).



Fig. 2. Zero-field cooled (ZFC) and field-cooled (FC) warming magnetization curve of (a) EG-Ni and (b) DEG-Ni nanoparticles. Magnetic hysteresis of (c) EG-Ni and (d) DEG-Ni nanoparticles at low and room temperatures. Inset in (d) shows variation of coercivity with the temperature of DEG-Ni.

The magnetic properties of the EG-Ni and DEG-Ni have been studied by performing both the temperature dependent zero-field cooling (ZFC) and field-cooled (FC) warming magnetization curve and magnetic hysteresis curves. ZFC and FC graph have been taken in the temperature range of 2 K - 300 K at H = 200 Oe for both EG-Ni and DEG-Ni (shown in Fig. 2(a-b)). ZFC curve of EG-Ni and DEG-Ni have broad hump at ~ 6 K and a sharp peak at ~ 17 K, respectively. The observed blocking temperature (T_B) is very close to the HCP-Ni nanoparticles prepared in PEG-200 (25 nm) $T_B \sim 12.5$ K which have size of ~ 25 nm.[2] The large magnetization value of EG-Ni, than DEG-Ni, indicates that EG-Ni is relatively more magnetic in nature than DEG-Ni.[6] The extracted value of the effective magnetic moment from the magnetization curves for DEG-Ni $\sim 0.021 \ \mu_B/f.u$ is less than the magnetic moment of EG-Ni $\sim 0.073 \ \mu_B/f.u$ at 300 K. The magnetic field dependence of magnetization for both DEG-Ni and EG-Ni at low temperature and room temperature are shown in Fig.2(c-d). The saturation magnetization for DEG-Ni ~ 9.54 emu/g is lower than the EG-Ni ~ 27.13 emu/g at T = 300 K and H = 5 T. The coercivity values of DEG-Ni ~ 140 Oe is larger than EG-Ni ~ 95 Oe at T = 300 K. The temperature dependence of the coercivity of DEG-Ni is shown in the inset of Fig.2(d). The values of coercivity obtained are: ~ 400 Oe, ~ 260 Oe, ~140 Oe at 5 K, 15 K, and 300 K respectively. The coercivity and

saturation magnetization of DEG-Ni decrease with increase in temperature. This shows that EG-Ni is more magnetic than DEG-Ni, which is perhaps because of the non-magnetic nature of DEG-Ni.[5] A clear exploration of the magnetic nature of absolute HCP-Ni is required for understanding the magnetic nature of HCP-Ni.

Conclusion

The optimization of synthesis of HCP-Ni with DEG and PVP has been done by isolating FCC-Ni from HCP-Ni to obtain a higher yield of HCP-Ni. The coercivity and hysteric behaviour of DEG-Ni decrease with increase in temperature. The processed DEG-Ni has less magnetization than EG-Ni (or FCC-Ni) and the magnetization in DEG-Ni is appearing from the mixed phase of FCC-Ni present with DEG-Ni.

Acknowledgement

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Phase Evolution in Sol-Gel Synthesized Barium Titanate Ceramics

Lickmichand M. Goyal and T. Garg*

Department of Physics, Vellore Institute of Technology, Vellore-632014

*Corresponding author: tarun.kulwant@vit.ac.in, lickmichand.m@vit.ac.in

Abstract

In this work sol-gel synthesized BaTiO₃ ceramics were studied for phase formation using X-ray diffraction. The effect of increase in calcination temperature was analyzed to see how BaTiO₃ crystallizes initially into cubic phase and then into tetragonal phase. Lower calcination temperatures below 500°C were not able to provide enough thermal energy required for formation of these ceramics. However, temperatures above 800°C lead to formation phase pure BaTiO₃. At sintering temperature of 1350°C, these ceramics predominantly crystallize into tetragonal phase.

Introduction

Barium titanate, BaTiO₃ (BTO) is one of the widely used materials known for its high dielectric constant, ferroelectric and piezoelectric properties[1-2]. It finds a variety of applications such as Multilayer capacitor (MLC), Dynamic Random-Access Memories (DRAM), charge-mediated biomedical applications, piezoelectric sensors, actuators and many more[1-3]. The tailor-need properties of these ceramics are strongly dependent on synthesis methods. Depending on the route chosen for synthesis, BaTiO₃ may crystallize into cubic or tetragonal or mixed phase. However, at room temperature, tetragonal phase is much desired due to its non-centrosymmetric nature leading to ferroelectric and piezoelectric properties. Most of the studies report evolution of tetragonal phase in BaTiO₃ at calcination temperatures above 1000°C[3-4]. However, current research is focused to have predominantly tetragonal phase at low calcination temperatures along with smaller grain size desired in some biomedical applications.

In this work, we have synthesized Barium titanate ceramics using sol-gel technique followed by calcination at different temperatures to obtain desired tetragonal phase with nanocrystalline grains. The samples were characterized using X-ray diffraction to estimate phase purity and crystallite size and lattice strain.

Methods and materials

 $BaTiO_3$ ceramics was synthesized using AR grade precursors. Barium acetate, Titanium isopropoxide (TTIP), glacial acetic acid, isopropyl alcohol and acetic acid were used as the starting materials. In first step, 0.1 M of TTIP was dissolved in 50 ml of Isopropyl alcohol followed by addition of 0.3 M glacial acetic acid and then magnetically stirred on a hot plate with magnetic stirrer at room temperature. In second step, 0.1 M Barium acetate was dissolved in 50 ml acetic acid and magnetically stirred. Both the solutions of titanium and barium precursors were mixed and stirred well until the transparent white solution is obtained. Then a drop of acetyl acetone was added to stabilize the sol. The temperature of the hot plate was increased to 90°C to induce gel formation. The formed gel was dried on the hot plate itself. Asprepared sample was calcined at 400, 600 and 800 °C. The calcined sample was subjected to X-ray diffraction to check the phase formation, average grain size and lattice strain. Furthermore 800 °C calcined sample was uniaxially pressed into a cylindrical pellet using a die at a pressure of 1 tonne. Polyvinyl alcohol (PVA) was used as a binder. The green pellet was sintered at 1350 °C for 4h in a muffle furnace. The green and sintered density of pellet were calculated and compared with theoretical density of BaTiO₃.

Results and discussion

X-ray diffraction patterns of 400, 600 and 800°C along with the 1350°C sintered sample are shown in Fig 1. The 400°C calcined sample shows the presence of BaCO₃ (JCPDS: 88-1175) which implies the need of higher energy of formation for BaTiO₃. While 600°C calcined sample shows the formation of BaTiO₃ with a cubic phase has been initiated however not completed. On further increase in calcination temperature to 800° C, the peaks of BaCO₃ and TiO₂ were diminished.



Fig.1 X-ray diffraction patterns of BTO calcined/sintered at 400, 600, 800 and 1350°C.



Fig 2. Peak splitting around 45° indicating phase transformation from cubic to tetragonal

Majority of the peaks could be indexed to $BaTiO_3$. However there were still small traces of $BaCO_3$ as indicated by peak around 24°. Furthermore the splitting of peak around 45° in (002) and (200) hints the improved tetragonality in crystal structure of BaTiO₃ as shown in Fig 2. [4-5]. X-ray diffraction pattern of the 1350°C sintered pellet shows no trace of BaCO₃. Moreover the splitting of all the characteristic peaks indicates that the tetragonal phase has increased substantially. Furthermore we also estimated the crystallite size and lattice strain for all the samples using Williamson-Hall plots and are listed in table 1.

 Table 1. Crystallite size and lattice strain of synthesized barium titanate

Temperature (°C)	Mean crystallite size (nm)	Mean lattice strain (%)
800	25	0.390
1350	45	0.292

We also calculated the green density and sintered density of the pellet sintered at 1350 °C. Green and sintered densities were found to be 3.87 and 5.96 g/cm³ respectively. Sintered density is nearly 99% of the theoretical density implying dense microstructure in the sintered sample.

Conclusions

In conclusion we have synthesized phase pure $BaTiO_3$ ceramics with predominantly tetragonal phase. Sintered density of these ceramics imply suitability of sintering temperature around 1300 °C.

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Synthesis And Characterization Of Lanthanum Modified Tungsten Trioxide And Its Efficient Antibacterial Performance

Pooja Nehra¹, Amita Khatri¹, Devina rattan Paul², Renu³, Kiran Nehra³, Pawan S. Rana^{1*}

 ¹ Dept. of Physics, Deenbandhu Chhotu Ram University of Science and Technology, Murthal -131039, Sonipat, Haryana (India)
 ²Dept. of Centre of excellence for energy and environmental studies, Deenbandhu Chhotu Ram University of Science and Technology, Murthal -131039, Sonipat, Haryana (India)
 ³Dept. of Biotechnology, Deenbandhu Chhotu Ram University of Science and Technology, Murthal -131039, Sonipat, Haryana (India)

*Corresponding author- <u>drpawansrana.phy@dcrustm.org</u>

Abstract

Present work is focused on the investigations of La doped WO₃ nanoparticles for their potentials applications in the field of antibacterial activity towards Escherichia coli (E. Coli) bacteria. Different doping concentration of Lanthanum (2%, 4%, 6% and 8%) in WO₃ was studied. The prepared samples were characterized by X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectroscopy (FTIR). Antibacterial activity towards E. Coli bacteria were studied at different concentrations using La incorporated WO₃ photocatalyst.

Introduction

Bacteria such as Escherichia coli (E. Coli) have adverse effects on human beings like it can causes bloody vomiting, diarrhoea and stomach cramps [1]. Although other metal oxides like ZnO were used as an antibacterial agent like yang et. al found that ZnO can act as a good antibacterial agent but it also kills mammals' cells by activating endoplasmatic stress response [2]. Therefore, another antibacterial agent with better compatibility needs to be explored. Tungsten trioxide has been bestowed with many properties such as optimum bandgap (2.4-2.8 eV). resilience to photo corrosion, good thermal and chemical stability, and its larger hole diffusion length as Pristine and compared to Titanium oxide [3]. Doping of rare earth metal ions results in induction of shallow energy levels between the valence band and conduction band which favours the separation of photogenerated electrons and holes which further play an important role in enhancing antibacterial activity. In the present work, pristine and a series of lanthanum modified WO₃ nanoparticles are synthesized by using the chemical co-precipitation method.

EXPERIMENTAL

Chemical Co-precipitation method was used to synthesize Pristine and Lanthanum (2%, 4%, 6% and 8%) doped Tungsten trioxide and were named as Pristine WO₃, 2WL, 4WL, 6WL and 8WL respectively. Take 7.121 gm of sodium tungstate in 100 ml of De-ionized water and stir for one hour at 80^oC on magnetic stirrer. similarly, we make

the solution of Lanthanum nitrate hexahydrate having optimum doping concentration and stir for one hour. Now add these two solutions and stir for 2 hours on hot plate at 80° C. Now we add Hydrochloric acid (HCl) dropwise into the solution until the pH reached up to 1. Thereafter kept the beaker overnight and on the next day, washed this slurry with ethanol and distilled water to remove all impurities from it and dry it in oven for 6 hours at 70° C. Now we calcined this powder at 550° C for 4 hour and used for further characterization.

RESULTS AND DISCUSSIONS

XRD AND FTIR

The XRD spectra of pristine and Lanthanum (2wt %, 4 wt. %, 6 wt.%, and 8 wt.%) doped Tungsten Trioxide is shown in fig.1. The main peaks appearing at $2\theta = 23.146^{\circ}, 23.699^{\circ}, 24.347^{\circ}$ in all samples corresponds to the plane (002), (020), and (200) respectively which indicates the formation of monoclinic Tungsten Trioxide and were fully matched with the JCPDS card no. 83-0951. Interestingly, the absence of any extra peak confirms that no extra phases or impurity are present in the synthesized sample therefore we concluded that doping of Lanthanum does not distort the crystal structure.



Fig.1. XRD pattern of pristine and La-doped WO₃

FTIR

Figure 2. shows the FTIR spectra of all the as prepared samples. From the graph, it is observed that there are strong or weak bands or shoulders at ~3435, ~1415, ~2925, ~2355, ~1620, ~780, ~ 830 cm⁻¹ in all the synthesized samples. The absence of any peak related to Lanthanum oxide in the spectra indicates that Lanthanum ions are successfully incorporated into the WO₃ structure.



Fig. 2. FTIR spectra of pristine and La-doped WO₃

Antibacterial activity toward E. Coli bacteria

Initially, varying concentrations of pristine and doped WO₃ nanoparticles including 10 μ g, 30 μ g, and 50 μ g were taken for evaluation their antibacterial activity against the E. Coli bacteria respectively. No effect was observed for 10 μ g and 30 μ g of pristine and doped WO₃ because of the highly resistant nature of E. Coli bacteria and hence we can check the other concentration of WO₃ i.e., 50 μ g. At this concentration, Pure and La-doped WO₃ was able to kill E. Coli bacteria effectively. From Table 1, it is observed that 4WL shows better antibacterial activity due to more availability of superoxide radicals. The antibacterial activity of Pure and doped Tungsten

pristine ar	id La doped WO_3	
S.No.	Sample	Inhibition Zone
		of E. Coli
1	Pristine WO ₃	(12.5 ±1) mm
2	2WL	(8±1) mm
3	4WL	(13 ±1) mm
4	6WL	(11 ±1) mm
5	8WL	(10.6 ±1) mm

Table 1: The Inhibition zone of E. (Coli I	by
pristine and La doped WO ₃		



Fig. 3. Inhibition zone of E. Coli bacteria

CONCLUSION

Synthesis of pristine and doped WO_3 is confirmed by XRD and FTIR. 4WL shows highest antibacterial activity towards E. Coli bacteria due to more availability of superoxide radicals and hence makes it an efficient and novel material in antibacterial applications.

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Impedance Spectroscopy of La doped BiFeO₃ Nanoparticles

Anju Kumari¹, Kavita Kumari², Jyotsna Sharma¹, Ankush Vij³, Shalendra Kumar^{3,4*}

¹Electronic Materials & Nanomagnetism Lab, Department of Physics, Amity School of Applied Sciences, Amity University Haryana, Gurgaon, 122413, India

²School of Materials Science and Engineering, Changwon National University, Changwon, Gyeongnam, 51140, Republic of Korea

³Department of Physics, College of Science, King Faisal University, *P.O Box 400*, Hofuf, Al-Ahsa, 31982, Saudi Arabia

⁴Department of Physics, University of Petroleum & Energy Studies, Dehradun, 248007, India

*Corresponding author: shailuphy@gmail.com

Abstract

We investigated the influence of La substitutional ions on the impedance spectroscopy properties of bismuth ferrite (BiFeO₃). Our compositions of $^{1.05}Bi_{1-x}La_xFeO_3$ (x = 0 to 5%) nanoparticles (NPs) have synthesized by sol-gel method. An increase in the dealing parameters of the rest time observed by electric analysis was established up to 5% La doped BiFeO₃ NPs. The impedance spectroscopy of La doped BFO is fitted with the R(C(R(QR)))(CR) model using cole–cole plots. It was found that a La-content of $^{1.05}Bi_{0.95}La_{0.05}FeO_3$ generated extra charged space that can across the threshold to initiate conduction due to these multiferroic materials.

Surface Plasmon Tunability of Green Synthesized Gold Nanoparticle Using Plasma Liquid Interaction

Parismita Kalita^{1,2*}, Palash Jyoti Boruah¹, and Heremba Bailung¹

¹Plasma Application Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology (IASST), Paschim Boragaon, Guwahati – 781035, Assam, India ²Academy of Scientific and Innovative Research (AcSIR), Ghaziabad – 201002, India

*Corresponding author: 2015parismitakalita@gmail.com

Abstract

High-quality and surfactant-free nanomaterial synthesis using Plasma – Liquid Interaction (PLI) technique is a rapidly growing interdisciplinary field in the interface between the plasma and material science. It offers single-step, rapid and large scale synthesis of nanomaterial of different shapes and sizes by simply controlling the physical as well as chemical parameters. One of the major advantage of this process is that it does not require any toxic reducing or stabilizing agent, due to which the process can be considered as a green process. This report involves the development of a plasma – liquid reactor for the fabrication of gold nanoparticles (Au NPs) of different sizes using PLI by controlling a physical and a chemical parameter that significantly influences the optical properties of Au NPs. OES spectra confirm the reactive species generated in the plasma zone.

Introduction

In recent years, a new method of generation of plasma via interacting with a liquid i.e., Plasma – Liquid Interaction (PLI), is becoming an increasingly important topic because of its potential applications in material, environmental and biological technologies [1]. In PLI, a wide range of short-lived and long-lived reactive species, UV radiations as well as low and high energetic electrons is formed [2]. It has been considered as a promising alternative for nanomaterial synthesis because of its flexibility in controlling both the physical (Plasma parameters) and chemical (solution parameters) properties. Using PLIs, desired shape and size nanomaterials (NMs) can be synthesized within few minutes. The reason behind the synthesis of various noble metal nanoparticles is that they have tunable Surface Plasmon Resonance (SPR) characteristics which can reach from visible to infrared. This unique property can be utilized in biological, optoelectronic and catalytic applications [3]. Petal et al. reported the synthesis of surfactant-free electrostatically stabilized Au NPs using HAuCl₄ solution [4]. Green synthesis of Au NPs to enhanced biological activities is reported by Pertiwi et al. [5]. Huang et al. studied the optical properties of Au NPs synthesize using PLI and its implementation in cancer diagnosis and photothermal therapy [6].

In this work, we have synthesized Au NPs of varying SPR bands. The various reactive species generated in the discharge zone, which plays a pivotal role as reducing agents during the formation of Au NPs is investigated by recording Optical Emission Spectra.

Experimental setup

Figure 1(a) and 1(b) depicts the experimental arrangement of the plasma – liquid reactor, which is placed in a magnetic stirrer for even distribution of the plasma generated species. An electrode arrangement with one electrode above the liquid (live electrode) and the other dipped into the liquid (grounded electrode) is coupled to the device, which is connected to a high voltage AC power supply (0 – 6 kV). Due to the generation of the discharge, the gap between the electrode and the liquid surface becomes conductive, which enables Plasma – Liquid Interaction to take place.





Optical Emission Spectroscopy (OES) (spectrometer: Andor SR303i-A having slit width 50 μ m and grating: 1200 lines/mm) is used to identify the emission of various plasma species. For optical characterization of the plasma synthesized Au NPs,

UV – Visible Spectrometer (UV-2600) is used. Structural characterization is employed using Transmission Electron Microscope (TEM) (Jeol, JEM 2100F).

Results and Discussion

The emission of various reactive oxygen and nitrogen (RONS) species such as OH, N_2 , N_2^+ , O as well as H_{α} lines are observed using OES [Fig. 2]. Intense emission of OH in the range 306 – 309 nm indicates the dissociation of water molecules [7].



Fig. 2. Typical OES spectra for natural air plasma.

A 50 ml solution of HAuCl₄ having concentrations 0.01, 0.05 and 0.1 mM is used to synthesize Au NPs. One minute of plasma discharge is sufficient for the formation of Au NPs. After plasma treatment, the color of the solution changes depending on the concentration of the precursor solution. The color change indicates the formation of Au NPs of different dimensions. With the increase of precursor concentration from 0.01 to 0.1 mM, the shifting of the SPR band of Au NPs towards a higher wavelength is observed [Fig. 3(a)]. It has also been observed that plasma treatment time can also affect the SPR band of the fabricated Au NPs, which shows a small redshift of the SPR band with the increase in treatment time [Fig. 3(b)]. Shifting of the plasmonic peak indicates the variation of nanoparticles' dimension [6]. For 1 and 7 minutes of plasma discharge at a fixed precursor concentration (0.05 mM), along with the visible range SPR peak, another low intense SPR peak around 750 nm is observed, which indicates the structural change of the Au NPs. TEM images of the Au NPs at different precursor concentrations are shown in fig 4(a). From TEM analysis, it is observed that the average particle size increases with the increase in precursor concentration [Fig 4(b)]. The reason can be understood in such a way that as the concentration increases, the probability of partially reduced HAuCl₄ interacting with growing NP is higher, which may be responsible for the increase in particle size. The mechanism of the formation of Au NPs can be explained by considering the following reactions [4].

$$\begin{array}{rcl} AuCl_4+3e^- \rightarrow Au^0+4Cl^-\\ e^-+H_2O \rightarrow H^-+OH \end{array}$$

$$\begin{array}{r} 20H \to H_2 O_2 \\ 3H_2 O_2 + 2Au^{3+} \to 2Au^0 + 6H^+ + 3O_2 \end{array}$$



Fig. 3. UV – Visible absorption spectra of plasma synthesize Au NPs at (a) different precursor concentration for 1 minute of plasma discharge (b) different discharge durations at a fixed precursor concentration (0.05 mM).



Fig. 4. (a) TEM image and (b) particle size distribution of Au NPs synthesize at different precursor concentration. Average particle size: 13 nm (0.01mM), 39 nm (0.05mM) and 49 nm (0.1 mM).

Conclusion

In this work, we report the development of a plasma – liquid reactor to synthesize different sized Au NPs. The process provides a rapid (few seconds) and green approach to nanomaterial synthesis as it does not require any chemical reducing or stabilizing agents. The size and optical properties (shifting of SPR band) of the Au NPs are found finely tunable through controlling a physical parameter (discharge duration) and chemical parameter (precursor concentration). OES spectra reveal the generation of different reactive species in the plasma zone that plays a crucial role in the formation process of Au NPs.

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Effect of Co-Doping (Y, Co) on Structural and Optical Properties of LaFeO₃

Daud Ahmad Ansari¹, Anand Somvanshi¹, Samiya Manzoor¹, and Shahid Husain^{1*}

Department of Physics, Aligarh Muslim University, Aligarh (INDIA), 202002

*Corresponding author: <u>s.husaincmp@gmail.com</u>

Abstract

The structural and optical properties of nanocrystalline La_{0.7}Y_{0.3}Fe_{0.7}Co_{0.3}O₃ sample, synthesized by sol-gel auto-combustion route, have been studied. The X-ray diffraction pattern shows that the sample was successfully formed in single phase perovskite structure. The value of tolerance factor (< 1) indicates the distortion and deviation from ideal perovskite structure. The Raman analysis reveals that the structure of the prepared sample is consistent with that of LaFeO₃ orthorhombic perovskite structure with *Pbnm* space group. Raman analysis reveals the compressive stress in the material. The Energy bandgap (E_g) as determined using Tauc's relation is found to be 2.93 eV.

Photodegradation of Methyl Orange Dye by Hydrothermally Grown CdS Nanoparticles

G. Sreedevi^{1,*}, Mohit Mittal², Badvath Purnesh², K.Aditya¹, V. Jayalakshmi²

¹Dept.of Freshman Engineering, PVP Siddhartha Institute of Technology, Vijayawada, A.P., India ²Department of Physics, NIT Warangal, Telangana, India **Corresponding author*: g.sridevimsc@gmail.com

Abstract

This paper focuses on the synthesis of CdS nanoparticles under hydrothermal route, studying their structural, morphological properties and photo degradation studies on the dye of methyl orange. Now day's methyl orange widely used dye in textile industry. For pollution free environment dye degradation is a one of the major component. From XRD studies CdS nanoparticles shows hexagonal phase with crystal lattice size of 12 nm and exhibiting the spherical spheres type morphology. A 400 watt halogen lamp is used to irradiate the CdS added dye solution to imitate the sunlight. For 100 ppm pure dye is on 464 nm showing the absorption value as 0.6235 respectively. This indicates that the absorption value is directly proportional to concentration. the concentration increases intensity of the peak increases. As the concentration of the dye and Irradiation Time increases the degradation percentage increases. We can also see the red shift for the 2nd peak after adding the nanoparticles. The peak shifted towards 460nm from 464nm in UV-VIS analysis. Which does mean the dye is getting degraded and colour is fading. By which we can conclude that CdS nanoparticles are acting as photocatalyst and breaking the dye complex structures into simpler compounds.

INTRODUCTION

In past few decades the role of material science is inevitable for the societal and technical development. When the sizes of materials reduce to nano regime they exhibit superior and excellent physical, chemical, electrical, optical properties, Among various inorganic semiconductors CdS experience tremendous development because of their unique band structure. CdS is a most important and interesting indirect energy bandgap (II-VI group) semiconductor of 2.42 eV and excited Bohr radius of 5.8 nm. CdS nanoparticles exhibit potential applications due to its excellent visible light absorption property in many fields such as light emitting diodes, lasers, photonics, photo catalytic, window layers in solar cells, photovoltaic cells, memory devices, switching devices, hydrogen storage, water and air purification. In this present study, we are discussing synthesis of CdS nanoparticles via hydrothermal method and discussing their structural, morphological properties and photo degradation studies of prepared nanoparticles

SYNTHESIS MECHANISM: To prepare CdS nanoparticles cadmium nitrate tetrahydrate $(Cd(NO_3)_2.4H_2O)$ and Thiourea (CH_4N_2S) are taken as precursors with AR grade of purity (>99%). All the chemicals weighed according to their

stoichiometry ratio and dissolved in 40 ml of deionized water in a beaker and stirred continuously with the help of a magnetic stirrer at room temperature. To produce transparent solution without any aggolemarization, sodium hydroxide solution (0.025M of NaOH in deionized water) is added slowly drop wise and stirried continuously for 2h. Now This aqueous solution turns into light yellow color without any precipitation, indicating the formation of CdS nano particles. This solution is transferred into autoclaves and maintained at a temperature of 120°C for 4h under autogenous pressure. It was cooled to room temperature and washed with distill water several times, filtered and then dried in hot air oven at 80°C for 6h finally grinding the prepared sample to get smooth powder.

RESULTS AND DISCUSSION

X-Ray diffraction & Morphological: Powder X-ray diffraction technique is a rapid analytical technique to determine the structure and phase of crystalline materials that gives information about unit cell dimensions. The X-ray diffraction pattern of CdS nanoparticles are shown in Figure 1. The X-ray diffraction pattern is analyzed by Xpert High Score Plus software. The strong and narrow peaks indicate that the prepared samples are well crystallized. X-Ray diffraction pattern shows various diffraction

peaks at 20 values 24.17°, 26.58°, 28.90°, 43.17°, 47.26°, 51.5° corresponding diffraction Plane is (100), (002), (101), (110), (103), (112) which are matched with the standard powder XRD data (PC-PDF file Numbers: 75-1545). The most prominent peak observed at 20 = 28.90°. The peaks of CdS are shown in Fig.1. The average size of crystallite is evaluated by Debye-Scherrer's formulae, $D = \frac{k\lambda}{\beta cos\theta}$

where k is shape factor, D is the average size of crystal lattice, λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) of X-ray diffraction peaks and θ is the Bragg's diffraction angle.CdS hexagonal system the lattice parameters are a=4.143A°, b=4.143A° and c=6.719A°. The average crystallite size (D) of the prepared sample is found as 21nm.



Fig.1. XRD of CdS Nanoparticles



Fig.2. Morphological structure of CdS Nanoparticles

DYE MATERIAL AND PHOTOCATALYTIC ACTIVITY:We have used methyl orange dye and distilled water to check the photocatalytic activity of CdS nano particles. Methyl orange dye absorption values has been found out using UV-VIS spectrometer. For pure dye the maximum value of absorption is at 464nm for both 100ppm and 200ppm CdS particles in distilled water. For 100ppm concentration of dye, CdS nanoparticles were added as 10, 20, 30, 40, 50mg respectively. After adding the nanoparticles, the absorption values have been noted immediately and after every half an hour up to 2hours using UV-VIS spectrometer. A 400watt halogen lamp is used to irradiate the CdS added dye solution to imitate the sunlight. The UV-VIS absorption spectra for 100 ppm pure dye is on 464nm showing the absorption value as 0.6235 respectively. Which indicates that the absorption value is directly proportional to concentration as the concentration increases the sharpness of the peak increases as well as the absorbance value. After adding the CdS nanoparticles in methyl orange dye solution, the absorption values have been noted immediately and after every half an hour up to 2 hours for every different concentration of dye with added different weight of CdS nanoparticles. As the irradiation time increases the absorbance value of each concentration decreases. Which implies the CdS nanoparticles acting as the photo catalyst and playing its part and breaking the complex structure of the dissolved dye in the solution. The dve degradation in 40mg and 50mg in 100ppm is in a progressive manner without any deviation. The dye degradation is increasing as the amount of irradiation time increases.

Fig.3. a) 10mg b) 20mg c) 30mg d) 40mg e) 50mg of



CdS nanoparticles added to 100 ppm solution.

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Synthesis Of ZnO Nanoparticles By Sol -gel and Co-precipitation Methods & Comparison Of Their Structural Properties.

Pawanpreet Kaur¹, Ritika Saini¹, Sakshi², Sikhardeep Kaur², Balwinder Kaur², Priyanka Sharma²

Department of Applied Sciences (Polywing) Sardar Beant Singh State University Gurdaspur- 143521 Punjab¹, Department of Applied Sciences Sardar Beant Singh State University Gurdaspur- 143521 Punjab²

*Corresponding author: ritika.saini23@yahoo.com

Abstract

Present work demonstrates the synthesis of Zinc oxide nanoparticles by co-precipitation and sol-gel methods. The prepared ZnO nanoparticls are further characterized by using X-ray diffraction technique. It has been observed from the X-ray diffraction data that both the variants exhibits hexagonal wurtzite structure. The particle size calculated for ZnO prepared by sol-gel is 29.90 nm and for ZnO prepared by co-precipitation is 20.66 nm. Furthermore it is found that the unit cell volume of ZnO nanoparticles prepared by sol-gel is smaller than the unit cell volume of ZnO sample prepared by co-precipitation method.

Introduction

Metal oxide nanoparticles have been the subject of focused research due to their unique electronic, optical, mechanical, magnetic, and chemical properties that are significantly different from those of their bulk counterpart. Metal oxides have attracted lots of attraction due to their ability to withstand harsh process conditions. Among various nanoparticles zinc oxide (ZnO) nanoparticles are of particular interest as they have large specific surface area, high pore volume, low cost, low toxicity and nanostructured properties. Nano ZnO make it a promising candidate, particularly in catalyst, photocatalysis, electrostatic dissipative coating, transparent UV protection films, and chemical sensors [1-4]. These remarkable properties form the basis for motivation of synthesis of ZnO nanaoparticles by sol-gel and co-precipitation method and to compare their structural properties.

Experimental Details

The Co-precipitation and the sol-gel methods were adopted for the synthesis of zinc oxide nanoparticles. Preparation by co-precipitation method: ZnO nanoparticles were synthesized by Coprecipitation method using 0.1M zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O) and 0.1M sodium hydroxide (NaOH) as precursors. 2.975g of zinc nitrate hexahydrate is dissolved in 100 ml of deionised water and 1g of NaOH in 250 ml of deionised water is added under magnetic stirring. When the addition is completed, the stirring is continued for 30 mins and then cooled with ice cold water. After the completion of the reaction, the solution is allowed to settle down for overnight. Then the precipitates formed are filtered and washed several times by deionised water to remove the any byproducts which are bound with the nanoparticles. The obtained precipitates are then allowed to dry at 60°C for 24 hrs and then calcined at 600°C for 2 hrs. Preparation by sol-gel method: 2.975 g of zinc nitrate hexahydrate is dissolved in 100 ml of deionised water and 1g of NaOH in 250 ml of deionised water is added under magnetic stirring. When the solutions are well mixed under the magnetic stirrer, 100 ml of ethanol which is filled in the burette is added drop wise to the solution of zinc nitrate and sodium hydroxide contained in a beaker. After the complete addition of ethanol, the solution is subjected to magnetic stirring for 30 mins and then cooled with ice cold water. After the completion of the reaction, the solution is allowed to settle down for overnight. Then the precipitates formed are filtered and washed several times by deionised water. The obtained precipitates are allowed to dry at 60°C for 24 hrs and then calcined at 600°C for 2hrs. The prepared samples are then characterized by x-ray diffraction (XRD) at room temperature.

Results and Discussion

The XRD patterns of the synthesized ZnO nanoparticle by both the methods are shown in Fig 1. where ZnO_a represents ZnO prepared by coprecipitation method and ZnO_b represents ZnO prepared by sol-gel method. The peaks at the crystal faces (100), (002), (101), (102), (110) assure the emergence of hexagonal wurtzite structure [4]. Furthermore, no impurity have been observed in the

prepared samples. The crystallite size (D) has been calculated by considering the most intense diffraction peak (101) in accordance with the Debye Scherrer formula [4] i.e

$D = 0.94 \lambda / \beta \cos \Theta$

where D is the average crystalline size, λ is wavelength, β the full width half maxima (FWHM) and Θ the diffraction angle. The crystalline size of the synthesized ZnO_a and ZnO_b samples are calculated as 20.66 nm and 29.90 nm respectively. From the Debye Scherer formula it is clear that there is an inverse relationship between the β and the D, which means narrower peaks are due to larger particles while broader peaks are obtained because of the smaller particles. This in agreement with the XRD peaks shown in Fig. 1. as XRD peaks of ZNO_a is broder than XRD peaks of ZnO_b.



Fig. 1. The XRD spectra of ZnO samples prepared by solgel (ZnO_b) and co-precitation methods (ZnO_a) .

 Table 1. Structural parameters of

ZnO nanoparticles		
Structural	ZnOa	ZnO _b
parameters		
Lattice	a= 3.4959	a= 3.4839
Constants(A ⁰)	c = 4.9411	c=4.9269
Unit cell Volume(A ⁰³)	52.2949	51.7872

The various calculated structural parameters are tabulated in Table1. It can be observed from the table that the unit cell volume of ZnO_b sample is smaller than that of ZnO_a sample same can be confirmed from the XRD patterns in fig 1. As the shift in most

intense peak position towards higher angle side is seen for the $ZnO_{\rm b}$ sample as compared to $ZnO_{\rm a}$ sample.

Conclusion

The nanoparticles of ZnO are successfully synthesied from both the methods i.e sol-gel and coprecipitation. The X-ray diffraction pattern confirms the hexagonal wurtzite structure for both the prepared samples. Broder XRD peaks of ZnO_a sample as compared to ZnO_b corresponds to smaller particle size i.e 20.66 nm for ZnO_a and 29.90 nm for ZnO_b, where ZnO_a represents ZnO prepared by coprecipitation method and ZnO_b represents ZnO prepared by sol-gel method. Moreover it is seen that the unit cell volume of ZnO_b sample is smaller than that of ZnO_a sample.

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STRUCTURAL AND MORPHOLOGICAL ANALYSIS OF NiCo2O4 PREPARED BY HYDROTHERMAL TECHNIQUE

D Pughal Selvi, S K Janani Sri, T Raguram and K S Rajni

Department of Sciences, Amrita School of Engineering, Coimbatore, Amrita Vishwa Vidyapeetham, India

*Corresponding author: ks_rajani@cb.amrita.edu

Abstract

In the present work, NiCo₂O₄ is prepared by hydrothermal method and its structural, morphological and electrochemical characteristics are analysed. From XRD, the average crystallite size changes from 17 to 9 nm when the nickel nitrate and cobalt nitrate ratio varies from (1:1, 1:2, 2:1). The surface morphology of the samples is imaged by a Field emission - scanning electron microscope. Most of the prepared particles are spherical in shape. As increases the Ni and Co concentration, the particles growth are from irregular to spherical in shape. Electrochemical studies is also carried out for the prepared samples. **Keywords:** Nanoparticles, XRD, FESEM, Optical Studies, Cyclic Voltammetry (CV).

Introduction

Supercapacitor which is also referred as supercap, Goldcap or ultra-capacitor is one of the energy storage device which have higher capacitance value than conventional capacitor i.e. electrolytic capacitor. Supercapacitor (SC) is a high capacity capacitor and can store 100 times more charge compare to electrolytic capacitor. It has more cyclic stability than rechargeable batteries i.e. it can have more charge discharge cycle's and can accept and release charge much rapidly than rechargeable batteries. [1, 2]. In this work, nickel cobalt oxide was synthesized as electrode material using hydrothermal synthesis method (a method for synthesis of single crystals (nano particles). When coupled together, nickel and cobalt could render the composites with rich redox reactions and improved electronic conductivity. Three different molar ratios of Ni and Co (nNi:mCo) were prepared to understand its important role in the development of fine nanostructures.

Experimental Techniques



Fig. 1 Synthesis procedure for Nickel Cobalt Oxide nanoparticles

Similarly, urea (of 2.1021 g) is dissolved in Deionized water (of 35 ml) and kept in stirrer for 1 hr. Then the solution containing urea was added drop wise to the sample solution and left for 1 hr in the stirrer. The solution was then transferred to a 100 ml Teflon Autoclave and kept inside the oven at 120 ° C for 4 hr. For cleaning, the solution was transferred to a beaker and kept in ultrasonic bath for 30 minutes. It was then kept in oven at 80°C for 12 hr, for drying. The dried sample was again cleaned three times using the above procedure. The final dried sample was kept in a muffle furnace for calcination process at 350° C for 2 hr. The above procedure was used to prepare all the three molar ratio samples. The samples 10 were later labelled as 1:1, 1:2 and 2:1. Fig.1 synthesis of NiCO₂O₄ nanoparticles

Results and Discussion

3.1. Structural Analysis



Fig. 2 PXRD pattern of NiCo₂O₄ nanoparticles

Fig. 2 shows powder X-ray diffraction pattern of all the three samples of Nickel Cobalt Oxide (NiCo₂O₄) prepared by varying the ratio of both nickel nitride (NN) and cobalt nitride (CN) by 1:1 (S1), 1:2 (S2) and 2:1 (S3). The peak corresponding to the planes matches well with the JCPDS data of NiCo₂O₄ (card no 20-0781) and NiO is observed in all the three ratios (card no 47-1409), respectively. The average crystallite size is calculated using Scherrer relation and it is noted that changes from 17 to 9 nm when the nickel nitrate and cobalt nitrate ratio varies from (1:1, 1:2, 2:1). Microstrain and dislocation density are directly proportional to each other and inversely proportional to the crystallite size. The hopping length at tetrahedral and octahedral sites decreases with the increase in nickel and then increases when the cobalt ion concentration which is attributed to the re-distribution of cations upon Ni and Co substitution [3].

3.4 FESEM Analysis



Fig. 3 FESEM images of (a) S1, (b) S2 and (c) S3 $NiCo_2O_4$ nanoparticles

From the Fig. 3, it can be seen from the images of all samples, most of the prepared particles are small spherical in shape. As NN and CN concentration changes, the particles grow from irregular to spherical in shape and in some places agglomeration is observed which is attributed to the synthesis process. It is noted that, the molar ratio of Ni: Co plays an important role in the morphology development of the nickel cobalt oxides which can be favourable to the applications.

3.5 Cyclic - Voltammetry Analysis

Cyclic voltammetry (CV) and galvanostatic (GV) charge/discharge tests are used to measure the electrochemical properties of the samples. Cyclic voltammetry (CV) and galvanostic (GV) test are done by software control. General setup consists of three-electrode, Ag/AgCl as the reference electrode, a Pt wire as the counter electrode and FTO coated with

NiCo₂O₄. 3 M KOH solution which is used as the electrolyte. A potential window in the range from - 0.04 V to 0.10 V is measured (Fig. 4). The CV measurements are performed at different scan rates varying from 1, 5, 10, 25, 50 and 100 mV/s. The peak potential at 0.10 V is called the anodic peak potential (E_{pa}), and it 23 is the potential when the surface of the electrode has been oxidized. The conventionally used materials for electrodes in pseudocapacitors which exhibits redox behavior [5, 6]. Thus, the graph exhibits pseudocapacitors behavior.



Fig. 4 CV analysis of (a) S1, (b) S2 and (c) S3 $NiCo_2O_4$ nanoparticles.

4. Conclusion

Nickel Cobalt Oxide nanoparticles are synthesized by varying the ratio of both nickel nitrate and cobalt nitrate (NN: CN) 1:1, 1:2, 2:1 using the hydrothermal method. The microstructural parameter confirms the cubic structure of the prepared samples, and the average crystallite size changes from 17.71 to 9.20 nm when the nickel nitrate (NN) and cobalt nitrate (CN) ratio are 1:1, 1:2, 2:1. Morphological analysis shows the synthesized samples are spherical in shape. The cyclic voltammetry studies are carried out for the prepared samples which exhibits the pseudocapacitors behavior.

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Synthesizing Silver Nitrate Nanocrystals from Rapidly Evaporating Microdroplets

Debashish Sarkar^{1*}, C. L. Prajapat¹, J. Bahadur² and Debasis Sen²

¹Technical Physics Division, Bhabha Atomic Research Center, Mumbai, 400085

²Solid State Physics Division, Bhabha Atomic Research Center, Mumbai, 400085

*Corresponding author: debashish@barc.gov.in

Abstract

Silver nitrate nanocrystals had been synthesized in large-scale by spray-drying an aqueous colloidal solution containing silver nitrate, polymer polyvinylpyrrolidone and ethylene glycol. The formation of silver nitrate nanocrystals had been confirmed using electron microscopy and x-ray diffraction. A small fraction of silver nanoparticles also formed during spray drying as confirmed by UV-Vis spectroscopy. Upon heat treatment, these silver nitrate nanocrystals reduced to silver nanocrystals as confirmed from x-ray diffraction and transmission electron microscopy. Thus, spray-drying can be used as an efficient and facile technique for large-scale production of silver nitrate and silver nanocrystals for various applications.

Charge Injection Mechanism in Semiconductor Memory Devices

Sandip Mondal*

Department of Electrical Engineering, Indian Institute of Technology, Mumbai 400076, India

*Corresponding author: phymondal@gmail.com

Abstract

Charge injection mechanism has been investigated in the two nonvolatile, semiconductor flash memory devices using a highspeed capacitance-voltage (HSCV) measurement system. The capacitance measurement process is fast in terms of measurement speed that it completes capturing the entire CV curve in less than 10 μ s. The system is capable of generating sequential pulsing sessions to inject the charges into the defect states and simultaneously measuring the HSCV curve. A continuous shift of the HSCV curve, as well as flatband voltage (V_{FB}) owing to injection of the charges into two terminal flash memory devices. The program state of memory devices is achieved due to the saturation of flatband voltage shift (ΔV_{FB}). The continuous charge injection helps to saturate the ΔV_{FB} . This mechanism confirms the availability of program and erase memory state in the semiconductor flash memory devices.

Effect of Gravity on the Vertically Flowing Down Water Jets

Wellstandfree K. Bani^{1, 2, *}, Shesstarwell K. Bani¹, and Mangal C. Mahato¹

¹Department of Physics, North-Eastern Hill University, Shillong-793022, India

²Department of Physics, Synod College, Shillong-793002, India

*Corresponding author: wellstandfreekbani@gmail.com

Abstract

A clean water jet flowing under gravity is allowed to impinge on the surface of deep water reservoir contaminated with tide detergent, a fluid pipe is formed on the jet extend up to some height from the surface of reservoir. The capillary waves appeared above the fluid pipe and the bulbous below which join the fluid pipe to the reservoir. We performed the experiment to measure the fluid pipe height H at various jet length L, flow rate Q, nozzle inner radius r_0 and concentration $c = 5 \text{ mg cm}^3$ of tidedetergent-water solutions in order to study the effect of acceleration due to gravity on the vertically flowing down water jets. We compare our experimental values of dimensionless fluid pipe height $\frac{H}{aRe}$ with the values of approximate expression using f_I = $\frac{2.73}{We_d^2}$ and $f_2 = \frac{2.73}{We_d^2} (1 + \frac{25.1}{We_d} + \frac{0.879}{SWe_d^2})^{-1}$ deduced by Hancock and Bush.

Introduction

A clean water jet flowing under gravity initially reduces its radius as the speed of the jet increase due to gravitational effect¹⁻³. However, with increasing Lthe jet become unstable and then develop necks and bulges due to the effect of capillary forces including acceleration due to gravity²⁻⁴. Recently, Dizes and Villermaux suggested that the capillary jet will exhibit the inertia dominated region and then gravity dominated region². Gravity plays a major role as it accelerates and stretches a vertically flowing down water jet^{5,6}. Thus, a falling water jet experiences many flow regimes² before break up into droplets leading to Plateau-Rayleigh instability⁴.

When a clean water jet impinges on the surface of water-detergent in the reservoir a fluid pipe is produced^{7,8}. The surface tension of the jet water is larger than that of water-detergent solution and thus causes *marangoni effect*^{7,8}. The vertical height of fluid pipe $\frac{H}{aRe}$ is controlled by viscous and *marangoni* stress⁸. We performed the experiment to measure the fluid pipe height and compare with the approximate expression in order to indirectly study the effect of gravity on a vertically flowing down water jet.

Experimental Method

The experimental setup is given elsewhere 9,10 . The experiment was performed with the same procedure as in case when a clean water jet impinges on the surface of water-detergent solution in the reservoir as explained in Ref.⁹. The experiment was performed for various L, Q, r_0 and $c=5 \text{ mg cm}^{-3}$ of tide-detergentwater solution. The capillary waves and fluid pipes are photographed using an ordinary (Nikon D5300)

camera^{9,10}. The photographs are digitally stored and calibrated before the measurement was begun.

The water-detergent solutions are prepared by mixing clean distilled water with commercially available tide detergent. All the measurements are done at room temperature of (25±0.5) °C and relative humidity of (80 ± 4) %. The flow rate Q was measured manually using the measuring cylinder. For our calculations, we have used the tabulated values of the dynamic viscosity μ =8.9×10⁻³ g cm⁻¹ s⁻¹, density of water $\rho=0.997$ g cm⁻³, kinematic viscosity $v=\frac{\mu}{2}$ =0.009 cm² s⁻¹ and the local acceleration due to gravity g=980 cm s⁻². The surface tension σ of (clean and contaminated) water was carefully measured using Jaeger's method⁹.

Experimental Results

In our experiment we use nozzles of various internal diameters $d_0=2r_0$ at their mouth, for example, $d_0=0.126$, 0.154 and 0.178 cm. For each of these nozzles we perform our experiment at various Q and L. The mean plug-flow jet speed u_0 at the mouth of the nozzle is calculated as $u_0 = \frac{Q}{\pi r_0^2}$ and the local jet speed at *L* as $u = (u_0^2 + 2gL)^{1/2}$ and local jet radius $r = r_0(\frac{u_0}{u})^{1/2}$. The entry speed *V* at the entrance of the fluid pipe can be calculated as V=u(L-H) and its radius as a=r(L - H).

The plots of $\frac{H}{aRe}$ and its approximate expressions f_1 and f_2 as a function of dynamic Weber number We_d for different r_0 , L and Q are shown in Fig. 1. Figure 1 show that for all Q values at smaller L the experimental values of $\frac{H}{aRe}$ is closer to f_I where the effect of gravity on the height of fluid pipe is ignored

but as *L* is increased the experimental values become closer to f_2 where the first effect of gravity is taken under consideration⁸. The plots show similar behaviour for all r_0 , *L* and *Q*. However, the plots of $\frac{H}{aRe}$ and its approximate expressions f_1 and f_2 as a function of *S* are shown in Fig. 2.



Fig. 1. Plot of $\frac{H}{aRe}$ and its approximate expressions $f_I = \frac{2.73}{We_d^2}$ and $f_2 = \frac{2.73}{We_d^2} (1 + \frac{25.1}{We_d} + \frac{0.879}{SWe_d^2})^{-1}$ as a function of dynamic Weber number $We_d = \frac{\rho a V^2}{\Delta \sigma}$, where the Stokes number $S = \frac{vV}{ga^2}$, Reynolds number $Re = \frac{aV}{v}$ and $\Delta \sigma$ is the difference of surface tension of jet water and the tide-detergent-water solution in the reservoir. The experimental parameters are: r_0 =0.063 cm, c=5 mg cm⁻³, Q=0.958, 1.208, and 1.458 cm³ s⁻¹. The inset shows the maximum diameter of the bulbous.



Fig. 2. Plot of $\frac{H}{aRe}$ and its approximate expressions f_I and f_2 as a function of *S*. The experimental parameters are: $r_0=0.063$ cm, c=5 mg cm⁻³ and Q=0.958 cm³ s⁻¹.

The plots of $\frac{H}{aRe}$ and its approximate expressions f_1 and f_2 as a function of We_d for different r_0 and $S=0.349\pm0.024$ are shown in Fig. 3. Figure 3 shows very similar behaviour with the earlier experimental results of Hancock and Bush⁸.



Fig. 3. Plot of $\frac{H}{aRe}$ and its approximate expressions f_1 and f_2 as a function of We_d for $S=0.349\pm0.024$. The experimental parameters are: $r_0=0.063$, 0.077 and 0.089 cm and c=5 mg cm⁻³.

Discussion and conclusion

Our experimental results of $\frac{H}{aRe}$ as a function of We_d are not in agreement with the earlier results of Hancock and Bush⁸. However, it shows very similar behaviour when $S=0.349\pm0.024$ which is very large compare to S=0.062 used in the earlier experiment⁸. The effect of gravity on the fluid pipe must be the same for all L (since L is small). However, the force due to gravity accelerates the jet as it falls downward. Thus these changes of experimental values of $\frac{H}{aRe}$ from f_1 to f_2 as a function of We_d with increasing L are presumed due to increase of local jet speed u and thus the speed V at the entrance of the fluid pipe.

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A GUI-based 2D-SAXS Data Analysis Software for Study of Anisotropic Structure in Mesoscopic Length-scale

Avik Das^{1,2*}, Jitendra Bahadur^{1,2} and Debasis Sen^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: avikd@barc.gov.in

Abstract

A graphical user interface based software package, named 'SAXS2D' has been developed for analysis of 2D small-angle X-ray scattering (SAXS) data. The software has been tailor-made for handling a large amount of SAXS data of the newly installed SAXS beamline of Indus-2 synchrotron both in interactive and batch mode. The unique feature of this Python language based software package is to analyze 2D-SAXS data, especially the anisotropic 2D-scattering patterns to reveal orientated and/or anisotropic structure in mesoscopic length scale. To demonstrate the performance of the software, the structural analysis of anisotropic pores distribution present in a shale-rock sample has been presented.

Modeling and Performance Analysis of Optical Microring Resonator for Chemical Sensing

Rajat Srivastava, Sangeeta Kale*

Department of Applied Physics, Defence Institute of Advanced Technology Girinagar, Pune-411025 *Corresponding author: sangeetakale2004@gmail.com

Abstract

The progress of technology from electronics to photonics is now evident more than ever, due to the ever increasing demands of faster and miniaturized technological gadgets; especially sensors. Several efforts have been made to optimize the selection of materials for such photonic applications. In this work, we have designed and simulated optical micro-ring resonators with different optical materials for their use as an efficient chemical and biological detector. We modeled an optical ring resonator with dimensions of the waveguides as small as 200 nm. Using this model, we studied the absorbance, reflectance and transmittance of resonator for materials like silicon nitride, silicon-on-insulator (SOI). We also conducted a study to analyze the behavior of device when exposed to ethanol on the sensor surface. After modifying sensing surface for ethanol sensing we observed a shift in resonating wavelength. For SOI based resonator the wavelength shift was 4.05 nm and for silicon nitride based resonator the shift 10.03 nm. The modeled device had a quality factor of 2129 and 556; the finesse was obtained to be 48 and 12 for SOI and Silicon Nitride based optical microring resonator structure respectively; the details of which will be discussed in this presentation.

Introduction

The characteristics of silicon photonics integrated circuits share many of its features with those of electronics integrated circuits. The integration of photonics and electronics integrated circuits [1] creates a possibility to develop a more efficient system for monitoring and controlling of various chemical and biological factors [2]. Optical microring resonators (OMR) are a type of microcavity sensors which has a straight waveguides coupled to a ring waveguide. The principle on which microcavity sensor works can be explained as the coupling of sensed light in a microcavity considering the condition for resonance [3]. The evanescent field of this confined light decays exponentially into the local surrounding [4]. Hence, the propagation of confined light is highly dependent on the characteristics like RI of the waveguide and reagents present in the surrounding of the waveguide [5]. The smaller size of optical micro-ring resonator provides the option to develop sensor arrays on a single sensor chip and perform multiplexed sensing. Along with Si, various other different materials having high refractive index like Lithium Niobate, high index nitrides and glasses, III-V semiconductors and some polymers [6] can also be used to integrate photonic circuits. This property of high refractive index possess a restriction on photonic circuit dimensions as even small variation in core's thickness and width may lead to unwanted effects of the circuit performance [7].

Since fabricating of an optical microring resonator is a complex task and requires huge accuracy, it is necessary to first study its behavior by performing simulation of the required structure. This can be done in several ways which include Finite Element Method, COMSOL Multiphysics and others. In this work, we have performed simulations in COMSOL simulation software because it gives an idea about the overall transmittance, absorbance and reflectance experienced by optical signal.

Modeling and Simulation

We have performed several simulation studies taking into consideration the RI contrast and material properties of Silicon Nitride and SOI waveguides. The simulation was performed using the Wave Optics module of COMSOL Multiphysics simulation software. In the performed simulation, the thickness of straight and ring waveguide was taken to be 200 nm each. The gap between the straight and ring waveguide near the coupling region was kept ~ 200 nm. The ring radius was kept to be 6 μ m in each case. The study was conducted for the excitation of 1550 nm laser source. The transmission spectrum was obtained for both the materials with the wavelength



Figure 1: Electric Field Intensity (a) SOI based OMR (b) Silicon Nitride based OMR

sweep enough to visualize the resulting plots.

The electric field intensity plot obtained in COMSOL Simulation is shown in Figure 1. For SOI platform, the plot shows the variation of and transmittance reflectance with varving wavelength for the studied device. It shows that maximum transmission loss is found to be around -32.85 dB at a resonating wavelength of 1554.77 nm (the accuracy till 2 decimal points is due to the simulation result outputs, and has less physical relevance). Similarly for Silicon Nitride based platform, maximum insertion loss was obtained to be -18.1 dB at a resonating wavelength of 1562.62 nm. When the whole ring surface is exposed to an ethanol sample, then the effective refractive index changes by a value of 0.03 RI unit and this change leads to shift in the resonating wavelength of the devices. For SOI based microring resonator, the shift in transmission power was obtained to be -7.98 dB along-with a shift in the resonating wavelength which was observed to be 4.05 nm. Also for Silicon Nitride based microring resonator, the resonant wavelength shift was observed to be 10.03 nm while negligible shift in transmitted power. The plot for the corresponding shift is shown in Figure 2(a) and Figure 2(b) for SOI and Silicon Nitride based microring resonators. The Free Spectral Range (FSR) for SOI based OMR was obtained to be 35.18 nm and silicon nitride based OMR was 36.37 nm as shown in Figure 2(c) and Figure 2(d). Also, the quality factor for SOI based resonator was 2129 which reduces drastically to 556 as the waveguide material changes to silicon nitride.



Figure 2: (a) Wavelength shift in transmission for SOI based OMR upon surface modification. (b) Wavelength shift in transmission for Silicon Nitride based OMR upon surface modification. (c) Transmission spectrum for SOI based OMR. (d) Transmission spectrum for Silicon Nitride based OMR.

Table I give tabulated information about different parameter variation between SOI based OMR and Silicon Nitride based OMR.

Table I: Different parameters of OMR.

Parameters	SOI based OMR	Silicon Nitride based OMR
λ	1554.77 nm	1562.62 nm
Δλ	4.05 nm	10.03 nm
Finesse	48	12
Quality Factor	2129	556

Conclusion

In this work, simulation of OMR based on two materials was performed. One of the structures has Silicon as waveguide while the other has Silicon Nitride as waveguide. It was observed that the OMR with silicon as waveguide showed a quality factor which is three times greater than that of silicon nitride Also, the finesse value for SOI based resonator is four times to that of silicon nitride based resonator. The sensitivity of the OMR sensor for SOI based waveguide was 4.05 nm and that of other sensor is 10.03 nm for a total change of 0.03 in effective refractive index. Due to better refractive index contrast, improved quality factor and sharpness of the peak, it can be said that OMR sensor based on SOI is better for sensing any chemical or biological analyte.

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Curved Structured 3D Printed Flexible Triboelectric Nanogenerator

Anand Babu, and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

3D printing is a versatile tool to fabricate any structure of desired shape and size, as a result an attempt has been taken to fabricate the triboelectric nanogenerator (TENG). We have prepared a curved structured TENG that exhibits superior flexibility and excellent mechanical energy harvesting capabilities. It is also expected to integrate with various parts of the body to monitor diverse human activities.

Introduction

Triboelectric nanogenerator (TENG), a kind of mechanical energy harvester, working under the combined concept of contact electrification and electrostatic induction. It is becoming very much popular in recent years due its high electrical throughput with wide choice of the materials of device fabrication.

Diverse techniques are used to fabricate a TENG, additive manufacturing is also one of them that draws attention due to easy availability of the low-cost materials, ease to fabricate the desired shape and size. Due to the limitations of the thickness of material and its stiffness, prepared from additive manufacturing, restrains the materials contact and further electrical output of TENG.

We have prepared a curved structured 3D-TENG, prepared with the help of 3D printing technique. It provides better contact area and flexibility to the device, consequently, it can able to produce peak to peak 15 V of voltage and 4.8 μ A of current output under the minimal force of 3 N. Further, a capacitor is also charged to demonstrate its energy harvesting capabilities, capacitance e.g., 2.2 μ F is charged up to 0.45 V in 15 s only.

Experimental Section

Polyethylene terephthalate glycol (PETG) and nylon 6 filament was purchased from eSUN. Ender-3 3D printer was used to print the two rectangular concave curved slabs of PETG and nylon 6 of dimension of 30 $mm \times 20 mm \times 2 mm$. The voltage and current responses were recorded from the digital storage oscilloscope (Keysight, X1102G) and source meter (Keysight, B2902A) respectively. Surface potential was measured from electrostatic voltmeter (Monroe Electronics, Isoprobe 279).

The two rectangular curved slabs of PETG and nylon 6 were sandwiched between the two aluminum

electrodes. The electrical connections were made by connecting the two copper wires with the aluminum electrodes, the schematic of 3D-TENG is illustrated in Figure 1(a).



Fig. 1: (a) Schematic of 3D-TENG. (b) Voltage and current responses of 3D-TENG under the repeating force amplitude of 3N.

Result and discussion

As evident from the schematic in Fig. 1(a), PETG and nylon 6 are used as a two tribolayers of 3D-TENG, in which PETG works as a tribonegative layer while nylon 6 as tribopositive layer. Tribonegativity or tribopositivity is defined by the materials property to lose or gain electrons, those materials which are more likely to lose the electrons known as tribopositive materials, while those are likely to gain the electrons designated as tribonegative materials. Based on its tribopositive or tribonegative nature, the materials are arranged in a series called as triboelectric series. To fabricate a TENG with high electrical output, it is primary requirement that the two materials are from the two ends of triboelectric series. Due to a large difference in position of PETG and nylon 6 in triboelectric series, 3D-TENG displayed a very good electrical performance and able to produce peak to peak open circuit voltage (V_{oc}) of 15 V and short circuit current (I_{sc}) of 4.8 μ A at a minimal force of 3N, showed in Fig.1(b). The electrical output, V_{oc} and I_{sc} of 3D-TENG is elucidated by the surface charge density of the comprised materials, as depicted by the following equations

$$V_{oc} = \frac{\sigma x(t)}{\varepsilon_0} \qquad a)$$

$$Q_{sc} = \frac{s\sigma x(t)}{d_0 + x(t)} \qquad b)$$

Where, V_{oc} represents open circuit voltage, σ is surface charge density, x(t) is distance between the two tribolayers, ε_0 is permittivity of free space, Q_{sc} is short circuit charge transfer, S is surface area under the area of contact, and d_0 is thickness of the material. The calculated surface charge density of PETG and nylon 6 is listed in the table 1.

Table 1. Surface charge density of comprisedmaterials in 3D-TENG.



Fig. 2: (a) Variation of voltage, current and power density as a function of different load resistances (inset shows the equivalent circuit diagram). (b) The transient repones of an external capacitor charging and discharging plot of 2.2 μF capacitance, capacitor connected to 3D-TENG via bridge rectifier (given in inset).

Because surface charge density of the materials linearly depends on the open circuit voltage and short circuit current, thus 3D-TENG is showing a superior electrical output.

To measure the electrical output characteristic of 3D-TENG, voltage and current are also measured passing through various load resistances. The voltage drop steadily increasing as the load resistance increasing and saturated at infinitely large resistance. However, output current gradually decreases as the load resistance increases. The instantaneous output power density of 3D-TENG is 9.8 μ w/cm² as illustrated in Fig. 2(a). Furthermore, to test the energy harvesting capabilities of 3D-TENG, a transient response of capacitor ($\sim 2.2 \ \mu F$) charging is recorded. The capacitor is able to reach the saturated voltage of 0.45 V within 15 s displayed in Fig. 2(b), where capacitor is connected via parallel connection through a full-wave bridge rectifier (inset of Fig. 2(b)). The output performances from 3D TENG indicating the potential mechanical energy harvesting abilities that pave the way of futuristic applications in self-powered technology.

Conclusion

A flexible 3D-TENG is fabricated by using additive manufacturing techniques, which shows excellent mechanical energy harvesting capabilities. Due its distinct structure, 3D-TENG can be also possible to use as wearable devices to monitor diverse human activities.

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Detector Performance Study for Cargo Scanning Applications using Monte Carlo Simulations

Amit Kumar and Anita Topkar*

Electronics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India *Corresponding author: anita@barc.gov.in

Abstract

Cadmium tungstate (CdWO₄) scintillator coupled to silicon PIN photodiode was investigated as a detector for Cargo Scanning applications for 6 MeV LINAC polychromatic X-ray spectrum. Monte Carlo (MC) simulation study was carried out for the generation and transportation of 6 MeV X-ray spectrum and to study energy deposition in CdWO₄ crystal. The penetration of 6 MeV X-rays through various thickness of steel was theoretically estimated. Images of stainless steel (SS) plates behind thick SS blocks were generated with the simulation data.

Introduction

LINAC based X-ray imaging systems with energy in a few MeV range are widely used for the inspection of cargo containers [1, 2]. The Cargo inspection system mainly comprises of X-ray LINAC as a source and detector array with back end electronics for line scan image generation. X-ray images of the cargo containers are obtained by passing them through X-ray fan beam and by measuring intensity of the attenuated X-ray beam as measured by the detector array. For the development of detectors for indigenous cargo scanners, we have studied the detector performance with 6 MeV LINAC spectrum for scintillator coupled silicon PIN photodiode detectors. Considering the energy of 6 MeV, CdWO₄ was chosen as a scintillator due to its high effective atomic number, wavelength matching to silicon, high radiation hardness, etc. Zeff, the geometrical parameters of the scintillator are important to obtain desired imaging performance. To study detector performance for cargo scanning, Monte Carlo (MC) simulation study was carried out to generate the 6 MeV X-ray spectrum and to estimate generation of signal in CdWO₄ photodiode detectors. The attenuation of signal due to SS objects of various thicknesses was also studied.

Simulation Modeling & Method

Monte Carlo based GEANT4 simulation tool was used to study generation and transportation of X-ray beams from 6 MeV LINAC. The code consists of several modular classes incorporating geometry (G4DetectorConstruction), primary beam (G4PrimaryGenerator), physics (G4EmStandardPhysics), user defined classes (G4EventAction & G4SteppingAction). C++ was as used to write the simulation code where codes are broken into several modules represented by various classes in object-oriented programming.

X-ray spectrum was generated from tungsten target using monochromatic 6 MeV electron beam. The CdWO₄ crystal was exposed to the 6 MeV X-ray spectrum and energy deposition in the crystal was calculated by varying the thickness of the crystal in order to optimize its thickness. The scintillation spectrum generated in the crystal due the energy deposited by X-rays was obtained by simulation. A Si photodiode was coupled to one of the longer faces of the crystal and other faces were coated with MgO to avoid leakage of scintillation photons. The scintillation photons were collected in photodiode and its spectrum was calculated. Subsequently penetration of the X-ray beam in steel was studied by varying the thickness of steel. The attenuation in the spectrum was calculated based on the energy deposition in CdWO₄ crystal by the transmitted photons. To generate images for penetration performance of a cargo scanner, SS plates of various thicknesses (20% of the block thickness) were kept behind SS blocks and energy deposited in the detector was calculated for the transmitted beam. For visual display of the data, gray scale images were generated with the gray values decided based on the energy deposited in the detector. The gray values were further scaled to get better contrast of the image.

Results and Discussion

The 6 MeV X-ray spectrum generated from the tungsten target is polychromatic with photon energy ranging from 0-6 MeV (Fig. 1.). The calculated average energy was about 1 MeV. The calculated energy deposition in CdWO₄ of cross section 5 mm x 5 mm with different thicknesses is plotted in Fig. 2. The energy deposition increases rapidly with the



Fig. 1. 6 MeV X-ray spectrum from tungsten target.



Fig. 2. Energy deposition in CdWO₄ crystal as a function of its length

thickness initially up to 4 MeV and slowly subsequently. The scintillation photon spectrum generated in CdWO₄ shows peak at 2.6 eV and these photons are collected in Si photodiode (PD) coupled to the scintillator. The spectrum collected in photodiode is shown in Fig. 3 and the photon collection was observed to be 80%.



Fig. 3. Scintillation photons reaching to photodiode. X-axis is energy & Y-axis is no. of photons

Fig. 4 shows the transmittance of total X-ray energy deposited in the scintillator through SS objects of thicknesses varying from 50 mm to 400 mm. It was observed that 400 mm steel attenuates X-ray by a factor of 10^{-6} .



Fig. 4. Attenuation of 6 MeV spectrum through SS with thickness varying from 100 mm to 400 mm.



Fig. 5. Gray image of 40 mm plate behind 200 mm SS block (left) and 60 mm plate behind 300 mm SS block (Right)

The gray scale images of SS plates behind SS blocks are shown in Fig. For 40 mm plate behind 200 mm SS the % signal difference is 65% and for 60mm plate behind 300 mm SS block the % signal difference is 78%. Since the signal was observed to be reduced by a factor of 1.4×10^{-3} for 200 mm SS block and 10^{-4} for 300 mm SS block, therefore further penetration in higher thicknesses became difficult to see in the simulation.

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Photoluminescence Properties of Orange Red Emitting LiSrP₃O₉:Sm³⁺ Phosphor

Payal Khajuria^{1,*}, Ankush Vij³, A. K. Bedyal¹, H.C. Swart², and Vinay Kumar^{1,2,*}

¹Department of Physics and Astronomical Sciences, Central University of Jammu, Rahya-Suchani, Samba-181143 (J&K), India ²Department of Physics, University of the Free State, P.O. Box 339, Bloemfontein, ZA9300, South Africa ³Department of Physics, University of Petroleum and Energy Studies, Dehradun, Uttarakhand 248007, India

*Corresponding author: Payal Khajuria (email: payalkhajuria99@gmail.com); Vinay Kumar (email: vinaykdhiman@yahoo.com)

Abstract

The Combustion method was used to synthesize the orange-red light emitting LiSrP₃O₉:xSm³⁺ (x = 1 mol%) phosphor. Powder X-ray Diffraction analysis was used to confirm the phase of the prepared LiSrP₃O₉:xSm³⁺ phosphor and photoluminescence (PL) properties were investigated under ultraviolet (UV) excitation (300–450 nm). The wavelengths 595 nm and 398 nm were used to record the excitation and emission spectra of the prepared phosphor. The emission spectra of LiSrP₃O₉:Sm³⁺ phosphors consist of series of sharp lines centered at 559 nm, 595 nm and 641 nm corresponding to ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ transitions of Sm³⁺ ion respectively. The CIE (Commission International de l'Eclairage) coordinates were calculated and determined to be x = 0.58, y = 0.42. Therefore, the LiSrP₃O₉:Sm³⁺ phosphor is a promising material for use in wLEDs.

Introduction

The use of White light-emitting diodes (wLEDs) for next-generation solid illumination devices, backlighting of liquid crystal displays etc have recently made significant progress. Phosphate compounds have been employed as host materials for fluorescent lamps for many years because of their low material cost, ease of synthesis and great stability for usage in lamp applications [1]. The Sm³⁺ ion with 4f⁵ configuration is regarded an essential activator for producing bright orange red light due to powerful ${}^{4}G_{5/2} \rightarrow {}^{4}H_{9/2}$ emission.

In the present work, we report on the structural and Photoluminescence properties of LiSrP₃O₉:Sm³⁺ phosphor synthesized by the Combustion method.

Experimental

The combustion method was used to prepare LiSrP₃O₉:xSm³⁺ (x=1 mol%) phosphor using urea as a fuel. Lithium nitrate(LiNO₃;99.0%), Strontium nitrate(Sr(NO₃)₂;99.0%), Ammonium dihydrogen orthophosphate(NH4H₂PO₄;99.0%), Samarium nitrate (Sm₂O₃;99.0%) and Urea(CH₄N₂O;99.0%) of Sigma Aldrich were the starting materials used in the synthesis. The raw ingredients were used as is, with no further purification, in proper stoichiometric ratio. The complete procedure of combustion method to prepare LiSrP₃O₉:Sm³⁺ phosphor has been reported in our previous work [2].

Powder X-ray diffraction (XRD) method was to analyze the phase development and purity of the material by using Bruker D8 Advance X-ray diffractometer. A Cary eclipse spectrophotometer with a Xenon lamp was used to record the photoluminescence (PL) spectra. Osram Color calculator software was used to plot the CIE chromaticity coordinates.

Results and discussion

XRD studies

Figure 1 depicts the powder XRD pattern of the $LiSrP_3O_9:xSm^{3+}$ (x = 1 mol%) phosphor annealed at 700 °C along with respective standard pattern. All the diffraction peaks of powder XRD patterns matched well with the standard patterns available on Crystallographic open database 7700884. The phosphor $LiSrP_3O_9:Sm^{3+}$ belongs to the triclinic phase with space group P1. The host material retains the structure and did not display any impurity peak of Sm^{3+} used as dopant.

Photoluminescence studies

Fig. 2 displays the excitation and emission spectra of LiSrP₃O₉:Sm³⁺ (1 mol%). The wavelength centred at 595 nm and 398 nm were used to record the excitation and emission spectra of LiSrP₃O₉:Sm³⁺phosphors. The excitation spectra consist of charge transfer band (O^2 - \rightarrow Sm³⁺) centred at

210 nm [3] and the intra-4f transitions from the ground state ${}^{6}\text{H}_{5/2}$ to higher energy levels of Sm³⁺ ion between 300 and 450 nm [4]. The absorption peaks monitored at 358 nm, 371 nm, and 398 nm, were due to the transitions from ${}^{6}\text{H}_{5/2}$ to ${}^{4}\text{F}_{9/2}$, ${}^{4}\text{D}_{5/2}$, and ${}^{4}\text{K}_{11/2}$ respectively of Sm³⁺ ions. The peak centred at 398 nm was found to have the highest intensity, hence blue LEDs can be used as an excitation source for this phosphor. The emission spectra show three major peaks on excitation with 398 nm wavelength [5]. The three dominant emissions were visible at 559 nm, 595 nm, and 641 nm, respectively, which correspond to the transitions ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$, ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ and ${}^{4}G_{5/2} \rightarrow {}^{6}H_{9/2}$. The peak centred at 595 nm with a bright orange-red emission is the most dominant of them. This matches well with the wavelength of n-UV based LEDs.



Fig. 1. PXRD patterns of LiSrP₃O₉:Sm³⁺ phosphor.



Fig. 2. Photoluminescence excitation and emission spectra of LiSrP₃O₉:0.01Sm³⁺ monitored at 595 nm and 398 nm.

The CIE coordinates of LiSrP₃O₉:Sm³⁺ phosphor was calculated by using Osram Color Calculator software and found to be (0.58, 0.42) at predominant wavelength of 595 nm which corresponds to orange

red color emission depicted in Fig. 3. Thus the phosphor was determined to be suitable candidates for orange- red LEDs.



Fig. 3. CIE coordinates for LiSrP₃O₉:Sm³⁺ phosphor.

Conclusions

Orange-red emitting $\text{LiSrP}_3\text{O}_9:\text{Sm}^{3+}$ phosphor was successfully synthesized by the combustion method. The PL results show an intense peak at 398 nm which matched well with the emission wavelength of near-UV LED's. Strong orange-red emission was observed at 595 nm in the prepared phosphors, with two additional peaks at 559 nm and 641 nm. Also, the calculated CIE coordinates were found to be (0.58, 0.42). The results show that the LiSrP₃O₉:Sm³⁺ phosphor can be used as a good candidate for orangered component in wLEDs.

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A transport measurements set up to probe single atomic/molecular junction at room temperature

Biswajit Pabi* and Atindra Nath Pal

S. N. Bose National Centre for Basic Sciences, Sector III, Block JD, Salt Lake, Kolkata - 700106

*Corresponding author: biswajitpabi1@gmail.com

Understanding the transport at the atomic limit (single atom or molecule) is the prerequisite to explore the future generation nanoelectronic applications. Among various experimental procedure, mechanically controllable break junction (MCBJ) is one of the well accepted experimental techniques to study and understand the atomic or molecular scale devices. In the present work, we demonstrate the fabrication and characterization of a gold atomic contact and 4, 4' bipyridine single molecular junction between gold electrodes using a homemade MCBJ experimental set up.

Deep Red Emitting Eu³⁺ Activated Sr₃B₂O₆ Phosphor for White Light Emitting Diodes

Isha Charak^{*}, M. Manhas, A. K. Bedyal and Vinay Kumar^{*}

Department of Physics and Astronomical Sciences, Central University of Jammu, Rahya Suchani, Samba, 181143

*Corresponding author: isha.charak96@gmail.com, vinaykdhiman@yahoo.com

Abstract

The Sr₃B₂O₆:xEu³⁺ phosphors were synthesized by the combustion technique. The structural and luminescent properties of the material had been explored using powder X-ray diffraction (XRD) and Photoluminescence (PL), respectively. The powder XRD results showed the formation of single-phase Sr₃B₂O₆:xEu³⁺ phosphors with rhombohedral crystal system and space group R-3c. PL results showed that under 394 nm excitation, the prepared Sr₃B₂O₆:xEu³⁺ phosphors give four characteristic emissions due to the 4f-4f transitions. i.e. ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1,2,3,4). The strongest emission peak at 614 nm is due to ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transitions which give intense red emission. The CIE coordinates for Sr₃B₂O₆:xEu³⁺ was (x = 0.65, y = 0.35) which falls in the red region of the horseshoe gamut with a color purity of 99.3%. The result shows that Sr₃B₂O₆:xEu³⁺ phosphor can be used in blue chips-based white LED's.

Introduction

In the development of solid state lighting, white Light Emitting Diodes (w-LEDs) have become a research hotspot because they have the ability of low energy consumption, rapid response, enhanced production performance, high durability, eco-friendly nature and many more and also it gives pure white light as compared to obsolescent incandescent lamps [1]. The phosphor converted w-LED's are cheap to produce, having high thermal and chemical stability and are environment friendly [2]. The inorganic phosphor plays an important role in the fabrication of w-LED's. The rare earth activated inorganic phosphors are widely used in UV/blue chips based w-LED's as they give specific emissions due to the shielding of 4f electrons by 5s and 5p electrons [3,4].

In the present work, $Sr_3B_2O_6$ host material is selected with Eu^{3+} activator ions because these phosphors can be easily excited with blue/UV chips to get pure red emission for application in w-LED's.

Experimental and Characterization

The Sr₃B₂O₆:Eu³⁺ phosphors were synthesized by solution combustion synthesis, the starting materials were Sr(NO₃)₂, H₃BO₃, CH₄N₂O, Eu₂O₃, taken in a stochiometric ratio such that oxidizer: fuel ratio is unity. The resulting materials were then ground to make a homogeneous paste and put it to preheated muffle furnace (600°C). The foamy product is produced with voluminous combustion with the emission of N₂, CO₂, H₂O. Finally annealed at 900 °C to get a white crystalline powder of Sr₃B₂O₆:Eu³⁺ phosphors.

The X-ray powder diffraction pattern was recorded by Bruker Advance D8 X-ray diffractometer with Cuk_a as source radiation, operated at 40 kV and 40 mA. The pattern is recorded in 2 θ range from 10°-70° with step size 0.02°. The excitation and emission spectra were recorded with Cary Eclipse Spectrofluorometer with a 150 W Xenon lamp.

Results and discussion

The XRD pattern for undoped and $Sr_3B_2O_6$:Eu³⁺ phosphors along with standard JCPDS is presented in Fig. 1.



Fig. 1. XRD patterns of undoped and Eu doped Sr₃B₂O₆ phosphors annealed at 900 °C with JCPDS standard pattern.

The diffraction pattern for undoped $Sr_3B_2O_6$ and $Sr_3B_2O_6$:Eu³⁺ (1.0 mol%) phosphors matched well with JCPDS 31-1343 standard pattern. The (hkl) values were assigned as per the standard data (31-1343), and no peak corresponding to impurity or any other phase was seen. Also, a small shift in these peaks towards a lower angle is observed due to the difference in ionic radii of Sr^{2+} ions (1.18 Å) and Eu³⁺ ions (0.94 Å) which causes strain in the lattice and results in to increase in lattice parameters. The lattice parameters were calculated with the Unit Cell Win program and

the obtained results were a = b = 9.061 Å and c = 12.609 Å and volume of unit cell = 896.688 Å³ having rhombohedral crystal system with space group R-3c. The crystallite size was calculated using Debye Scherrer formulation and the estimated value was 52 ± 0.62 nm.

The excitation spectrum of $Sr_3B_2O_6:Eu^{3+}$ (1.0 mol%) phosphor was recorded in the range 225-450 nm shown in Fig. 2(a) by monitoring emission at 614 nm. The excitation spectrum shows a broadband centered at 261 nm which is due to charge transfer band as charge get transferred from $O^{2-}\rightarrow Eu^{3+}$ ion. The sharp peaks observed at 320 nm ($^7F_0 \rightarrow {}^5H_3$), 362 nm ($^7F_0 \rightarrow {}^5H_6$), 382 nm ($^7F_0 \rightarrow {}^5D_4$), 394 nm ($^7F_0 \rightarrow {}^5L_6$), 416 nm ($^7F_0 \rightarrow {}^5D_3$) belong to intrinsic 4f \rightarrow 4f transitions of Eu³⁺ ion [3]. From these excitations, it can be assumed that these phosphors can be easily excited with blue chips with a 380-410 nm range.



Fig. 2. Photoluminescent (a) Excitation spectra and (b) emission spectra of $Sr_3B_2O_6$:Eu³⁺ phosphors

The emission spectrum of Sr₂B₂O₆:Eu³⁺ phosphor under 394 nm excitation shows four sharp emissions peaks centered at 593 nm, 614 nm, 654 nm & 704 nm corresponding to transitions from excited ⁵D₀ state to ground ${}^{7}F_{1}$, ${}^{7}F_{2}$, ${}^{7}F_{3}$ and ${}^{7}F_{4}$ states as shown in Fig. 2(b). The emission around 593 nm is due to magnetic dipole allowed transitions and around 614 nm is due to electric dipole allowed transitions. The ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition is hypersensitive and strongly depends on the nature of the host than the less sensitive ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$ transitions as these transitions are parity allowed [3]. This intense red emission under UV excitation demonstrates the possibility of the potential use of this phosphor in w-LED's. The CIE coordinates of $Sr_3B_2O_6:Eu^{3+}$ phosphors were (0.65, 0.35) with high color purity of 99.3% as shown in Fig. 3.

Conclusion

Single-phase Eu^{3+} ions activated $Sr_3B_2O_6$ phosphors were successfully achieved by solution combustion synthesis. The photoluminescent studies revealed that these phosphors having strong absorption at 394 nm corresponding to ${}^7F_0 \rightarrow {}^5L_6$ transitions and the most intense emission peak positioned at 614 nm corresponding to electric dipole allowed ${}^5D_0 \rightarrow {}^7F_2$ transitions, which offer pure red colored emission to the phosphors.

The CIE coordinates were calculated using the OSRAM color calculator and the obtained values were (0.65,0.35), these coordinates positioned in the red region of the horse gamut (shown in Fig. 3). The color purity was evaluated using the following formula:

color purity =
$$\frac{\sqrt{(x-x_i)^2 - (y-y_i)^2}}{\sqrt{(x_d-x_i)^2 - (y_d-y_i)^2}} \times 100$$

Where (x, y) = (0.6, 0.4) are the CIE color coordinates, $(x_d. y_d) = (0.652, 0.348)$ are coordinates of dominant wavelength $(x_i, y_i) = (0.310, 0.3162)$ are coordinates of illuminant point and the color purity is calculated to be 99.3 %.



Fig. 3. The CIE 1931 Chromaticity diagram for $Sr_3B_2O_6$: Eu³⁺ phosphors under 394 nm excitation.

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Biofilm Thickness Measurement by Doppler Optical Coherence Tomography (D-OCT) and Speckle Interferometry

Athira.A¹, Keerthi Nakkalil², Aiswarya P M³, S Gajalakshmi^{*3}, Alok Sharan^{*1}

^{1,2}Department of Physics, Pondicherry University, Puducherry, India, 605014

³Centre for Pollution Control and Environmental Engineering, Pondicherry University, Puducherry, India, 605014

*Corresponding author: athira7rythm@gmail.com / aloksharan@gmail.com

Abstract

Optical coherence tomography (OCT) utilizes low coherent light source to capture two and three-dimensional images of biological tissues with micrometre resolution. We present our estimate of the thickness of a biofilm as measured by speckle interferometry technique and also by using our locally developed Doppler OCT (D-OCT) system. The results are comparable with those obtained from SEM cross sectional images and are found to be in close agreement.

INTRODUCTION

Tomography technology has evolved considerably over the last 50 years. Computed Tomography (CT) and Magnetic Resonance Imaging (MRI) have already been used in radiology and medical diagnostics, to investigate anatomy and physiology [1]. Optical Coherence Tomography, being a noncontact and non-invasive imaging technique, is a relatively new technology which demonstrates better axial resolution in comparison to other existing tomography technologies. Thanks to its micrometre resolution and millimetre penetration depth, OCT technology has revolutionized biomedical imaging to produce highresolution cross-sectional images by measuring optical reflections [2]. In our design, we have measured the thickness of a biofilm developed by speckle interferometry and also designed a D-OCT setup with a narrowband diode laser of 670 nm wavelength, which produces optical Doppler shifts produced by applying different waveforms to the mirror mounted on PZT, using an Agilent DSO-X 2014A digital oscilloscope.

PRINCIPLE

When a plane wave strikes a film with a thickness of *d*, the waves reflected from the upper surface interfere with those reflected from the lower surface. It is obvious that the wave reflected from the film's lower surface travels over an additional optical path of 2nd, where *n* is the refractive index of the film's surface. When the film is placed in air, the wave reflected off the upper surface of the film undergoes a rapid shift in phase of π . Then the condition for destructive or constructive interference will be given by,

 $2nd = \begin{cases} m\lambda & Destructive Interference \\ \left(m + \frac{1}{2}\right)\lambda & Constructive Interference \end{cases}$

where m = 0, 1, 2, ... and λ represent the wavelength. θ is the angle of refraction and *n* is refractive index of the medium [3].

Measurement of thickness of the biofilm using

Speckle Interferometry: In order to measure optical thickness of the biofilm, a PCO Pixelfy CCD camera of pixel resolution 6.45 µm X 6.45 µm (horizontal X vertical) is used as a detector at the screen of Michelson interferometer. Optical thickness is measured by recording the fringes set at zero path difference onto CCD. The fringes are recorded using camware 64 software, set to an exposure time of 1 ms. First, glass slide is placed on two arms of the Michelson interferometer setup and adjusted to zero path difference to obtain the fringes due to the glass slide. After that the glass slide on which the biofilm is mounted is placed and the fringes are recorded. The recorded image with glass slideglass slide is subtracted from the images with those of glass slide-film so as to get the fringes due to the film only, using MATHLAB R2013a. The difference between two points on consecutive bright or dark fringes along x axis and y axis and this difference multiplied by the pixel resolution of 6.45 μm gives the optical thickness. The experimental arrangement is shown in Fig.1. Reflected images from biofilm are scattered and are like speckle.



Fig.1. Basic experimental setup for Speckle Interferometry and D-OCT. (P: Polarizer, BE: Beam Expander, M: Mirror, BS : Beam Splitter)

Measurement of thickness of the biofilm using Doppler OCT (D-OCT): In the above Speckle interferometer setup we replace one mirror with piezo(PZT) mounted mirror. The main idea was to input various waveforms to the piezo at different frequencies and peak voltages and observe the corresponding Doppler shifts by plotting a frequency response curve of the PZT. Here a triangular waveform at an input frequency at 93 Hz (saturation region of PZT) and peak-to-peak voltage of 2.5V (voltage corresponding to exactly one fringe shift corresponding to diode laser wavelength of 670nm, during one complete oscillation of the input signal) was applied to the PZT. The interference fringes produced by the superposition of a reference beam (coming from the reference arm) and the Doppler shifted beam (response of piezo to the applied triangle waveform) are recorded by the CCD in 2 stages: with the glass slide – glass slide, and then with the biofilm coated on glass slide and glass slide.

RESULTS AND DISCUSSION

The thickness measurement of three different samples of a biofilm was measured using the described techniques. For this, refractive index of biofilms was obtained using Brewster angle method. The Brewster angle was estimated from the plots of voltage(v) versus angle(θ) for the three sets of the biofilm. From the curve the angle corresponds to minimum intensity referred to as Brewster angle, and refractive index is obtained using the relation $\tan \theta_B = n_2 / n_1$. Refractive index of the samples named as FR, FC and MC are 1.37, 1.11 and 1.19 respectively. The low value of refractive index of biofilm is due to its vast voids in between the stands comprising the biofilms. The images of the fringes obtained after image processing for the biofilm sample set are shown in **Fig.2**. and **Fig.3**. respectively and the thickness of biofilm are shown in the **Table 1**.



Fig.2. Fringe pattern using Speckle Interferometry



Fig.3. Fringe pattern using Doppler-OCT (D-OCT)

The SEM images of the three samples of biofilm at 5μ m resolution is shown in **Fig.4**. Cross-sectional images showing thickness of biofilm and it is obtained as 496 μ m, 340.5 μ m and 116 μ m for FR, FC and MC respectively.



Fig.4. SEM images of biofilm

Table 1. Thickness of Biofilm

Biofilm	Speckle Interferometry (µm)	D OCT (µm)	SEM (µm)
FR	397	483	496
FC	322	356	340
MC	369	188	116

CONCLUSION

In our work, we presented an experimental arrangement to find out the thickness of films. The thickness of the biofilm was measured using speckle interferometer and a Doppler OCT system developed. The range of values of the thickness measured by both these techniques fall in the range of SEM measurement values.

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Thermographic Studies of CaSr₂(PO₄)₂:Sm³⁺ Phosphor for High Temperature Sensing

Rajan Singh*, A. K. Bedyal, M. Manhas and Vinay Kumar*

Department of Physics and Astronomical Sciences, Central University of Jammu, Rahya Suchani, Samba, 181143

*Corresponding author: rajan.jamwal9@gmail.com, vinaykdhiman@yahoo.com

Abstract

This work presents the synthesis of $CaSr_2(PO_4)_2:Sm^{3+}$ phosphors prepared via solution combustion method and the photoluminescence (PL) properties had been investigated to explore its potential application in luminescence thermometry. The PL studies reveal that the phosphor had a strong absorption in the ultraviolet region and sharp emission peaks at 562 nm, 600 nm, 645 nm and 706 nm due to the 4f-4f transition of the Sm³⁺ ions. Further, temperature dependent PL studies were done to examine the phosphor for thermometry application. The fluorescence intensity ratios (FIRs) between the emissions of the Sm³⁺: ${}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (600 nm) were calculated as a function of temperature in the range of 323-473K. The sensitivity obtained had a maximum value of 0.00116 K⁻¹ indicating that the prepared phosphor is a promising candidate for optical thermometry.

Introduction

Rare earth activated phosphors have gained a lot of attention in the scientific community because of their unique photophysical properties such as large Stoke's shift, tunable luminescence, high photostability and long excited-state lifetime [1,2]. Based upon the above photophysical properties, they are being widely exploited in the field of health, solid-state lighting, scintillators, sensors, etc. Much attention has been granted to the development of optical temperature sensors based on the fluorescence of rare earth ions.

In the optical thermometry method, Fluorescence Intensity Ratio (FIR) technique has allured great heed in numerous fluorescent temperature sensors as it improves the sensitivity. FIR technique focuses on the measurement of the fluorescence intensity ratio of the fluorescence from the two excited thermally coupled energy levels (TCLs) of the active rare earth ions. Among the rare earth activated phosphors, Sm³⁺ doped materials have significant applications in optical thermometry [3]. Sm³⁺ is luminescent activators that have coupled energy levels required for application in optical temperature sensors. These ions easily accommodate a variety of different host materials.

In this work, $CaSr_2(PO_4)_2:Sm^{3+}$ phosphor had been prepared by the combustion method and its photoluminescence properties are explored. The main objective is to use $CaSr_2(PO_4)_2:Sm^{3+}$ phosphor for temperature sensing based on the FIR technology.

Experimental Details

The solution combustion method had been adopted for the synthesis of $CaSr_2(PO_4)_2:Sm^{3+}$. The raw

materials calcium nitrate $[Ca(NO_3)_2.4H_2O]$, strontium nitrate $[Sr(NO_3)_2]$, samarium nitrate $[Sm(NO_3)_3.6H_2O]$, urea (H_2NCONH_2) and ammonium dihydrogen orthophosphate $(NH_4H_2PO_4)$ of Analytical Reagent (AR) grade were taken in the stoichiometric amounts. After thorough mixing and grinding, the mixture was placed in a preheated muffle furnace at 650 °C to produce the phosphors by undergoing flaming combustion.

Characterization

Photoluminescence excitation and emission recorded via Cary-Eclipse spectra were Spectrofluorometer attired with a 150 W Xenon flash lamp as the excitation source. The temperature dependent photoluminescence measurements were carried out using an assembly containing an optical furnace to heat phosphor fitted with a diode laser (404 nm) as an excitation source and a spectrophotometer (Ocean Optics) to record the spectrum produced by heated phosphors.

Results and Discussion

The photoluminescence excitation spectrum of CaSr₂(PO₄)₂:Sm³⁺, shown in Fig.1. The excitation spectrum was measured within the wavelength range of 200-450 nm, by monitoring the dominant emission at 600 nm. The broad absorption band centered at 205 nm, assigned to the charge transfer (CT) band due to $O^{2-}\rightarrow$ Sm³⁺ interaction into the host lattice. The other peaks are located at 344 nm, 362 nm, 375 nm, 403 nm and they correspond to the transition states of ${}^{6}H_{5/2}$ to ${}^{6}H_{7/2}$, ${}^{6}P_{7/2}$, ${}^{6}K_{11/2}$ respectively. The prominent excitation peak is located at 403 nm. The emission spectrum comprises of three emission bands by the intra 4f transitions of Sm³⁺ centered at 562 nm,

600 nm, 645 nm, 706 nm which are assigned to the ${}^{4}G_{5/2}$ to ${}^{6}H_{J}$ [J = 5/2, 7/2, 9/2, 11/2] transition respectively. CaSr₂(PO₄)₂:Sm³⁺ phosphor exhibit a strong emission fixed at 600 nm ascribed to ${}^{4}G_{5/2}$ to ${}^{6}H_{7/2}$ transition.



Fig. 1. PL excitation and emission spectra of $CaSr_2(PO_4)_2:Sm^{3+}$.

Temperature dependent PL Studies

Fig. 2. depicts the photoluminescence emission spectra of the phosphors excited at 403 nm in the temperature range from 323-473 K. From Fig. 2, we can see that with the increase of temperature, the



Fig. 2. Emission spectra of $CaSr_2(PO_4)_2:Sm^{3+}$ phosphors as a function of temperature.

the peak position of four emission bands located at 562 nm, 600 nm, 645 nm remain constant, but the intensity of the peaks declined. The reason behind the decline in intensity is the thermal quenching effect.

To explore the temperature sensing potential of $CaSr_2(PO_4)_2:Sm^{3+}$ phosphors, the FIR between the thermocouple levels ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ (564 nm) to the $Sm^{3+}: {}^4G_{5/2} \rightarrow {}^6H_{7/2}$ (600 nm) were calculated as a function of temperature in the range of 323-473K as depicted in Fig. 3. The prime parameter that

determines the performance of the material for temperature sensing is sensitivity which is defined as the rate of change of FIR. It can be expressed as:

$$S = \frac{d[FIR]}{dT}$$

From Fig. 3 we can see that the overall trend for S is decreasing with the increment of temperature, and the maximum sensitivity of the $CaSr_2(PO_4)_2:Sm^{3+}$ phosphor is 0.00116 K⁻¹ at 323 K. This means that the $CaSr_2(PO_4)_2:Sm^{3+}$ phosphor can be used as a potential material for optical temperature sensors.



Fig. 3. Depicts the variation of FIR (562/600) and Absolute sensitivity of thermally-coupled levels as a function of temperature from 323-473 K.

Conclusion

The CaSr₂(PO₄)₂:Sm³⁺ phosphor has been successfully prepared via solution combustion synthesis. PL results revealed that phosphor is excited by 403 nm with intense orange-red emission with the highest peak at 600 nm. The temperature responses of emission ratio from ${}^{4}G_{5/2} \rightarrow {}^{6}H_{5/2}$ (564 nm) to the ${}^{4}G_{5/2} \rightarrow {}^{6}H_{7/2}$ (600 nm) of Sm³⁺ was characterized by the FIR technique. The maximum sensitivity obtained for the phosphor was 0.00116 K⁻¹ at 473 K.

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Efficiency improvement of heat pipe with Graphene/R-410a working fluid

Aruna Veerasamy^a, Kanimozhi Balakrishnan^{a*}, Godwin Antony^b

^{a,a*} Sathyabama Institute of Science and Technology, Chennai, Tamil Nadu, India-600119 ^b K.Ramakrishnan College of Technology, Trichy, Tamil Nadu, India – 621112 *Email: kanihwre@gmail.com

Abstract: This paper aims to improve the thermal efficiency of heat pipe (HP) by using graphene / R 410a nanorefrigerant. In this study graphene nanoplatelets (0.75% volume concentration) with R 410a refrigerant is used as a working fluid. Different heat power (60W, 80W) and inclination angles (0^{0} , 45^{0} , 90^{0}) are implemented to HP in order to validate the thermal resistance, thermal efficiency. Based on this study, nanorefrigerants enhance thermal efficiency, at the same time decrease thermal resistance. Thus the study suggests that HP with nanorefrigerants are well suitable for cooling techniques in all industries.

Key words: Heat pipes, nanorefrigerant, thermal efficiency, thermal resistance.

INTRODUCTION

Cooling electronic devices and industrial equipments is a very big challenge in recent years. Esspecially cooling devices and compenents in industries utilize large surface area and higher procedure involved for installation. In order to rectify these difficulties, HP's technology was implimented. HP is a heat transfer equipment having thermal conductivity and phase transition. HP efficiently tranfer the heat from one plase to another without energy loss, and zero maintenance. Plenty of research is going on regarding HP in past decads.

Jihad et al [1] experimentally investigated HP with graphene oxide nanofluid. They adding 0.075% weight concentration of graphene oxide into DI water (base fluid). From their investigation, graphene oxide nanofluid significantly increase the thermal efficiency than DI water can be used for cooling system in high heat applications. Lukasz et al [2] discussed HP with R404A and R407C refrigerants. From their experimental result and thermographic analysis heat pipe with R404A (10% filling ratio) enhanced the thermal efficiency than R407C (5% filling ratio). Vivek K.S et al [3] compared R600a to DI water by varying input heat from 20W to 140W. From their result HP with R600a enhanced heat transfer coefficient decreased thermal resistance by 27%. Author suggested that heat pipe with R600a working fluid is suitable for electronic gadgets cooling techniques.Nivedan et al [4] used R134a and R600a refrigerants as a base fluid instead of DI water. Authors found that, presence of nano sized TiO₂ particles in R600a drstically reduced thermal resistance and enhance thermal conductivity of HPHE at low heat input and low concentration of nanoparticles.

EXPERIMENTAL SETUP

Schematic diagram of HP is shown in fig 1. HP





consist of evaporator (60mm), adiabatic (60mm) and condenser section (80mm). power supply is given to evaporator section by using electric coils. Coils are connected to power supply. Nanorefrigerant (0.75% graphene + $\hat{R}410a$) was prepared by two step. The working fluid, which is injected into an evaporator has heated and reaches to pool boiling condition. Phase change working fluid reaches the condenser section in order to release the latent heat. Here water is used as a cooling medium. K-type thermocouples are brassed to the HP and attached to the data logger. The data logger is used to detecting the temperature in various parts of the HP which is connected to personal computer. All the connections are perfectly arranged and power supply is applied to HP, and experimental values are predicted.

RESULT AND DISCUSSION

The type of HP is selected, designed, manufactured. HP is under vacuum before filling the working fluid (nanorefrigerant). Filling ratio of working fluid is 50%. HP performance are evaluated and validated thrice for precision. Fig 2 exhibits the thermal resistance of HP at 60W and 80W with 0^{0} , 45^{0} , and 90^{0} inclination angles. At horizontal position thermal resistance of HP was 0.95 ($^{\circ}C/W$) for 60W and 0.61($^{\circ}C/W$) for 80W. Increasing inclination angle decreases thermal resistance to $0.72(^{\circ}C/W)$ and $0.58(^{\circ}C/W)$, $0.69(^{\circ}C/W)$ and $0.44(^{\circ}C/W)$ for

refrigerant. Thermal resistance for nanorefrigerant were 0.61(°C/W) and 0.58(°C/W), 0.44(°C/W) and 0.54(°C/W), 0.48(°C/W) and 0.4(°C/W) in 60W and 80W respectively. The presence of nanoplatelets in the base fluid could diminish thermal resistance. Basically, nanoparticles are reduced thermal resistance but increase the thermal performance of HP's [3], [5]. At high heat power, pool boiling condition in evaporator and condensation in condenser happened rapidly and diminish thermal resistance.



FIGURE 2. Rth Vs incination angle of R410a and nanorefrigerant at 60W and 80W heat power



FIGURE 2. η Vs incination angle of R410a and nanorefrigerant at 60W and 80W heat power

Thermal efficiency of R410a and nanorefrigerant at different heat power and inclination angles are displayed in fig 3. From the graph thermal efficiency of HP with R 410a were 34.7%, 39.5%, 42.7% for 60W and 35.4%, 44.2%, 60.8% for 80W at 0^{0} ,45°, 90°. Following, for nanorefrigerant 39%, 41.4%, 46.4% for 60W and 41.1%, 52%, 74.7% respectively. An interfical layer between the graphene nanoplatelets surface and refrigeration can diminish migration ratio and increase the thermal efficiency. Therefore increasing an inclination angle and heat power significantly enhance the thermal efficiency [1], [2].

CONCLUSION

From experimental study, thermal resistance and thermal efficiency of HP was perdicated and validated. Results clearly prove that nanorefrigerant can enhance thermal efficiency by 20.5% than R410a in HP. And higher inclination angle and heat power enhance the performance of HP. Thus the paper suggest that HP with nanorefrigerants is suitable cooling device for industrial and electronic cooling applications

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Synthesis Of Strontium/Barium Titanate ((Sr/Ba)TiO₃) Nanoparticles Using New Sol-gel Technique And Study Of Their Optical Properties

Akhilesh Kumar Yadav¹ and Chandana Rath^{1,*}

¹School of Materials Science and Technology, Indian Institute of Technology (BHU), Varanasi, 221005, India

*Corresponding author: <u>chandanarath@yahoo.com, akhileshkumaryadav.rs.mst19@itbhu.ac.in.</u>

Abstract

Strontium/barium titanate ((Sr/Ba)TiO₃) nanoparticles have been successfully synthesized by employing a new, facile, easy and cost-effective sol-gel technique using Titanium isopropoxide (TIP), nitrates of Sr/Ba and ethanol and water as solvent. The structures of the prepared samples were confirmed using XRD. It revealed the formation of pure cubic phase of SrTiO₃ and tetragonal phase of BaTiO₃ after calcining the sample at 800° C for 5hrs and then 1200° C for 10hrs. The optical properties of the synthesized (Sr/Ba)TiO₃ were demonstrated using FTIR and UV-Visible spectroscopy. The band gap of SrTiO3 and BaTiO3 was 3.08 and 3.26 respectively. The band gap of SrTiO3 is in the visible region which makes it a potential candidate for photocatalytic applications.

INTRODUCTION

The structure and the application of perovskite compounds (ABO₃) in optoelectronics devices have been generating immense interest. SrTiO₃ and BaTiO₃ are the most important thermoelectric materials having implicit use in thermoelectric generators [1]. Moreover, they have a high low dielectric loss, high nonlinear optical coefficient, static dielectric constant, and good insulation which paved their use in capacitors [2]. SrTiO₃ is an important n-type semiconductor having an indirect band gap of 3.2eV and exceptional optical transparency in the visible region and high charge storage capacity which makes it a suitable candidate for the application in photocatalytic and microelectronics [3, 4]. For the synthesis of (Sr/Ba)TiO₃ nanoparticles, several methods have been reported such as sputtering [5,6], conventional solid-state method, solgel[7,8], auto combustion sol-gel[9], screw-capped method [10], etc. All the synthesis methods use complicated processes. In one paper, first titanyl nitrate is synthesized by dissolving TIP in nitric acid and then use that to synthesize SrTiO₃

In this paper, our focus is on the synthesis and structural characterization of (Sr/Ba)TiO₃ nanoparticles via a simple sol-gel technique. There are so many papers that reported the synthesis method for (Sr/Ba)TiO₃ nanoparticles but we have used the minimum number of chemicals, simple and easy process to synthesize nanoparticles and we have confirmed this using different characterization techniques i.e. XRD, FTIR, UV-Vis spectroscopy.

EXPERIMENT

 $(Sr/Ba)TiO_3$ was synthesized via a new modified sol-gel method. In this method, two solutions were prepared by taking the calculated amounts of Sr/Ba nitrate and TIP. Solution (a) contained Sr/Ba nitrate (Himedia, >97%) dissolved in double distilled water and solution (b) contained TIP (Sigma- Aldrich, >97%) dissolved in absolute ethanol with constant stirring. A few drops of nitric acid were added to the solution (b) to catalyze the hydrolysis reaction of TIP. After 3 hrs of rigorous stirring, solution (a) was dropwise added to the solution (b) with continuous stirring. After the complete dissolution of the solutions, the reaction mixture was transferred to a gel. The obtained gel was left for aging for 24 hrs, then finally dried at 110° C. The obtained sample was subjected to calcination at different temperatures 800, 1200 and 800+1200°C for 10 hrs (@3°C/min) and grinded using mortar-pestle to obtain a fine powder which was used for further characterization.

The TIP to ethanol molar ratio was 1:4 and barium nitrate was dissolved in water at temp 100° C because of its low solubility at room temp.

The phase and crystal structure of the samples were determined by X-ray diffraction using CuK α radiation (λ =1.5406 Å, current =40 mA, voltage=40 kV) and FTIR in the range 400-4000cm⁻¹ (@ 4cm⁻¹). UV-2600 UV-visible double beam spectrophotometer was used to study the optical properties of the (Sr/Ba)TiO₃ samples.

RESULT AND DISCUSSION

XRD



Fig.1. X-ray diffraction pattern of (a) BaTiO₃ (b) SrTiO₃

Fig.1 presents the XRD pattern of the prepared samples $BaTiO_3$ (fig. 1.a) and $SrTiO_3$ (fig. 1.b). From the figure, it is manifested that the pure cubic phase (according to ICSD-080873) of $SrTiO_3$ formed after calcining the sample at 800^{0} C for 5 hrs and then at 1200^{0} C for 10hrs while $BaTiO_3$

has a tetragonal phase (ICSD-073644). It can be seen from the figure that after calcining the sample at 800 and 1200^oC alone there are still impurity peaks are present. That's why we have chosen to calcine the sample twice with an intermixing using mortar and pestle. The average crystallite size of SrTiO3 and BaTiO3 were found to be 18nm and 22.18nm (estimated using Scherrer's equation) respectively.

FTIR

The FTIR analysis is shown in fig.2. The spectrum of uncalcined (as prepared) and calcined (at 800+1200°C) of strontium and barium titanate is plotted. It can be seen from the fig.2 that there are no peaks in the range 400-600 of uncalcined (as prepared) sample while after calcination, sharp absorption peaks are observed. These absorption peaks between 400-600 cm⁻¹ can be attributed to the Ti–O– Ti bond stretching vibration (in $[TiO_6]^{-2}$ octahedron) of (Sr/Ba)TiO₃ nanostructures and Sr/Ba–O bonds as reported earlier [11]. The peak around 1480cm⁻¹ is because of the of alcohol use in the process [12].



Wavenumber(cm⁻¹)



UV-VISIBLE SPECTROSCOPY

The UV-Vis absorption spectra and Tauc plot of $SrTiO_3$ and $BaTiO_3$ in fig.3. Kubelka –Munk algorithm was used to plot absorption spectra from diffuse reflectance data.



Fig.3. (a) UV-Vis absorption spectra of SrTio₃ and BaTiO₃ (b) Tauc plot of SrTiO₃ and BaTiO₃

From fig. 3.a it can be seen that both the samples present higher absorbance in the wavelength shorter than 400nm which is the result of electron transition from the valence band to the conduction band [3]. Fig. 3-b shows the Tauc plot using which the band gap energy of both the sample is calculated. Since SrTiO3 has an indirect band gap so the plot is in between $(\alpha h\nu)^{1/2}$ and h ν whereas BaTiO₃ has a direct band gap so the plot is in between $(\alpha h\nu)^2$ and h ν where (α -absorbance and h ν -photon energy). The band gap energy estimated from the plot for SrTiO₃ is 3.08eV and for BaTiO₃ 3.26eV.

CONCLUSION

We have synthesized strontium and barium titanate nanoparticles using a new facile and easy sol-gel method which has not been reported to the author's best knowledge. The formation of the pure phase of SrTiO₃ and BaTiO₃was established via XRD and FTIR. We have found the band gap of SrTiO₃ is in the visible region (3.08 eV) and band gap of BaTiO₃ is 3.26eV. Further, we will also study the dielectric properties of both the samples and the photocatalytic deterioration of the most common organic dyes like congo red (CR) methylene blue (MB) and rhodamine B (RhB) using strontium titanate nanoparticles under the sunlight and UV light.

ACKNOWLEDGMENT

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Design and commissioning of neutron time-of-flight spectrometer at Dhruva reactor

Mala N Rao^{1,3}, Shraddha S Desai¹, Rohit Chandak¹, S S Naik¹, V Kulkarni¹, S K Mishra^{1,3}, Santosh Kumar¹, S Mitra^{1,3}, P Goel¹, R Mittal^{1,3}, Somesh Rai², R Mukhopadhyay^{1,3}, and S L Chaplot^{1,3}

¹Solid State Physics Division, ²Refuelling Technology Division, Bhabha Atomic Research Centre, Mumbai-400085, ³Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094,

*Corresponding author: mala@barc.gov.in

Abstract

The neutron time-of-flight spectrometer commissioned recently at Dhruva reactor provides high throughput in terms of higher neutron flux at the sample position and a large solid angle of detector coverage. This instrument incorporates focusing monochromator, neutron Fermi chopper, an array of linear position sensitive detectors, and position encoding and time-read out electronics. Background scattering has been minimized with adequate shielding of all components. Comparison of the measured data with the results of Monte Carlo simulations is demonstrated.

Introduction

At Dhruva reactor, under the National Facility for Neutron Beam Research, inelastic neutron scattering measurements are mainly carried out on a triple axis spectrometer (TAS). With a focusing monochromator Cu(111), a Pyrolytic graphite analyzer, and a single detector placed in an end-on configuration, the energy resolution of TAS is around 15% of the incident neutron energy. In order to augment the inelastic neutron scattering facilities, a time-of-flight (TOF) spectrometer was designed for obtaining enhanced flux, improved energy resolution, and enabling rapid surveys of the (momentum transfer, energy transfer) space.

A description of the design considerations, and components of the spectrometer is given and initial measurements to determine the performance of the spectrometer and comparison with simulations is described.

Design considerations

The TOF spectrometer is developed on a thermal neutron beam at the Dhruva reactor. The requirements were neutron flux of around $10^7 \text{ n/m}^2/\text{s}$ at the sample position, and an energy resolution of at least 4-5 meV. A combination of focusing monochromator (Fig. 1a) and a neutron Fermi chopper consisting of neutron-absorber coated slats rotating at high speed in the path of the monochromatic neutrons creating pulses of intense neutrons to fall onto the sample was considered an ideal configuration. The simulations were carried out employing the McStas software [1]. Fig 1b shows the (Q, ω) space accessible to the spectrometer. A bank

of position sensitive neutron detectors (PSD) positioned around the sample leading to high throughput, and position-encoding and time-recording electronic modules help to determine the time-of flight (Time of flight= 252.78 $\lambda L \mu s$, with λ in Å and L in m), and the momentum transfer. The characteristics of the spectrometer are given in Table 1.

Table 1.	Characteristics	s of neutron	time-of-flight
spectrom	neter		

Component	Material/Value	
Monochromator	Doubly curved	
	Cu(111)	
Wavelength	1.2 Å	
Energy resolution	5 meV	
Maximum speed of Fermi	30000 rpm	
chopper		
Beam size on sample	$4 \text{ x} 4 \text{ cm}^2$	
Maximum scattering angle	110°	
Sample-to-detector distance	2 m	
Detector array	40 mm dia tubes,	
	1 m long PSDs	

Components of the spectrometer

The monochromator (Fig. 1a) is a doubly focussing assembly with fifteen Cu [111] crystals. The neutron Fermi chopper allows collimation of the beam up to 1.5° . The neutrons scattered by the sample reach the detectors through a shielded flight chamber made of thin aluminum. The detectors are mounted on a curved detector stand, ensuring that the flight paths of the scattered neutrons are almost constant.

The PSDs, developed in-house are arranged vertically (Fig. 3) and allow large solid angle coverage. The PSDs are with coaxial geometry and

completely welded cathode in SS and fine 25 μ m diameter of resistive anode (NiCr). 20 PSDs are filled with gas ³He (2 bar) + Kr (1.5 bar) and 20 PSDs are with 1.1 bar BF₃ gas. Two PSDs are looped to treat it effectively as a single PSD. This arrangement reduces the number of electronic modules needed to half. These PSDs (Position resolution 6 mm FWHM) have uniform operating parameters; which suits the looping arrangement.

The Fermi chopper controller has a BNC output on the front panel which gives a once per revolution signal. This chopper pulse starts the reference timer and the periodic time window ticks generated by the timer circuit defines the time window (here $l\mu$ s) and are used for measurement of flight time of neutrons detected in all the PSDs.



Fig.1.(a) Doubly focusing monochromator assembly (b) Accessible (Q, ω) space (c) Simulated neutron intensity map at sample position (d) Neutron image of beam at sample

The charge division method is employed for position encoding. The time of arrival of neutron with respect to the zero-time pulse is used to estimate its energy [2] and build histogram of scattered neutrons. A five channel NIM module (Fig. 2) caters to these needs. The radiation shielding (Fig. 3) around the detectors comprises alternate layers of High Density Polyethylene and borated rubber.

Instrument Performance

Fig 1(c) shows simulated neutron intensity map at the sample position. This is in very good agreement with the neutron image of the beam at the sample position, shown in Fig 1 (d). Fig 4 shows a measured energy

spectrum of ammonium chloride. The elastic peak is followed by a continuous spectrum and two peaks at energy transfers of 24 meV and 48 meV correspond to the translational and librational modes of the NH_4 ion respectively [3].



Fig. 2. Five channel data acquisition module



Fig. 3. Photographs of (a) the neutron time-of-flight spectrometer, (b) the arrangement of PSD array



Fig. 4. Measured energy spectrum of ammonium chloride.

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Microstrip Line Based Complementary Resonant Structure For Dielectric Characterization

Subhadip Roy, Pronoy Das, Puspita Parui, Anuvab Nandi and Chiranjib Mitra*

Department of Physical Sciences, Indian Institute of Science Education and Research, Kolkata, India

*Corresponding author: chiranjib@iiserkol.ac.in

Abstract

In this work, a complementary resonant structure etched on the ground plane of a microstrip line is proposed for characterizing dielectric materials. The resonant sensor is designed to operate in S-band (2 – 4 GHz). The sensor is designed in an electromagnetic simulator to generate its transmission response, electric and magnetic field maps. A numerical model of the sensor is established to extract the electric permittivity of dielectric samples. The sensor is fabricated on a soft microwave laminate using a rapid photolithography technique. The electric permittivity values of wood, Teflon, and RT/duroid[®] 5880LZ are determined by using the sensor. The permittivity values are found consistent with those available in the literature.

Role of Natural Dye in Photovoltaic Performance of Dye Sensitized Solar Cell

Varsha Yadav^{1, 2 a}, Yashaswi Soni¹, Chandra Mohan Singh Negi¹, Saral Kumar Gupta¹ and Upendra Kumar³

¹Department of Physical Sciences, Banasthali Vidyapith, Banasthali, 304022, INDIA ²School of Applied Science, Shri Venketashwar University, Gajraula (Amroha), 244221, U.P.INDIA ³Department of Applied Sciences, Indian Institute of Information Technology (IIIT) Allahabad, Prayagraj-211015, U.P. INDIA

*Corresponding author: ^avarshayadav616@gmail.com

Abstract

Investigating cost-effective alternatives to organic dyes for use in dye-sensitized solar cells (DSSC) could help to lower the overall cost of the devices. This manuscript deals with optical and structural properties of novel natural dye extracted from harda fruit. The optical absorbance, emission and functional group of natural dye has been studied using UV-Vis. spectroscopy, photoluminescence and Fourier transform infrared (FTIR), respectively. The DSSC has been fabricated using natural dye as photo-sensitizer and studied their photovoltaic performance. The power conversion efficiency (PCE) for DSSC has been achieved up to 2.7%. Although the use of natural dye in DSSC improved the better short-circuit current density (Jsc) and open-circuit voltage (Voc). Understanding these fundamental properties of natural dye could pave the way for the development of natural dyes based solar cells.

Automated Thermally Stimulated Current Measurement Setup for Characterizing Photovoltaic Materials

Vikas Jain¹, S. Raj Mohan¹, M. O. Ittoop¹, T. S. Dhami¹, M. P. Joshi^{1,2}

¹Laser Materials Processing Division, Raja Ramanna Centre for Advanced Technology, Indore-452013 ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400094

*Corresponding author:vikasj@rrcat.gov.in

Abstract

Investigating the trap distribution in semiconducting materials is very important because of its influence on various optoelectronic properties and on the efficiency of the fabricated devices. Thermally stimulated current (TSC) experiment is a versatile technique for investigating the electronic trap states in semiconducting materials. This work reports the development of a LabVIEW based automated TSC experimental setup with sub-pA current sensitivity. The developed setup is used to obtain trap activation energies of Poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenyle and Methyl Ammonium Lead Iodide perovskite materials.

XANES study of gamma irradiated CaSO4:Dy for dosimetry

P. K. Sahani¹, Haridas G.², M. K. Nayak², V. Srihari³, S. N. Jha⁴, M. S. Kulkarni² and R. K.

Sahu¹

¹Indus Operation Division, Raja Ramanna Centre for Advanced Technology, Indore-452013

²Health Physics Division, ³High Pressure & Synchrotron Radiation Physics Division, ⁴Atomic & Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai-400085

*Corresponding author: pksahani@rrcat.gov.in

Abstract

CaSO₄:Dy thermoluminescence (TL) dosimeter has a linear dose response up to 30 Gy using the TL dosimetry technique. X-ray Absorption Near Edge Structure (XANES) technique is explored to extend its useful dose range to higher gamma dose. The present study is carried out up to gamma dose of 5 kGy and the XANES results are presented. The study indicates that the XANES technique provides a linear response up to 1 kGy.

Introduction

CaSO₄:Dy commonly is а used thermoluminescence (TL) material for radiation dosimetry of ionizing radiation. Because of its high sensitivity and low fading, CaSO4:Dy disc based TLD badge is used for personnel and environmental dosimetry at radiation facilities in India. The disc is prepared from CaSO₄:Dy powder added with 0.05 mol% Dysprosium (Dy) and using Teflon (PTFE) as the binding medium. The PTFE to CaSO₄:Dy ratio is maintained at 3:1 ^[1]. The dose evaluation from the irradiated TL disc is done through measurement of TL counts under the glow curve using a TLD reader. Dosimetry using CaSO₄:Dy is limited to linear dose response up to ~ 30 Gy because of its non-linear response above 30 Gy followed by TL saturation at ~kGy dose level ^[2]. Therefore the high dose evaluation from CaSO4:Dy discs using TL technique is cumbersome and highly erroneous.

In our previous study ^[3], investigation on effect of high gamma ray dose up to 1 kGy on CaSO₄:Dy TL dosimeter using X-ray Absorption Near Edge Structure (XANES) is reported. It was observed from the XANES spectrum that pre-edge gives a direct evidence of Dy³⁺ transition to Dy²⁺ on gamma ray irradiation and confirms the redox model proposed by Nambi et al ^[4]. Also increase in the white line was observed in XANES spectrum with increasing dose up to 1 kGy which can be calibrated for high dose dosimetry. However the investigation was limited up to 1 kGy and thus the present study was initiated to extend the investigation in the dose range 1 to 5 kGy.

Materials and Methods

Annealing of CaSO₄:Dy in powder and disc form was performed at 400 0 C for 1 hour. These annealed TL

materials were irradiated with Cobalt-60 gamma rays in the dose range 1 - 5 kGy in a gamma irradiation chamber at BARC, Mumbai. X-ray Absorption Near Edge Structure (XANES) measurements at Dy L3edge of CaSO4:Dy TL discs were carried out at Scanning Extended X-ray Absorption Fine Structure beamline (BL-9) of Indus-2 synchrotron source at RRCAT, Indore. The absorption measurement was carried out through X-ray fluorescence mode. In order to study the changes in the lattice structure due to gamma irradiation, X-ray diffraction (XRD) measurement of the irradiated CaSO₄:Dy powder samples was carried out at Protein Crystallography beamline (BL-21) of Indus-2. CaSO4:Dy powder samples were used in XRD measurements instead of the TL discs as the TL discs have high PTFE (as binder) and generates high amorphous background signal as compared to the powder sample.

Results and Discussion

The XANES spectra of the CaSO₄:Dy samples along with the Dy₂O₃ (standard) was measured in fluorescence mode using Si drift detector (VORTEX-EX) placed at an angle of 45° with respect to the disc sample at BL-9. The beamline uses Si (111) based double crystal monochromator (DCM) for energy selection from the white (full spectrum) synchrotron radiation generated in Indus-2 and capable of delivering photons in 5-20 keV energy range with an energy resolution better than 10⁻⁴. The fluorescence counts were normalized with the incident flux, I₀ (measured using an ionization chamber) and the absorption coefficient $\mu(E)$ of the sample was obtained through energy scanning in the range 7750 to 7870 in steps of 1 eV. The normalised XANES spectra (absorption coefficient) from the irradiated CaSO₄:Dy samples in the dose range up to 5 kGy along with

unexposed and the standard Dy_2O_3 is shown in Figure 1.



Fig. 1. Normalized XANES spectra of Dy₂O₃ and CaSO₄:Dy samples at different gamma doses.

The pre-edge indicating Dy^{2+} state due to quadrupole (QP) transition is observed only in CaSO₄:Dy samples and is completely absent in the Dy₂O₃ (Figure 1), which is in concurrence with the earlier study ^[3]. The white line at 7791 eV of the spectra increases up to 1 kGy which can be attributed to the transition from $2p_{3/2}$ state to the continuum state. However at higher dose level from 1 to 5 kGy, the intensity of the white line shows a falling trend (Figure 2).



Fig. 2. Areas under the white line of XANES spectra as a function gamma dose.

XRD measurement was performed for unexposed and gamma irradiated CaSO₄:Dy sample at 5 kGy dose to study structural changes due to irradiation. The XRD spectra obtained are shown in Figure 3. From the figure, it is observed that no change in the orthorhombic phase of the CaSO₄ crystal took place up to 5 kGy but variation in the peak intensities is observed due to structural recrystallization after gamma irradiation.



Fig. 3. XRD spectra of unexposed and gamma irradiated CaSO₄:Dy samples.

Conclusion

The XANES spectra from gamma irradiated CaSO₄:Dy TL dosimeter up to 5 kGy were obtained from SEXAFS beamline (BL-9) at Indus-2. The study indicates that due to non-linear effects, the area under the white line shows a decreasing trend beyond 1 kGy. This may be due to saturation of Dy^{3+} to Dy^{2+} transition. This is in contrast to our earlier study (up to 1 kGy) where the area under the white line was found to increase linearly with gamma dose. Thus the studies conclude that using XANES technique, absorbed dose from the CaSO₄:Dy disc can be accurately evaluated up to 1 kGy against 30 Gy by conventional TL technique.

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Carbon-nanomaterial-based Ternary Composite as Photoactive Layer

Minakshi Sharma, P. A. Alvi, S.K. Gupta and C.M.S. Negi*

Department of Physical Sciences, Banasthali Vidyapith, Banasthali, 304022, India

*Corresponding author: nchandra@banasthali.in

Abstract

Here, we prepared the reduced graphene oxide (rGO): carbon nanotubes (CNTs): Buckminsterfullerene (C60) based all carbon ternary composites with the aim to study the optoelectronic properties, in order to utilize them in the photoactive layer of optoelectronic devices. The facile solution processing method has been used to prepare the composite thin film. Field emission scanning electron microscopy analysis validates the development of ternary composite. The as-prepared composites were used to fabricate the two kinds of device, one comprising the photoactive layer made by composites of rGO, C60, and single-walled type CNTs and in another device, everything was the same except the single-walled CNTs were replaced by multiwalled type CNTs. The device containing multiwalled CNTs demonstrated greater optoelectronic performance compared to that of the device comprising single-walled CNTs. The lower ideality factor of the multiwalled CNTs composite-based device suggests better interface quality, therefore better interface quality might be attributed to the superior optoelectronic performance.

Measurement of Neutron Fluxes Incident on Neutron Transmutation Doped Si Samples Irradiated in Apsara-U Core

Kapil Deo^{1*}, Deep Bhandari¹, Rajeev Kumar¹, U. Kannan¹, Y.S. Rana², Tej Singh², Sajin Prasad³, Saurav³ and Ranjit Sharma³

¹Reactor Physics Design Division, ²Research Reactor Services Division, ³Health Physics Division, Bhabha Atomic Research Centre, Mumbai, INDIA-400085 *: kapil@barc.gov.in

Abstract

Irradiations of Neutron Transmutation Doped-Silicon (NTD-Si) samples were carried out at core positions of newly commissioned Apsara-U (Apsara-Upgraded) reactor at BARC. This was part of feasibility studies carried out for NTD-Si production at Apsara-U. For proper characterisation of the irradiated NTD-Si samples, it is very important for continuous monitoring of neutron fluxes at the irradiation locations. Using thermal and fast neutron activation monitors, neutron fluxes were measured during NTD-Si irradiations at two core positions (G4 and H7) of the reactor. The fluence seen by the sample, thus estimated, were further utilised for resistivity characterisation of the irradiated Si-samples.

Luminescence investigations on low energy He⁺ ion irradiated ZrO₂ Sujoy Sen^{1*}, Ranjini Menon³, P. Jegadeesan¹, S. Amirthapandian^{1,2}, P.Gangopadhyay^{1,2}

¹Materials Science Group, Indira Gandhi Centre for Atomic Research, ²HBNI-Kalpakkam, Kalpakkam – 603 102, ³Accelerator Physics Group, VECC, Kolkata-700064

*Corresponding author: sujoy@igcar.gov.in, sujoy.2006.sen@gmail.com

Abstract

In the present work, monoclinic zirconia was irradiated with 100 keV He⁺ ions and during ion irradiation, the ionoluminescence experiments were carried out with the ion fluence interval of $\sim 1.49 \times 10^{15}$ ions/cm². Photoluminescence (PL) and Raman scattering measurements were carried out before and after ion irradiation. Raman scattering results reveals that, the structure of zirconia is monoclinic form, and upon ion irradiation, slight shift in the Raman mode along with broadening is observed, however, monoclinic to tetragonal phase transformation was not observed. Ionoluminescence and photoluminescence experiments are consistent, with defect cluster formation and its growth, the intensity of luminescence signal is quenched.

Diffusivity measurement in Zr-2.5%Nb alloy using Neutron Radiography

Shefali Shukla, T. Roy, P. Singh, Y.S.Kashyap, M. Shukla & M.R.More

Technical Physics Division, Bhabha Atomic Research Centre, Mumbai

*Corresponding author: shefali@barc.gov.in

Abstract

Zirconium alloys have long been used in nuclear industry owing to their special properties. They however suffer from the problem of hydrogen embrittlement which results in reduced service life and issues. Hydrogen estimation in Zr-alloys is an area long studied using several techniques. Neutron radiography offers the advantage of being a nondestructive technique which provides bulk hydrogen information in a short span. Apart from hydrogen concentration study of its redistribution under different types of gradients like stress, temperature and concentration is especially important. Here we present evaluation of the diffusivity value of hydrogen in Zr-2.5%Nb alloy at 673K. Studies have been carried out on samples from pressure tube which were precharged electrolytically and annealed for a definite time at said temperature to generate a diffusion profile.

EOS and Mechanical Properties of Cu-Ti Alloy under Dynamic Loading

Swati Gandhi^{1*}, D. Mukherjee¹, A. S. Rav¹ and K. D. Joshi^{1,2}

¹Applied Physics Division, Bhabha Atomic Research Centre, Mumbai, India 400085 ²Homi Bhabha National Institute, Mumbai, India 400094

*gandhis@barc.gov.in

Abstract

The shock compression study in the pressure range of 4.92GPa- 14.28GPa has been conducted on Cu-5%Ti alloy via plateimpact experiments using single-stage gas-gun facility. The experiments were designed to create both compressive and tensile stresses in the sample so as to measure mechanical strength properties such as Hugoniot elastic limit (HEL) and spall strength apart from determining Hugoniot data. From the free-surface velocity profiles of the target measured by Photon Doppler velocimeter (PDV), the HEL and spall strength is determined to be in the range 1.32GPa-1.76GPa at strain rates 3.56×10^4 10.56×10^4 s⁻¹ and 2.12GPa-2.34GPa at strain rates of 2.33×10^4 - 4.05×10^4 s⁻¹, respectively. The comparison of the generated Hugoniot data of this alloy with pure copper indicates that the addition of 5%Ti slightly influence the EOS. However, the dynamic strength properties, i.e., HEL and spall strength differed significantly from that of pure Cu.

Photoluminescence Study of Eu³⁺ Activated Ca₂CeNbO₆: Red Emitting Double Perovskite Phosphor for LED Application

Naresh Degda^{1,*}, Nimesh Patel¹, Vishwnath Verma¹, M. Srinivas¹ and K. V. R. Murthy²

¹Luminescence Materials Laboratory, Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390002, India.

²Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara-390001, India.

*Corresponding Author: <u>degdanaresh65@gmail.com</u>

Abstract

 Eu^{3+} doped Ca₂CeNbO₆ double perovskite phosphors were synthesized via high temperature combustion method, in which urea is taken as a flux. The synthesized phosphors have polycrystalline structure with homogeneous particle size. The structural and crystalline parameters have been determined from the x-ray diffraction patterns. Prepared phosphors have orthorhombic structure. It is observed that the crystallite size increases with increasing doping concentration of Eu^{3+} . The photoluminescence (PL) properties of the phosphors have been investigated using 467nm excitation wavelength. The phosphor shows high intense red emission at 614nm when phosphor was excited with 467nm wavelength. Having intense red emission due to the characteristic electric dipole and magnetic dipole transition of Eu^{3+} ion at 467nm excitation would signify its LED application.

Introduction

The solid-state lighting has got an extensive interest by the researchers in present days, particularly to develop the white light emitting diodes (WLEDs) as they are considered as the fourthgeneration solid-state lighting sources. Currently, most of the WLEDs are made by employing the blue LED chip with YAG: Ce³⁺ (Y₃Al₅O₁₂: Ce³⁺) yellow emitting garnet [1]. This combination suffers from the low color rendering index and high correlated color temperature due to the lack of the red component in the emission spectra. Therefore, the phosphor under study is in high demand to compensate the red component with outstanding luminescence emission. The phosphor doped with Eu³⁺ shows very good luminescence that can be considered as a red emitting phosphor.

The perovskite materials get immense demand for the development of efficient lighting devices. The importance of double perovskite material is that they have very good semiconducting property which is the basic need for the preparation of the phosphor. In the basic perovskite formula ABO₃, when exactly half of the B-site cation getting replaced by B'-cation forms the double perovskite A₂BB'O₆. This will make even broader structural array of perovskite. The successful red emitting double perovskites have been developed by doping Eu³⁺ ions.

In this paper, the photoluminescence properties of the Eu^{3+} doped Ca_2CeNbO_6 are presented for exploring the application as a red emitting LED phosphor, and the present investigation shows that the phosphor exhibits high efficient emission which can be used as a red LED material.

Experimental

Eu³⁺ doped Ca₂CeNbO₆ phosphors have been synthesized by high temperature combustion synthesis method, CaCO₃, Ce(NO₃)₃·6H₂O, Nb₂O₅ and Eu₂O₃ were taken as starting materials in stoichiometric ratio. Urea was taken as a flux with the starting materials (15% wt. of the mixture) to increase the combustion rate. The mixture of starting material was transferred in to the alumina crucible and calcined at 1200°C for 6 hr in muffle furnace. After that samples were allowed to cool at room temperature and the resultant material is been grinded powder. The mandatory obtain white to characterization has been carried to explore the behavior of phosphors.

Results and Discussion

I. X-ray Diffraction



Fig. 1. xrd patterns of pure and Eu³⁺ doped Ca₂CeNbO₆

The x-ray diffraction patterns of the Ca₂CeNbO₆: x Eu³⁺ (x=1-5 mol%) along with the host matrix are shown in Fig.1. All the reflection peaks of the x-ray profile are indexed to the orthorhombic structure of the Ca₂CeNbO₆. The good agreement between observed and calculated d-spacing confirms the orthorhombic phase with crystallite lattice parameter a = 9.332 Å, b = 6.628 Å, c = 6.775 Å and $\alpha = \beta = \gamma = 90^{\circ}$ [2]. There is no substantial change observed in xrd patterns of pure and Eu³⁺ doped Ca₂CeNbO₆ signifies the formation of pure phase of all phosphors.

The identification of orthorhombic structure of the double perovskite phosphor has been confirmed by calculating tolerance factor using Goldschmidt formula. The calculated value of tolerance factor is found to be nearly 0.80 which is also recognized the orthorhombic phase of the phosphors. The crystallite size of the prepared phosphors has been determined from W-H plot which is increase with doping concentration and ranging from 80-125 nm. The particle size of the phosphors is measured through Malvern zeta sizer instrument which is ranging from 500nm $(0.5\mu m)$ to 900nm $(0.9\mu m)$.

II. Photoluminescence



Fig. 2. (a) PL excitation spectra of pure and Eu³⁺ doped Ca₂CeNbO₆, under λ_{em} = 612 nm

Fig. 2(a) and 2(b) shows the excitation and PL emission spectra of the pure and Eu^{3+} doped Ca₂CeNbO₆ phosphor respectively. The excitation spectra is composed of two well defined sharp absorption peaks located 396nm and 467nm in violet-blue region, due to the characteristics 4f-4f transition of Eu^{3+} ion. The excitation peaks located at 396nm and 467nm are attributed to the ⁷F₀-⁵L₆ and ⁷F₀-⁵D₂ transition of Eu^{3+} ion respectively.

PL emission spectra is essentially recorded under 467nm excitation wavelength comprise of welldefined emission peaks located at 582, 593, 614 and 632nm. The emission yield due to the magnetic and electric dipole transition of Eu^{3+} from ${}^{5}D_{0}{}^{-7}F_{J}$ (J=1,2). Emission peaks at 582 and 593nm are assigned due to the ${}^{5}D_{0}{}^{-7}F_{1}$ magnetic dipole transition, while the most intense emission peak at 614nm is attributed to the hypersensitive ${}^{5}D_{0}{}^{-7}F_{2}$ electronic dipole transition of Eu³⁺. The emission peak located at 632nm is assigned due to the electric dipole transition of Eu³⁺ ${}^{5}D_{0}{}^{-7}F_{2}$ [3].



Fig. 2. (b) PL emission spectra of pure and Eu³⁺ doped Ca₂CeNbO₆, under λ_{ex} = 467 nm

The emission intensity due to the magnetic dipole transition is quite lower than that of electric dipole transition, indicates that the Eu^{3+} is located at non-inversion symmetric site in crystal having structure of Ca₂CeNbO₆ [4]. The intense PL emission intensity implies that the doping concentration substantially enhanced the PL properties of the Ca₂CeNbO₆. The results revealed that the absorption and emission rate increases with increase in doping concentration which signifies that the phosphor can be effectively used as LED with intense red emission.

Conclusion

In order to develop efficient red emitting phosphor, Eu^{3+} doped Ca_2CeNbO_6 phosphors have been successfully synthesized by combustion method which have pure orthorhombic phase. Eu^{3+} doped Ca_2CeNbO_6 phosphor gives profound PL emission at 614nm signifies the phosphor is potential for red LED application.

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Metal Nitride Heterostructure for UV-B Photodetection

Jyotisman Bora*, Santanu Podder and Arup R. Pal

Plasma Nanotechnology laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Paschim Boragaon, Garchuk, Guwahati 781035, Assam, India

*Corresponding author: jyotismanb512@gmail.com

Abstract

Interband transition generated carriers of plasmonic nanostructure offer a new scope for the detection of higher energy photons. In this report, an effort has been made to utilize the interband carriers of titanium nitride (TiN_x) for UV detection by fabricating a metal-semiconductor heterostructure (TiN_x/TaN_x) . The active components of the device are synthesized by pulse DC magnetron sputtering technique, and subsequent photoelectrical characterization confirms the generation of photocurrent by UV light. The maximum performance of the detector is found to be in UV-B region where $X_5 \rightarrow X_2$ transition (3.9 eV) of TiN_x takes place. The excitonic carriers of semiconducting tantalum nitride (TaN_x) also contributes and enhanced the overall performance in this region.

Introduction

Plasmonic metal-semiconductor heterostructures are primarily used for sub-bandgap photodetection. Here, the hot carriers generated from the metal surface move towards the semiconductor due to a built-in electric field at interface which helps to detect the lowenergy photons. In contrast, the detection of highenergy photons with the same arrangement is not in the forefront research yet. Till date, most of the low cost UV (high energy photons) detectors are based on high band gap semiconductors, but in terms of performance they are not sufficient enough to fulfill all the criteria. To enhance the performance of such detectors, researchers are trying to combine the interband carriers of metal nanostructure with the existing excitonic carriers of semiconductor, so that the benefit of both the materials can be achieved at a same time. In 2020, Podder et al. successfully reported a selfpowered UV detector where the interband carriers of plasmonic Au and the excitonic carriers of ZnO simultaneously participated. They have found that the contribution of interband carriers drastically improved the detector performance compared to the pristine semiconductor device.¹

Metal nitrides as a potential alternative to the conventional plasmonic metals, get enormous attention in recent times due to their promising mechanical as well as electrical properties. The semiconductor compatible feature of these nitrides provide an additional advantage to explore its usability further.² Titanium nitride (TiN_x) is a well-known plasmonic material and it shows various interband transition in the UV region.³ In this work we have utilized these interband carriers of plasmonic titanium nitride (TiN_x) to fabricate a UV detector by forming a heterojunction with tantalum nitride (TaN_x). Tantalum nitride (TaN_x) used in this configuration behaves as a semiconductor which helps in the transportation of

charge carrier. The selection of active component as a nitride plasmonic and a nitride semiconductor further enhances the durability of the detector.

Experimental Details

The fabrication process of the photodetector comprises of a series of steps where all the components are synthesized by pulse DC magnetron sputtering technique. In the first step, a very thin layer of TiN_x nanostructures are deposited on a patterned ITO substrate at a pressure of 0.1 mbar. In order to separate the generated charge carriers from this TiN_x, a suitable semiconductor is required. So in the second step, a smooth semiconducting thin film of TaN_x is deposited at 0.05 mbar pressure. In the third and final step, Ag is deposited as a counter electrode. So, the final device has the configuration ITO/TiN_x/TaN_x/Ag.

Results

X-ray diffraction pattern of the synthesized TiN_x and TaN_x are shown in **Fig. 1 (a)**. The diffraction peak at 42.9^o is assigned to the (200) lattice plane of TiN_x whereas TaN_x shows a broad peak at 33.9^o corresponds to the (111) crystal plane.^{4, 5}

Fig. 1(b) shows the optical reflectance of the synthesized samples as a function of wavelength. The reflectance spectrum of TaN_x film (violet coloured spectrum) shows a gradual decrease in its reflectance value below the wavelength 400 nm and reaches its minimum value at ~300 nm. The strength of this minima becomes very prominent after the addition of nanostructured TiN_x. The red coloured spectrum represents the combined optical behavior of TiN_x/TaN_x heterostructure, which shows two reflectance minima in the UV and Visible region respectively. Theoretical study confirms that L₃→L₃ (5.6 eV), X₅→X₂ (3.9 eV) and $\Gamma_{15}\rightarrow\Gamma_{12}$ (2.3 eV) are

the mostly occurred interband transition in TiN_{x} .³ So, the minima in the UV region corresponding to 310 nm (~4 eV) is mainly associated with $X_5 \rightarrow X_2$ (3.9 eV) transition of TiN_x . The minima in the visible region around ~520 nm depicts the well-known plasmon excitation of TiN_x .



Fig.1. (a) XRD pattern of the synthesized samples, (b) Reflectance spectra of the active component (TiN_x/TaN_x)

Fig. 2. (a) & (b) shows the 3D topographic image and the roughness histogram of the synthesized TiN_x and TaN_x . A comparative study of both the images clearly indicates that the high-pressure growth favours titanium nitride to form large number of nanostructure. These nanostructures are mainly responsible for the plasmonic behaviour of the TiN_x . On the other hand, a lower-working pressure provides a continuous film of tantalum nitride which is very much essential for the smooth transportation of carriers. The RMS roughness value of both TiN_x and TaN_x are measured to be 11.5 nm and 3.61 nm respectively.



Fig. 2. AFM image with the roughness histogram of (a) ${\rm TiN}_x$ (b) ${\rm TaN}_x$

The photoelectrical measurements of the device is carried out in self-powered configuration with the help of a Keithley 2634B sourcemeter. The time dependent (I-t) photoresponse of the fabricated detector is recorded by switching different wavelength LED at a fixed intensity of 0.5 mW is shown in **Fig. 3 (a)**. The fabricated detector exhibits very low dark current (~4 nA) and shows an excellent consistency with switching effect. At 310 nm, the device offers a

maximum value of photocurrent and it is measured to be 472 nA. The photosensitivity parameter of the detector i.e. $(I_{light}-I_{dark})/I_{dark}$ is also calculated and presented in **Fig. 3 (b)**. The nature of the photosensitivity spectrum is completely opposite to the reflectance spectrum of the active material and it suggests that the performance of detector follows the light absorption nature of the active material. The maximum photosensitivity value of the detector at 310 nm is found to be 70.



Fig. 3. (a) I-t characteristics, (b) photosensitivity of the photodetector at different wavelengths.

Conclusion

In summary, this study experimentally demonstrates the interband transition generated carriers of TiN_x mediated UV-B detector where TaN_x is used as a base semiconductor material. The photocurrent obtained by the detector is found to be maximum at 310 nm with a photosensitivity value of 70. This result shows the way toward the design of different optoelectronic devices by combining interband carriers of nitride plasmonic materials with appropriate semiconductors for deep UV photodetection.

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Magnetodielectric Ni_{0.5}Zn_{0.3}Co_{0.2}Fe₂O₄ and SrFe₁₂O₁₉ Composite for Ferrite Resonator Antenna Applications

Jijin K. Raj¹, Athira Rajan¹, and Subodh G. ^{1*}

¹Department of Physics, University of Kerala, Thiruvananthapuram, Kerala, India 695 581

*Corresponding author: <u>gsubodh@gmail.com, gsubodh@keralauniversity.ac.in</u>

Abstract

A conventional solid-state sintering method is adopted for the fabrication of x Ni_{0.5}Zn_{0.3}Co_{0.2}Fe₂O₄–(1–x) SrFe₁₂O₁₉ composite with x = 0.5, with appreciable density and their broadband electromagnetic properties were deciphered. X-ray diffraction analysis revealed the presence of Ni_{0.5}Zn_{0.3}Co_{0.2}Fe₂O₄ (NZCFO) and SrFe₁₂O₁₉ (SFO) phases in the composite along with minor impurity phases. The composite possesses a stable real permittivity of 8.9, dielectric loss in the order of 10^{-2} , permeability greater than 2 and magnetic loss tangent in the order of 10^{-1} in the broadband region. A ferrite resonator antenna based on NZCFO-SFO composite has been simulated and fabricated. The fabricated resonator antenna operates at 13.4 GHz presented an exceptional return loss of -28.5 dB with a wide impedance bandwidth of 1.7 GHz.

Introduction

Over the last few decades magnetodielectric materials, particularly ferrites materials have gained popularity in the field of wireless communication owing to their excellent physical as well as chemical properties. One particular and interesting application of ferrites is that these materials can be used to fabricate ferrite resonator antenna (FRA), a device capable of radiating effectively at a higher frequency range. Nickel zinc cobalt ferrite is a spinel ferrite exhibiting many applications in various field of physics, particularly for radio and microwave communications owing to its high permeability and high resistivity¹. On the other hand, strontium hexaferrite, which is an M-type hexagonal ferrite is a potential candidate for various applications in the high frequency region of the microwave band due to its appealing properties such as high saturation magnetization, high uniaxial magnetic anisotropy, and high Snoek's limit². In this work, we have investigated broadband electromagnetic response the of $Ni_{0.5}Zn_{0.3}Co_{0.2}Fe_2O_4$ - SrFe₁₂O₁₉ composite. The electromagnetic properties of this spinal-hexaferrite composite is further explored to simulate and fabricate an FRA designated for Ku-band applications.

Experimental

The ferrite powders of $Ni_{0.5}Zn_{0.3}Co_{0.2}Fe_2O_4$ (NZCFO) and $SrFe_{12}O_{19}$ (SFO) were synthesized by conventional solid-state reaction route. Stoichiometric amounts of high purity NiO, ZnO, Co_3O_4 , Fe_2O_3 were used as the starting materials for the synthesis of NZCFO, while high purity Sr_2O_3 and Fe_2O_3 were used for the synthesis of SFO. The ball milled and dried mixture of the reagents was calcined at 1150 °C for 3 hours and 1000 °C for 4 hours, respectively for the synthesis of SFO and NZCFO. 0.5NZCFO-0.5SFO composite is prepared by sintering the properly mixed and pelletized powder mixture of NZCFO and SFO at a temperature 1200 °C for 2 hours. The phase purity of ferrites and composite were characterized using X-ray diffraction (XRD). The broadband electromagnetic parameters of the 0.5NZCFO-0.5SFO composite in the frequency range of 10 MHz to 1 GHz was analyzed using a Keysight E4991B impedance analyzer with a 16453A dielectric and 16453B magnetic test fixture. The FRA design simulations were carried out using the ANSYS Electromagnetics Suit 2019 R2 version HFSS software. The antenna measurements were carried out using the Keysight PAN-L N5234B Vector Network Analyzer (10 MHz to 43.5 GHz).

Results and discussion



Fig. 1. XRD patterns of NZCFO, SFO and 0.5NZCFO-0.5SFO composite.

Figure 1 shows the XRD patterns of NZCFO, SFO ferrites and 0.5NZCFO – 0.5SFO composite. The formation of ferrites as well as existence of hexagonal SFO and cubic NZCFO in the composite is confirmed by comparing the reflection peaks of the obtained XRD patterns of the respective ferrites and the composite with that of the standard ICDD files of SFO (ICDD file No: 00-033-1340) and NZCFO (ICDD file No: 00-033-1340). However, the presence of small extra peaks around $2\theta=36^{\circ}$ in the XRD pattern of 0.5NZCFO – 0.5SFO composite suggests the formation of additional phases in the composite.



Fig. 2. Frequency dependence of a) real part of permittivity and permeability, b) imaginary part of permittivity and permeability, c) dielectric and magnetic loss tangent of 0.5NZCFO-0.5SFO composite and d) return loss of simulated and fabricated FRA (inset shows fabricated antenna).

Figure 2 (a) – (c) shows the broadband electromagnetic parameters as well as dielectric and magnetic loss tangent of 0.5NZCFO - 0.5SFO composite. The *ɛ*' of the composite remains approximately 8.9 through the entire broadband region which could be attributed to the relaxation of various polarization mechanisms in the high frequency region. The ε and tan δ_{ε} exhibits a similar trend and the loss is found to around 10^{-2} in the wide bad region, which can be ascribed to the to the electron exchange interactions between the Fe^{2+} and Fe^{3+} ions in the composite^{2,3}. The μ of the composite shows a similar trend as that of a typical spinal ferrite with a high permeability value maintained to a certain frequency then start reducing as the frequency increases due to the ceasing of domain wall motion⁴. The ferromagnetic resonance frequency (FMRF) of NZCFO is near 700 MHz and SFO is greater than 1 GHz^{3,4}. 0.5NZCFO-0.5SFO present relatively high and sustained value of 3.7 up to 200 MHz, which lowers to 2.1 near 1 GHZ with an increase in magnetic loss to 0.6. The reduction in the

FMRF of the composite and the higher tan δ_{μ} may be assigned to the presence of additional phases present in the composite. However, the comparably high permeability, stable permittivity, low dielectric loss and characteristic impedance as high as 0.5 of the composite point towards its applicability as a resonator for antenna applications. Hence, a multiband FRA with the major band resonating around 13.4 GHz has been designed, simulated and fabricated. The simulated antenna possesses a return loss (RL) of -36.55 dB and an impedance bandwidth (BW) of 4.3 GHz, while the fabricated antenna has a RL of -28 dB and BW of 1.7 GHz, as shown in figure 2(d). The variation between simulated and experimental results may be associated with the air gap between the resonator and the substrate which will inhibit proper coupling of energy between the patch in the substrate and the resonator. The results acquired through this study points towards the fact that spinal-hexaferrite combinations are excellent candidates for wideband FRA applications despite with the presence of smaller additional phase formation.

Conclusions

In summary, $0.5Ni_{0.5}Zn_{0.3}Co_{0.2}Fe_2O_4 - 0.5SrFe_{12}O_{19}$ composite were synthesized and broadband electromagnetic properties were studied. XRD analysis of the composites confirmed the existence of the dual phase in the composite along with smaller fraction of additional phases. Based on the EM properties of the composite, a ferrite resonator antenna is fabricated based on the composite. The fabricated FRA resonated at 13.4 GHz with a RL of -28 dB and a wide BW of 1.7 GHz, proposing the application potential of the ferrite resonator antenna in the Ku-band region.

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MEMS based pressure sensor for detection of negative pressure wave in subsea pipelines

Sumit Sunil Kumar^{*}, Dhyan Patel, Rugved Katole, Ujwal Gandhi

Department of Mechanical Engineering, Birla Institute of Technology and Sciences - Pilani, Goa 403726

*Corresponding author: f20180029@goa.bits-pilani.ac.in

Abstract

Design analysis and simulation of a MEMS based capacitive pressure sensor for detection of a negative pressure wave (NPW) has been presented for leak detection in subsea pipelines. A capacitive pressure sensor measures the change in pressure through a calibrated circuit due to displacement of the membrane. Capacitive pressure sensor involves two coupled physics, namely Electrostatics and Solid mechanics. COMSOL Multiphysics was used to simulate the sensor behavior under various conditions. A negative pressure wave, modeled in MATLAB, was imported as an input load to study the change in impedance and its sensitivity to different parameters. The parameters chosen for sensitivity analysis were (a) the material of the capacitor membrane and (b) the gas-filled in the cavity. Simulation study showed that the maximum displacement occurred at the center of the sensor membrane and reduced radially outwards; also a change in the capacitance due to the change in membrane material is also observed. While the same deflection and capacitance was observed when the cavity was filled with air and noble gases, there was improved total capacitance when the cavity was filled with Nitrogen. We conclude that a change in the dielectric material of the cavity and membrane material has a positive effect on the sensor.

Introduction

Oil and gas industry has one of the largest contributions in the world economy through supply of oil barrels and different gases. These pipelines travel very long distances through deep seas and lands, leakages in these pipelines could cause disastrous consequences as they carry hazardous substances and can cause damages to sea life and also to habitats nearby. Subsea pipelines are designed in such a way to sustain harsh environments.

It is very important to develop a reliable system to detect leakages in these pipelines. When there is a leak in the pipeline there is a sudden change in the density of gas, resulting in creation of a negative pressure wave. This negative pressure wave travels upstream and downstream. Detection of a negative pressure wave by sensors can be used to calculate the location of leak. Detection of negative pressure waves using pressure sensors based on Fiber Bragg Grating (FBG) has been reported in [1]. Rao et al [2] presents design and simulation of MEMS capacitive pressure sensors in harsh environments. Material selection for the design of sensors plays an important part, this has been reported in [3]. Pressure wave behaviour and leak detection has been reported in [4]. In harsh environments like the sea, MEMS based pressure sensors [2] are more reliable than pressure transducers. The work in this paper uses negative pressure waves for an approximate estimation of the location of the leak in a pipeline by improving sensitivity of the MEMS based pressure sensor.

Leak Detection

Figure 1 shows a pipe with two pressure sensors at a distance L. If a leak happens, the negative pressure wave is divided into two damping waves flowing in opposite directions. The amplitude of the damping wave and the time difference between two consecutive peaks can be used to detect the location of the leak.Consider the velocity of the fluid is u and the pressure wave velocity is V: Then,V-u and V+u are the upstream and downstream velocities respectively. Let t_1 (t_2) be the time at which the upstream (downstream) sensor detects pressure change. The location of the leak, x can be derived using equation (1)

$$\mathbf{x} = (t_{1} - t_{2}) \frac{V^{2} - u^{2}}{2V} + L \frac{V - u}{2V}$$
(1)



Design Methodology of the Sensor

The sensor uses two capacitors, where one capacitor is fixed and the other is variable, which provides
detectable leak. A simple schematic diagram of the MEMS based pressure sensor used is shown in Figure 2. It has a pressure membrane, anchors to hold and clamp the membrane onto the substrate, a cavity, two electrodes, and a dielectric layer. The two electrodes and the dielectric makes one of the capacitors whose capacitance (C₁) is constant (capacitance $C = \mathcal{E} \frac{A}{d}$). Another capacitor results from the membrane, upper electrode and the cavity shown by the air gap, which is a variable capacitor (C_2) as the distance between the plates varies due to change in pressure subjected by the membrane. Using COMSOL multiphysics a parametric study is performed to check the effect of change in the material in the cavity and the change in membrane material on the sensitivity of the sensor. The substrate, membrane, electrodes and dielectric are circular in shape. The cross-sectional view of the model is shown in Figure 3.



Fig. 2 Schematic diagram of the MEMS sensor



Fig 3. CAD model and its dimensions.

Results and Discussions

The simulation was conducted for coupled electrostatics and solid mechanics simultaneously. A dynamic convergence criteria was used by COMSOL. Applied pressure in the NPW model was 120kPa. Figure 4 shows displacement of the membrane varied from maximum at the center to no displacement as we moved away from the center. With Si₃N₄ dielectric, the capacitance of the fixed capacitor C₁ = (8.85E-12) * (7.5) * (7.85E-09) / (1.00E-05) = 5.21E-14 F. Table 1 and 2 provide displacement and variable capacitance (C₂) for varying cavity gas and membrane material.



Fig 4. Displacement of the membrane **Table 1** Displacement and Capacitance for different gases

Membrane Material	Cavity Filled	Displacem ent (m)	Capacitanc e (C ₂) F	Total Capacitance
Silicon	Air	7.99E-08	3.62E-14	8.84E-14
Silicon	Nitrogen	8.06E-08	4.16E-14	9.38E-14
Silicon	Krypton	7.99E-08	3.62E-14	8.84E-14
Silicon	Argon	7.99E-08	3.62E-14	8.83E-14
Silicon	Helium	7.99E-08	3.62E-14	8.83E-14

Table.2 Displacement and Capacitance for membrane

Membran e Material	Displacement of membrane(m)	Cavity Remaini ng (m)	Variable Capacita nce (C ₂)(F)	Total Capacita nce (F)
Silicon	7.99E-08	1.92E-06	3.62E-14	8.83E-14
Aluminum	1.20E-07	1.88E-06	3.70E-14	8.91E-14
Polysilicon	1.10E-07	1.89E-06	3.68E-14	8.89E-14

Conclusion

With silicon membrane and different gases in the cavity, nitrogen provides the highest displacement and capacitance. When the cavity gas is fixed and varying membrane material, aluminum membrane provides better displacement and capacitance thereby increasing sensitivity of the sensor.

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Niobium Doped Bismuth Titanate Ceramic Piezo-Elements For High Temperature Transducer Application

Babita Tiwari, M. Sonawane, A.K. Chauhan

Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India

*Corresponding author: babitat@barc.gov.in

Abstract

Polycrystalline ceramics of bismuth titanate Bi₄Ti₃O₁₂ (BIT) doped with 3 mol% Nb were synthesized by solid state sintering method. Synthesis process was optimized to get phase pure material. Piezoelectric properties of this material were studied. Sintered pelletized BIT discs were polled and used as an active piezo element. In initial experiments these BIT discs were tested for ultrasonic transducer application using pulse echo method. Results of study indicate that prepared piezo ceramic has potential to be used for high temperature transducer applications.

Structural Characterization of Pure Monazite Phase in LaPO4

Y. Kumar^{1,2,*}, S. Tripathi¹, M. Nand^{1,2}, A. Arya^{2,3} and S. N. Jha^{1,2}

¹Beamline Development & Application Section, Bhabha Atomic Research Centre, Mumbai, India – 400085

²Homi Bhabha National Institute, Anushaktinagar, Mumbai, India - 400 094

³MSD, Bhabha Atomic Research Centre, Mumbai, 400085, India

* Corresponding author: kumaryogeshbhu@gmail.com

Abstract

We report Rietveld refined data of X-ray diffraction experiments performed on monazite LaPO₄, which is considered to be a potential host material for immobilization of metallic actinides produced as nuclear waste products. The sample was synthesized via solid state reaction method with starting material as La_2O_3 and $(NH_4)_2HPO_4$ at elevated temperature of 1550°C followed by sintering in air atmosphere. X-Ray diffraction measurements revealed the phase purity and crystallinity of sample. Energy dispersive X-ray analysis technique was used to determine any chemical impurity present and elemental composition. The sample was found to be in monoclinic crystal structure with space group number 14 and symmetry $P2_1/n$ with the lattice parameters close to the expected ones (standard bulk). Present studies would be used as a basis for further characterization of this material to understand its suitability as a host for waste immobilization.

Introduction

Disposal of high-level nuclear wastes obtained from nuclear reactors, research reactors, hospitals and military applications is one of the major concerns of present time. One of the most important ways of such disposal is deep burial of the radioactive nuclear waste that contains these actinides doped in the suitable host. But these applications require specialized materials that can sustain high pressure and temperature conditions as well as have low leaching rates. For example, the rare earth-based monazite structure $LnPO_4$ (where Ln = light rare earth lanthanides) crystallizes in monoclinic crystal structure and is a highly stable material with the capability of bonding with different kinds of dopants including actinides. Among these, LaPO₄ shows high stability against chemical as well as radiation damage (self-irradiation due to radioactivity of the dopant actinides) and in naturally found monazite, it exhibits high stability for billions of years. It has been seen that monazites can easily incorporate trivalent and tetravalent actinides.

However, any host can be considered for commercial applications only when its suitability and compatibility is fully tested at laboratory level. To do this, surrogate materials are generally chosen to avoid the complexity and possible radiation exposure if radioactive actinides are used directly. For this, the properties of pure host material need to be characterized before using them for doping purpose.

LaPO₄ has been chosen for the present study in view of its stability, compatibility with nuclear waste, possibility of pure phase formation and many others. Here, we report the laboratory synthesis and initial measurements carried out to understand the structural and compositional properties using solid-state chemical reactions technique, energy dispersive Xray analysis method and X-ray diffraction (XRD) technique.

Experiments

LaPO₄ sample was synthesized by using hightemperature solid-state reaction method in which La₂O₃ (dehydrated at high temperature) and $(NH_4)_2HPO_4$ were mixed and ground for few hours. The mixed powder was then calcined at 1350°C followed by grinding. Finally, pellets were prepared and sintered at 1550 °C for 10 hrs. Energy dispersive X-ray analysis (EDAX) measurement on Cu coated pellet was done on Element EDAX system of the FE-SEMs instrument with the incident energy of 18 KeV inside high vacuum.

After checking the sample purity using EDAX, Xray diffraction (XRD) measurements were performed on Indus-2 XRD beamline (BL-11) of Synchrotron radiation source (SRS), RRCAT, Indore, using photon energy of ~15.7 KeV [3]. The measurements were done at room temperature. Rietveld refinement was performed using GSAS-II software [4].

Results and Discussion

Figure 1 depicts the EDAX spectrum of LaPO₄ bulk sample (coated with ultra-thin layer of Cu to make it conducting). The spectrum shows only the elemental peaks from compositional elements and their fine transitions are marked at respective positions. The highest intensity peak observed can be attributed to oxygen as also evident from the standard composition (La: 16.7 at%, O: 16.7 at%, P: 66.6 at%). However, owing to the low sensitivity of EDAX towards low atomic number elements, the composition as observed can be slightly different from the standard composition and it was reflected in the present case, where the composition was found to be La: 19.3 at%, O: 17.1 at% and P: 63.6 at%.



Fig. 1. EDAX spectrum of LaPO₄.

Figure 2 exhibits the comparison of experimental and theoretically simulated XRD patterns along with the residual of the fitting. The Rietveld refined data shows that all the Bragg reflections are matching well with those obtained experimentally and hence validates the fitting parameters. No additional peak was found apart from the compositional peaks of LaPO₄ confirming the phase purity as well as complete transformation of starting chemicals into the final product. This was also in agreement with the observations from EDAX.



Fig. 2. Rietveld refined XRD pattern of LaPO₄.

The standard data file corresponding to this monoclinic crystalline phase was taken from COD (Crystallography Open Database) as the initial guess. The weighted profile factor (R_{wp}) comes out to be ~ 6.5% and the volume (V)= 309.98 Å³. The standard deviation in the lattice parameters a, b and c is ~ 0.0001 Å. Other lattice parameters as the cell dimensions (a, b and c and angle β) are provided in

table-1.	As	seen	from	the	table-1,	the	lattice
paramete	ers ar	e close	e to the	stand	lard ones.		

Table-1 Rietveld refined lattice parameters of LaPO4			
Parameter	Standard values	LaPO ₄	
a (Å)	6.84	6.86	
b (Å)	7.08	7.10	
c (Å)	6.51	6.53	
β (°)	103.32	103.30	

Conclusions

LaPO₄ pellet was synthesized using solid-state reaction method followed by calcinations and sintering processes. The elemental purity was confirmed from EDAX analysis which showed the presence of elemental peaks related to La, P and O absorption transitions along with the absence of any other element except Cu that was used as coating to make the sample conducting.

Further measurements with X-Ray Diffraction exhibited monoclinic crystal structure with space group number 14 (symmetry $P2_1/n$). Detailed analysis was performed using Rietveld refinement, which showed that lattice parameters were close to the standard bulk and there was no crystalline phase impurity in this sample. These observations confirmed the formation of highly stable, single crystalline phase of LaPO₄ that matches well with the reported monazite structure. Further experiments based on this material as a host for actinide doping are being planned and will be performed based on these initial results.

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G Phonon Mode Splitting in Doped Bilayer Graphene Probed by insitu Transport Measurement and Raman Spectroscopy

Shubhadip Moulick^{*1}, Shubhrasish Mukherjee¹, Sreyan Raha², Achintya Singha² and Atindra Nath Pal¹

¹Department of Condensed Matter Physics & Material Sciences, S.N. Bose National Centre for Basic Sciences, Sector III, Salt Lake, Kolkata, 700106, India, ²Department of Physics, Bose Institute,93/1,A.P.C Road, Kolkata, 700009, India,

*Corresponding author: moulick.shubhadip94@gmail.com

Abstract

Two dimensional material like graphene, TMDC's have shown a lot of promises due to their excellent electrical and optical properties. Graphene devices fabricated so far relied on lithographic techniques which always leave an unintentional residue on the graphene surface. Here, we have created a bilayer graphene device avoiding the conventional lithographic procedure by transferring the graphene layer directly on top of the metal electrodes. We tune the carrier density by the application of an electrolyte top gate, and a high doping level ($\sim 10^{13}/\text{cm}^2$) can be accessed due to the formation of a nanometer-thick Debye layer. We performed in-situ Raman spectroscopy by varying the carrier concentration. A prominent blue shift of the characteristic G peak was noticed with increasing carrier concentration, originating possibly due to enhanced electron-phonon interaction. Moreover, we observed a splitting of the G peak at higher doping concentration, may arise due to mixing of symmetric and antisymmetric modes by breaking the layer symmetry of the bilayer graphene.

High Efficiency, Zero Dead Space, Square Cathode Neutron Detector For Triple Axis Spectrometer

Shraddha Desai^{*1}, Mala N Rao^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, ²Homi Bhabha National Institute, Anushaktinagar, Mumbai-400094

*Corresponding author: ssdesai@barc.gov.in

Abstract

Neutron scattering instrument with optimized detectors enhances the instrument through put. Position sensitive detectors show considerable gain in beam time utilization, whereas few experiments such as Triple Axis Spectrometer need point detector in step scan mode for recording the neutron intensity in variable (Q,ω) space. Use of focusing monochromator, planar beam monitor for integral beam intensity counting and efficient neutron detector with zero dead space and square cross section area are of advantage. Neutron efficiency, beam interception area and shielding volume put constraints on the overall design of the detector. It is essential to have compact detector with high neutron detection efficiency, indicating position $in(Q,\omega)$ space and high beam interception. Square cross section neutron counting detector is designed and developed for use at Triple Axis Spectrometer. The present detector also gives the advantage of reduced shielding weight on movable arm of detector.

Synthesis and characterisation of GdTaO₄ using XRD, Raman, and first principles calculation

Saheli Banerjee^{1*}, Alka B Garg^{1,2}, H.K. Poswal^{1,2}

¹Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India. saheli@barc.gov.in

Abstract

In recent times, the family of Ternary oxides RBO₄ (R = Gd, Eu, Dy and B = Nb, Ta) has drawn special attention because of their potential application in field of solid-state fuel cells, scintillating crystals, anti-laser radiation area and so on. We have synthesized polycrystalline GdTaO₄ by solid state reaction method and characterized same compound by using XRD, and Raman techniques. First principles calculations have been performed using Quantum espresso and the structural parameters and Raman mode frequencies, obtained from DFT calculations corroborates well with our experimental findings.

Internal Field Nuclear Magnetic Resonance: Versatile tool to Estimate the Fe³⁺ ions concentration in Ferrites

Manjunatha M¹, and K P Ramesh²

¹Department of Physics, SG College Koppal, 583231. ²Department of Physics, IISc, Bengaluru, 560012.

*Corresponding author: manjuna999@gmail.com

Abstract

To determine the concentration of Fe3+ ions in the ferrimagnetic materials there are only few limited tools: one such is Internal Field Nuclear Magnetic Resonance (IFNMR). To estimate the concentration we have chosen two ferrimagnetic materials Nickel ferrite and Lithium Ferrite. The determined concentration of Fe3+ ions is in good agreement with the existing tools such as XRD and Mössbauer etc.

Development of In-situ X-ray Imaging and µ-CT facility for Sample Studies Under Tensile/Compressive Load Conditions

Payal Singhai^{*}, Ashish K. Agrawal, B. Singh, Yogesh Kashyap, Mayank Shukla

Technical Physics Division, Bhabha Atomic research centre, Mumbai 400085

* spayal@rrcat.gov.in

Abstract

X-Ray micro tomography is versatile tool for study of properties of materials like density, micro structure etc. There is great demand in studies related to change in the properties of materials under various loading conditions (such as mechanical stress and temperature). An In-Situ X-Ray imaging and u-CT facility with compression and tensile loading stage have been developed at imaging beamline Indus -2. This facility allows study of material micro-structures under compression and tensile load conditions. This papers describes in details about the facility developed.

INTRODUCTION

Study of physical properties like micro-structures of materials are necessary for understanding bulk properties of the materials. These micro-structures changes under various loading conditions like temperature and pressure, these changes in microstructures can alter physical properties as a bulk. Hence it is of great interest to know the changes in micro-structures. Steel fiber entanglements, and fatigue in Al alloys at room temperature were studied in [1] using In-situ experiments. Propagation of cracks in alloys and composite materials were studied in detail using in-situ tomography in [2,3,4]. These studies are necessary in development of light weight metal matrix composites with improved mechanical properties and wear resistance, which are demanding in automobile and aircraft industry.

An In-Situ load cell setup have been augmented to the existing micro-tomography facility existing at imaging beamline Indus – 2. This setup has been reported with results in BARC news letter March – April 2021. In this paper details of the facility are reported.

IN-SITU LOADING FACILITY

In-Situ Loading device shown in Fig 1. currently operational at imaging beamline Indus – 2. Currently 500N and 3000N load cells are available for use with this system. Load can be varied in 1000 steps upto maximum range, with an accuracy of 1%, at rates ranging from 0.1mm / min to 1mm / min.

This facility is operated remotely from control room's remote terminal. All the experiments are automated using labview. The control panel is developed dedicated to be used for in-situ loading is shown in fig 2. All the parameters such as maximum load, load step size, and imaging parameters such as exposure time, sub area imaging can be set via this control panel.



Fig. 1. In-Situ Load Cell and X-ray imaging camera.

This developed program is capable of sample alignment, take reference and background images which are necessary during the post-processing and 3D reconstruction. The flowchart of is shown in figure 3.



Fig. 2. Graphical Use Interface.

This facility has software tools like ImageJ for postprocessing of images (normalization, background correction, flat field correction, sticting). Octopus software for 3D reconstruction from tomography images. Dhristi for 3D visualization of reconstructed data. With these software tools we are capable to deliver details of the parameters such as porosity, pore size and shape, crack propagation to the users.



Fig. 3. Flowchart

An example usage of this facility is shown in figure 4. It shows radiographs of PU foam under various loading condition.



Fig. 4. Radiograph of PU foam under different loading conditions

CONCLUSION

In-Situ X-Ray imaging and u-CT facility for sample studies under stress and compressive load conditions have been developed.

Acknowledgment

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Characterization of Polystyrene based Plastic Scintillator for Neutron Detection Applications

Lizbeth Alex¹, P. Rajesh^{1*}, Mohit Tyagi²

¹Centre for Crystal Growth, Department of Physics, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Tamilnadu, 603110

²Crystal Technology Section, Technical Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085

*Corresponding author: rajeshp@ssn.edu.in

Abstract

A polystyrene based plastic scintillator of 4.5 cm diameter and 2.5 cm length was successfully synthesized using thermal polymerization reaction. The radioluminescence measurement of the synthesized sample exhibited a very strong emission band in the wavelength range from 320 to 450 nm with a peak maximum at 420 nm for different voltages. The fast scintillation decay time of the fabricated plastic scintillator was investigated using γ -rays from ¹³⁷Cs source. Pulse height spectra were recorded using different gamma ray sources such as ¹³⁷Cs and ⁶⁰Co. The results showed that the above-mentioned material is a promising and a potential candidate for scintillation and neutron detection applications.

In vitro bioactivity of bismuth containing borate-based glasses

Sathaiah Murimadugula and P. Syam Prasad

Department of Physics, National Institute of Technology Warangal, Warangal-506004

*Corresponding author: syam9405@gmail.com

Abstract

Bismuth containing borate-based glasses were prepared by conventional melt-quenching technique and characterised to know their biological activity suitable for tissue engineering applications. Bioactivity of glass samples was examined *in vitro* by the apatite mineralization ability in simulated body fluid (SBF). The glass samples were analysed by XRD, FTIR and SEM-EDS before and after immersion in SBF. The obtained results revealed that the developed bismuth containing borate-based glasses have shown excellent hydroxyapatite layer (HAP) formation in SBF for lower content of bismuth. Therefore, the prepared bismuth borate glasses are appropriate for the development of bioactive implants.

1. Introduction

Bioglasses have wide range of applications in orthopedics for the repair and regeneration of bone and in dentistry for dental repair. When the bioactive glass surface interact with the biological environment, hydroxyapatite is formed, which mimics the mineral phase in natural bone [1].

Many bioactive glasses such as silicate, phosphate and borate-based glasses etc., have been developed for various hard and soft tissue repair and regeneration purpose. Boron affects the osteoblast activity as well as functioning of several metabolic enzymes. Boron absence causes the abnormal bone growth. Appropriate amounts of boron improve the bone health and stimulates wound healing. Different concentrations of boron in bioactive glasses have significant effect on glass network parameters, bioactivity, biocompatibility, and degradability. [2].

Bismuth has been used in pharmacy production of biomedical applications. It acts as an antimicrobial agent and anticancer agent. Bismuth plays a key role in bone formation depending on its concentration [3]. Therefore, in the present study, we aimed to synthesize bismuth borate-based glasses by varying bismuth concentration.

2. Materials and methods

Glasses with composition $(60-X)B_2O_3-25CaO-15Na_2O-XBi_2O_3$ (where X = 0, 2, 4 and 6 mol. %) were prepared. The mixture of oxide powders (Sigma Aldrich) were melted in a platinum crucible at 1100 °C for 3 h. The melt was then poured into pre-heated stainless-steel moulds and then annealed at 350 °C. For *In vitro* bioactivity analysis the SBF was prepared as per the protocol given in the reference [4]. Glass samples were incubated in SBF at a ratio of 0.15g/150 ml at 37 °C for 7, 14 and 21 d. After that,

Samples were removed from SBF and dried for characterization.

The phase identification of glass samples was carried out by X-ray Diffractometer. The surface was studied using scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Infrared spectrum was recorded using Fourier transform infrared (FT-IR) spectroscopy.

3. Results and discussion

XRD patterns of the glass samples exhibited typical broad halos, no sharp peaks were observed, indicating amorphous nature of glasses before immersion in SBF (Fig.1).



Fig. 1. XRD patterns of as prepared grass samples

After soaking in SBF glass samples exhibited the diffraction peaks as shown in Fig. 2. The peaks have been identified and assigned to standard crystalline hydroxyapatite phase (JCPDS: 09-0432). It can be observed that all the sample have shown well-defined diffraction peaks of hydroxyapatite phase, while the intensity of peaks slightly decreased with increasing Bi content from 2 to 6 mol. %. The results indicating that the addition higher concentration of Bi reducing the mineralization rate of hydroxyapatite layer. The SEM images of glass powders demonstrated that

glass particles are irregular in shape (Fig. 3). Further, EDS spectra confirmed the chemical composition of glass samples with the presence of B, Ca, Na, O and Bi. The Bi content is also increased from Bi2 to Bi6.



Fig. 2. XRD patterns of glasses after soaking in SBF 21 d



Fig. 3. SEM-EDS of glass powders

After immersion in SBF the surfaces of the samples covered with white globular precipitates, which confirmed the formation of HAP layer (Fig. 4) according to the earlier reports [5]. EDS spectra showed the presence of P content in addition to the elements present in glass composition.



Fig. 4. SEM-EDS of glasses after soaking in SBF 21 d

Fig. 5 illustrates the FT-IR spectra of glass samples before and after soaking in SBF. The bands in the region 760-1160 cm⁻¹ are attributed to B-O stretching vibration of BO₄ units and the bands in the region 1200–1500 cm⁻¹ are related to B-O stretching of trigonal BO₃ units. The small band at 700 cm⁻¹ is due to bending vibration of B-O-B in symmetric BO₃ triangles. The variation of bismuth content in the glass network did not showed any significant changes. FT-IR spectra of glass samples after immersion in SBF for 21 days exhibited several new infrared bands. The peaks observed at 1418, 1487 and 875 cm⁻¹ were assigned to carbonate group. The bands at 1093, 1033, 603 and 563 cm⁻¹ were assigned to the phosphate group of HAP. The bands at 1642 and 3434 cm⁻¹ corresponded to the OH stretching vibrations. The results of FT-IR analysis in combination with XRD and SEM-EDS analysis conformed the formation of hydroxyapatite (HAP) on the glass samples in SBF solution.



4. Conclusion

Bismuth containing borate-based glasses was synthesized. *In vitro* bioactivity of these glass samples was examined in SBF. The apatite forming ability was studied using XRD, FTIR and SEM-EDS. The results revealed that these glasses showed good bioactivity by forming bone like hydroxyapatite layer on their surface in simulated body fluid environment. However, it is further inevitable in terms of its cytotoxicity and osteogenesis to ensure the potential of these glasses for orthopedic or dental applications.

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$\gamma\text{-ray}$ Induced Defects in $Yb^{3+}\text{-}Sm^{3+}$ Co-doped Borate Glass

Nimitha S. Prabhu¹, H.M. Somashekarappa², Sudha D. Kamath^{1*}

¹Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India.

²Centre for Application of Radioisotopes and Radiation Technology (CARRT), Mangalore University, Mangalagangothri, Karnataka, India.

*Corresponding author: sudha.kamath@manipal.edu

Abstract

The 10BaO-20ZnO-20LiF-49.4B₂O₃-0.1Yb₂O₃-0.5Sm₂O₃ glass was studied for the structural and optical changes after 1 kGy γ -dose exposure. Post-irradiation, the Fourier Transform Infrared spectroscopy indicated the upsurge in Non-Bridging Oxygens while the optical absorption spectroscopy revealed the occurrence of color centers and rise in defects. The defect centers were distinguished as Non-Bridging Oxygen Hole Center and Boron *E*'-center from the Electron Spin Resonance analysis.

Introduction

The study of the glass properties pre-and postirradiation is valuable for understanding the changes in the intrinsic glass structure under the influence of radiation [1]. These changes in the form of defects may arise due to atomic displacement by momentum and energy transfer, charge trapping, and radiolysis [2,3]. From a practical point of view, the knowledge of radiation-induced changes is useful for the evolution of the glass under long-term application in a radiation environment like dosimetry, vitrification matrix, optical fibers in space, etc. [1,4]. In our previous work [4], the BaO-ZnO-LiF-B₂O₃-Yb₂O₃-Sm₂O₃ glass system had been examined for thermoluminescence (TL) features. The material was well-suited for TL dosimetry application. In this work, the same glass has been analyzed for the radiation-induced changes through Fourier Transform Infrared (FTIR) spectroscopy, optical absorption, and Electron Spin Resonance (ESR) characterizations.

Synthesis and Characterization

10BaO-20ZnO-20LiF-49.4B2O3-0.1Yb2O3-The 0.5Sm₂O₃ (ZLBBY0.1S0.5) glass was synthesized by melt-quench method. The glass synthesis and optimization has been discussed earlier [4]. The glass was irradiated with 1 kGy γ -dose from Co-60 source in a gamma irradiation chamber (GC-5000, BRIT, Mumbai, India). The dose was optimized from TL analysis [4]. FTIR spectroscopy was done using a Shimadzu FTIR 8300 spectrometer, by KBr pellet technique between 400-4000 cm⁻¹. Optical absorption spectroscopy was recorded by a Perkin-Elmer Lambda 750s UV-Vis-NIR spectrophotometer between 250-2000 nm. ESR profile was recorded by a JEOL-JES FA200 CW ESR Spectrometer at room temperature, X-band (9.44 GHz) frequency, modulation frequency 100 kHz, field center 400 mT, modulation width 0.35 mT, time constant 0.03 s, and sweep time 2 min.

Results and discussion

The FTIR profile of the ZLBBY0.1S0.5 glass preand post- 1 kGy γ -irradiation is shown in **Fig.1**. Between 500 and 1700 cm⁻¹, the broad band was deconvoluted (**Fig.1 inset**) and the peak assignments [1] are listed in **Table 1**. Irradiation did not cause any significant peak shifts. The fraction of BO₃ and BO₄ units (N₃ and N₄) were respectively determined [1] as 0.93 and 0.07 pre-irradiation, and 0.96 and 0.04 postirradiation. This indicates the change of BO₄ units to BO₃ units post-irradiation by the creation of Non-Bridging Oxygens (NBOs) [1].

The optical absorption spectra of the ZLBBY0.1S0.5 glass pre- and post- 1 kGy yirradiation is shown in Fig.2. The spectra revealed the presence of 13 transitions. Twelve of them were assigned to the Sm³⁺ ion from its ⁶H_{5/2} ground state to the excited levels ${}^{4}P_{3/2}$, $({}^{4}H_{9/2}, {}^{4}D_{7/2})$, ${}^{4}D_{3/2}$, ${}^{6}P_{7/2}$, ${}^{6}P_{3/2}$, $^6F_{11/2}, \ ^6F_{9/2}, \ ^6F_{7/2}, \ ^6F_{5/2}, \ ^6F_{3/2}, \ ^6H_{15/2}, \ and \ ^6F_{1/2},$ respectively at 318, 346, 359, 375, 403, 975, 1081, 1227, 1373, 1475, 1521, and 1590 nm [1]. The only transition of Yb³⁺ ion ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$ superposed at 975 nm with the Sm³⁺ transition. The glass absorbance improved after irradiation, particularly in the UV-Vis regions. This could be due to the origination of 'color centers'. These centers/structural defects may form traps which demonstrate preferential light absorption due to the transitions between them and valence band, within them, and/or between them and conduction band [1]. The absorption edge was red-shifted from 273 to 291 nm which could be due to the origination

of NBOs [3]. The indirect bandgap from Mott and Davis model [5] and Tauc's plots (**Fig.2 inset**) reduced from 4.49 to 4.14 eV while Urbach energy [6] increased from 0.55 to 0.60 eV post-irradiation. The results confirm the rise in defects post-irradiation.



Fig. 2. Optical absorption spectra. inset: Tauc's plots of the ZLBBY0.1S0.5 glass.

The ESR profile of the ZLBBY0.1S0.5 glass before and after 1 kGy γ -irradiation is shown in **Fig.3.** While pre-irradiation no specific signals were detected, post-irradiation two distinct signals emerged at g=2.0170 and g=1.9869. The signal at g=2.0170 may correspond to the hole trapped on NBO or Non-Bridging Oxygen Hole Center (NBOHC) [1] which could be formed as below [2]*irradiation*

$$\equiv B - OH \xrightarrow{array} \equiv B - O \cdot + H^{a}$$

The signal at g=1.9869 may correspond to the Boron E'-center ($\equiv B \cdot$) [1] formed as follows [2]-

 $\equiv B - O - B \equiv \xrightarrow{irradiation} \equiv B \cdot \cdot O - B \equiv$ The presence of the two signals post-irradiation confirms the occurrence of the pair of hole and electron defect centers because of radiolysis.



Table 1. FTIR peak assignments and position (cm⁻¹) in the ZLBBY0.1S0.5 glass pre-and post-irradiation.

Peak assignments	Non- irradiated	1 kGy
	IITaulateu	
BO ₃ -O-BO ₄ bending	738	752
B-O-Metal ion stretching	945	945
[BO ₄] stretching	1074	1074
B-O ⁻ stretching in [BO ₃] units	1224	1217
	1318	1320
NBO stretching in [BO ₃] units	1405	1430
B-O anti-symmetric stretching	1504	1517
in [BO ₃] units		
H stretching in OH groups	2707	2689
Stretching of free OH ⁻ groups	3566	3565

Conclusion

The γ -irradiation of 1 kGy on the Yb³⁺-Sm³⁺ codoped glass system increased the defects. The ESR profile revealed two defect center signals originating from NBOHC and Boron *E*'-center.

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Dielectric and AC Conductivity Studies of CdZnTe Quantum Dots Doped Silica Matrices

Kiran John U¹, and Siby Mathew¹

¹Department of Physics, Sacred Heart College, Thevara, Cochin, 682013

*Corresponding author: smphy250@gmail.com, smphysics@shcollege.ac.in

Abstract

CdZnTe quantum dot doped silica matrices synthesised through sol-gel route using acid catalyst. The prepared silica matrices with different concentrations of CdZnTe quantum dots were characterized using FTIR and EDX spectrum. The effect of CdZnTe nanocrystals doping on the dielectric properties of sol-gel silica glasses was studied for a frequency range of 100 Hz- 5 MHz at room temperature. The frequency dependence of dielectric constant real part, loss tangent and A.C conductivity were investigated. The conductivity curve obeys Jonscher's power law and power law parameters were found out.

Introduction

The last few decades have witnessed the extensive use of the sol-gel technique. The motivations for the synthesis of sol-gel derived matrices are primarily due to higher purity, homogeneity, lower processing temperature and control over microstructure associated with sol-gel technology compared with other traditional methods like melt quenching, ion implantation, ion exchange, and high-temperature fusion techniques etc. Sol-gel matrices doped with metal, mare earth and semiconductor nanoparticles find a variety of optical applications like solid-state lasers, platforms for chemical and biosensors, dielectric materials etc.

Semiconductor nanoparticles doped in sol-gel silica matrices is a very extensive research area. The nano-sized semiconductors exhibit quite different physicochemical properties compared with the bulk material. Exploration of efficient composition tuneable temary quantum dots becoming an excellent tool to design new nanomaterials with exciting properties. Among the temary II-VI quantum dots, ZnCdSe, CdZnS, ZnCdS, ZnSTe and CdZnTe alloyed quantum dots are greater interest because of their wider adjustable band gap and high quantum yield compared with binary quantum dots

Experimental

The sol-gel technique used to synthesis the silica matrices. TEOS precursor was used as the source of silica. The CdZnTe quantum dots were prepared using 3-MPA as the capping agent and Na₂TeO₃ as the source of tellurium under open atmosphere conditions. The prepared CdZnTe precipitated using alcohol and the precipitate redispersed in water. The silica matrix loaded with 1,3 and 5 weight percentage of CdZnTe quantum dots labeled as czt1, czt3 and czt5 respectively.

Results and Discussion

The presence of silanol and silane peaks confirmed through FTIR which indicates the glass formation. EDX confirm the presence of Silicon, Oxygen, Cadmium, Zinc, and Tellurium.



Fig. 1. FTIR spectrum and inset shows the EDX spectrum of sample czt3.



Fig. 2. Frequency variation of dielectric constant real part (ε') for the samples.

The real part of dielectric constant (ϵ ') and AC conductivity of the samples found out using the equations given below

$$\varepsilon' = \frac{c_p d}{\varepsilon_0 A} \qquad \qquad \text{a)}$$

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon' tan\delta \qquad b)$$

$$\sigma_T = \sigma_0 + A\omega^s \qquad \qquad \text{c)}$$

Where, 'd' is the sample thickness, 'A' is the area, 'f' is the frequency of the applied signal, ' C_p ' is the measured parallel capacitance, ' ϵ_0 ' is the permittivity of free space and 'tanð' is the loss tangent. The frequency variation of real part of the dielectric constant at room temperature is given in Fig. 2. The real part found to be decreasing with increasing frequency for all three samples. Also, the real part decreased with increasing the weight percentage of CdZnTe quantum dots. The increasing dopant concentration effectively reduces the dipole-dipole interaction and causes decrease in dielectric value.

Using the real part of the dielectric constant and loss tangent tan δ the AC conductivity was found using the equation b. The frequency dependence of the conductivity illustrated in Fig. 3. The conductivity values were increasing with frequency. The sample czt1 which have low dopant concentration showed higher conductivity values at high frequency range compared to the samples czt3 and czt5.

The frequency dependence of conductivity curves can be effectively explained using the universal powerlaw equation which is proposed by Jonscher given as equation c with the terms, σ_T - total conductivity; σ_0 -DC conductivity; 'A' and 's' are material and temperature depended parameters The conductivity curves of the samples fitted using the power-law relation.



Fig. 3. Frequency depended Conductivity curves for the samples.

The fitting gives the power-parameters σ_0 , A and s. The power-law parameters obtained given in Table 1. The dc conductivity of the samples found of the order of 10⁻⁷ S/cm. The sample czt3 showed a higher value compared to other samples. The parameter 's' value of samples found in the range 0.41-0.54 which indicate good frequency dependence of the conductivity values.

Table 1. Power-law Parameter	ers.
------------------------------	------

Sample	σ0	Α	S
czt1	2.5x10 ⁻⁷	1.6x10 ⁻⁸	0.53
czt3	4.0×10^{-7}	2.2×10^{-8}	0.41
czt5	1.4x10 ⁻⁷	4.0x10 ⁻⁹	0.54

Conclusion

CdZnTe quantum dots doped silica glasses were prepared by acid catalyst Sol-gel route. FTIR spectra confirm the SiO₂ bond formation. EDX study reveals the respective elements confirmation. The dielectric constant is found to be influenced by the dopant concentration and it is decreasing towards higher frequency region. The dielectric studies confirm that the dielectric properties can be altered by varying the CdZnTe concentration. The dielectric parameters are frequency dependent.

The conductivity curves were frequency dependent and increasing towards higher frequency region. The conductivity curves obey Jonschers power-law equation and the power-law parameters σ_0 , A and s were extracted from the power-law fitting. The power-law parameters vary with the dopant concentration. The dielectric and AC conductivity studies suggest the CdZnTe-silica composites can placed as potential materials for dielectric applications.

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Effect Of Te Content On The Optical, Structural And Morphological Properties Of Ag_(60-x)Se₄₀Te_x Thin Films

Subhashree Das1*, P. Priyadarshini¹, Ramakanta Naik¹

¹Department of Engineering and Materials Physics, ICT-IOC, Bhubaneswar, 751013, India

*Corresponding author: subhashreedasiocb@gmail.com

Abstract

In the present work, $Ag_{60-x}Se_{40}Te_x$ (x=0, 5,10 at %) ternary film of thickness ~800 nm was prepared by thermal evaporation technique. The structural analysis was done by X-ray diffraction that revealed the amorphous nature of the films with Te addition. However, the Raman shift showed the changes in the vibrational modes in the films. The surface morphological studies carried out by atomic force microscopy and scanning electron microscopy showed the changes with Te content. The optical studies of the thin films done by UV-Vis spectroscopy revealed the decrease in transmittance and optical bandgap. The Te content influenced the absorption coefficient as well as the other optical parameters.

INTRODUCTION

Chalcogenide films have increased demand in the field of optoelectronics and memory devices nowadays due to their peculiar linear and non-linear properties. The different types of doping elements are added to the chalcogenide material to increase their diverse optical properties in a prominent way[1]. Among all the chalcogens, selenium (Se) is a highly sensitive material that is commonly used for imaging and biomedical applications. Silver is a good conductor and is frequently used in electronics and is a good choice for the binary semiconductor material with selenium. Silver selenide (I-VI) Ag₂Se group produced a special type of semiconductor which shows high detectivity, low voltage photodetector for optoelectronic applications [2]. The structural stability enables high thermoelectric performance of Ag₂Se at room temperature [3]. Tellurium is considered as third element of Ag-Se-Te ternary compound as it improves machinability and is resistant to oxidation by air and non-volatile. Recent studies on Ag2Te1-xSex solid solution showed high thermoelectric performance [4]. The optical properties were influenced by the addition of Ag into Se₉₀Te₁₀ thin films [5]. So, the addition of Te into host $Ag_{60}Se_{40}$ compound and investigating the corresponding optical and structural changes is the primary aim of this study.

EXPERIMENTAL PROCEDURES

The bulk $Ag_{60-x}Se_{40}Te_x$ (x=0,5,10%) samples were prepared by the conventional melt quenching method followed by thin film preparation on glass substrate by thermal evaporation method from the bulk sample at a vacuum of 10^{-5} Torr. The thickness of the films was ~800 nm. The structural study was done by X-ray diffractometer (XRD) and Raman spectroscopy while the optical measurements were done by UV-VIS spectrophotometer over the range of 500-1100 nm. The topographic changes were investigated by atomic force microscope (AFM) and the surface morphology by Field emission scanning electron microscopy (FESEM). The elemental composition was checked by the EDX facility attached to the FESEM.

RESULTS AND DISCUSSION

The XRD patterns as shown in Fig.1 confirms the amorphous nature of the Te doped films. AFM pictures as shown in Fig.1 (inset) clearly shows the variation of surface topography with change in the mean surface roughness. Its value decreased (40.98 nm for 5% Te and 27.33 for 10% Te) with Te content as compared to the as-prepared one (53.16 nm for 0% Te).



Fig. 1. XRD and AFM images of Ag_{60-x}Se₄₀Te_x films.

The Raman spectra show the change in peak position that signifies the effect of Te addition. The peak at 251 cm^{-1} refers the Ag₂Se and pure Se-Se bonds which decreased for the 10% Te due to the dominant peak at 167 cm⁻¹ [6]. This peak corresponds to the Ag-Te vibrational mode in expense of the Ag-Se bond and the increase in intensity for the peak at 205 cm⁻¹ (Se-Te vibrational mode) is due to doping of Te. The presence of Ag, Se and Te was confirmed from the EDX picture (Fig.2 inset) and the composition of the film is nearly equal with the calculated At. % with an error of ~3%. The FESEM image of 10% Te as shown in Fig.2

(inset) infers the homogeneous and uniform distribution of particles in the film. The transmission (T) spectra of the films are shown in fig. 3 which shows the increase in transmission % with Te addition and shift of the absorption edge towards higher wavelength thus inferring the reduction in bandgap. Optical density (OD) is related to the potential of the material to absorb the electromagnetic radiation through distance. The OD value is calculated from the product of absorption coefficient (α) and thickness of the film (OD=d x α) where ' α ' was calculated by using the relation, $\alpha = (1/d) \ln [(1/T])$ (1)

where d and T are the thickness and transmittance of the films. The OD value decreased up to the characteristic wavelength and then saturated as shown in Fig.3(inset). The OD value was found to be increased with Te concentration indicating the increase in the absorbing ability of the incident radiation.



Fig. 2. Raman, EDX and FESEM picture of the studied films

The indirect allowed optical bandgap is calculated by using the Tauc relation by using the equation [7]

$$(\alpha h v)^{1/2} = B^{1/2} (h v - E_g)$$
 (2)

where h, v, E_g and B are the Planck's constant, frequency, optical band gap, and Tauc parameter respectively. The straight-line fitting of dependence between $(\alpha hv)^{1/2}$ and photon energy (hv) provided the indirect optical bandgap values such as 1.46 eV (Ag₆₀Se₄₀), 1.41 eV (Ag₅₅Se₄₀Te₅), and 1.28 eV (Ag₅₀Se₄₀Te₁₀) for the studied thin films [Fig.3 inset]. The reduction in E_g value with addition of Te is due to the modifications in localized energy levels due to the increase in disorder. The addition of Te replaces the heteropolar bonds to form homopolar bonds that increase the density of defect states in the gap and thus reduced the optical band gap. This is also due to the decrease in average coordination number and shift in the Fermi level [8]. The average coordination number (CN_{ave}) of the compound as calculated by the formula

$$CN_{ave} = Xa + Yb + Zc/(X + Y + Z)$$
(3)

where X, Y and Z are the % at. wt. of Se, Ag and Te respectively and a, b and c are their respective coordination

numbers. The coordination numbers for Se, Te and Ag are 2, 2 and 4 respectively. The decrease in E_g is also explained by the chemical bond approach. According to the chemical bond approach, the bond energies are additive in nature due to which there is decrease in cohesive energy with increase in Te content that leads to the decrease in bandgap [9].



Fig. 3. Transmission, bandgap and optical density variation with Te content

CONCLUSION

The addition of Te in thermally evaporated $Ag_{60-x}Se_{40}Te_x$ (x=0,5,10%) films bring changes in the optical parameters whereas the structure remains amorphous in nature. The reduction in bandgap with Te content is due to the increase in disorder and density of defect states that increased the width of the localized states. The average coordination number decreased whereas the transmittance and OD increased. The surface roughness decreased with Te addition.

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Structural and Nuclear Radiation Shielding Properties of Barium-Sodium-Alumina-Borate Glass System

Sukhpal Singh^{*}

Department of Basic and Applied Sciences, Punjabi University, Patiala, India-147002

*Corresponding author: sukhpal@pbi.ac.in

Abstract

In the present study, physical and structural parameters of Barium-Sodium-Alumina-Borate glass system such as density, molar volume, oxygen packing density (OPD), oxygen molar volume (OMV), ion Concentration, Polaron radius, inter-ionic distance and field strength have been calculated. The elastic parameters namely Young, bulk, shear moduli, and Poisson's ratio of the glass samples have also been calculated using the Makishima and Meckenzie model. Further, in order to study the application of selected glass system in the field of nuclear radiation shielding and design, the values of attenuation parameters and fast neutron removal cross-section ($\sum R \text{ cm}^{-1}$) were calculated and compared with standard radiation shielding materials.

Introduction

The excessive exposure of nuclear radiations may have several redundant effects on the living organisms and the environment. Keeping this in view, various technologists and researchers have paid frightful efforts in designing, characterizing and evaluating shielding properties of newly developed materials to protect human and surrounding environment from detrimental effects of such radiations. Glasses have been emerged as promising materials in this regard. Glasses are amorphous materials which have stiffness like solids but have a structure which is identical to those of liquids. The development of high elastic modulus glass compositions for the manufacturing of strong glass has instigated numerous researchers to work on a theoretical model that would enable an a priori determination of elastic moduli. Glass materials unique physical and mechanical possessing advantages like high transparency, hardness, excellent corrosion resistance, high density and high effective atomic number, non-toxicity particularly lead free glasses, low coefficient of thermal expansion, excellent resistance to environmental conditions, resistant to acids, alkaline solutions and chemicals. Moreover, glasses are low cost, easy to manufacture and could have been tailored physical and shielding properties by incorporating different chemical compositions.

Boric acid (B_2O_3) is one of the important glass raw materials that can form glass at low melting point, high transparency chemical resistance and thermal stability. Sodium oxide assist ion exchange thereby decreases the melting temperature of the melt, hygroscopic nature of the borate glasses and increases the glass forming region and chemical stability of the glasses. Use of aluminium oxide modifies the host matrix and can improve the crystallization ability, chemical durability and mechanical strength of the resultant glass matrix. Due to high atomic numbers, barium oxide glasses have been extensively studied for their nuclear radiation shielding properties. Barium oxide (BaO) based glasses are found to be non-toxic, non-hazardous and pro environment.

In the present study, physical, structural and elastic properties of the xBaO+0.15Na₂O+0.15Al₂O₃+(0.70-x) B₂O₃ [x = 0.10(S1), 0.15(S2), 0.20(S3), 0.25(S4) and 0.30(S5) mol fraction] have been studied using the Makishima and Meckenzie model [1]. The values of radiation attenuation parameters have also been calculated by using winXCOM software [2]. Further, the values of fast neutron removal cross-section ($\sum R cm^{-1}$) were also calculated [3] and compared with standard shielding materials [4, 5].

Theoretical formulism

Physical and Structural Parameters

The density of the glass samples can be calculated by using the following relation: $\rho = 0.53 \frac{\Sigma M_i x_i}{\Sigma v_i x_i}$, where M_i is molar weight (g/mol), x_i is molar fraction (mol %), V_i is packing density factor (cm³/mol). Molar volume is calculated using formula $V_m = \frac{M}{\rho}$, where ρ is density of sample. Oxygen packing density gives information about the tightness of glass network and is determined by $OPD = 1000C \left(\frac{\rho}{M}\right)$, where C is total number of oxygen atoms, ρ is a measured density of studied glass system. Molar volume of oxygen is calculated using following formula $V_o = \frac{V_m}{\Sigma x_i n_i}$, where x_i is molar fraction of every constituent, n_i is number of oxygen atoms in each component oxide. The packing density is given by the relation $V_t = \frac{\sum V_i x_i}{V_m}$. The Barium ion concentration (N), Polaron radius (r_p), inter-ionic distance (r_i), and field strength (F) in a glass sample were computed by using following mathematical relations, respectively: $N = \frac{x_{Ba} \times \rho \times N_A}{M}$; $r_p = (\pi |48N)^{1/3}$; $r_i = (1|N)^{1/3}$; $F = A/r_p^{-2}$, where A is the mass number of barium.

Further, Young's (E), bulk (K), shear (S), Poisson's ratio (σ) and hardness (H) have been calculated by using the following formulae: $E = 83.6V_tG_t$; $K = 100.32V_t^2G_t$; $S = \frac{300V_t^2G_t}{(10.2V_t-1)}$; $\sigma = 0.5 - (\frac{1}{7.2V_t})$;

Shielding Parameters:

The linear attenuation coefficient (μ) is determined using Beer-Lambert Law $I = I_0 e^{-\mu t}$, where I_0 and I are incident and transmitted intensities, t is material's thickness and μ is linear attenuation coefficient. The FNRC value is given by $\sum_R = \sum_i \rho_i (\sum_R |\rho)_i$, where, ρ_i and $(\sum_R |\rho)_i$ are the density and mass removal cross-section of the ith constituent, respectively.

Results and discussion

Physical and structural properties

The density of the prepared samples increases from 2.305 gcm⁻³ to 3.025 gcm⁻³, as Boric acid (69.62 g/mol) is replaced, in steps, with Barium oxide (153.33g/mol), so more dense glass samples have been obtained. The molar volume decreases from 35.443 cm³ to 32.538 cm³ with the increase of BaO content in the glass matrix. This reduction in molar volume values is a sign of more tight structure of the resultant glss matrix. Oxygen packing density (OPD) is the measure of tightness of an oxide network. For the present glass matrix, the value of OPD shows a decrease (70.535-64.540 g. atom/litre) with the increasing content of BaO. The value of OMV increases from 14.675 cm3 /mole for glass sample S1 (0.10 mol % of BaO) to 15.496 cm3 /mole for glass sample S5 (0.30 mole %) confirms the the presence of more non-bridging oxygens in the structure. Similarly, the decrease in the polaron radius (0.78 A° -0.49 A°) with the increasing molar fraction of BaO advocate the decreased free space within the glass structure i.e. the glass structure becomes tightly packed. For the present glass matrix, the value of Poisson's ratio shows a constant value (0.238) suggests that the prepared glass samples possess satisfactory strength and rigidity.

Radiation shielding parameters

The shielding effectiveness of the prepared glasses have been compared in terms of half value layer values with some standard shielding concretes [4] available in literature used in the field of radiation protection. The ratio (Γ_G / Γ_{SMC}) of HVL for the glass samples (Γ_G) and steel–magnetite concrete (Γ_{SMC}) has been examined for selected incident gamma photon energies and is shown in Fig. 1. This figure clearly depicts that the value of the ratio (Γ_G / Γ_{SMC}) is less than one for all samples at all energies, which confirms that for all the glass samples, the values of HVL are lower than steel-magnetite concrete.

Further, the glass samples found to possess neutron removal cross-section ($\sum R \text{ cm}^{-1}$) values in the range of 0.0856 -0.0889 cm⁻¹. These values are compared with some commonly used neutron shielding materials available in literature [5]. It has been found that glass samples exhibit higher value of removal cross-section than graphite but lesser than hematite serpentine concrete (HSC) and water.



Fig.1. Ratio (Γ_G / Γ_{SMC}) of HVL for the glass samples (Γ_G) and steel–magnetite concrete (Γ_{SMC}) at selected energies.

Conclusions

On the basis of the obtained results, it has been reported that the chosen glass samples possess satisfactory physical reliability and superior shielding efficiency against gamma rays and fast neutrons as compared to conventional shielding materials.

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Structural Studies of Silver Doped Lithium Bismuth Borate Glasses

Alan.B.Samuel¹, Ameer Nasih KV², and V.V.Ravi Kanth Kumar³

¹Department of Physics, Pondicherry university, Puducherry, 605014, India

*Corresponding author:ravi.phy@pondiuni.edu.in

Abstract

Silver oxide doped lithium bismuth borate glasses have been prepared by the conventional melt quenching method with compositional range $30\text{LiF}-40Bi_2O_3-(30-x)B_2O_3-xAgNO_3(x=0,0.1,0.5 \text{ and } 1 \text{ mol}\%)$. Structural studies were characterized using FTIR spectroscopy. The density of glasses were determined. The incorporation of silver causes some structural rearrangement in the glass network leads to formation of BO₄ and BO₃ structural units. It is observed that with progressive silver doping there is appearance and disappearance of some IR bands in the BO₄ spectral region. Silver acts as network modifier as it promotes the conversion of four coordinated to three coordinated boron initially and reversed afterwards.

Introduction

The Bismuth borate glasses are of great interest due to their low melting point, higher refractive index and improved non linear properties leads to vivid applications in LEDs, optoelectronic devices^[1].

The inclusion of alkali earth metals in suitable concentrations leads to structural modifications in the glass matrix. Hence, we can tailor the properties of glass system for our specific applications.

Basically, borate glasses are of high phonon energy. The inclusion of heavy ions like Bi_2O_3 and also the addition of fluoride to oxide glasses reduces their phonon energy and leads to an enhancement in chemical durability and optical properties of glass.^[1,2]

B₂O₃ is a glass former and the addition of modifier oxides causes a change in the coordination number of boron atoms leads to the formation of different cyclic units like diborate ,tetraborate ,pentaborate groups.^[3]

The aim of this paper is to prepare and investigate the effect of doping silver on the structural properties of $Li_2O-Bi_2O_3-B_2O_3$ glass system.

Materials and Methods

The glass system with the chemical composition $30LiF-40Bi_2O_3-(30-x)B_2O_3-xAgNO_3$ where

x=0,0.1,0.5 and 1 mol% abbreviated as BBL, BBLA1, BBLA5, BBLA10 where prepared through melt quenching technique. Stoichiometric amount of analytical grade Bi2O3,H3BO3,LiF and AgNO3 were taken in a silica crucible and melted in a muffle furnace at a temperature of 900°C for 40 minutes. The melt is then quenched by pouring into a preheated stainless-steel plate and pressed with another to form a glass. The prepared glasses were annealed near glass transition temperature for 3hrs to reduce the internal stress. The obtained glass samples were grounded to thickness around 1.5 mm and then polished to obtain good optical quality glasses.

The density of glass is measured by Archimedes principle using distilled water as immersion liquid. FTIR spectrum of the sample is recorded in Shimadzu FTIR 8700 spectrometer in the range of 400-1600 cm¹ using the KBr pellet technique.

Results and Discussions

Density and molar volume

.Measurement of density is powerful tool to look into the structural compactness of the glass^[4].From Table1 it is observed that both the molar volume and density increases with silver concentration. The observed results were due to the formation of non-bridging oxygen(NBOs).^[4]

Table 1. Measured Physical pro	perties of Ag d	oped glasses
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Glass Sample	Density(gcm ⁻³)	Molar Volume(cm ³ mol ⁻¹)
BBL	5 52	38 77
BBLA1	5.53	38.82
BBLA5	5.55	38.88
BBLA10	5.57	38.93

FTIR Studies

The deconvoluted FTIR spectra of the samples using gaussian distribution are shown in Fig1. BiO_6 , BiO_4 , BiO_3 are the major structural units present in bismuth borate glasses. The broad absorption band around 460 cm⁻¹ is due to the vibration of Bi-O and Bi-O-Bi bond in BiO₆ octahedral units.

There are mainly three IR spectral region where the vibration of borate networks is active such as midinfrared 1200-1450 cm⁻¹, 850-1200 cm⁻¹ and 600-800 cm⁻¹.^[5] From the FTIR spectrum it is observed that there is vibration in the region 800-1200 cm⁻¹ centered around 940cm⁻¹ and these are due to the B-O bond stretching of the tetrahedral BO₄ units^[5]. There exists vibration of B-O bonds in BO₄ structural units as tri, tetra and pentaborate groups depend on the concentration and the nature of modifiers added in the glass matrix.^[6]

The peaks in the region 1320-1340 cm⁻¹ are attributed to the asymmetric stretching vibration of B-O bond in BO_3 units.^[5]



Fig.1.Deconvoluted FTIR Spectra of (a)BBL (b)BBLA1 (c)BBLA5 and (d)BBLA10 glasses

The absence of boroxol ring peak at 806 cm⁻¹ implies that the addition of modifiers leads to breakage of these rings and there is a progressive transition towards BO₃ and BO₄ units formation.^[5]

The structural changes related with the inclusion of AgO can be analyzed by taking the ratio of relative content of BO₄ to BO₃ or BO₂O borate species. The ratio(R) of the integral of the spectra in the region 740-1190 cm⁻¹ corresponds to BO₄ to 1190-1600 cm⁻¹ related to BO₃ are tabulated in Table 2.

Table 2. The calculated R values of the glass samples

Glass Sample	Ratio(R)
BBL	2.50
BBLA1	2.37
BBLA5	2.14
BBLA10	2.20

From Table2, it is observed that most of the R values are above 2 showing the dominance of BO_4 structural units. With progressive inclusion of silver there is decrease in R value till x=0.5 mol% and slight increase afterwards for x=1 mol%. This is due to the isomerization process between 3 and 4 coordinated boron units as follows

$$BO_2O^- \leftrightarrow BO_4$$
 (1)

When the percentage of silver increased from x=0 to 0.5 mol% there is a slight shift in reaction towards left

side of equ.1 as more BO_3 units are formed. While the concentration of silver varies from x=0.5 to 1 mol% there is shift in reaction towards right side showing that the 4 coordinated boron atoms are more predominant than the 3 coordinated ones. It is also noted that there is a shift in the bands corresponding to the addition of silver.

From the FTIR spectra Fig.1(b) it is observed that with the incorporation of silver there comes appearance of multiple bands in BO₄ spectral region i.e,from 800 to 1200 cm⁻¹.This is due to the initial formation of BO₄ tetrahedral groups and subsequent addition of silver leads to destruction of these peaks favours the formation of non-bridging oxygen(NBO) containing units^[7].The small peak at 695 cm⁻¹ is due to the angle bending vibration of B-O-B from pentaborate groups. And the peak around 1340 cm⁻¹ is assigned to the B-O stretching vibrations of BO₃ units in pyroborate groups^[4].

Conclusion

Silver doped Lithium Bismuth Borate glasses were prepared and the structural peculiarities of glasses were analyzed using FTIR technique.It is observed that BO₄ are the major structural unit in the glass matrix and with the inclusion of silver there is a shift towards formation of BO₃ units at initial concentration and reversed afterwards due to isomerization process. Further the addition of silver leads to appearance of tetraborate groups peaks initially and disappear afterward due to the formation of NBOs favouring structural units.Thus the incorporation of silver leads to structural rearrangements in glass network.

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A frequency-dependent dielectric study on the amorphous biopolymer electrolyte membrane

M. Infanta Diana¹, D. Lakshmi¹, P. Christopher Selvin^{1*}, S. Selvasekarapandian², M. Vengadesh Krishna²

¹Luminescence and solid state Ionic Laboratory, Department of Physics, Bharathiar University, ²Materials Research Center, Coimbatore

*Corresponding author: csphysics@buc.edu.in

Abstract

The present work studies the dielectric properties of NaSCN incorporated sodium alginate-based amorphous biopolymer electrolyte membranes. From the impedance measurements, frequency-dependent real and imaginary parts of the dielectric permittivity and electric modulus have been calculated. The dielectric permittivity of the electrolyte membrane is high at the low-frequency region which validates the electrode-electrolyte polarization. The electric modulus for the salt-concentrated membranes gets decreased with respect to frequency. The investigation divulges the frequency-dependent behavior of the ions in the sodium alginate biopolymer system.

Introduction

The ionic conductivity of the electrolyte fondly depends on the lattice energy of the salts and the dielectric constant of the host polymer [1]. The ion dissociation and association are the major apprehensions that unswervingly distress the ionic conductivity. This eventually gets linked with frequency-dependent properties dielectric properties. The present article is the extension of our previously published work which unveiled the high ionic conductivity of the sodium alginate-NaSCN biopolymer membrane [2]. Understanding the dynamics of ions and dielectric properties is perplexing due to polymer-salt complexation. Hence this work focuses to evaluate the frequencydependent properties such as dielectric constant (ε'), dielectric loss (ε ["]) to obtain an insight into the salt's dynamics in the matrix.

$$\varepsilon^* = \varepsilon' \cdot j\varepsilon''$$
 a)

where ε' and ε'' are the real and imaginary part of the dielectric permittivity which is obtained from,

$$\varepsilon' = \frac{-Z''}{\omega C_{\circ}(Z'^{2} + Z''^{2})}$$
 b)

$$\varepsilon'' = \frac{Z''}{\omega C_{\circ}(Z'^{2} + Z''^{2})}$$
 c)

The complex permittivity of the solid polymer electrolyte provides an essential understanding of the polarizing ability of the material on application of field and about energy loss in lining up the molecular dipoles in the direction of the field. The ionic conductivity of the biopolymer membranes gets increased with an increase in NaSCN concentration supported by amorphous phases of the biopolymer system. All the coordinated ions follow up the field and respond differently.

Method and Instrumentation

The amorphous polymer electrolyte membranes have been prepared according to our previous study [2]. The AC impedance analysis (42 Hz - 5MHz) employing stainless steel blocking electrodes has been carried out to explore the frequency-dependent factors.

Results and Discussion

The variation of dielectric constant and dielectric loss against frequency for the prepared solid biopolymer electrolyte is shown in Fig. 1.



Fig. 1. Frequency-dependent real part (ϵ_r) of complex permittivity.

It is observed that ε' is high at a low-frequency window. Sodium alginate-based biopolymer electrolytes consist of dissociated Na⁺ - SCN⁻ and polar groups of the sodium alginate chains as the source of dipoles. On application of AC field, the dipoles tend to accumulate at the electrode-electrolyte interface creating a space charge region which is due to the availability of adequate time for the dipole orientation. On increasing the frequency, the dipoles become incompetent with fast reversal of the field and they are unable to orient themselves in the direction of the field. This behavior eradicates the electrode polarization and pave way for a relaxation mechanism thereby attaining a steady-state [3]. Also, the solid polymer electrolyte membrane which attained the highest conductivity (30 wt% sodium alginate: 70 wt% NaSCN) possesses the highest dielectric strength. The dielectric loss with respect to frequency is shown in Fig. 2. It is observed that dielectric loss decreases with an increase in frequency for all the sodium alginate membranes owing to the absence of ion diffusion in the field direction.



Fig. 2. Frequency-dependent imaginary part (ε ") of complex permittivity.



Fig. 3. Frequency-dependent real part (M') of the Modulus.

Periodic reversal of the field at a high-frequency window generates internal heat which contributes to the dielectric loss. The dielectric loss increases with an increase in the concentration of NaSCN. The decrease in ε_r , ε_i at high frequency defines the non-Debye behavior of the prepared membranes [4]. The depressed electrode polarization region in the complex permittivity can be analyzed with the help of modulus formulation which is expressed as

$$M^* = 1/\varepsilon^* = M' + jM''$$
 d)

A long tail is perceived in the low-frequency region from Fig. 3. The ion migration via the segmental motion of the polymer chains changes the electric potential in the polymer-salt environment which affects the adjacent ions.



Fig. 4. Frequency-dependent imaginary part (M'') of the Modulus

The increase in the length of the tail evidences the formation of polarization. The rapid increase at high frequency is due to the hopping of ions from one coordinating site to another [5].

Conclusion

The amorphous biopolymer membrane with the highest ionic conductivity possesses the highest dielectric constant which deduces the high capacity of charge storage. The high dielectric strength also endorses ion dissociation thereby lowering ion aggregation propensity. The modulus spectra signal the occurrence of increased capacitance and ion migration.

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Study Of Optical Constants Of Ge₂₅S_{75-x}Sb_x(x=0, 10, 20) Amorphous Chalcogenides For Optical Applications

Anjani Kumar¹, S. Shukla², Sudhir K. Sharma¹, R.K. Shukla¹ and Rajeev Gupta³

¹ Department of Physics, Harcourt Butler Technical University, Kanpur-208002, India,
 ²Department of Physics, U. I. E. T. C.S.J.M. University, Kanpur-208024, India,
 ³Materials Science Programme, Indian Institute of Technology, Kanpur-208016, India.

*Corresponding author: anjanikumar.hbti@yahoo.com

Abstract

Amorphous $Ge_{25}S_{75-x}Sb_x(x=0,10,20)$ chalcogenides are processed by familiar melt quenching approach and vacuum thermal evaporation approach for preparing alloys and then thin films respectively. An optical transmission experiments have been done in the given samples. Swanepoel method has been used to calculate various optical parameters. Tauc's relation has been used for the estimation of optical band gap. An indirect optical transition has been found for present glassy system and on the basis of optical parameters the suitability has been discussed for various optical applications.

Introduction

Multitudinous amorphous chalcogenides have immersed potential applications in optoelectronics, phase-change memories, electronics and emerging optical applications due to their individual features such as amorphous nature, high optical homogeneity, large optical nonlinearities, high infrared transparency, substantial photosensitivity, original guiding, capability of high doping and metal alloying [1-5].

Authors motivated towards non-oxide chalcogenides due to absence of strong chemical bonds of chalcogens in amorphous non oxide chalcogenides. Although amorphous chalcogenide materials have required availability from last many years but they have used in industry due to their unique optical properties. Shukla et. al. [6] have found that chalcogenides have a prominent impact on modern era in technological importance and development in optical applications on the basis of optical parameters. Thus the present research work directed towards the optical measurements of Ge₂₅S₇₅₋ _xSb_x (x=0, 10, 20) glassy system and their optical applications.

Experimental

A well known melt quenched technique have been used for preparation of glassy alloys of $Ge_{25}S_{75}$. _xSb_x (x=0,10,20) chalcogenide material. A familiar vacuum thermal evaporation [7] approach was used for obtaining thin films of above mentioned samples on glass substrate at room temperature. Then annealing (more than 24 hrs) of deposited thin films was done [8]. XRD and EDS were also performed on the prepared samples. UV-VIS-NIR spectrophotometer was used for optical transmission characterization of thin films of given samples in the wavelength range 300nm-3100nm.

Results and Discussion

Well-defined optical transmission curves of thin films of Ge-S-Sb glassy system are represented by Fig. 1. These curves show interference phenomena at various wavelengths. A well known envelope method [9,10] is used for analysis of curves.

The refractive index (n) of the film for $(\alpha = 0)$ region i.e. transparent region is given by formula:

$$n = [N + (N^{2} - s^{2})^{1/2}]^{1/2}$$
(1)
And $N = (2s/T_{m}) - (s^{2} + 1)/2$ (2)



Fig. 1. Optical transmission curves of $Ge_{25}S_{75-x}Sb_x$ (x=0,10,20) thin films.

In the above eq. (2), T_m represents the lower envelope wavelength values and s represents the refractive index of substrate material. In medium and weak absorption region ($\alpha \neq 0$), eq. 2 becomes as:

 $N = [2 s (T_M - T_m) / T_M T_m] + (s^2 + 1) / 2$ (3)

Where T_M represents the upper envelope wavelength values. If n_2 and n_1 represent the refractive indices of two adjacent minima and maxima for respective wavelengths λ_2 and λ_1 , thus basic equation for interference phenomena will be: $2nd = m \lambda$, where 'm' is an computational digit and thickness can be addicted as: $d = \lambda_1 \lambda_2 / 2(\lambda_1 n_2 - \lambda_2 n_1)$. The thickness of thin films and refractive index were calculated by using above equations [9,11].

The extinction coefficient (k) is evaluated by the following liaison $x = \exp(-4\pi kd/\lambda)$. Here,

 $\mathbf{x} = [\mathbf{E}_{\mathbf{M}} - \{\mathbf{E}_{\mathbf{M}}^2 - (\mathbf{n}^2 - 1)^3 (\mathbf{n}^2 - \mathbf{s}^4)\}^{1/2}] / [(\mathbf{n} - 1)^3 (\mathbf{n} - \mathbf{s}^2)]$ (4)where $E_M = [(8n^2s/T_M) + (n^2-1)(n^2-s^2)]$ (5)

The values of n and k with wavelengths have been calculated for given sample and found to be decreases with good grace in λ which shows normal dispersion behavior and results of calculation of n & k with Sb are addicted in Table 1.

The constants of dielectric [real (ε ') and imaginary $(\varepsilon^{"})$] are related with n and k and relations are given as: $\varepsilon' = n^2 - k^2$ and $\varepsilon'' = 2nk$. Results show that fluctuation of ε ' and ε '' with respect to the λ , followed by n & k characteristics with λ . Results of ε ' and ε '' for present samples have been addicted in Table 1.

Table 1. Calculated values of n, k, ε ' and ε '' of Ge₂₅S₇₅₋ $_x$ Sb_x (x=0, 10, 20) thin films

		-			
х	n	k	ε`	ε"	
0	2.06	6.22×10^{-3}	4.32	0.0222	
10	2.05	6.17×10^{-3}	3.74	0.0247	
20	1.70	7.67×10^{-3}	3.69	0.0318	
					_

A well known formula $k = \alpha \lambda 4\pi$ has been used for evaluation of absorption coefficient (α) of Ge₂₅S_{75-x}Sb_x (x=0, 10, 20) thin films. Results show that there is proportionality relation of α with hv and calculated results have been listed in given Table (2).

Tauc [12] pointed out that for high absorption arena where $\alpha = 10^4$ cm⁻¹, the relation of α and band gap (E_g) is addicted by equation: (6)

 $\alpha h \nu = B (h \nu - E_g)^p$

Here B is a parameter of band tailing and p is taken 2 for indirect transition (in our case). Fig. 2 represents the graphs of $(\alpha hv)^{1/2}$ vs. hv for Ge₂₅S_{75-x}Sb_x (x=0, 10, 20) films. The value of E_g has been calculated by taking the intercept on the X-axis. The values of Eg, are addicted in Table (2). It is easy to perceive from the table that Eg becoming fewer with incorporation of Sb content in Ge-S glassy system and this can be justified on account of bond energy as already discussed by many research groups [13-15].

Table 2. Calculated values of E_g and α of $Ge_{25}S_{75-}$ $_x$ Sb_x (x=0, 10, 20) thin films.

X	E _g (in eV)	α (in cm ⁻¹)
0	2.42	0.1306×10^4 at 480nm
10	1.89	0.2518×10^4 at 510nm
20	0.84	0.1855×10^4 at 846nm

The optical applications [16] for the given system are as active fibers that produce Infrared light and show non linear effect and developed as micro structured optical fibers and IR transmitting optical fibers. It has been observed that these are used in electro-optic applications such that photonic integrated circuits and optoelectronic logic circuits etc. Thin films can also be used in photonics and photovoltaic applications.



Fig. 2. $(\alpha h\nu)^{1/2}$ vs. hv graphs for Ge₂₅S_{75-x}Sb_x (x=0, 10, 20) thin films.

Conclusions

Optical transmission curves have been plotted and various optical frame works like n, k, α , $\epsilon', \epsilon'', E_g$ have been premeditated in the measured range of wavelength 300nm-3100nm. It have been found that present Ge-S-Sb glassy system can be used for emerging optical applications in optics and electrooptics.

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Structural and Optical analysis of Cadmium Bismuth Borate glass system

Vijeta Bhatia¹, Harpreet Singh¹, Dinesh Kumar¹ and Supreet Pal Singh^{1*}

¹Department of Physics, Punjabi University Patiala, Punjab-147002

*Corresponding author: spsmudahar@gmail.com

Abstract

Cadmium doped sodium bismuth borate glasses have been synthesized by melt quenching technique. Physical, optical and structural properties have been explored by UV-Vis spectroscopy, X-ray diffraction (XRD) and Fourier Transform Infrared spectroscopy (FTIR). Interesting results are observed; thereby confirm the change in structure of the host glass with addition of Cadmium.

Structure determination of Lead Iron Phosphate Glasses

Sourabh Wajhal^{1,*}, A. B. Shinde¹, A. C. Hannon² and P. S. R. Krishna¹

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085 ²ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 OQX, UK

*Corresponding author: swajhal@barc.gov.in

Abstract

Reverse Monte Carlo modelling of total neutron diffraction data of Lead Iron Phosphate glasses have been performed to determine the structural origin of high leaching resistance behaviour shown in these glasses. Effect of Fe_2O_3 concentration on the atomic structure and its correlation on leaching resistance is probed.

Glass transition temperature dependence on coordination number for Se-Te-Ge-Pb chalcogenide alloys

Priyanka Vashist¹, Balbir Singh Patial^{1,*}, Suresh Bhardwaj², S.K. Tripathi³ and Nagesh Thakur¹

¹Department of Physics, Himachal Pradesh University Summerhill, Shimla, H.P.-171005 India ²UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore, M.P. 452001 India ³Centre of Advanced Study in Physics, Panjab University, Chandigarh 160014 India

*Corresponding author email: <u>bspatial@gmail.com</u>

Abstract

In the present work, differential scanning calorimetry (DSC) is employed for thermal study of $(Se_{80}Te_{20})_{94-x}Ge_6Pb_x(x=0, 1, 2, 4, 6, 8, 10 and 12)$ bulk samples under non-isothermal conditions. Glass transition temperature (T_g) of investigated alloys has been deduced theoretically using Tanaka approach and modified Gibbs DiMarzio relation. Dependence of T_g on average coordination number (<r>) is analyzed. Trends of experimental and theoretical results are not in agreement with each other which show T_g does not solely depend on <r>.

Synthesis and Characterization of Semiconducting Iron Tellurite Glasses

Navjot Kaur¹, Atul Khanna^{1*}

¹Department of Physics, Guru Nanak Dev University, Amritsar, 143005, Punjab, India

*Corresponding author: atul.phy@gndu.ac.in

Abstract

 xFe_2O_3 -(100-x)TeO₂ (where x = 15 and 30 mol%) glasses were prepared by normal quenching technique. The samples were characterized by X-ray diffraction, DSC, Raman spectroscopy and dc electrical conductivity studies. The density of glasses decreases from 5.34 to 5.14 gcm⁻³ and glass transition temperature increases from 659 to 710 K as the concentration of Fe₂O₃ is increased from 15 to 30 mol%. Raman studies reveal that the Te-O coordination number decreases from 3.55 to 3.48 while the room temperature electrical conductivity increases from 1.79×10^{-7} to $4.00 \times 10^{-5} \Omega^{-1} m^{-1}$ with an increase in concentration of Fe₂O₃ from 15 to 30 mol%.

Introduction

TeO₂ based glasses have been widely studied due to their useful properties such as low melting points, high refractive indices, high chemical durability, high dielectric constants and low phonon energies [1] which makes them attractive for various useful properties. Tellurium oxide is a conditional glass former that forms glasses on addition of modifier oxides which enhances its glass forming ability and forms glasses at low quenching rate of ~10² K s⁻¹ [1].

Owing to the electronic conduction, various transition metal oxide based tellurite glasses have been studied [2-4]. The conduction process in these glasses is explained on the basis of small polaron hopping (SPH) model [4]. Due to the conducting behaviour, TMO based glasses can be used as cathode materials in secondary batteries [3, 5].

The electrical conductivity of xFe_2O_3 -(100x)TeO₂ (x = 10 and 20 mol%) have been reported and it is observed that the room temperature conductivity increases from 3.54×10^{-10} to $3.28 \times 10^{-7} \ \Omega^{-1}m^{-1}$ an increase in Fe₂O₃ concentration [3]. The present work reports structural, thermal and electrical properties of iron tellurite glasses with 15 and 30 mol % of Fe₂O₃.

Experimental

Glass samples of xFe_2O_3 -(100-x)TeO₂ system (where x = 15 and 30 mol%) were prepared by melt quenching technique [3]. The glasses were melted at different temperatures i.e; $15Fe_2O_3$ - $85TeO_2$ (sample code: 15FeTe) at $920^{\circ}C$ and $30Fe_2O_3$ - $70TeO_2$ (sample code: 30FeTe) at $1100^{\circ}C$. The density of the glasses were measured by Archimedes principle using dibutyl-pthalate oil as an immersion fluid.

X-ray diffraction studies of iron tellurite glasses were carried out on Bruker D-8 Focus X-ray diffractometer with $CuK_{\alpha 1}$ ($\lambda = 1.5406$ Å) and $CuK_{\alpha 2}$ ($\lambda = 1.5406$ Å) radiations at 40kV and 30mA in the 2 θ range of $10^{\circ} - 70^{\circ}$.

Thermal properties were studied on SETARAM Labsys Evo DSC instrument using sample of amount 10-30 mg at a heating rate of 10 K min⁻¹ under Ar flow conditions. Raman spectra were recorded using Renishaw In-Via Reflex micro-Raman spectrometer using 488nm Argon laser, 2400 lines/mm diffraction grating, an edge filter to record the Stokes spectra and a Peltier cooled CCD detector.

The dc electrical conductivity of 15 and 30 mol% iron tellurite glasses were measured on two probe setup (TPX-600, SES Instruments Pvt. Ltd., Roorkee, India) as discussed elsewhere [3].

Results and Discussion

The XRD patterns of iron tellurite glasses are shown in **Fig. 1**. The broad humps shows that samples are amorphous in nature.

The density of iron tellurite glasses decreases from 5.34 to 5.14 gcm⁻³ as the concentration of Fe_2O_3 increases from 15 to 30 mol%. This is because lighter Fe ion replace the heavier Te ions [3].



Fig. 1. XRD pattern of xFe_2O_3 -(100-x)TeO₂ (x = 15, 30 mol%).

The glass transition temperature (T_g) increases from 659 K to 710 K as the concentration of Fe₂O₃ increases from 15 to 30 mol% because the bond enthalpy of Fe-O (409 kJ/mol) is higher than Te-O (391 kJ/mol). The values of crystallization temperature (T_c) and melting temperature (T_m) are shown in **Fig. 2** and **Table 1**.



Fig. 2. DSC patterns of xFe_2O_3 -(100-x)TeO₂ (x = 15 and 30 mol%).

The Raman spectra of iron tellurite glasses are shown in **Fig. 3**.



Fig. 3. Raman spectra of xFe_2O_3 -(100-x)TeO₂ (x = 15 and 30 mol%).

The peak at 72 cm⁻¹ is the boson peak. The peaks at 107 cm⁻¹ are due to bending vibrations of Te-O bonds in TeO₃ trigonal bipyramidal units. The peak at 653 cm⁻¹ is assigned to the Te-O stretching vibration in TeO₄ units whereas the peak at 748 cm⁻¹ is due to Te-O stretching vibrations of TeO₃₊₁ and TeO₃ units. The relative intensity of peak at 653 cm⁻¹ decreases whereas the intensity of 748 cm⁻¹ peak increases with an increase in concentration of Fe₂O₃ from 15 to 30 mol % and this is due to the structural transformation from TeO₄ to TeO₃ units. The Te-O coordination number decreases from 3.55 to 3.48 [3]. The room temperature dc electrical conductivity increases from 1.79×10^{-7} to $4.00 \times 10^{-5} \Omega^{-1} m^{-1}$ with an increase in concentration of Fe₂O₃ from 15 to 30 mol% [**Fig.4** & **Table 1**]. Further the electrical conductivity of 30 mol% Fe₂O₃ sample is higher than the iron tellurite glasses containing 10 and 20 mol% Fe₂O₃ [3].



Fig. 4. Variation of dc electrical conductivity with temperature of xFe_2O_3 -(100-x)TeO₂ (x = 15 and 30 mol%).

Table 1. Thermal and electrical properties of iron tellurite glasses

Sample	Tg [K]	T _c [K]		T _m [K]		$\sigma \ [\Omega^{-1}m^{-1}]$	
		T _{c1}	T _{c2}	T_{m1}	T_{m2}	313K	423K
15FeTe	659	767	836	889	-	1.79 ×10 ⁻⁷	4.00×10 ⁻⁵
30FeTe	710	-	-	957	970	2.60 ×10 ⁻⁵	2.06 ×10 ⁻³

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XAFS Characterization Of Self-irradiated Gadolinite

Debdutta Lahiri¹, Parasmani Rajput², S. N. Jha², Pranesh Sengupta³ and Nandini Garg¹

¹High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Mumbai 400085
 ²Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai 400085
 ³Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085

*Corresponding author: dlahiri@barc.gov.in

Abstract

Immobilization of radioactive wastes in suitable hosts is pressing industrial demand. We have conducted XAFS investigation for (Fe, Y)-site resolved structure and valence information in such a potential host - Karatupatti metamict gadolinite ($FeO_{10}Be_2Y_2Si_2$) from (South India) .We detected multi-site configuration that drives large disorder of Fe(Y)-O-Si linkage. Implications of large disorder for actinide immobilization and its thermal recovery are discussed.

Structure property relations in (As₂Se₃)_x(GeTe₄)_{100-x} glasses

Shweta Chahal^{*}, K. Ramesh

Department of Physics, Indian Institute of Science, Bangalore-560012, India

*Corresponding author: shwetachahal@iisc.ac.in

Abstract

 $(As_2Se_3)_x(GeTe_4)_{100-x}$ glasses were prepared over the entire composition range $0 \le x \le 100$. As_2Se_3 is an excellent glass former and its increase is expected to improve the glass forming ability (GFA) of $(As_2Se_3)_x(GeTe_4)_{100-x}$. In contrast, GFA shows an opposite trend. Initial addition of As_2Se_3 (x < 40) depolymerises the network and affects the glass forming ability. Glass transition (T_g) shows a decreasing trend for x < 40 and the network is mainly dominated by Ge-Te units. For $40 \le x \le 60$, the network is modified from Ge-Te to As-Te based units. The structural network also begins to polymerize but the average bond energy becomes low. In this range, T_g is found to remain unchanged as both network connectivity and average bond energy compete with each other. For x > 60, T_g is found to increase as both the average bond energy and the network connectivity are increasing. From the Raman studies, the presence of GeTe_(4/2), GeSe_(4/2), Te-Te, AsTe_(3/2), Se-Te and AsSe_(3/2) structural units are inferred. The glassy network is dominated mainly by GeTe_(4/2) for x < 40, and for x > 60, the network is dominated by AsSe_(3/2) structures. Glasses in the intermediate compositions $40 \le x \le 60$ are composed of mixed structures GeSe_(4/2-k/2)Te_(k/2), Te-Te and AsTe_(3/2-m/2)Se_(m/2). These results bring out the dominance of chemical composition effects over the network connectivity in a critically coordinated network.

Introduction

Chalcogenide glasses which find wide range of applications in many areas like phase change memory, infrared sensing, and detection can be prepared over a wide composition range. By varying the composition, the short-range order (SRO) and medium range order (MRO) can be altered by which the properties can be tuned to a desired level [1]. The variation properties as a function of composition is well explained by the constraint counting theory (CCT) proposed by Philips and Thorpe [2-3]. The CCT model predicts that the covalent network undergoes transition from floppy to a rigid structure at the average coordination number ($Z_{av} = 2.40$). It is suggested and also experimentally observed that the properties of these glasses are mainly dictated by the average coordination or the connectivity. The chemical composition effects are seen only at higher coordination numbers ($Z_{av} > 2.40$). In this work, $(As_2Se_3)_x(GeTe_4)_{100-x}$ have been prepared over the entire composition range $0 \le x \le 100$ between the two binary ends. The Z_{av} or the connectivity of all the glasses prepared in this tie-line is 2.40. The fixed connectivity in this tie-line helps to understand the effect chemical composition and average bond energy in modulating the physical and structural properties. The variation in thermal and structural properties are discussed based on the dominant structural units present in these glasses revealed by Raman spectroscopic measurements.

Experimental

Bulk glasses $(As_2Se_3)_x(GeTe_4)_{100-x}$ $(0 \le x \le 100)$ were prepared by melt quenching method. The amorphous nature of the samples was confirmed by X-ray diffraction (XRD). Differential scanning calorimeter (DSC) was used to measure the thermal properties at a scan rate of 10 °C/min. About 15 mg of sample taken in an aluminum pan was sealed with a crimper. An empty crimped aluminum pan was used as a reference. The density (ρ) of the glasses was determined by Archimede's principle. Raman spectroscopy (LabRAM HR system) measurements were performed using a 532 nm line LASER with a CCD detector in backscattering geometry in the range of 100 to 400 cm⁻¹. The spectral resolution of the instrument was 0.5 cm⁻¹.

Results and Discussion

Fig.1(a) shows the variation of T_g with As_2Se_3\% in (GeTe₄) glasses. T_g is related to the network connectivity and consequently reflects the network rigidity. Highly cross-linked and rigid networks have high values of T_g. Interestingly, T_g of various chalcogenide glasses plotted as a function of Z_{av} falls on the same line and does not show much variation upto $Z_{av}=2.40$. This indicates that the chemical composition effects are minimal and the connectivity plays a major role till the critical coordination $Z_{av} = 2.40$. The chemical composition effects are realized for glasses with $Z_{av} > 2.40$. In the present (As₂Se₃)_x(GeTe₄)_{100-x} glasses, T_g varies between 162 °C and 100 °C. With the increase of As₂Se₃, T_g decreases in the range ($10 \le x \le 40$) and reaches a minimum value in the range $40 \le x \le 60$. For x > 60, T_g starts increasing and saturates for x \geq 80. When the As₂Se₃ is added initially $(10 \le x \le 40)$, Se prefers to bond with Ge by replacing the Te in GeTe_(4/2) tetrahedral units. The bond energy of GeSe is higher than Ge-Te and hence the average bond energy of the network increases. This should reflect as an increase in T_g but a decrease in T_g is observed. The effect of de-polymerization is maximum in the range $10 \le x \le 40$. This indicates that the network forms more of an open like structure. The continuous decrease in density also infers the



Fig. 1. T_g , and ρ plotted as a function of As₂Se₃. (a) T_g decreases and reaches its minimum value in the range $40 \le x \le 60$. (b) ρ shows a monotonic decrease. Lines are drawn between the points as guide to the eyes.

decrease in the network rigidity. In the $40 \le x \le 60$ range, the decrease in Tg is arrested. This could be attributed to the increase in network connectivity. So, an increase in Tg is expected for x > 40, but T_g remains constant in the $40 \le x \le 60$ range. In this region the network is dominated by As-Te based structure. As the bond energy of As-Te is low as compared to the bond energy of Ge-Te, As-Se and Te-Te, there is a decrease in average bond energy. Hence, the average bond energy and the network connectivity act against each other. This makes the T_g invariant in this range. For x >60, the structural network is dominated by the AsSe(3/2) units. The bond energy of As-Se higher than the bond energy of Ge-Te and Te-Te. This increases the rigidity and the mean bond energy and hence Tg starts increasing upto x = 80. For x > 80, T_g almost remains constant. For x > 60, the structural network is dominated by AsSe_(3/2) structural units [4]. Glasses with $x \ge 70$ do not show crystallization reaction. The network is rich with As₂Se₃ in the composition range $70 \le x \le 100$. Raman spectra in the range 40-310 cm⁻ ¹ are shown in Fig.2 for different concentration of As₂Se₃ supports the above discussion. For lower content of As₂Se₃, the spectra show bands at 125 cm⁻ ¹ and 157 cm⁻¹ which are commonly observed in GeTe₄ glassy material. In the intermediate range, new bands at 140 and 198 cm⁻¹ are observed. For higher concentration of As₂Se₃, bands at 209 and



Fig. 2. Raman spectra of $(As_2Se_3)_x(GeTe_4)_{100-x}$ $(0 \le x \le 100)$ glasses. The structural variations in the three regions can be very well seen.

240 cm⁻¹ are observed which are characteristic of As_2Se_3 vibrational units.

Conclusions

Various composition having an average coordination Z_{av}=2.4, were studied in pseudo-binary joint $(As_2Se_3)_x$ -(GeTe₄)_{100-x}. T_g show a minimum in the range $40 \le x \le 60$. The density of these glasses continuously decreases with the increase of As₂Se₃. For $0 \le x \le 30$ (Range I), the network mainly consists of GeTe₄ and for $40 \le x \le 60$ (Range II) the network is dominated by AsTe_{3/2} and Te-Te units. For $70 \le x \le 100$ (Range III) the network is dominated by AsSe(3/2) structural unit. In Range I, structural network undergoes de-polymerization resulting in the decrease of Tg. In Range II the network connectivity and mean bond energy compete with each other which make the Tg invariant. In Range III the polymerization and mean bond energy act together to increase the Tg. This study underlines the influence of chemical composition effects in quaternary glasses (Ge/As/Se/Te) prepared at the critical coordination $Z_{av} = 2.40$, which results in reducing the rigidity of the network.

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Elastic constants for the inhomogeneous amorphous states of the hard-sphere system

Faizyab Ahmad^{*}, and Shankar P. Das

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

*Corresponding author: faizya47_sps@jnu.ac.in

Abstract

We study the high frequency elastic constants for the metastable amorphous states of the hard-sphere liquid. The disordered states are identified using the classical density functional theory(DFT) model modified to consider the highly inhomogeneous states. We observe a cross in the behavior of the DFT elastic constants for the two qualitatively different types of amorphous states signifying different degrees of mass localization in the system. We also obtain the high-frequency elastic constants for the homogeneous state using the well-known Mountain-Zwangig formula.

Introduction

When a liquid is cooled, either a crystalline solid or an amorphous solid is formed depending upon the type of liquid and the conditions under which solidification takes place. The density distribution in normal liquid is spatially uniform. In a regular crystal, the mass localization at each lattice site is the same with long range order. The formation of crystal takes place through the thermodynamic first order phase transition at a temperature T_{m.} The amorphous solid is formed by bypassing crystallization that occurs through the quenching process. The mass localization in amorphous solid/glass is not the same on the randomly distributed lattice sites $\{\mathbf{R}_i\}$ with short range order. The classical density functional theory (DFT)[1] presents a theoretical model for understanding the freezing transition by treating inhomogeneous density function $\rho(\mathbf{r})$ as an order parameter[2]. In our work, we take $\rho(\mathbf{r})$ as a sum of Gaussian density profiles centered around the lattice sites[3].

$$\rho(\mathbf{r}) = \sum_{i} \phi(|\mathbf{r} - \mathbf{R}_{i}|) \tag{1}$$

where {**R**i} signifies the underlying lattice. ϕ (r) is a normalized Gaussian function given by

$$\phi(r) = \left(\frac{\alpha}{\pi}\right)^{3/2} e^{-\alpha r^2}$$
(2)

The parameter α is the mass localization parameter that determines the width of the Gaussian densities. For uniform liquid, $\alpha \rightarrow 0$.

In this paper, the total free energy of the amorphous system for different mass localization is calculated by using the Modified density functional approach. We have also calculated the thermodynamic properties like pressure and elastic constants like shear modulus, bulk modulus using standard DFT formulation.

Elasticity of the localized state

The elastic constants of the amorphous metastable state plays a key role in understanding its solid-like behavior. The bulk modulus K of the amorphous solid is written in terms of the second derivative of the free energy with respect to ρ_0 as

$$K = \rho_0^2 \frac{\partial^2 f}{\partial \rho_0^2} \tag{3}$$

The pressure is obtained as the first derivative of the free energy as

$$P = \rho_0 \frac{\partial f}{\partial \rho_0} - f \tag{4}$$

Here, we have used the modified weighted density functional approximation(MWDA) for calculating the total free energy *f* of the metastable states[4]. In MWDA, the nonuniform solid is mapped to an equivalent homogeneous liquid of lower density. In the canonical ensemble, for calculating the excess free energy density(f_{ex} =F_{ex}/N) using MWDA, a self-consistent integral equation is obtained for calculating the density of the effective liquid $\hat{\rho}$ numerically. In terms of packing fraction $\hat{\varphi} = \pi \hat{\rho} \sigma^3/6$, eq. becomes

$$\hat{\varphi} = \frac{I(\hat{\varphi}, \alpha)}{2f'_{ex}(\hat{\varphi}) + \hat{\varphi}f''_{ex}(\hat{\varphi})}$$
(5)

where $f_{ex}(\hat{\varphi})$ is an excess free energy density function and I is defined as
$$I = N^{-1} \int d\mathbf{x} \int d\mathbf{x}' \rho(\mathbf{x}) \rho(\mathbf{x}') c(|\mathbf{x} - \mathbf{x}'|; \hat{\varphi}) \qquad (6)$$

For solving Eq.(5), the following standard form of excess free energy of a hard-sphere $f_{ex}(\phi)$ is taken

$$f_{ex}(\varphi) = \frac{3}{2} \left[\frac{2 \varphi - \varphi^2}{\left(1 - \varphi\right)^2} \right] - \ln\left(1 - \varphi\right) \tag{7}$$

We have used the Percus-Yevick solution for the hard-sphere system for calculating the direct correlation function c(r).

For a fixed value of ρ_0 , the MWDA total free energy(sum of respective ideal and excess parts) is calculated over a range of the width parameter α values[5,6]. The elastic constants are calculated according to the nature of the local free energy minima. MWDA minima are depicted in Fig.1.



Fig. 1. A Plot of MWDA free energy *f* of a hard sphere system vs width parameter α (in units of σ^{-2}) for φ =0.552(dashed),=0.580(solid) and =0.615(dot-dashed).

The DFT results for K, P, and G are shown in the main panel and in the two insets of Fig.2. For low packing fractions (ϕ <0.580), the less localized (low α_{min}) has higher values for the elastic constants. For high packing fractions (ϕ >0.580), the corresponding elastic constants are higher for the sharply localized (high α_{min}) state. The corresponding pressure does not show any cross-over like the elastic constants, i.e the pressure for the less localized state is always more than that for the sharply localized state[7].

The correlation function $g_B(R)$ as obtained by Bennett algorithm[8] is used for generating Bernal's random structure[9]. We use the random structure $g_s(R)$ through the following relation

$$g_{s}(R) = g_{B}[R(\varphi/\varphi_{0})^{1/3}]$$
 (8)



Fig.2. A Plot of DFT elastic constants K(main panel), shear modulus(Inset II), and Pressure(Inset I)[all in units of $\rho_0 k_B T$] for the metastable states of hard-sphere system vs packing fraction ϕ is shown. Solid(dashed) lines are for the metastable state corresponding to low α_{min} (high α_{min}). The vertical arrows in the main panel and inset II correspond to packing fraction ϕ =0.552, 0.580, and 0.615 for which the respective free energy curves are shown in Fig.1.

In all our calculations of MWDA free energy, we have used ϕ_0 =0.68.

The well-known Mountain-Zwangig formulas[10,11] are used for calculating the high-frequency elastic moduli of continuous potential systems. They are expressed in terms of pair potential $\varphi(r)$ and the radial distribution function g(r). The standard expressions are

$$G = \rho_0 T + \frac{2\pi\rho_0^2}{15} \int_0^\infty dr \, r^3 g(r) [ru''(r) + 4u'(r)] \quad (9)$$

$$K = \frac{5}{3}\rho_0 T + \frac{2\pi\rho_0^2}{9} \int_0^\infty dr \, r^3 g(r) [ru''(r) - 2u'(r)] (10)$$

The first terms correspond to the kinetic contribution(ideal gas parts) and the second terms are the excess contribution(configurational parts). For the soft-sphere potential system, having form $u(r) \propto r^{-n}$, the corresponding reduced form of MZ elastic constants are[12]

$$G_{\infty} = 1 + \frac{\Lambda}{5} (n-3) \tag{11}$$

$$K_{\infty} = \frac{5}{3} + \frac{\Lambda}{3}(n+3) \tag{12}$$

where $P/\rho_0 K_B T = Z(\phi)$ and $\Delta = Z(\phi) - 1$. From Eq. (11), (12), we can easily see that if n becomes large

then both G_{∞} and K_{∞} will diverge. So the hard sphere limit of MZ is not good[13]. Therefore, for the hard sphere system, we calculate the high-frequency elastic constants given by Miller. He did the long wavelength expansion of the stress tensor in terms of strains and retained only those terms that were independent of the wavelength[14]. The generalized forms of Miller's elastic constants are

$$G_{\infty} = 1 + \frac{\Delta}{5} [\tilde{n} - 3]$$
(13)

$$K_{\infty} = \frac{5}{3} + \frac{\Delta}{3} [\tilde{n} + 3] + \frac{2}{3} \Delta [\Delta + 2]$$
(14)

If we use the Carnahan-Starling equation of state (CS) i.e.

$$Z(\varphi) = \frac{1 + \varphi + \varphi^{2} - \varphi^{3}}{(1 - \varphi)^{3}}$$
(15)

then $\tilde{n}=3+\frac{9 \varphi(1+\varphi)}{(1-\varphi)}$. If we use the equation of

state according to the Percus-Yevick theory using compressibility equation (PY-C) i.e.

$$Z(\varphi) = \frac{1 + \varphi + \varphi^2}{(1 - \varphi)^3}$$
(16)

then $\tilde{n}=3+\frac{18\,\varphi(1+\varphi)(2-\varphi)}{(1-\varphi)(\varphi^2-2\,\varphi+4)}$. Both of these

elastic constants are depicted in Fig3.



Fig.3. In the main panel, the plot of high-frequency elastic constants(in units of $\rho_0 k_B T$) for the uniform hard-sphere liquid vs packing fraction φ is shown. Bulk modulus K_{∞} ;

PY-C(dashed line) and CS(solid line). Shear modulus G_∞ is same for both CS and PY-C and is shown with dot-dashed line. In the inset, the plot of thermodynamic pressure P(in units of $ρ_0 k_B T$) for the uniform hard-sphere system vs packing fraction φ is shown. Here dashed line is for PY-C

and solid line is for CS.

We have also studied the free energy landscape for the Hertzian potential system[15] used generally for soft-sphere systems and obtained the phase diagrams of these continuous potential systems. We have studied how such systems approach the hard-sphere limit.

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Replica theory for Structural Glass Transition using density functional Hamiltonian

Prakash Vardhan*, and Shankar P. Das

School of Physical Sciences, Jawaharlal Nehru University, New Delhi 110067, India

*Corresponding author: al091188@gmail.com

Abstract

We study microscopic replica field theory of the disordered system without quenched disorder. The sharp fall of configurational entropy of a many-particle system is analyzed with the scenario of spontaneous ergodicity breaking, in which the free energy landscape of the many-particle system splits into distinct basins of local minima. The field theoretic model is formulated in terms of a density field, and a nonlocal free energy functional used in classical density functional theory (DFT) up to third order in density fluctuation $\delta \rho$ is the key input in the calculation. Using a mapping into a composite system of *m* replicas, and idea of an an auxiliary field, first suggested by R. Monasson, we compute the configurational entropy S_c of the supercooled liquid. The configurational entropy S_c sharply falls with increase of packing fraction η . The Kauzmann point η_{k_i} (at which extrapolated entropy S_c vanishes) obtained in the model, is in agreement with other works.

Introduction

Understanding the non-ergodic state and entropy paradox that frequently occur in spin glass [1] and structural glass systems [1-4] has sparked decades of theoretical and experimental research. The replica analysis of spontaneous ergodicity breaking in structural glass without quenched disorder [2,4] is studied, the principle was originally developed for spin glass.

A hard sphere interacting molecular fluids below a ergodicity breaking point η_c , undergoes a transition to vitrification. Viscosity increases sharply below η_c due to high packing fraction results in diverging relaxation time and a dynamic crossover is observed [4]. The theme of present work is based on replica theory, where FEL fragments into exponentially large number of minima of metastable states N, originally emphasized by Kauzmann [5].

In the present work, configurational entropy is taken as $S_c = \ln \Omega$ rapidly falls as we depart from the freezing point towards a highly metastable state with extremely sluggish dynamics. We show how, in the case of a hard sphere system, ergodicity breaks spontaneously and S_c decreases as density increases. To calculate the Kauzmann point, we extrapolate S_c to zero.

Configurational entropy

In the present work, we consider three dimensional hard sphere liquid of *N* particles in a volume \mathcal{V} . $\rho = \{\rho_1, \rho_2, ..., \rho_N\}$ is a vector whose components are liquid's coarse grained density field $\rho(\mathbf{x})$. defined by the Hamiltonian $H[\rho]$. The corresponding equilibrium

Gibbs free energy functional is, $\int D\rho \exp\{-\beta H[\rho]\} =$ $-\beta F_{\rho}$. Derivative of free energy functional with respect to density field $\rho(\mathbf{x})$ provides an equilibrium state. Following the hypotheses [1,2], at quite high density η_c , below freezing point of liquids, ergodicity breaking occurs provided crsytallization is avoided. As a result of ergodicity breaking, underlying FEL fragments into large number of local minimas for metastable states. Counting number of minima provided by $\rho(\mathbf{x})$ contributes to partition function of the system is obtained through Monasson's seminal work [2]. A symmetry breaking field $\psi(x)$ is coupled to $\phi(\mathbf{x})$ quadratically with a coupling constant term g. The free energy functional F is minimum when $\psi(\mathbf{x})$ is equal to the configuration $\phi(x)$. Consider a system of m replicas of the original system is represented as $\{\rho^{a}\} = \{\rho^{1}\}, \{\rho^{n}\}, \{\rho^{m}\}$. Spanning $\Psi's$ function space pick up the contribution coming from minima of different meta stable states in FEL. Treating F_{ψ} as Hamiltonian, the corresponding free energy yields

$$\beta F(m\beta) = \lim_{g \to 0^+} \ln \left[\int \prod_{\{a=1\}}^m D\rho^a \exp\{-\beta \sum_{a=1}^m H[\rho^a] - \frac{g}{2m} \sum_{a < b} \int (\rho^a(\mathbf{x}) - \rho^b(\mathbf{x}))^2 \right] dx$$
(1)

at some temperature $m\beta$, m being some integer. The coupling term g enforces all replicas to remain in the same meta-stable minima of FEL, eventually leads to glass phase after putting $g \rightarrow 0$ at the end of the calculation.

The corresponding internal energy at temperature $m\beta$ is, $U = -\frac{\partial}{\partial m} \{mF[m, \beta]\}$, with β being treated

as a constant. With definition, $S_c = \beta(U - F)$, the configurational entropy of the metastable liquid in the limit m approaching 1 is defined as,

$$S_c = \beta \frac{\partial}{\partial m} \{ mF[m, \beta] \}$$
(2)

Understanding the physical interaction among replicas, defining two point correlation matrix *G* in real space, $G_{ab} = \langle \delta \rho^a(x) \delta^b(y) \rangle$. Constructing direct matrix *G* in replica space with diagonal and off-diagonal components such as G = (G - F)I + FE. I is $m \times m$ identity matrix, and **E** is a matrix having all the elements equal to unity of same size. In the following, we use free energy functional in addition to external field ν to generate two point correlation function, which is written in polynomial expansion form as,

$$F_{\nu}[\Psi] = \frac{1}{2} [\sum_{12} G_0^{-1}(12)\Psi(1)\Psi(2)] \qquad (3)$$

+
$$\frac{1}{3} [\sum_{123} V(123)\Psi(1)\Psi(2) \ \Psi(3)] - \sum_{1} \nu(1)\Psi(1)$$

where we denote field $\Psi(1) \equiv \delta \rho^a(\mathbf{x})$, with a = 1, to m, and 1 stands for spatial point \mathbf{x}_1 etc. The Gaussian matrix $G_{0^{-1}}$, and symmetrized cubic vertex V(123) are obtained in terms of the direct correlation functions $c^{(2)}$ and $c^{(3)}$, using Ramakrishnan-Youssouff free energy functional [6]. The correction to zeroth order correlation function G_0 is provided by non-linear term and replicated Schwinger Dyson's equation is obtained as, $G^{-1ab}(k) = G_0^{-1ab}(k) - \Sigma(k)$. In the *m* replica space, Σ has similar structure to matrix *G*, with Σ_G and Σ_F denoting diagonal and off diagonal elements respectively. Comparing the Schwinger-Dyson's eqn with direct matrix *G* in the limit $m \to 1$ leads to self consistent off diagonal correlation function,

$$F(k) = G(k) - \Lambda(k) \text{ with,}$$
(4)

$$G^{-1}(k) = G_0^{-1}(k) - \Sigma_G(k) \text{ and,}$$

$$\Lambda^{-1} = G^{-1} + \Sigma_F(k)$$

Translation and isotropic property of the system has been used, and expression for Σ_F obtained with *u* is the angle between vectors **k** and **q** - **k**, as,

$$\Sigma_F(k) = \int \left[\{ \rho_0^{-2} + c^{(3)} (k, q - k, u) \}^2 \times F(k) F(q - k) \right] \frac{d^3 k}{(2\pi)^3}$$
(5)

Further, we obtained the replicated free energy F(m) and configurational entropy S_c , follows as,

$$F[m] = \frac{1}{\beta m} [Tr \ln G^{-1} - Tr(\Sigma G) + C_0(m)]$$
(6)

 $S_C = S_0 + \int_k [3\ln(1 + G\Sigma_F) - (3G - 2F)\Sigma_F]$ (7) The data of S_c fits to power law $A_0(\eta - \eta_k)^{\mu}$ as

shown by solid and dashed lines in Fig.1. From input

of intra-replica correlation from Verlet-Weiss(VW) method, we obtained Kauzmann point η_k .



Fig. 1. Configurational entropy S_c scaled with constant S_0 vs. packing fraction η , for input structure factors from VW (open circles). Power law fits extrapolating to zero at S_c with exponent $\mu = 0.03$. Inset: structure factor G(k)(solid), F(k)(dashed) vs. $k\sigma$ at $\eta_c = 0.524$.

In summary, following field theoretic model for studying super-cooled liquid using DFT free energy functional with inclusion of three body correlation plays crucial role in determining transition. Further, replica approach is used to understand the entropy paradox based on the structural information of the uniform liquid. Below η_c , we obtain non-ergodic term, *F* signifies overlap between distinct replicas. Overlap between replicas getting stronger with increase of density and condense in deep minima of free energy and causes for formation of glassy phase. Thermodynamic transition η_c is obtained with sharp fall of S_c in a first principle calculation.

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Bi₂O₃ Glasses: Gamma Ray Shielding Properties

Mridula Dogra

Department of Physics, Baring Union Christian College, Batala, Punjab, India

mriduladogra@yahoo.co.in

Abstract

Quaternary glass systems containing oxides of bismuth based glass systems: S1 ($3Bi_2O_3-62B_2O_3-15Li_2O-15K_2O-5M_2O_3$), S2 ($3Bi_2O_3-62B_2O_3-15Li_2O-15K_2O-5V_2O_5$ and S3 ($0.65Bi_2O_3-0.15B_2O_3-0.15Na_2O-0.05BaO$) have been prepared by melt quenching technique using AR grade chemicals. Gamma ray shielding parameters in terms of mass attenuation coefficient, HVL and MFP have been calculated at photon energies 356, 662, 1173 and 1332 keV. Prepared samples provide better radiation shielding properties than some standard concretes.

Effect of Neodymium Loading in Iron Phosphate Glass

Akhilesh C Joshi,^{1,2} Mainak Roy^{1,2} and Dimple P Dutta^{1,2*}

¹Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushakti Nagar, Mumbai-400094, India

*Corresponding author: dimpled@barc.gov.in

Abstract

A series of iron phosphate glass (IPG) samples loaded with different mole percent of Neodymium (Nd) oxide were prepared by melt quench technique with a view to test the feasibility of high-level waste immobilization in them since Nd is considered to be a chemical surrogate for actinides like Curium (Cm). Typically, for a batch of 25g, the constituent oxides in stoichiometric ratio are melted at a temperature of 1323K, quenched in air and vitrified on a steel plate. Scanning electron micrographs of representative samples showed that they were homogeneous in terms of composition, devoid of any noticeable precipitation of crystalline phase and nodule formation up to 8mol%. The observation was further confirmed from the overlapping EDS elemental mapping of the samples. Amorphous nature of the samples was ascertained from their respective X-ray diffraction patterns which showed broad hump in between $20^{\circ}-30^{\circ}$. Thermogravimetric analysis of the samples confirmed their stability over a wide range of temperatures, which was further substantiated from their glass transition temperatures (T_g), liquidus temperature (T_L) and crystallization temperature (T_x) obtained through the calculation of *K*_H, *K*_W and *K*_{LL} parameters. It was observed that the IPG matrix got structurally modified upon incorporation of Nd.

Introduction

Till date, vitrification remains the principal mode of disposal for high level nuclear waste (HLW) wherein HLW retrieved from the fuel rods are mixed with glass-formers, melted and quenched inside a stainless steel canisters. Borosilicate glass matrix is widely used for the immobilization of HLW. In recent times, iron phosphate glass (IPG) matrix is being explored as a potential substitute for borosilicate glass because of its higher waste-loading capacity and lower processing temperatures [1,2]. A lower temperature not only favors energy economy but also prevents volatilization of wastes. Further, it has been observed that loading of IPG matrix with heavy metals tends to modify the P-O-P linkages in such a way that its durability against atmospheric moisture and corrosive environment gets enhanced significantly.

Neodymium (Nd) is a chemical surrogate for actinides like americium (Am) and curium (Cm) present in HLW. The objective of the present study was to find out the optimum Nd loading in IPG without getting it devitrified that in turn would hint upon the viability of immobilization of wastes such as Am and Cm in IPG. It has been demonstrated Nd may be incorporated into IPG matrix up to 8mol% without onset of crystallization. Thermogravimetric analysis of the samples confirmed their stability over a wide range of temperatures.

Experimental

The base IPG glass samples were prepared by melt-quench technique using AR grade $NH_4H_2PO_4$, and Fe₂O₃ as the starting materials. For a typical batch of 25g, the reactants were mixed in 60% -40% ratio, homogenized by grinding in Ar atmosphere for 2h. The homogenized mixture was preheated at 873K for 1h followed by further heating at 1273K for 1h. The resultant melt was air quenched and finally vitrified on steel plate. For Nd loaded IPG, Nd₂O₃ was added to the base composition in different mole percent.

Results and Discussion

Fig. 1 shows the XRD pattern in the 2θ range of 10°-70° of a representative IPG sample loaded with 8mol% of Nd. The pattern exhibits a broad hump extending between 20°-30° indicating of its amorphous nature. Absence of any sharp peak in the XRD pattern due to a possible crystalline phase forbids the co-



Fig. 1. XRD pattern of IPG loaded with 8mol% Nd.

existence of any precipitated phase and hence devitrification of the glassy matrix at least up to 8mol% Nd loading.

The observation is further evidenced from the scanning electron micrograph of the 8 mol% Nd loaded sample (Fig. 2a) which shows it is homogeneous in composition and devoid of any noticeable nodule formation from a possible parasitic crystalline phase. Similarly, EDS elemental mapping (Fig. 2b) over the scanned sample area confirms homogeneity in sample composition.



Fig. 2 (a) SEM micrograph of IPG loaded with 8 mol% Nd, **(b)** Elemental mapping of the same sample, **(c)** SEM micrograph of IPG loaded with 15 mol% Nd and (d) EDS spectrum of IPG loaded with 8mol% Nd.



Precipitation of crystalline phases is however observed

Fig. 3. TG graph of IPG loaded with 2, 5 and 8 mol% Nd.

in the sample loaded with 15mol% Nd (Fig. 2c), indicating of the initiation of crystallization between 8 to 15mol%. Fig. 2d shows the EDS spectrum of the 8mol% sample for stoichiometric composition.

Thermogravimetric (TG) analysis of three representative IPG samples loaded with 2, 5 and 8mol% of Nd (**Fig. 3**) shows minimal mass loss ($\leq 8\%$) over a wide range of temperatures confirming appreciable stability of the samples. Different thermal stability parameters viz. K_H, K_W and K_{LL} for the glass samples were calculated from glass transition temperatures (T_g) , liquidus temperature (T_L) and crystallization temperature (T_x) of the respective samples as obtained from their DTA analysis (not shown). Structural modification leading to enhanced thermal stability of the glassy matrix have been extensively studied using different spectroscopic techniques.

Conclusion

Nd loading up to 8mol% of Nd in iron phosphate glass without sacrificing amorphous nature of the sample, as evidenced from its XRD, SEM and EDS analysis has been successfully demonstrated. TG- DTA analysis shows thermal stability of the samples over a wide range of temperatures, which was further confirmed from complementary spectroscopic investigations.

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Gamma Attenuation by Cadmium Chloride filled Polymeric Blend Composite at Specific Gamma Photon Energies – A Computational Approach

Basavarajeshwari M. Baraker¹, Blaise Lobo¹

¹UG & PG Department of Physics, Karnatak University's Karnatak Science College, Dharwad 580001, India

blaiselobo@kud.ac.in

Abstract

The mass attenuation coefficient and half value layer thickness of composite films comprising polyvinyl alcohol - polyvinyl pyrrolidone blend reinforced with cadmium chloride has been explored by a computational method at specific gamma photon energies, equal to 14.4, 31, 59.54, 80, 122, 356, 511, 662, 835, 1173, 1274 and 1332 keV. Data from NIST- XCOM has been used to extract the necessarv basic information in order to perform the computations. The FLs of cadmium chloride in the polymeric blend considered for the computational study are 5.4, 10.2, 15.5, 21.5, 30 and 40 Wt%, which were selected based on the composites prepared for earlier microstructural studies on this system. The half value layer thickness decreases on the increased incorporation of filler into the host polymeric blend, at all the gamma photon energies of interest, implying that the material can be effectively used as a gamma shielding material.

Introduction

X-rays and radio-isotopes emitting gamma rays are increasingly being used in various applications like food preservation, imaging, determination of purity of materials, investigation of defects, medical diagnosis and treatment, in addition to being encountered in nuclear power industry, different types of fission reactors and research laboratories. Ionizing electromagnetic radiation like x-rays and gamma rays pose a health hazard to humans, and therefore there is a need to utilise proper radiation shields in order to protect personnel and other users from the damaging effects of ionizing radiation [1-4]. In this direction, lead (Pb) is being commonly used due to its high atomic number (Z), its low cost and easy processability. However, the toxic effects of Pb have outweighed its utility as a gamma shielding material, and there are attempts to develop safer shielding materials. In this direction, the formation of polymeric composites with high Z and medium Z additives are being investigated by various research groups. The use of medium Z element like cadmium in a polymeric composite serves the dual purpose of a strong thermal neutron absorber as well as a good gamma shield reasonably [5]. The microstructural changes which occur when cadmium chloride hexahydrate (CdCl₂. 6 H₂O) is filled in polyvinyl alcohol (PVA) - polyvinyl pyrrolidone (PVP) blend has been extensively investigated. The composite material shows interaction of the filler species with the polymeric molecules at low and moderate filler levels (FLs), but exhibit a

homogeneous distribution of the filler in the host polymeric blend above a filler level of 15.5 Wt%. Thus, the FLs employed for this computational study of gamma attenuation parameters of CdCl₂. $6H_2O$ filled PVA-PVP blend is mainly in the FL range from 15.5 Wt% up to 50.5 Wt%, but also includes two lower FLs, namely, 5.4 Wt% and 10.2 Wt% for the purpose of completeness.

Details of Computational Work

The mass density (ρ) of the prepared polymer composite, at different FLs has been computed by using Eq. (1).

$$\rho = \frac{100}{\left[\frac{M}{\rho_m} + \frac{F}{\rho_f}\right]} \tag{1}$$

In Eq. (1), M is mass percentage (%) of the host polymeric blend, F is mass percentage (%) of the filler, ρ_m is density of the host polymeric matrix and ρ_f is the mass density of the filler. Polymeric composites are well known for good overall performance when used for different applications although they have light weight, a property arising due to their low mass density. To check the heaviness of these composites, Pb was assumed as the standard. The percentage of heaviness (% H) of the polymer composite films has been calculated by using Eq. (2).

$$\% H = \frac{\text{Density of the given material}}{\text{Density of lead}} \times 100$$
(2)

The data required for the computations are extracted from the NIST-XCOM site. The computations are performed using mixture rule to obtain the values of mass attenuation coefficients at certain gamma photon energies, from which the mass attenuation coefficients at the desired specific gamma photon energies have been determined using logarithmic interpolation formula.

Table 1.Mass density and percentage of heaviness of CdCl₂. 6H₂O filled PVA-PVP blend composites, at different FLs.

FL	ρ	%Н
(Wt%)	(g/cm^3)	
0.0	1.200	10.57
5.4	1.243	10.95
10.2	1.284	11.31
15.5	1.332	11.74
21.5	1.391	12.26
30.0	1.485	13.08
40.0	1.612	14.20

The attenuation of the collimated mono energetic gamma radiation passing through a material of effective thickness 'pt' is given by the Lambert-Beer- Bouger's law

$$I = I_0 e^{-\mu_m \rho t} \tag{3}$$

In Eq. 3, I_o and I are the incident and transmitted gamma beam intensities respectively, and μ_m is the mass attenuation coefficient. Mass attenuation coefficient of any mixture or compound can be theoretically calculated by using Eq. 4.

$$\frac{\mu}{\rho} = \sum_{i} W_{i} \left(\frac{\mu}{\rho}\right)_{i} \tag{4}$$

In Eq. (4), W_i is the weight fraction of the ith element and $\left(\frac{\mu}{\rho}\right)_i$ is the mass attenuation coefficient of the ith constituent element. The mixture rule is applicable when the additives added to the polymeric host do not interact chemically with the molecules of the host, but only forms a physical mixture. The values of half value layer (HVL) and tenth value layer (TVL) thickness are calculated using Eq. 5 and Eq. 6, respectively.

$$HVL = \frac{ln2}{\mu}$$
(5)

$$TVL = \frac{ln10}{\mu} \tag{6}$$

The specific gamma photon energies of interest are the gamma photons equal to 14.4, 31, 59.54, 80, 122, 356, 511, 662, 835, 1173, 1274 and 1332 keV, which are emitted by commonly used laboratory sources of radiation, namely, cobalt- 57, americium – 241, barium -137, caesium -137, sodium -22, manganese - 54 and cobalt-60. The results of measurement are represented in Fig. 1a and Fig. 1b.



Fig. 1a. Variation of mass attenuation coefficients with gamma photon energy, for different FLs of CdCl₂. $6H_2O$ in PVA-PVP blend. **b.** Variation of half value layer thickness with gamma photon energy, for different FLs of CdCl₂. $6H_2O$ in PVA-PVP blend.

It is noticed that the value of μ_m decreases significantly with increase in photon energy (see Fig. 1a), and there is an increase in HVL with increase in photon energy, at all FLs, as expected. However, with increase in FL at specific energy, it is noted that μ_m increases and HVL decreases (Fig. 1b), implying that the incorporation of cadmium salt in the polymeric blend improves its gamma shielding effectiveness.

Conclusions

The mass attenuation coefficient and half value layer of composite films formed by incorporating cadmium chloride hexahydrate in a polymeric blend of polyvinyl alcohol and polyvinyl pyrrolidone has been computed using the mixture rule and logarithmic interpolation formula, for specific gamma photon energies of interest. The results reveal that the half value layer thickness decreases significantly with an increase in filler content, implying that the material can be used as a gamma shield at these energies.

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Nano Silver (Ag⁺) Ion-Exchange Composite Glass for Enhanced Linear and Nonlinear Optical Properties

D. Manikandan¹, P. Manikandan², G. Kavitha³, J. Naseer¹, R. Namachivayam¹,

E. Manikandan⁴

¹Dept of Physics, Arignar Anna Government Arts College, Villupuram-605602. ²Dept of Physics, Krishnasamy College of Engineering &Technology, Cuddalore-607109. ³P.G.& Research Dept. of Physics, A. M. Jain College, Chennai, ⁴Dept of Physics, TUCAS Thennangur-604408, Thiruvalluvar University, Vellore, Tamil Nadu.

*Corresponding author: <u>maniphysics@gmail.com</u>

Abstract

Silver nanocomposite (Ag-NCs) glasses are formed by sequential ion-exchange and thermal annealing technique. The dielectric containing the metal nanoclusters are well investigated by optical absorption (OA) showed the signatures of Ag^+ clusters embedded in the glass-matrix exhibiting OA peak due to dipolar Surface Plasmon Resonance (SPR). Low frequency Raman Scattering (LFRS), which stems from the quadrupolar acoustic vibrations of the embedded Ag-nanoclusters and PL band centered at 445 nm. Open aperture *z*-scan measurement shows the transmitted light was recorded as a function of the sample position along the focal plane. The spectrum was fitted using the theory and the magnitude of the nonlinear absorption coefficient was determined from it.

Different Models For Calculating The Refractive Index And Band Gap For Chalcogenide Glasses

Chandresh Kumari¹, S.C. Katyal¹, Pankaj Sharma²

Department of Physics & Materials Science, Jaypee Institute of Information Technology, Noida - 201309, India
 Applied Science Department, National Institute of Technical Teachers Training & Research, Chandigarh - 160019, India.

*Corresponding author: chandreshphy14@gmail.com

Abstract

Optical analysis plays an important role in the development of optoelectronic materials. In this paper, some relations have been studied for optical parameters for erbium based GeSbSe system. These relations are based on the particular models suggested for calculating doped, co-doped *etc.* chalcogenide systems for a given energy gap range. These models predict refractive index values and are compared to the experimental analysis of chalcogenide glasses. The experimental refractive index for $Ge_{17}Sb_8Se_{75-x}Er_x$ (x=0, 0.4 and 0.8) thin films varies from 2.45 to 2.67 and have good agreement with the relationships proposed by several researchers.

Introduction

VI group elements of the periodic table such as S (sulphur), Se (selenium) and Te (tellurium) etc. in combining with electropositive elements such as Sb, Ge, As, Ga etc. form chalcogenide glasses (ChGs) [1,2]. ChGs are good candidates for photonic as well as optical applications [3]. Doping of ChG with rare earth elements like erbium, ytterbium, holmium etc. [4-6] used in amplification devices [5,6], optical waveguide [7], optical converter [8,9], sensor and detector [10] etc. Refractive index (n) and the optical energy gap (E_{σ}) are two important parameters that have been used to predict the optical and electrical properties of semiconductors. These parameters are crucial in optoelectronic materials such as optical fibres, photodiodes etc. The bandgap has a complete impact on the refractive index (n) of a semiconductor. Both are inversely proportional to each other, and the material is excellent for optoelectronic applications.

The goal of this study is to utilize the various models suggested for revealing the relationship in optical bandgap and refractive index for $Ge_{17}Sb_8Se_{75-x}Er_x$ (x=0, 0.4 and 0.8) thin films. This research will support in the identification of theoretical models for calculating optical properties.

Experimental Details

Melt quenching technique has been used for the synthesis of amorphous glasses. High purity elements Ge, Sb, Se and Er (5N Purity, Alfa Aesar) were weighed with desired proportion and sealed in the quartz tube. Ampoules were placed inside the muffle furnace and the temperature was raised to 1000°C with 2-3°C/min heating rate. The ampoules were regularly shaken at this temperature for 14 hr. The quenching was performed in chilled water [11]. Thin films of bulk

samples were deposited on glass substrates using the thermal evaporation method (HINDHIVAC model 12A4D India).

Results and Discussion

In amorphous semiconductors, the energy gap and refractive index are the crucial parameters. There are different methods to find relations between refractive index and bandgap. Moss made the first attempt, known as Moss relation [12]. Moss suggested an idea that in the solids energy levels are scaled-down by $1/E_{eff}^2$ here E_{eff} indicates dielectric constant. Moss equation is given as:

$$\frac{n_o}{\lambda_a} = 77 \mu \mathrm{m}^{-1}$$
 (I)

In case of energy gap E_g, Eqn. (I) can be written as: $n_0^4 E_q = \text{k.eV}$ (II)

Where E_g , n are the energy gap and refractive index, the value of k = 95 eV. Ravindra and Gupta [13] improved the Moss relation by proposing a new value of k. Refraction loss has been calculated by using this relation for the improvement in conversion efficacy in a solar cell. Ravindra and Gupta [13] estimated that, in Moss formula, value of k = 108 eV the modern experimental data indicates good fitting.

 $n_0^4 E_g = 108.\text{eV}$ (III) Here E_g is band gap of the system, value of band varies from 1.907 for x=0, 1.85 for x=0.4 and 1.815 for x=0.8.

Because Moss relationship limited the validity of Ravindra equation [12], Ravindra and Gupta established a third linear relationship. The difference between average energy gap and optical energy gap, (IV)

according to Ravindra et al., remains constant. They postulated the following relationship [14] based on this theory:

$$n = 4.084 - 0.62E_g$$

Moss [10] then examined equation (IV) and argued that it is applicable for bandgap smaller than 4 eV and that it produces unsatisfactory consequences for both low and high band gap E_g values. Reddy and other authors [15] presented a different relation, in terms of exponential term.

$$E_g e^n = 36.3 \tag{V}$$

Kumar and Gupta [16] reported that the given idea might be applicable for optoelectronics uses for several semiconducting devices.

$$\mathbf{n} = \mathbf{K} \mathbf{E}_{g}^{c} \tag{VI}$$

In Eq. (VI) the value of c = -0.32234 and K = 3.3668.

Table 1. Refractive index of $Ge_{17}Sb_8Se_{75-x}Er_x$ (x = 0, 0.4 and 0.8) system with four theoretical approaches.

X	Present value (n)	Moss work	Ravindra work	Ravindra & Gupta work	Kumar & Singh work
0	2.45	2.65	2.74	2.90	2.73
0.4	2.68	2.67	2.77	2.93	2.76
0.8	2.67	2.68	2.78	2.95	2.77



Fig. 1. Refractive index with band gap for $Ge_{17}Sb_8Se_{75-x}Er_x(x = 0, 0.4 and 0.8)$ by Moss, Ravindra, Ravindra & Gupta, Kumar & Singh.

In this paper, the refractive index values vary from 2.45 to 2.67 so these relationships can apply to $Ge_{17}Sb_8Se_{75-x}Er_x$ (x=0, 0.4 and 0.8) films. The optical

band gap (E_g^{opt}) values is calculated by using Tauc method for Ge₁₇Sb₈Se_{75-x}Er_x (x=0, 0.4 and 0.8) thin films, the values of bang gap are 1.90 eV, 1.85 eV, 1.81 eV. By using the above relations from (I) to (VI) the refractive index (n) has been calculated for the Ge₁₇Sb₈Se_{75-x}Er_x (x=0, 0.4 and 0.8) films shown in Table 1. From Fig. 1 it is clear that for the present system the refractive index values from Moss relations, Ravindra & Gupta, Ravindra, and Kumar et al. are closely approaching to experimental value.

Conclusion

For design of optical devices, the estimation of refractive index (n) is crucial. Refractive index of the system was determined using experimental optical band gap of $Ge_{17}Sb_8Se_{75-x}Er_x$ (x = 0, 0.4 and 0.8) deposited films in this present study using several methodologies. These experimental values are reasonably close to the result. Calculated value is shown a decent resemblance with experimental data.

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Spin-Coated ZnO Nanocrystalline Thin Films: Effects Of (Sn, Ni) Co-Doping On Their Microstructural And Optical Properties

Aradhana Tiwari and P.P. Sahay

Department of Physics, Motilal Nehru National Institute of Technology Allahabad, Prayagraj-211004

*Email: aradhana.bindu@gmail.com

Abstract

In this paper, the effects of (Sn, Ni) co-doping on the microstructural and optical properties of the spin-coated ZnO thin films have been investigated. The crystallinity of the films has been found to be maximum in the undoped ZnO film with preferred orientation along (0 0 2) plane. Upon doping and co-doping, the film crystallinity decreases. The energy band gap value of the undoped ZnO film is found to be 3.26 eV, which decreases slightly upon doping and co-doping. The refractive index values of the doped and co-doped ZnO films are found to be more than that of undoped ZnO film.

Introduction

Zinc oxide (ZnO), an II-VI group compound semiconductor, is an important multifunctional metal oxide, which has got potential applications in chemical gas sensors, photocatalysts, optoelectronic devices, and so on [1, 2]. An effective approach to control the properties of ZnO is the diffusion of the appropriate dopant species in the ZnO lattice. The incorporation of various dopants and co-dopants in ZnO lattice has been studied to improve the functionality of ZnO [3, 4].

In the present investigation, the incorporation of two heterovalent cations (Sn, Ni) in ZnO lattice and its impact on the microstructural and optical properties of ZnO films have been studied.

Experiment

The films were produced on quartz substrates employing a spin coating unit [Make: Milmam, Model: 2000S]. The dopant Sn:Ni atomic percent with respect to Zn atomic concentration were taken 1:0, 1:1, 1:3, 3:1, and 0:1. Accordingly, the films deposited are referred to as 1TZO, 1T1NZO, 1T3NZO, 3T1NZO and 1NZO, in addition to the undoped ZnO film. The films were characterized for their microstructural and optical properties using XRD, FESEM, AFM, and UV-Vis spectroscopy.

Results and Discussion

All the peaks in the XRD profiles of the films agree well with the standard peaks of JCPDF Card No: 36–1451, inferring that the films are polycrystalline in nature and possess a hexagonal wurtzite structure of zinc oxide. No additional peak associated with dopants or their compounds is observed in the profiles. The crystallinity of the films has been found to be maximum in the undoped ZnO

with preferred orientation along (0 0 2) plane. Upon doping and co-doping, the film crystallinity decreases and is least for 1NZO film. Further, the positions of XRD peaks in the doped and co-doped ZnO films are slightly shifted towards lower diffraction angles with respect to undoped ZnO. This may be due to the incorporation of dopants and co-dopants in ZnO lattice as the ionic radii of Sn^{4+} (0.69 Å) and Ni^{2+} (0.69 Å) is different to that of Zn^{2+} (0.74 Å).

The average crystallite size, D, of the films has been determined from the Scherrer plot using a well-known Scherrer formula:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad \dots \qquad \qquad \text{a)}$$

where λ is the wavelength of CuK_{a1} radiation (1.5406 Å), β is the full width at half maximum (FWHM) of the diffraction peak of the sample in radians, and θ is the angle of diffraction in radians.

Lattice constants, a and c, have been determined using the plane spacing equation for the hexagonal structure. A very small increase in lattice constants has been observed in the doped and co-doped films relative to undoped ZnO, which is attributed to the introduction of dopants and co-dopants in ZnO lattice. The structural parameters of the films are listed in Table 1.

Table 1. Structural parameters of the ZnO films

Samples	Lattice constants [Å]	Crystallite size, D [nm]	Lattice strain, ε [%]
ZnO	a = b = 3.2334 c = 5.1754	1.601	0.0064
1TZO	a = b = 3.2654 c = 5.1972	1.592	0.0100
1NZO	a = b = 3.2383 c = 5.1990	1.605	0.0072
1T1NZO	a = b = 3.2459	1.602	0.0073

	c = 5.1987		
1T3NZO	a = b = 3.2471	1.620	0.0096
	c = 5.2588		
3T1NZO	a = b = 3.2275	1.606	0.0076
	c = 5.1840		

Fig. 1 presents the transmittance and reflectance spectra of the films in the wavelength range 300-800 nm. It is evident that the transmittance of the films improves upon doping and co-doping. The observed variation in transmittance of the films arises due to the surface roughness and the structural defects in the films. In all the films, the transmittance decreases rapidly near the ultraviolet region due to the band gap absorption, inferring that the incident photons get absorbed by the electrons in exciting them from the valence band to the conduction band.



Fig. 1. Transmittance and reflectance spectra of the ZnO films.

The energy band gap value of the undoped ZnO film is found to be 3.26 eV, which decreases slightly upon doping and co-doping in ZnO films. The energy band gap value is found to be least (3.03 eV) in 1T3NZO film. A decrease in the energy band gap value reveals the formation of localized energy states near the bottom of the conduction band.

Fig. 2 presents the spectral dependence of refractive indices of the films. As is seen, the refractive index values of the films are higher in the

absorption region due to a strong interaction of incident photons with the electrons in the films. Furthermore, the refractive index values of ZnO films are found to increase with the dopants and codopants, which can be explained in terms of microstructural changes that occurred in the films due to the incorporation of dopants and co-dopants.



Fig. 2. Spectral dependence of refractive indices of the films.

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Evaluation of Optical Parameters of ZnSe Thin Film

H. N. Desai^{1,2}, S. P. Sikligar², P. D. Patel², H. M. Patel^{1,2}, P. B. Patel^{1,2*}, J. M. Dhimmar², B. P. Modi²

¹C. B. Patel Computer College and J. N. M. Patel Science College, Bharthana, Surat ²Department of Physics, Veer Narmad South Gujarat University, Surat

*Corresponding author: p.b.patel2276@gmail.com

Abstract

Zinc Selenide (ZnSe) thin film was fabricated onto an ultrasonically clean glass substrate by physical vapour deposition method under high vacuum. The value of optical band gap was found to be 2.62 eV evaluated using absorption spectra. The low value of Urbach energy and the interference pattern in absorption spectra the film has a good surface smoothness, low defects and is uniformly deposited onto glass substrate. Also, the position of conduction band and valence band of ZnSe thin film was calculated using semi-empirical relation.

Introduction

The II–VI semiconducting compound has novel physical properties with wide range of optoelectronic applications due to its wide range optical band gap (1.4 eV-2.7 eV) and low electrical resistivity [1]. Among them, ZnSe has been recognized as a promising substitute material to CdS as buffer layer in Cu(InGa)Se₂ based hetero-junction solar cells [2]. So, it is important to study different properties of ZnSe which affects the performance of the material for various applications.

In the present work, ZnSe thin film was synthesized by thermal evaporation method. The optical absorption spectra within the wavelength range of 400 nm-1200 nm have been utilized to study the optical parameters such as energy band gap, Urbach energy and the locations of conduction band and valence band respectively.

Experimental detail

Thin film of ZnSe was fabricated under a vacuum of 10^{-5} mbar by a physical vapour deposition technique onto a glass substrate with the help of HINDHIV:15F6D system. Pure ZnSe powder (99.99%, Sigma Alrich, USA) was used as a source material and was kept in a boat made up of molybdenum and was evaporated at high temperature. The thickness and deposition rate were measured by quartz crystal monitor. The deposition rate was uniformly kept nearly about 3-5 Å/s throughout deposition process with substrate temperature of 473 K. The thickness of deposited ZnSe thin film is 10340 Å. UV-Visible spectra acquired using CARRY- Varian 300 (Australia) was

utilized for the optical characterization of ZnSe thin film.

Result and Discussion

The optical parameters of ZnSe thin film were studied in the wavelength range of 400 nm-1200 nm using absorption spectra as shown in Fig. 1. The crystalline nature of ZnSe thin film was confirmed by the interference pattern in the absorption curve and also by a sharp fall in absorption at the band edge.

Using the relation; $\alpha = 2.303$ A/t, the absorption coefficient (α) of the film was evaluated. Here, A is the absorption and t is thickness of the film. For allowed direct transition, the fundamental absorption relation corresponding to valence band-conduction band transition is specified as follows [3];

$$\alpha h v \propto (h v - E_g)^{1/2}$$
 a)

Where hv is the photon energy. A plot of $(\alpha hv)^2$ versus hv is represented in the Fig. 2.



Fig. 1. Absorption spectra of ZnSe thin film



Fig. 2. Plot of $(\alpha h \upsilon)^2$ versus h υ (inset: ln α versus h υ) of ZnSe thin film

The value of optical band gap was found by extrapolating the linear portion of the curve to $(\alpha h \upsilon)^2$ = 0. Due to the effect of quantum confinement, the evaluated direct band gap value found to be 2.62 eV in ZnSe thin film is slightly different from bulk ZnSe material. The density of the localized defect states is analysed by estimating the tail width. The relation between coefficient of absorption (α) and the energy of photon (hu) is given by [4];

$$\ln \alpha = \frac{hv}{E_u} + C \qquad \qquad b)$$

Where C is a constant and E_u is the Urbach energy. The plot of $\ln \alpha$ versus hu is linear near to the optical band edge as shown in inset of Fig. 2. The slope of this linear plot will yield the value of $1/E_{\mu}$ and hence giving the value of Urbach energy (E_n) calculated to be 86.28 meV for ZnSe thin film. The locations of conduction band and valence band of ZnSe thin film can be determined if the affinity energy of electron and the energy of ionization of the elements are known.

For ZnSe film, these positions is calculated by using the following relation [5]; $E_{CB} = E_e - X + 0.5E_a$

Where.

$$X_M = \frac{1}{2} (E_{EA} + E_{ion}) \tag{d}$$

c)

$$X_{ZnSe} = [(X_{Zn})^p x (X_{Se})^q]^{1/(p+q)}$$
 e)

Where, E_{CB} is the conduction band potential, E_e is a constant taken to be 4.5 eV [5], X is composition dependent energy parameter, E_{EA} is the affinity energy of electron and Eion is the ionization energy of the Zinc (Zn) and Selenium (Se) elements. Values of affinity energy of electron for Zn and Se elements are 20 kJ/mol and 195 kJ/mol respectively while the energy of ionization for these elements is 906.4 kJ/mol and 941 kJ/mol.



Fig. 3. Schematic diagram of valence band and conduction band position of Bulk ZnSe and ZnSe thin film

Energy parameter (X) and the potential of the conduction band (E_{CB}) as well as the potential of valence band (E_{VB}) of ZnSe film are noted in Table 1 and it is schematically represented in Fig. 3.

Table 1. Optical parameters of ZnSe thin film

Sample	Eg (eV)	X	Ecb (eV)	Evb (eV)
Bulk ZnSe	2.70	5.3164	-0.5336	2.1664
ZnSe Thin Film	2.62	5.3164	-0.4936	2.1264

Conclusion

Thin film of ZnSe are successfully fabricated by thermal evaporation method. Different optical parameters of ZnSe thin film are evaluated using optical absorption spectra and it was found that the thin film has high absorption. The pattern of interference in absorption spectra revealed that the film is uniformly deposited throughout the surface. The value of optical band gap of fabricated thin film was lower than the value its bulk counterpart due to confinement of particles. The low value of Urbach energy shows that the thin film has excellent surface smoothness with lower defects. Positions conduction band and valence band was traced.

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Induction Time Induced Modifications in Physical Properties of Chemically Grown Nanorystalline PbS Thin Films

N.M. Gosavi¹, K.R. Sali², S.R. Potdar³, R.A. Joshi⁴ and S.R. Gosavi^{2,*}

¹Department of Applied Science & Humanities, Govt. College of Engineering, Jalgaon-425001, ²Materials Research Laboratory, C.H.C. Arts, S.G.P. Commerce and B.B.J.P. Science College Taloda

Dist. Nandurbar-425413,

³UGC-DAE CSR, University Campus, Indore-452001,

⁴Department of Physics, Toshniwal Arts, Commerce and Science College, Sengaon Dist. Hingoli-431542

*Corresponding author: srgosavi.taloda@gmail.com

Abstract

Nanocrystalline lead sulfide (PbS) films are prepared on glass substrate by using simple, low cost chemical bath deposition (CBD) technique by varying the induction time. The induction time induced effects on physical properties are studied with the help of X-ray diffraction pattern (XRD), Raman spectroscopy and UV-Vis spectroscopy. From the XRD patterns, it can be seen that the as the induction time of thin films increased the nature of appearance turned into polycrystalline in nature with cubic phase, while the average crystallite size observed to be ~22nm. Raman spectrum analysis confirms that CBD method suits best for synthesis of stiochiometry nanocrystalline PbS thin films. The electronic transitions studied using the optical absorbance spectra shows that the absorbance coefficient increases with increase in induction time.

Introduction

Lead sulfide (PbS) is one of the semiconducting chalcogenides belonging to class IV-VI compound which attracts attention of researchers over the past few decades because of their novel electrical and optical properties originating from significant size dependent and tunable band gap [1], thus making it a potential candidate for application in photovoltaics [2], photodetector [3] and solar control coatings and display devices [2]. Recently, synthesis of PbS in nanostructured form have attracted much interest due to its size dependent properties for fabrication of possible devices. Also, as compared to other chalcogenides, a quantum confinement effect is more notable in PbS even for relatively larger particle sizes.

In this viewpoint, many researchers have shown a great interest in the synthesis of nanocrystalline PbS thin films by several physical and chemical methods [4], but chemical bath deposition (CBD) method has its own advantages over the others like large area deposition, ease of synthesis control, simple, low cost and user friendly method. Since very few research have been done in the context of studying the effect of induction time on physical properties of CBD deposited PbS thin films, we intend to study the modifications arising when the induction/nucleation time of PbS thin films is varied. These different thin films synthesized at different deposition time are characterized for structural, Raman spectroscopy and optical properties.

Experimental details

AR grade lead (II) acetate trihydrate $[(CH_3COO)_2Pb.3H_2O]$, thiourea $[(NH_2)_2CS)]$ and 25% ammonia (NH₃) were used for the preparation of nanocrystalline PbS thin films and glass was selected as the substrate.

For the synthesis of nanocrystalline PbS thin films, the chemical bath contains 20ml of 0.1M solution of (CH₃COO)₂Pb.3H₂O in which few drops of 25% ammonia slowly added for complex formation under constant stirring for 20 minute. Subsequently, 20ml of 0.1M solution of (NH₂)₂CS was added into this mixture and stirred well for few minute. Then, this reaction mixture of dark brownish color was transferred into a 100ml beaker, in which the well cleaned glass substrates were kept vertically. The deposition was carried out at constant temperature $(50^{\circ}C)$ by keeping the chemical bath in a thermostat water bath for different time durations i.e. 20, 30, 40, and 50 min. Such chemically grown films were examined and characterized by means X-ray diffraction (D8 Advanced, Powder XRD), Raman spectroscopy (Horiba Jobin-Yvon HR 800, JAPAN), UV-visible light spectrometer (JASCO V-630).

Results and Discussion

In order to study the growth mechanism, we have studied the variation of the film thickness as a function of deposition time for chemically synthesized nanocrystalline PbS thin film. The deposition time varied between 20 to 50 min with the interval of 10min. The trend observed shows that the film thickness increases upto deposition time of 40 min, thereafter it starts slight decrease may be due to the excess ion stabilizes the complex ions and reduces the growth rate and hence decrease in film thickness. The PbS film has maximum terminal thickness is of the order of 734 nm.

XRD was used to confirm the crystalline structure of nanocrystalline PbS thin films deposited on glass substrates at different deposition time. For all films, cubic structure characterized with (1 1 1) and (2 0 0) planes as preferred orientation (JCPDS No. 78-1901). As a result of increase in deposition time and film thickness, there is a change in the intensity of the peaks were observed. The film deposited for 20, 30 and 40min shows atmost similar intensity of the peaks while for film deposited for 50 min reflects variation in intensity and dissimilation of peaks. It is observed that the crystallite size increases from 18.04 to 22.20 nm as deposition time increases from 20 to 40 minute and again it decreases to 16.03 nm for higher deposition time.



Fig. 1.XRD patterns of PbS thin films for deposition time i.e. a) 20 min, b) 30 min, c) 40 min, and d) 50 min.

Fig. 2 shows typical Raman spectra of nanocrystalline thin films synthesized with 20 minute deposition time. From Raman spectra, we can notice that there are two Raman modes in which intense modes are situated at 95 and 142.78 cm⁻¹. The major Raman mode positioned at 95 cm⁻¹ are related to combination of Longitudinal and Transverse (LA+TA) acoustic phonon modes while the mode positioned at 142.78 cm⁻¹ are related to combinational Longitudinal Optical (LO) and Transverse Optical (TO) acoustic bands in PbS thin films [5]. This study confirms the prepared sample consists of pure PbS without the presence of sulphates.

The optical absorbance of the nanocrystalline PbS thin films was studied in the wavelength range of 500 nm to 1000 nm. It is observed from the inset of fig. 2 that the increase in deposition time (till 40 min) increased the absorbance of nancrystalline PbS thin films. This could be due to increase in the crystallite size at higher deposition time as evident from XRD study. Further, at higher deposition time i.e. at 50

min, the absorbance of nancrystalline PbS thin films is found to be decreased. The high absorbance characteristics nancrystalline PbS thin films in the visible region indicate that the deposited material may play vital role in thin film solar cells as a good absorber layer [6].



Fig. 2.Typical Raman spectra of PbS thin films. (Inset figure shows plot of absorbance verses wavelength)

Conclusion

PbS thin films were deposited successfully using CBD technique by varying the induction time. From XRD studies, it is confirmed that obtained films have a cubic phase with (111) and (200) as preferential orientation and films are nanocrystalline in nature. The Raman study confirms formation of pure PbS without the presence of sulphates. The absorption spectrum shows the variation of absorption edge with the deposition time. These results suggest that the induction time for obtaining the good thin film of PbS could be 40min.

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Proton Ion Irradiation Induced Changes In Optical And Morphological Properties Of As₄₀Se₅₀Sb₁₀ Thin Films

Deviprasad Sahoo^{1*}, S. Sahoo², R. Naik¹

¹Department of Engineering and Materials Physics, ICT-IOC, Bhubaneswar, 751013, India ²Institute of Physics, Bhubaneswar, 751004, India

*Corresponding author: deviprasad.sahoo2019@gmail.com

Abstract

The impact of proton irradiation (30 KeV) upon the optical and morphological properties of thermally evaporated As40Ses0Sb10 thin films was observed in our study. The transmittance and RMS roughness of the irradiated films significantly increased with higher fluence. The optical bandgap and refractive index changed with fluence. The tuning of different optical parameters and surface modifications with proton ion fluence are suitable for optical applications.

INTRODUCTION

Ion irradiation, photo irradiation, thermal annealing are the most familiar methods which are used as a tool for tuning the structural, optical, and morphological properties of the material. The ion irradiation that depends upon the ion species, ion energy, and properties of the target material is most useful to study these changes [1]. It is either based on low-energy ions (energy ranging from few tens of KeV to hundreds of keV) or high energy ions (energy ranging from few tens of MeV to GeV) for material modifications. The low energy ion undergoes elastic collision while interacting with the matter that leads to the material modifications due to the nuclear energy loss. Whereas, the high energy ion undergoes inelastic collision and transfers energy to the lattice that results in material modifications due to the electronic energy loss [2]. Ivan et al. have studied the deuterium interaction upon the optical parameters of AsSe films due to their sensitivity towards relatively low energy [3]. The influence of 120 MeV Ag swift heavy ion on As-Se-Bi films showed significant changes in the optical, electrical as well as the structural changes [2]. Similarly, the low energy 40 keV Ag ion irradiation in Bi/GeSe2 film formed new Bi₂Se₃ phases [4]. However, the proton ion irradiation on such films is very few and this encouraged us to investigate the impact of low-energy proton irradiation on thermally evaporated As₄₀Se₅₀Sb₁₀ chalcogenide thin films. The choice of As-Se-Sb thin films lies in their application for optical switching and memory devices [5].

EXPERIMENTAL PROCEDURES

The bulk $As_{40}Se_{50}Sb_{10}$ samples were prepared by the conventional melt quenching method. Thin films of thickness ~800nm were prepared from the bulk by thermal evaporation method a vacuum of under 10^{-5} Torr. The thin films were irradiated with 30 KeV proton ion using low energy ion implanter at two different fluences i.e. 5×10^{15} ions/cm² and 5×10^{16} ions/cm² under high vacuum pressure of 10^{-11} Torr inside the chamber. The structural study was done by X-ray diffractometer (XRD) and the optical measurements of the proton irradiated samples were

performed by UV-VIS spectrophotometer over the range of 550-1100 nm. The topographic changes were investigated by atomic force microscope (AFM).

RESULTS AND DISCUSSION

The transmittance (T) and reflectance (R) spectra of asprepared and proton irradiated samples at different fluence are shown in fig. 1. The transmittance value increased and reflectance decreased after proton irradiation. The absorption edge of 5 x 10^{15} ions/cm² irradiated film shifted towards higher wavelength region and again changed to lower wavelength region upon 5 x 10^{16} ions/cm² fluence which infers the ion irradiation impact. Such changes influenced the absorption coefficient and optical bandgap of the film. The value of absorption coefficient (α) was calculated by using the relation,

$$\alpha = (1/t) \ln \left[(1-R)^2 / T \right]$$
 (1)

where t, R, and T are the thickness, reflectance, and transmittance of the films.



Fig. 1. Transmittance and reflectance spectra of as-prepared and proton irradiated thin films

The obtained absorption coefficient is of the order of 10^4 cm⁻¹ that agrees well with most of the results. The Tauc relation were used to evaluate the indirect optical bandgap of the material by using the equation [6]

$$(\alpha h v)^{1/2} = B^{1/2} (h v - E_g)$$
 (2)

where h, v, E_g and B are the Plank's constant, frequency, optical band gap, and Tauc parameter respectively. The straight-line fitting of dependence between $(\alpha hv)^{1/2}$ and photon energy (hv) provided the indirect optical bandgap values such as 1.73 eV (as-prepared), 1.62 eV (5 x 1015 ions/cm²), and 1.65 eV (5 x 10¹⁶ ions/cm²) for the thin films [Fig.2]. The modifications in localized energy levels due to the change in disorder by ion irradiation effect caused the change of absorption edge and optical bandgap [2,4]. The Tauc parameter $(B^{1/2})$ gives the information regarding the degree of disorder. The linear refractive index of the films was obtained from the Swanepoel envelope method [7]. The abrupt reduction in refractive index displays the impact of proton irradiation and increases with further increasing the irradiation fluence. The increase in refractive index is due to the structural modifications in localized defect states as a result of the proton irradiation effect [8].



Fig. 2. Bandgap calculation and variation in refractive index (inset) for the films.

The XRD patterns of the studied film (Fig.3) shows the amorphous nature of the films after ion irradiation also. This signifies the change in disorder with ion fluence. The AFM analysis provides the 3D profile of the topography of a sample by measuring the forces between sharp probes and surfaces at a very short distance. The 5 µm x 5 µm threedimensional scans of as-prepared and proton irradiated films (fig.3) shows the impact of the ion irradiation upon its topography. The RMS roughness of the asp, 5 x 10^{15} ions/cm^{2,} and 5 x 10¹⁶ ions/cm² fluence samples were found to be 6.125 nm, 8.987 nm, and 9.824 nm respectively. It clearly shows the impact of the proton-irradiation with increasing the fluence and represents the overall increase in roughness of the samples. It also indicates that the energy of the projectile ion is sufficient enough for material surface modification [4]. Such type of study indicates the lowenergy proton irradiation can also act as a useful tool for material surface modifications. This changes in optical parameters in such films can be used in optical applications. It would be also interesting to observe the tuning of nonlinear optical parameters via low-energy ion irradiation.



Fig. 3. XRD and AFM images of as-prepared and proton irradiated thin films

CONCLUSION

In summary, we have studied the impact of proton irradiation on thermally evaporated $As_{40}Se_{50}Sb_{10}$ thin films. The change in transmittance and absorption coefficient with different ion fluence tuned the refractive index and optical band of the as-prepared film. The amorphous structure remained unaffected by ion irradiation while the surface roughness increased. The disorder in the film influenced the density of defect states in the localized state region and changed the bandgap.

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Bovine Serum Albumin/Lysozyme (BSA/Lys) Complex Thin Film Raktim Jyoti Sarmah^{*}, Sarathi Kundu

Soft Nano Laboratory, Physical Sciences Division, Institute of Advanced Study in Science and Technology, Vigyan Path, Paschim Boragoan, Garchuk, Guwahati, Assam 781035, India.

*Corresponding author: raktimsarmah1@gmail.com

Abstract

The protein complex formed by mixing two globular proteins, bovine serum albumin (BSA) and lysozyme (Lys), is studied using Langmuir-Blodgett method. The surface pressure (π)-specific molecular area (A) isotherm of the monolayer formed at the airwater interface at a subphase pH \approx 9.0 shows a rise in surface pressure at $A \approx 52 \text{ mm}^2$ /molecule and a plateau-like feature is observed at $\pi \approx 18 \text{ mN/m}$. Atomic force microscopy (AFM) gives an average height of 1.26 nm and a total height of 4.28 nm, whereas x-ray reflectivity analysis gives a thickness of ≈ 41 Å of the deposited complex film in single up-stroke. Thus a stable protein complex film can be formed at the air-water interface which may have potential applications.

Introduction

The complexation between two oppositely charged biopolymers has gain a lot of attention in the recent decade due to its more desirable physicochemical properties than exhibited by the individual biopolymers. The significance of these complexes can be seen in many naturally occurring biological systems, such as providing outer shell coating of sand castle worms and mussels, in biomedical applications such as tissue engineering and drug delivery, as biodegradable films in food industry etc. [1]. Although a wide variety of complex systems such as protein-polymer, nucleic aciddendrimer, nucleic acid-polymer etc. have been investigated and reported, however, complexes made of oppositely charged proteins or protein-protein complexes have emerges as a new topic of interest to many researchers [2]. Such heteroprotein complex formation is mainly driven by the electrostatic interactions and is a fully reversible process [3]. The formation of these complexes are greatly influenced by the variation in pH and also ionic strength as they can affect the surface charge density of the molecules. Complexes formed between globular proteins, such as bovine serum albumin (BSA) and lysozyme (Lys) are widely studied as they proved to be a versatile agent for many technological applications when used as a microencapsulation agent, besides adding functional and nutritional value to a product. Lysozyme is a globular glycoprotein found in high concentrations in egg whites. It has an isoelectric point (pI) around 10.7 with various antimicrobial properties [4]. On the other hand, BSA is a globular protein found in abundance in blood plasma and is extensively studied due to its structural similarity with human serum albumin (HSA). It has

an isoelectric point (pI) around 4.8 [5]. In this work, Langmuir monolayer of BSA-Lys protein complex is formed, and their structure and morphology is studied after depositing on solid surface.

Experimental Details

The BSA-Lys complex was prepared by dissolving the desired amount of BSA and lysozyme sample in ultrapure water, and by changing the pH of the solution to pH \approx 9.0. Required amount of the complex solution was spread on the water surface in a double barrier Langmuir trough made of Teflon (Apex Instruments). Monolayer formed at the airwater interface was transferred onto silicon substrates at a control subphase pressure of 18 mN/m, at a room temperature of $\approx 24^{\circ}$ C and at a subphase pH ≈ 9.0 . Surface topography of the deposited complex films were analysed using an atomic force microscopy (NTEGRA Prima, NT-MDT Technology) in semicontact mode. X-ray reflectivity measurements were done using an X-ray diffractometer (XRD) setup (D8 Advanced, Bruker AXS).

Results and Discussion

The effect of pH on the turbidity while forming the complex is visible within the pH range of 8 – 10.5, however, maximum elevation in the turbidity is obtained at a pH of around 9.0 due to the favourable electrostatic interaction between the protein molecules. Surface pressure (π) - specific molecular area (*A*) isotherm of the complex monolayer formed at the air-water interface at a subphase pH \approx 9.0 is shown in fig.1. As the area per molecule goes on decreasing, the surface pressure increases and a rapid increase in the surface pressure is observed at $A \approx 52$ nm²/molecule. A plateau-like feature is also visible in



Fig. 1. Surface pressure (π) - specific molecular area (*A*) isotherm of BSA-Lys complex at pH \approx 9.0.

the isotherm at a higher surface pressure of $\pi \approx 18$ mN/m as seen from the fig.1. Such plateau-like feature indicates the formation of molecular rearrangement or alignment around that point, thereafter the surface pressure increases nearly linearly up to the maximum barrier position.



Fig. 2. (a) AFM image of BSA-Lys complex film (scan area: $1x1\mu$ m²) (b) X-ray reflectivity data (circles) and corresponding fitted curves (solid line) deposited on Si (001) substrate at $\pi = 18$ mN/m at a subphase pH ≈ 9.0 .

The in-plane morphology of the deposited complex film is characterized by AFM. Deposition is carried out in a single up-stroke of the hydrophilic silicon substrate through the monolayer covered water at a subphase pH of \approx 9.0 and at a control surface

pressure of 18 mN/m by LB method. Fig.2 (a) shows the AFM image of the complex film having nearly globular-like morphology. An average height of 1.26 nm is obtained from the deposited film from the height histogram (inset of the image), whereas a total height of 4.28 nm is obtained from the total height scale or Z-scale (right hand side of the image).

Out-of-plane structure of the complex film is obtained from the x-ray reflectivity (XRR) analysis. XRR data (open circles) and the corresponding fitted curve (solid line) for the complex film are shown in fig.2 (b). The electron density profile (EDP) extracted from the XRR data is shown in the inset of fig.2 (b). A BSA-Lys complex film of thickness of ≈ 41 Å is obtained from the EDP.

Conclusion

The BSA/Lys complex monolayer is studied at the air-water interface at a subphase pH of around 9.0 by Langmuir-Blodgett method. The surface pressure (π) – specific molecular area (A) isotherm of the monolayer shows a rapid increase in the surface pressure at $A \approx 52 \text{ nm}^2/\text{molecule}$ and a plateau-like feature at $\pi \approx 18\text{mN/m}$. The complex monolayer is deposited on hydrophilic Si (001) substrates at a control surface pressure of 18 mN/m for further study. AFM image shows globular-like morphology of the deposited film and an average and total height of 1.26 and 4.28 nm respectively. EDP extracted from the XRR analysis shows the thickness of the complex film is around 41 Å, which nearly match with the AFM result.

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Influence Of The Substrate Temperature On The Structural, Optical, And Morphological Properties Of (101) Oriented ZnSe Thin Films For Solar Window Applications

Ganesha Krishna V S, and Mahesha M G*

Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Udupi, 576104 India

*Corresponding author: mahesha.mg@manipal.edu

Abstract

Structural, optical, and morphological studies of spray deposited zinc selenide (ZnSe) thin films at various substrate temperatures are reported. Films were characterized using energy dispersive analysis (EDX), x-ray diffractogram (XRD), and UV-Vis spectra. ZnSe thin films showed a strong preferred (101) orientation with an excellent crystallite size of 57.4 nm at a deposition temperature of 673 K. Composition of Se/Zn was 0.8. A transmittance of nearly 75% was observed in the visible regime, with a wide band gap of 2.7 eV; the prepared samples were assessed for window layer in solar cells.

Effect of Oxygen Annealing on Ultrafast Carrier Dynamics of Pr_{0.5}Ca_{0.5}MnO₃ Thin Films

Monu Kinha, Malay Udeshi, Rahul Dagar, and D. S. Rana^{*}

Department of Physics, Indian Institute of Science Education and Research, Bhopal, M. P., 462066

*Corresponding author: dsrana@iiserb.ac.in

Abstract

We report the effect of oxygen annealing and epitaxial strain on the ultrafast carrier excitation and relaxation mechanism of holedoped manganite $Pr_{0.5}Ca_{0.5}MnO_3$ (PCMO) as investigated by optical pump-Terahertz (THz) probe measurements. PCMO thin films of 60 nm thickness, both pristine and oxygen annealed, were prepared using pulsed laser deposition technique. Transient THz transmittance is negative for both the films. As fitted by the sum of exponentials, the fast relaxation time constant is found to be fluence independent while the slow relaxation time constant decreases with pump fluence for both the films and is less for the annealed film suggesting that the relaxation in PCMO strongly depends on strain and oxygen content.

Structural and Magnetic Properties of Bi₂FeReO₆ Double Perovskite Thin Films

Rahul Dagar, Jayaprakash Sahoo, Monu Kinha, and D. S. Rana*

Department of Physics, Indian Institute of Science Education and Research, Bhopal, M. P., 462066

*Corresponding author: dsrana@iiserb.ac.in

Abstract

Ferromagnetic insulators (FMI) are the most promising candidates for the application in the field of dissipation less electronics as well as spintronics. Devices operating at practical conditions are highly desirable. In this context, we have examined the effect of epitaxial strains on magnetism of Bi_2FeReO_6 (BFRO) thin films prepared by the pulsed laser deposition technique. The effects of crystallographic orientations on structural and magnetic properties were investigated. Our studies reveal that the magnetization of these thin films is strongly dependent on tensile and compressive strains as well as on crystallographic orientation along strain is induced.

Optimization of Spray deposited Ca-Doped SnO₂ thin films for Ethanol Gas Sensor Application

R. Kavitha, G. Karthi², R. Chellakumar², K. Ravichandan^{2a)}, and R. Ramarajan^{1b)}

¹Department of Materials Science, University of madras (Guindy Campus), Chennai, India 600025 ²Department of Nuclear Physics, University of madras (Guindy Campus), Chennai, India 600025

*Corresponding author: ravi21068@unom.ac.in (a), ramarajan.2005@gmail.com (b)

Abstract

The Ca-doped SnO₂ (CTO) thin films are spray deposited on glass substrate as a function of solution concentration for the ethanol gas sensor Applications. The X-ray diffraction pattern of the film deposited from 0.2 M, 0.5 M, and 1.0 M solution concentration possesses the SnO₂ phase with a tetragonal crystal structure. The surface morphology of the spray deposited thin films confirms nanoparticle formation with the lower surface roughness. The ethanol gas fabricated using a 0.5 M solution (CTO-2) exhibits the maximum sensitivity of 69.7 % with a response and recovery time of 114/98 s. Hence, the optioned results confirm the applicability of CTO thin film as an ethanol gas sensor.

Introduction

Thin film-based Gas Sensor (GS) is an indispensable device for modern technology. It is widely used in industries, factories, research labs, and environment monitoring due to many benefits such as controlling toxic gas level, reducing the chemical explosions, and food safety.¹ The thin film-based gas sensor is the resistive devices in which resistance of the film changed in response to adsorbed gases.¹ Recently, doped SnO₂ thin film has been explored for different gas sensors applications due to its easily tunable physicochemical properties and also SnO₂ source material is earth-abundant element.² More interestingly, it is easy to get high quality SnO₂ thin film by adjusting the several deposition parameters. Several researchers investigated the doped SnO₂ film for different gas sensor applications.² However, For the better detection limit, selectivity, and low response/recovery time still need to improve for the better sensitivity of the SnO₂ based GS using facile deposition methods and doping process.³

In this article, we reported the optimization of Ca doped SnO_2 (CTO) films on glass substrate by a cost-facile spray pyrolysis technique as a function of solution concentration. Further, optimized CTO thin films structural, surface, optical, electrical transport properties are characterized by various analytical techniques. Finally, optimized CTO film suitability were tested for the ethanol gas sensor application.

Method and Characterization

Stoichiometric amount of $SnCl_2 2H_2O$ and $CaCl_2 2H_2O$ (2, 5, and 10 wt. %) were weighted for prepare 0.2 M, 0.5 M, and 1.0 M solutions. An 80 ml of ethylene glycol and, 2 ml of HCl were added into each stock solutions and stirred well until a

homogenous transparent precursor solution. These precursor solutions were used to form a CTO thin film onto ultrasonically cleaned glass substrates. Totally 150 numbers of spray deposited for each solution. The duration of the spray about 0.5 s in an interval of 30 s, and substrate to nozzle distance about 18 cm. Films deposited at three different solution of 0.2 M, 0.5 M, and 1.0 M were labelled as CTO-1, CTO-2, and CTO-3 respectively. Further, these films are inspected by characterization techniques such as XRD, and SEM analysis. Finally, the CTO thin film suitability tested for homemade gas sensor setup.

Results and discussion

Structural analysis

Figure 1a shows the XRD of the CTO films with tetragonal crystal structure matched well with the standard JCPDS file No: 41-1445 with the space group P42/mnm.¹ No secondary peak of dopant element Ca, Ca₂O₃ and or Ca₂SnO₄ are showed in the XRD patterns indicating that the perfect incorporation of Ca ions into the SnO₂ interstitial lattice site.⁴ However, the atomic radii of Sn^{+4} (0.69 Å) is much lower than the ionic radii of Ca^{2+} (1.06 Å). The intensity of the peaks increased as a function of solution concentrations are shown in Fig. 1a. With increasing solution concentrations, the peak position shifts to lower angle side (Fig. 1b). Similar trend was also reported for Sb and Ba-codoped SnO₂ thin film.⁴ The average crystallite size (L) of the films was estimated using Scherrer's formula and the values are given in Table 1. The incorporation of Ca into SnO₂ lattice site may also influence the lattice parameter. The small variation in lattice parameter causes more variation in crystallite size.⁴



Fig. 1. XRD patterns of the CTO thin films (a), peak shift of the (110) plan (b).

Surface morphology analysis

The SEM images of the spray deposited CTO thin films shown in Fig. 2 a, b, c and its exhibit nanoparticle surface morphology with significant variation upon solution concentrations. The particle size of the films was also found increase upon solution concentrations. The size of the particulates on the surface of the CTO-1 film was found to be smaller compared to other films. The elemental mapping confirmed the presence of Sn, O, and Ca in desired stoichiometric ratio with uniform distribution over the entire region without segregation or clustering (Fig.2 d, e, f).



Fig. 2. SEM and elemental mapping of CTO films.

Ethanol Gas sensor Analysis

Ethanol gas sensing properties of as deposited CTO films were studied at the operating temperature of 100 °C with desired ethanol concentration of 100 ppm. Sensitivity (S %) is estimated by measuring the change in resistance of the films when purged with ethanol.² The sensitivity of the sensor measured by standard gas sensor equation.¹ The operating temperature is an important parameter which determines the response and recovery period of the sensor.¹ To determine the optimal temperature of operation of the sensors, we first studied the response (T_{res}) and recovery (T_{rec}) time of the sensors at 100 °C (Fig. 3). Maximum sensitivity obtained in the CTO-2 film of 69.7 % for 100 ppm with the response/recovery

time of 114/98 s (Table 1). The CTO thin films show in significant variation in sensitivity due to its variation of structural and surface properties of the films.³



Fig. 3. Ethanol response of CTO thin films at $100 \,^{\circ}$ C with an ethanol concentration of $100 \, \text{ppm}$ (a).

 Table 1. Structural and gas sensitivity properties of CTO thin films.

Films	(L) Size	Tres (s)	Trec (s)	S %
CTO-1	62.29	173	212	20.4
CTO-2	73.81	114	98	69.7
CTO-3	96.33	129	90	53.4

Conclusion

In summary, Ca-doped SnO₂ thin films have been deposited by facile spray pyrolysis. The structural and surface properties of the films are investigated as a function of solution concentrations. The applicability of the CTO thin film as an ethanol gas sensor has been tested at 100 °C. The obtained results have provided several clues for further enhancing sensitivity of the CTO film in the near future.

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In-situ RHEED study of reactively sputtered ScN thin films

Susmita Chowdhury¹, Rachana Gupta¹, Yogesh Kumar², Shashi Prakash¹ and Mukul Gupta^{2*}

¹Applied Science Department, Institute of Engineering and Technology, DAVV, Indore, 452 017, India, ²UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India

*Corresponding author: mgupta@csr.res.in

Abstract

We report a nascent real time structural analysis of reactively sputtered ScN thin films through in-situ RHEED. Samples were grown on single crystalline MgO (001) substrates at different substrate temperatures (T_s). Notably, at room temperature, the adatom mobility was insufficient leading to a polycrystalline growth. However, increasing the T_s to 523 and 773 K enhances the crystalline growth and self-sustaining the epitaxial nature along the [100] azimuth up to a comparatively high thickness. However, at T_s = 973 K, resulting films again show the polycrystalline growth due to N out-diffusion leading to a N-deficient Sc-N phase.

Oxygen Pressure dependence of the growth of La_{0.66}Sr_{0.34}MnO₃ thin films and their magnetic anomalies

Ankita Singh, Ram Prakash Pandeya, Srinivas C Kandukuri, and Kalobaran Maiti*

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, India 400005 *Corresponding author: <u>kbmaiti@tifr.res.in</u>

Abstract

We have setup a ultra-high vacuum pulsed laser deposition system and have grown La_{0.66}Sr_{0.34}MnO₃ films on SrTiO₃ (001) substrate under different oxygen partial pressures. The samples show good crystallinity and mosaicity. The lattice parameter of the films decreases with the increase in oxygen pressure. Curie temperature, T_C of the deposited films are found to be below the room temperature which is much lower than the reported values for both bulk and thin film samples. Interestingly, *M*-*H* isotherm at 300 K shows clear hysteresis. Such anomalous behavior indicates the presence of some magnetic order even above T_C of this system.

Impact of Post MgI₂ Treatment on Properties of CdS Films for Solar Cells

Suman Kumari^{1,2,*}, D. Suthar², Himanshu², S.L. Patel², N. Kumari¹ and M.S. Dhaka²

¹Department of Chemistry, Mohanlal Sukhadia University, Udaipur-313001, India

²Department of Physics, Mohanlal Sukhadia University, Udaipur-313001, India

*Corresponding author: <u>pgsumangodara@gmail.com</u>

Abstract

The polycrystalline pristine thin films consist of large amount of grain boundaries which are detrimental for devices and need passivation by CdCl₂ chloride treatment. The toxic nature of CdCl₂ emphasizes to expose its alternative compounds, and therefore in this study, an impact of post deposition MgI₂ (Magnesium iodide) treatment on the structural, optical and electrical properties of thermally evaporated CdS thin films is undertaken. XRD patterns reveal that the CdS thin films consist of hexagonal phase with (110) preferred orientation where the crystallite size is observed in range of 37-48 nm. The electrical analysis showed the linear change in current with voltage with decreased conductivity. Optical study demonstrated that direct optical energy bandgap of MgI₂ passivated CdS films is increased from 2.2 to 2.5 eV with temperature. Thus, MgI₂ treatment has influenced the properties of CdS films at a great deal, and consequently, CdS thin films annealed at 200°C are found appropriate for window layer in Cd-based thin film solar cells.

Keywords: Cd-based thin films; Thermal evaporation; MgI2 treatment; Physical properties; Solar cells

Introduction

Cadmium sulfide (CdS) is a fascinating and building block material for the fabrication of various optoelectronic and photovoltaic devices due to its peculiar characteristics like high transmittance, low absorbance, direct optical band gap of ~2.42 eV, high electron affinity, n-type conductivity, high chemical stability etc. It is widely used as window layer in CdTe and CIGS based solar cells in order to transmit maximum irradiance to absorber layer concerned [1-2]. In order to develop the CdS thin films, various deposition techniques are available such as resistive heating thermal evaporation, spray pyrolysis, electrochemical, chemical bath deposition, sputtering, closed spaced sublimation etc [1-5] where the thermal evaporation is easy to handle and provide high quality films with control on deposition rate. The pristine polycrystalline thin films usually carry defects such as grain boundaries which behave as trap states for charge carriers. Halide treatment is known to be a crucial step in order to reduce these defects and enhance the physical properties of Cd-based thin films for solar cell applications [6]. An extensive work is undertaken on exploration of chloride treatment using CdCl₂, MgCl₂ and NH₄Cl while the impact of other halogen atoms (X=F, Br, I) and subsequent halide treatment (CdX₂, MgX_2) is still unexplored so far [3, 7-8]. In the present study, as an alternative to chlorides, the effect of MgI₂ activation on CdS films is undertaken in order to improve the physical properties for solar cell applications.

Experimental Details

The CdS thin films were grown on pre cleaned glass and Indium doped Tin oxide (ITO) glass substrates using thermal vacuum evaporator (HHV SMART COAT 3.0) under the high vacuum of 2×10^{-5} mbar that was attained with the help of rotary and diffusion pumps. Prior the deposition, substrates, substrate holder, vacuum chamber and boat were cleaned by acetone and iso-propanol to get

rid of any contamination. During the deposition, the substrate holder was continuously rotated for achieving uniform films. The thickness and average growth rate of deposited thin films were found as 200 nm and 5-6Å/sec respectively which were measured with the help of inbuilt digital thickness monitor (DTM-101). The pristine CdS films were subjected to 0.2M MgI2 treatment followed by annealing in temperature range of 100-300°C for one hour in a muffle furnace (SONAR) and then these films were cleaned by hot DI water for 15 minute at 50°C. The crystallographic study was performed in the 2 theta range of 20-80° by Rigaku Ultima-IV X-ray diffractometer having CuK_a source (λ =1.5406Å) whereas an Agilent source-meter (B2901A) was used to measure the current and voltage via two probe method. The Shimadzu (UV-1780) UV-Vis. spectrophotometer was used to analyze optical properties in wavelength range of 300-900 nm.

Results and Discussion

The XRD patterns of pristine and treated films are shown in Fig. 1(a) where hexagonal phased diffraction peaks are originated at diffraction angles (20) of 29.36°, 38.14°, 44.44°, 47.50°, 64.93° and 77.81° corresponding to the (101), (102), (110), (103), (203) and (204) orientations, respectively which are indexed according to JCPDS card number 41-1049. The obtained peaks showed good agreement with previously published works [7, 9]. The intensity of preferred orientation (110) is increased slightly with MgI₂ annealing temperature which demonstrates improvement in crystallinity of films. However, no change is observed in the 2θ value i.e. position of preferred peak. Various crystallographic parameters are calculated using formulae concerned [3,9] and charted in Table 1. The lattice constant (a) of MgI₂ treated CdS films is found almost constant (4.07-4.08Å) indicating minimum lattice mismatching with substrate. The obtained lattice constant is found in good agreement with the standard one (4.14Å) and previously reported work [9].

Samples	2θ(°)	a(Å)	D (nm)	δ×10 ¹⁴ m ⁻²
Pristine	44.48	4.07	37	7.3
100 °C	44.48	4.07	41	5.9
200 °C	44.48	4.07	48	4.3
300 °C	44.47	4.08	48	4.3

TABLE 1. Structural parameters of pristine and MgI₂ treated CdS films corresponding to preferred orientation.

The pristine thin film indicates the lowest crystallite size and MgI₂ treatment enhanced the grain size from 37 to 48 nm which is possibly due to strong passivation of grain boundaries by segregations of Iodine atoms. The appearance of different peaks (i.e. polycrystalline nature) of CdS films might be due to MgI₂ induced recrystallization. The decrement in dislocation density and microstrain further support the better crystallization through MgI₂ treatment [10].

The impact of MgI_2 treatment on electrical properties of CdS films is undertaken by performing current (I) - voltage (V) characteristics in -5V to +5V range (Fig. 1(b)) where linear behavior notifies the ohmic nature of thin film contacts. The I-V curves for pristine and 100°C annealed films are appeared almost similar that revealed to the less effect of iodide treatment at such low temperature [11]. The conductivity of CdS films is found to be decreased with increase in temperature of MgI₂ passivation.



Fig. 1. (a) XRD patterns and (b) I-V curves of MgI₂ treated CdS thin films.



Fig. 2. Variation in (a) Optical transmittance and (b) Tauc's plots for MgI₂ treated CdS thin films.

A sharp increment in optical transmittance is seen in wavelength range of 350-525 nm then transmittance is slightly varied upto 600 nm, and became constant in 600-800 nm range. The annealing of MgI₂ treated films enhances the transmittance and reduces the absorbance upto 200°C, however, the treated films showed lower transmittance vis-à-vis to pristine films. Fig. 2 (b) shows Tauc's plots which indicated that the optical energy band

gap is increased from 2.2 eV to 2.5 eV. The MgI_2 might introduce new defect levels owing to difference between ionic radii and electronegativity of CdS and MgI_2 which might promote free electrons in the crystal. The free electrons could generate carrier gradient (Moss-Burstein effect). The Moss-Burstein effect demonstrates the mechanism for bandgap increment [7]. The direct energy band gap of CdS films activated at 200°C is observed as 2.41 eV which is near to bulk counterpart (2.42 eV) [4].

Conclusions

The present study highlighted the influence of MgI₂ treatment on the physical properties of thermally evaporated CdS thin films having thickness 200 nm. All the CdS thin films (pristine and MgI₂ treated) demonstrated hexagonal (wurtzite) phase with (110) preferred orientation. The grain growth is observed for CdS films with treatment temperature. The optical band gap is blue shifted (towards lower wavelength) from 2.2 to 2.5 eV with increasing temperature. The MgI₂ treatment led to variation in transmittance and absorbance. In this way, the MgI₂ treatment significantly affected the properties of CdS thin films. The findings showed that the 200°C annealed films have potential candidature to be used as window layer in the development of high efficient Cd-based thin film solar cells.

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Annealing Induced Properties of ZnTe:Cu Back Contact Layer for Solar Cells

Deepak Suthar^{1,*}, Himanshu¹, S.L. Patel¹, A. Thakur², and M.S. Dhaka¹

¹Department of Physics, Mohanlal Sukhadia University, Udaipur-313001, India ²Department of Basic and Applied Sciences, Punjabi University, Patiala-147002 India *Corresponding author: deepusuthar1993@gmail.com

Abstract

In order to realize the entire potential to the CdTe thin film solar cells, the development of environmentally stable, low-resistive, and easily manufactured back contact is required. The Cu doped zinc telluride i.e. ZnTe:Cu interface layer is most suitable for back contact applications between the CdTe and the metal contact. The annealing is proved to be an effective way for improving the properties of films. Therefore, the present work demonstrates the physical properties of ZnTe:Cu 5% films where films are deposited thermal evaporation technique and annealed in air ambient in 100-300°C temperature range. The developed films showed (103) preferred orientation where the crystallite size is found in the range of 38-44 nm. The transmittance of ZnTe:Cu 5% films is varied with temperature and optical energy band gap is estimated in the range of 2.71-2.80 eV. The electrical analysis of ZnTe:Cu 5% films confirmed their ohmic behavior.

Keywords: ZnTe:Cu thin films; Back contact layer; Solar cells; Physical properties.

Introduction

In the past few years, the solar cells and modules incorporating thin films of CdTe absorber have shown substantial improvements in the conversion efficiency. One challenging task to further improve the performance of CdTe solar cell is development of back contact with low resistance and high stability. The CdTe has a large electron affinity (χ =4.5eV) and low carrier density, therefore, CdTe absorber layer contributes to the formation of a back contact Schottky barrier. This barrier limits hole collection at the back contact, causes losses in open circuit voltage and fill factor. The CdTe absorber needs the metal contact materials having work function >5.9 eV to construct an ohmic contact on p-type CdTe since the direct metallic contact with low work function leads to development of Schottky barrier related negative band bending at the back contact region [1, 2]. To address this problem, thin interfacial back contact layer is grown between the metal contact and the CdTe absorber layer. The ZnTe is one of the potential materials for the back contact layer since it has suitable energy band gap (2.26 eV) and high chemical stability where the Cu doping could be done to improve the conductivity. The valence bands of ZnTe and CdTe could be easily aligned in order to enabling facile hole transport [3]. Therefore, in the present work, the ZnTe:Cu 5% films are developed using thermal evaporation and their properties are investigated as a function of annealing temperature.

Experimental

The ZnTe:Cu 5% material is synthesized using melt growth method. The resistive heating based thermal evaporation technique (model: Hind High Vacuum, SMART COAT 3.0) was employed to deposit the ZnTe:Cu 5% films. During deposition, the ZnTe:Cu 5% powder was placed in Molybdenum boat and the glass and ITO substrates were stacked to substrate holder in the vacuum chamber. The high vacuum (~ 1.5×10^{-5} mbar) was achieved by the rotary and diffusion pumps. The average deposition rate of ~6-10 Å/sec is maintained where the thickness of films is measured as 200 nm. The pristine ZnTe:Cu 5% films are thermally annealed at 100°C, 200°C and 300°C for one hour in Sonar muffle furnace in air atmosphere. The structural, electrical and optical properties of pristine and treated ZnTe:Cu 5% films were characterized employing different amicable tools.

Results and Discussion

Structural and electrical properties

The XRD patterns of pristine and annealed ZnTe:Cu 5% films are depicted in Fig. 1(a) where the diffraction peaks are found nearly at 37.06°, 44.40°, 64.89° , and 77.87° corresponding to the (102), (103). (203), and (300) planes respectively as per JCPDS card 80-0009. The intensity of preferred (103) orientation is varied with temperature which indicates the variation in crystallinity of ZnTe:Cu 5% films. The structural parameters are calculated using equations concerned [3] and presented in Table 1. The crystallite size (D) is observed in the range of 38-44 nm where the maximum crystallite size is found (44 nm) for ZnTe:Cu 5% thin films annealed at 200°C. The increment in crystallite size is due to improvement in the crystallinity and decrease in lattice imperfections. The augmented mobility of adatoms due to supplied high thermal energy by annealing is also possible reason for enhanced crystallite size [4-5]. Later, it is decreased to 42 nm at 300°Cannealing temperature due to introduction of lattice imperfections in these films. The increment in FWHM or decrement in crystallite size might be due to the increased nucleation density [3]. The dislocation density (δ) is also varied and found minimum at 200°C. The higher crystallite size at 200°C revealed to better crystalline quality as needed for fabrication of high-efficiency solar cell device.



Fig. 1 (a) X-ray patterns and (b) I-V characteristics for pristine and annealed ZnTe:Cu 5% films.

Table 1: Structural parameters of ZnTe:Cu 5% films.

Sample	2θ (°)	a(Å)	D(nm)	$\delta \times 10^{14} (m^{-2})$
Pristine	44.55	12.6	40	6.3
100°C	44.55	12.0	38	6.8
200°C	44.40	13.9	44	5.2
300°C	44.55	13.2	42	5.7

The variation in current with voltage for pristine and annealed ZnTe:Cu 5% films is displayed in Fig. 2(b). The electrical conductivity is slightly enhanced for 100°C and 200°Cannealed ZnTe:Cu 5% films and the enhancement in conductivity is owing to a slight reduction in grain boundaries [3] whereas conductivity of 300°C annealed films is found almost same as that of the pristine films.

Optical properties

The investigation of optical properties of ZnTe:Cu 5% films is important in order to find its suitability for back contact applications. Fig. 2(a) shows the variation in transmittance with wavelength and annealing temperature. The transmittance of annealed films is decreased up to 550 nm with the increasing the annealing temperature whereas it is varied in higher wavelength region. The decrement in the transmittance may be attributed to the increased scattering of photons by crystal defects [6]. The optical energy band gap (E_g) is determined from Tauc's plots ($(\alpha h \upsilon)^2$ vs. h υ plots) as displayed in Fig. 2(b). The calculated E_g of ZnTe:Cu 5% films is found as 2.75 eV, 2.80 eV, 2.71 eV, and 2.73 eV for pristine, 100°C, 200°C, and 300°C annealed films, respectively. The optical energy band is strongly affected by the crystallinity and various structural parameters. The increment and decrement in band of films is due to corresponding decrement and

increment of crystallite size. The optical energy band gap of these ZnTe:Cu 5% films is also affected due to presence of Cu dopant [7].



Fig. 2 (a) Variation in optical transmittance (b) Tauc's plots of pristine and annealed ZnTe:Cu 5% thin films.

Conclusions

The present work demonstrates a concise study on annealing induced properties of ZnTe:Cu 5% films for back contact applications in order to enhance the efficiency of the CdTe thin films. The ZnTe:Cu 5% film deposition (having thickness 200nm) was carried out by thermal evaporation technique. The ZnTe:Cu 5% films are found to have cubic phase with zinc blende structure where the crystallite size is found in range of 38-44nm. The optical transmittance was observed to be varied with annealing and the direct energy bandgap was estimated in the range of 2.71-2.80eV. The I-V characteristics indicated ohmic nature of the films. The findings revealed that 200°C treated films have larger crystallite size, band gap, and electrical conductivity, consequently, these films could be utilized as back contact layer in CdTe solar cells.

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A Sensitive NH₃ Sensor Using MoSe₂/SnO₂ Composite

Sukhwinder Singh^{1*} and Sandeep Sharma¹

¹Department of Physics, Guru Nanak Dev University, Amritsar, Punjab,-143005, India

*Corresponding author: sukhwinderphy@gmail.com

Abstract

In this report, we demonstrate the use of $p-MoSe_2/n-SnO_2$ heterojunctions as sensitive and selective chemiresistive ammonia sensor operating at room temperature. The $MoSe_2/SnO_2$ composite was synthesized via a two-step synthesis approach. Structural analysis was confirmed by Raman spectroscopy. Two-terminal devices were made on an alumina substrate with pre-deposited gold contacts. The resulting composite device showed n-type semiconductor behavior. Surprisingly, the composite based sensing device exhibited enhancement in ammonia sensing as compared to $MoSe_2$ (p-type) and SnO_2 (n-type) counterparts. The device also displayed excellent response and recovery features together with a superior selective nature towards ammonia as compared to ethanol, acetone, and formaldehyde. The current study demonstrates the potential application of composite-based heterostructures for NH_3 detection.

Effect of Pyrochlore phase on Magnetic Properties of PMN-PT/LSMO Thin film

Ganesha Channagoudra and Vijaylakshmi Dayal

Department of Physics, Maharaja Institute of Technology Mysore, (Aff. VTU-Belagavi), Karnataka, 571477, India.

*Corresponding author: drvldayal@gmail.com

Abstract

In this paper, we demonstrate the effect of the pyrochlore phase on magnetic properties of La_{0.30}Sr_{0.70}MnO₃ in PMN-PT/LSMO bilayer thin film grown on (001) oriented LAO single crystal substrate using pulsed laser deposition technique. The formation of the pyrochlore phase at 34⁰ in thin-film probed using X-ray diffraction θ -2 θ scan. There is a reduction in Ms value and enhancement of T_C occur in PMN-PT/LSMO/LAO thin film compared with LSMO/LAO. The pyrochlore phase relaxes the strain and induces oxygen deficiency in both the PMN-PT layer and PMN-PT/LSMO interface, which restore the Mn-O-Mn bonding and create an imbalances in Mn³⁺/Mn⁴⁺ valance ratio, thus reducing the magnetization value of LSMO. The compressive strain of LSMO in PMN-PT/LSMO/LAO (ϵ_{out} =1.03%) thin film is less than LSMO/LAO (ϵ_{out} =1.28%), which might be shift the T_C of bilayer thin film towards bulk value (365 ^oC).

Introduction

Artificially designed multiferroics materials, consisting of piezoelectric and magnetostrictive components having various architectures such as; thin-film heterostructure, laminate, particulate ceramic composites, and nanostructured materials, have piqued the interest of researchers in recent years due to their intriguing fundamental physics and industrial applications [1,2]. Among them thin-film heterostructures are the most sophisticated kind, with high ME coupling and fast switching capabilities. Thin-film heterostructures with a combination of ferroelectric (FE) layers (e.g., PZT, BTO, PMN-PT) and ferromagnetic (FM) layers (e.g., LSMO, LCMO, CFO) were investigated widely [3,4]. The lead-based FE materials such as PZT and PMN-PT, although toxic, have gained importance due to their high dielectric and piezoelectric coefficient value [5]. However, lead (Pb) being highly volatile, and if it evaporates during film deposition, leads to the formation of the pyrochlore phase in the heterostructures. Basically, from the technological point of view, it is equally important to study the impact of such a phase on the magnetic behaviour of the FM layer in the heterostructure.

For this study, we have grown $150nm/100nm 0.67Pb(Mg_{1/3}Nb_{2/3})O_3-0.33PbTiO_3/La_{0.70}Sr_{0.30}MnO_3$ (PMN-PT/LSMO) bi-layer on (001) oriented LAO single crystal substrate using pulsed laser deposition (PLD) technique. Compared to our previous report [6] on PMN-PT/LSMO (100nm/100nm), bi-layer structure, we observed that, when PMN-PT layer thickness increased to 150 nm, there is the formation of pyrochlore phase. In this paper, we

present the impact of such a phase on the magnetic behaviour of the FM LSMO layer.

The film deposition methodology is described in our previous published paper [6]. Initially, the LSMO layer of thickness 100nm grown on LAO substrate and later 150nm PMN-PT layer was deposited over LSMO layer with deposition rate 1.5nm/min, and film represented by PMN-PT/LSMO/LAO.

Results and discussions:



Fig. 1. θ -2 θ scanned X-ray diffraction patterns of PMN-PT/LSMO/LAO bi-layer thin film along with LAO substrate.

The thin film's structural orientation and lattice strain are investigated from the XRD θ -2 θ scan pattern and shown in Fig. 1. The appearance of PMN-PT and LSMO (001) peaks in the pattern corresponds to LAO single-crystal, indicating that both layers are oriented towards the c-axis. The extra diffraction peak appears approximately at 34⁰ belongs to the (400) peak of cubic pyrochlore Pb₂Nb₂O₇ phase [5], which is the most prominent secondary phase that appears during the PMN-PT thin film synthesis. The deficiency of lead during depositions is the leading cause of the pyrochlore phase. Moreover, in high thickness film (t > 100 nm), re-evaporation of PbO
from the substrate occur due to energetic bombardment between atoms and ions in the plasma; there is a loss in the stoichiometry of the target resulting in the formation of pyrochlore phase. The out of the plane (OOP) lattice parameter (c) of both PMN-PT and LSMO layers are 4.0201Å and 3.9161Å, respectively. The 'c' value of PMN-PT is similar to the bulk value (c_{bulk}=4.20Å), which indicates that the PMN-PT layer is completely relaxed. The considerable thickness (t=150nm) and pyrochlore phase formations may relax the PMN-PT layer. A slight 1.03% compressive strain existed on LSMO.



Fig. 2. The 2D and 3D AFM images of PMN-PT/LSMO/LAO bilayer thin film.

AFM is an ideal technique for qualitative measurement of surface roughness and morphology of thin film. The 2D and 3D AFM images with scanning area $2\mu m \times 2\mu m$ and height 18nm of bilayer thin film are shown in Fig. 2. It is observed from the figure; the surface is very smooth and free from microcracks and defects. The average and route mean square (rms) roughness of thin film are 6.78 and 1.75 nm, respectively, which ascribe due to the lattice mismatch at the PMN-PT and LSMO interface.

Magnetic Properties:

The temperature-dependent magnetization in both zero-field-cooled and field-cooled states measured at 50 mT is shown in Fig. 3. The film shows a saturation magnetization (M_S) 38 kA/m at 5K, and further increasing the temperature magnetization decreases, indicating that phase transition from FM to paramagnetic state. The minima of the dM/dT vs T curve suggest the T_C of about 338K. The room-temperature MH loop indicates the soft FM nature with Ms value 26 kA/m. However, the observed value is less than the reported LSMO/LAO thin film (105 kA/m) [6].

The reduction in the M_s value and enhancement of T_c occur in PMN-PT/LSMO/LAO thin-film compared with LSMO/LAO thin-film previously published [6]. This non-piezoelectric pyrochlore phase degrades the piezoelectric properties of the FE phase, which affects the ME coupling of the heterostructures [5]. We understand here that, the formation of the pyrochlore phase relaxes the strain and induces oxygen deficiency in both the PMN-PT layer and PMN-PT/LSMO interface leaving only a small amount of compressive strain in the LSMO layer, which exists due to lattice mismatch with the substrate. Additionally, the oxygen deficiency at the interface restores the Mn-O-Mn bonding and imbalances the Mn³⁺/Mn⁴⁺ valence ratio, reducing the magnetization value of LSMO [7]. The quantified compressive strain of LSMO in PMN-PT/LSMO/LAO is found to be ε_{out} =1.03%, which is less than that existed in LSMO/LAO film (ε_{out} =1.28%), may shift the T_C of bilayer thin film towards bulk value (365 K).



Fig. 3. The temperature-dependent magnetization of PMN-PT/LSMO/LAO thin film was measured at 50 mT. In inset (a). The minimum of the dM/dT vs T plot shows the T_C. (b). MH loop measured at room temperature.

Conclusion:

The PMN-PT/LSMO/LAO bilayer thin film was prepared using the PLD technique. The XRD pattern shows that the extra peak near 34^{0} indicates the formation of the pyrochlore phase in the thin film. The pyrochlore phase reduces the strain and enhances the oxygen deficiency in bilayer thin film; consequently, reduction in the M_S value and enhancement T_C occur compared to single-layer LSMO/LAO thin film.

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Electrochemical impedance spectroscopy study of protective aluminium thin film coatings on AZ31 Mg alloy against corrosion

Sundeep Kumar Marndi¹, Hema Palani¹ and Thangadurai Paramasivam^{1,*}

¹Centre for Nanoscience and Technology, Pondicherry University, Kalapet, Puducherry- 605014, India

*Corresponding author: thangaduraip.nst@pondiuni.edu.in / thangadurai.p@gmail.com

Abstract

Magnesium is the lightest structural element that struggles for its proper application because it is highly corrosive under wet environment. A good protective surface coating on it would help to improve its corrosion inhibition capability. In this direction, aluminium metal coating on the Mg alloy AZ31 is chosen in this work. Thermal evaporation technique was employed to achieve aluminium coating of varying thicknesses in the range from 50 nm to 200 nm. Scanning electron microscopy studies showed a uniform Al coating on the AZ31 substrate. Electrochemical impedance spectroscopy technique was used to study the corrosion behaviour of the coatings. The coatings were exposed to corrosive environment for 12 h and their performance was evaluated.

Introduction

Located in the group IIA of the periodic table, magnesium (Mg) is the lightest structural metal, having the density of 1.74 g/cm³ ^[1]. Unfortunately, magnesium is the most chemically active among the structural metals thus restraining it for applications in automobile, aerospace industries and electronic devices ^[2]. Corrosion of Mg alloys is extremely high with poor formability and the oxide layer formed is not stable enough to protect the alloy from further corrosion reaction. A role of protective aluminium film, that can effectively inhibit corrosive solution to penetrate the surface of the alloy without majorly altering the properties of the alloys, is studied in this work.

Experimental Procedure

The AZ31 Mg alloy plates were cut to a size of 1.5 \times 1.5 cm² coupons and polished to grit size of P2000. Further cleaning and sonication in 2-propanol was done to remove debris from the surface of the coupons. The coupons were dried using a hot air blower.

A thermal evaporator (Hind High Vacuum) was used to coat the aluminium thin films of different thicknesses in vacuum. Pure aluminium metal pieces in tungsten helical coil were used as target material. The coating thickness was monitored using a quartz crystal digital thickness monitor. The details of the thin film samples on AZ31 are coded as follows: the just polished bare AZ31 without Al deposition is coded as Mg2 whereas the Al film of thickness 50, 100, 150 and 200 nm coated AZ31 are coded as MgA1, MgA2, MgA3 and MgA4, respectively.

The microstructure of the surface was analyzed by a field emission scanning electron microscopy (FE-SEM). A 3.5 wt.% NaCl solution was used as electrolyte and an area of 1 cm² working electrode (AZ31 coupons) was exposed for electrochemical measurements. The Ag/AgCl and Pt mesh were used as reference and counter electrodes, respectively. Solartron SI1260 with SI1287 was used for electrochemical impedance spectroscopy (EIS) studies. A potential of 10 mV at 11 steps/decade under standard temperature conditions of 25 °C were used for the EIS measurements.

Results And Discussion

FE-SEM

The FEM micrographs surface showing microstructural features of Mg2, MgA1, MgA2, MgA3 and MgA4 are presented in Fig. 1. The Mg2 surface shows the fine polishing lines on the surface, few particles visible on the surface may be unwanted debris or unavoidable corrosion products formed during processing. The grains of aluminium coating are observed on the surface of the coupon that is coated with Al films. There is a clear difference between coated and uncoated specimens' surface. However, the polishing lines are still visible on the film coated surface, which highlights that the coating is thin.

EIS

EIS measurements were performed continuously for 12 h by acquiring EIS data at every 1 h interval while exposing to 3.5wt. % NaCl solution. The Bode plots obtained at 0 h for each coupon are shown in Fig. 2. From Fig. 2 (a) the magnitude of impedance is shown to vary in the low frequency region. The resistance at the lower frequency region shows the ability to resist corrosion ^[3], hence the order of corrosion capability is found to follow, MgA3> MgA1> MgA4> Mg2> MgA2. In the case of higher thickness, MgA4 is expected to be higher than MgA3 but the resistance of the latter is higher. Hence, Al coating corrosion rate vary with thickness but it is not directly proportional to the thickness.

The resistance values extracted by fitting the EIS data with Cole-Cole function *vs* exposure time are shown in Fig. 3. The impedance remains high for the initial period showing the ability of the Al coating to resist corrosion in AZ31. After 2 h, the resistance decreases and saturates showing that the film breakdown has occurred, allowing the electrolyte to react with the substrate.



Fig. 1. FE-SEM micrographs of the AZ31 alloys with aluminium coating of thickness (a) bare, (b) 50 nm, (c) 100 nm, (d) 150 nm and (e) 200 nm



Fig. 2. Bode plots (a) magnitude vs freq. (b) phase vs freq. of polished AZ31 alloy and with coatings of aluminium varying in thickness.

Conclusions

AZ31 Mg alloy were coated with aluminium of different thicknesses using thermal evaporation SEM micrographs showed an even method. aluminium coating was achieved on the surface of the polished AZ31 Mg alloy. Continuous 12 h of EIS measurement were performed on the substrate with coating and it showed that the 150 nm thick was able to resist corrosion better than all the other coatings. After 2 h, the resistance behaved relatively similar for every coupon showing that the electrolyte was able to corrode the surface. This work signifies that appropriate aluminium coating can inhibit corrosion effectively and the optimum thickness is 150 nm. Further work is going on to understand the mechanism of corrosion prohibition by Al films.



Fig. 3. Resistance values obtained by fitting the EIS data with Cole-Cole function for the AZ31 alloy with aluminium coatings of varying in thickness for 12 h of exposure to corrosive environment.

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Blue shifted photoluminescence emission of ion beam modified InGaP thin film

K. Saravanan^{1,*}, Sujoy Sen², B. Sundaravel², N. V. Chandra Shekar^{1,2}

¹UGC-DAE Consortium for Scientific Research Kalpakkam Node, Kokilamedu - 603104, Tamilnadu. ²Materials Science Group, Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam - 603102, Tamilnadu.

*Corresponding author: sara@csr.res.in

Abstract

In this report we have studied the photoluminescence (PL) property of the ion beam modified InGaP ternary thin film grown on GaAs substrate. The sample is irradiated with 200 keV N⁺ ions and subsequently ion beam annealed with 2 MeV He⁺ ions. The pristine InGaP sample exhibits PL emission in the near IR region centered around 670 nm, whereas, the irradiated sample exhibits PL emission in the visible region centered around 520 nm. The Rutherford backscattering spectrometric analysis of the samples evidenced that there is no significant change in the composition or thickness of the film upon ion irradiation. Thus our studies have shown that ion irradiation can alter the local electronic structural property of the ternary film which results a large blue shift in the PL emission.

Introduction

In recent research the application of ternary compounds has shown interesting and remarkable improvements in the field of solar cell, light emitting diode, laser and many optoelectronic devices [1-4]. In particular, InGaP ternary film with its interesting physical and chemical properties is a potential material in wide variety of applications including junction solar cells, visible laser applications. The electronic band structure of this compound is highly dependent on the Ga content. InGaP is a direct band band gap material when the Ga content is low and it becomes indirect band gap material when the Ga content exceeds the limit ~0.7 [3]. Further, the strain induced in the film due to lattice mismatch can also significantly affect the band structure of the film. Hence the growth of the InGaP thin film on the minimum lattice mismatch is a challenging issue and is important for the device fabrication application.

In this report we have studied the photoluminescence property of N^+ ion implanted and subsequently ion beam annealed InGaP thin film grown on GaAs substrate.

Experimental detail

InGaP thin film of thickness ~700 nm has been grown on GaAs substrate using metal-organic chemical vapour deposition growth technique. This film was irradiated with 200 keV N⁺ ion beam using 200 kV Accelerator (HVEE, The Netherlands) up to a fluence of 1×10^{14} ions/cm². The range and straggling of 200 keV in InGaP estimated from the Monte Carlo simulation SRIM software is found to be 350 nm and 140 nm respectively. Then the film annealed by ion beam annealing technique using 2 MeV He⁺ ions, from 1.7 MV Tandetron accelerator, up to a fluence of 1×10^{15} ions/cm². The electronic energy loss of 2MeV He in InGaP is found to be ~30 eV/Å. The film thickness and elemental compositional analysis have been studied using Rutherford backscattering spectrometry (RBS) technique. Photoluminescence excitation (PLE) measurements were performed with a fluorescence spectrometer (F980, Edinburgh Instruments). A Xe arc lamp with double monochromator was used as excitation source. Photoluminescence (PL) properties have been analyzed using WiTech alpha300RA microscope with 355 nm line from HeCd laser as an excitation source at room temperature.

Results and Discussion



Fig. 1. RBS spectra of the pristine and ion beam modified InGaP thin film. The bottom panel depicts the elemental concentration of the pristine and ion beam modified films extracted from RBS.

The elemental compositions and film thickness have been studied using RBS technique. Fig. 1 shows the RBS spectra of the pristine and N ion implanted InGaP samples. The RBS spectra were simulated to extract the thickness and the compositions. The bottom panel of Fig. 1 depicts the concentration of the elements in the pristine and ion beam modified InGaP films extracted from the simulation of RBS spectra. The estimated quantities of the elements in the N implanted samples are found to be almost same as that of pristine film. The estimated thickness of the film is ~700 nm. From the RBS analysis it is clear that N ion implantation does not alter the composition of the film. This might due to the mass of the implanted N, which is considerably smaller than the mass of other film elements. However, the implantation process produces a lot of point defects such as vacancies, interstitials due to the electronic energy loss and nuclear energy loss of the incident ion in the matrix. It should be noted that the energy loss of the incoming ion may anneal out the defects present in the matrix, so called ion beam annealing. Thus ion irradiation can be employed in many ways depending upon its energy. These point defects play a major role in the alteration of electronic band structure which can be easily studied by the photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopic analyses.



Fig. 2. PL spectrum of the pristine InGaP film recorded with $\lambda_{exc} = 355$ nm.

The PL spectrum of the pristine film is shown in Fig. 2. The pristine film exhibits a sharp emission centred around 670 nm (1.85 eV) which is significantly less with the band edge emission of InGaP. PLE spectrum of the pristine InGaP film is shown in Fig. 3. The PLE intensity reached maximum at the excitation wavelength (λ_{exc}) 460 nm (2.69 eV), which indicative of the pristine film is under stress/strain which alters the band edge emission to near IR region. However, the N implanted and subsequently ion beam annealed film exhibits a broad and blue shifted PL emission centred around 520 nm (2.38 eV). The FWHM PL emission is ~150 nm. The broadened PL emission of the ion beam modified InGaP film may due to the introduction of the point defects (vacancies,

interstitials) by the N implantation and blue shift might due to the release of the stress/strain in the film.



Fig. 3. PLE spectrum of the pristine InGaP film.



Fig. 4. PL spectrum of the ion beam modified InGaP film recorded with $\lambda_{exc} = 355$ nm.

Conclusion

In summary, the effect of ion beam modification on the photoluminescence property of the InGaP ternary film has been studied using PL and PLE analyses. The pristine film exhibits a PL emission in the near IR region whereas the ion beam modified film exhibits in the visible region. Thus ion irradiation method can be effectively employed altering of the electronic band structure without significant modification of the film composition/concentration.

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Characterization of Interface of Corn-Husk Film Reinforced Composites

Harwinder Singh¹ and Arobindo Chatterjee²

¹Bannari Amman Institute of Technology, Sathyamangalam, Erode, 638-401 ² Dr BR Ambedkar National Institute of Technology, Jalandhar, 144011

*Corresponding author: harwindersinghs@bitsathy.ac.in

Abstract

There is abundance of lignocellulose-based biomass globally, but the most challenging task is to increase the quality of the interface between reinforcement and matrix in order to achieve desired properties from the selected combination of filler and matrix as a whole. In present research interface between corn-husk film (CHF) and epoxy matrix is characterized through SEM and dynamic mechanical analysis. SEM micrographs of fractured samples of treated CHF show better interphase between CHF and epoxy as compared to untreated CHF. Alkali treatment enhances the fibre surface texture and reduces impurities on the external surface of the fiber which resulted in improved interface and as well as mechanical interlocking between matrix and reinforcement. Dynamic properties improve with addition of CHF in the composites and the best results are obtained at 6wt % CHF and 45⁰ angle of orientation of CHF. The improved interface between CHF and epoxy matrix widens its scope for applications in automobile and construction sector.

Introduction

Different chemical treatments are used to enhance the surface roughness and to reduce impurities on the external surface of the fibrous matter which helps in increasing its interphase with the matrix. In the recent past many researchers worked on lingocellulosic fibers such as kenaf [1], rice husk [2], wheat straw [3], sisal [4], coir [5], jute [6] etc. as reinforcement with the polymer matrices. Alkali treatment of corn husk has been done earlier for fiber extraction [7–10] but in present research corn husk after alkali treatment is used in film form for reinforcement in the epoxy matrix.

Fabrication of composites

The composites are fabricated by using hand lay-up technique. After pouring the initial layer of epoxy resin and hardener, CHF is placed on to it followed by another layer of resin thus forming a laminate structure which is left for curing for 4 h at room temperature followed by oven drying at 60 °C for 4 h. Composites are prepared at three different weight percentages of CHF loadings (3%, 6% and 9%) by weight and three angles of orientation of CHF with respect to longitudinal direction of mould (0⁰, 45⁰ and 90⁰).

Characterization Techniques

The X-ray diffraction is recorded on Empyrean diffractometer by Melvern Panalytical (2 θ range-10° to 30°). FTIR is carried out on Agilent 630 spectrophotometer (wave number range 400-3800 cm⁻

¹). SEM micrographs of fractured surfaces are obtained by JEOL (6510LV) at 35x and 500µm. Water absorption testing of the composites is done as per ASTM D570 standard. Dynamic mechanical analysis is conducted using DMA1 (Mettler Toledo) in single cantilever mode in the temperature range of 30 °C -120 °C with heating rate 3°C /min at 1 Hz frequency.

Characterization of interface

The diffraction peak at $2\theta = 16.72^{\circ}$ corresponds to the amorphous part whereas at $2\theta = 21.87^{\circ}$ represents both crystalline and amorphous part of CHF [12]. In case of treated CHF the crystallinity is increased as compared to untreated CHF sample, due to the reduction of amorphous content with delignification and partial removal of hemicellulose after the alkali treatment. FTIR spectra of treated CHF shows reduction in hydroxyl groups compared to untreated CHF.



Fig. 1. SEM images of fractured surfaces of a) treated and b) untreated CHF epoxy composites

The fractured surface morphology of treated CHF composites highlights good interface between CHF and epoxy (Fig. 1.a) whereas in case of untreated CHF epoxy composites (Fig. 1.b) poor interphase between

the reinforcement and the matrix can be seen. The alkali treatment of CHF promotes the interface between CHF and epoxy, which provides more opportunities for mechanical interlocking between CHF and matrix [14, 15] and consequently improves the performance of the composites.

Viscoelastic behavior of the composite is shown in Fig. 2 with respect to neat epoxy. The best results for storage modulus (SM) of alkali treated CHF epoxy composites are obtained in case of 6 wt% CHF loading and 45° angle of orientation of CHF (634 MPa), which is 2.1 times more than neat epoxy (302 MPa). SM of treated CHF epoxy composites, as well as neat epoxy reduces with increase in temperature but the extent of decrease is different in both the cases [20]. The reduction in the SM at high temperatures is caused by the softening of the polymer due to the increase in the chain mobility of the polymer matrix [21]. The incorporation of CHF restricts the relaxation of the polymeric chains of matrix and enhances the SM which results in reduced damping (tan delta) [22]. In case of treated CHF epoxy composites a positive shift of around 10°C in the tan delta peak is observed compared to neat epoxy which shows the effectiveness of reinforcement [23].



Fig. 2. Curves of Storage Moduli and Tan delta of Neat Epoxy and treated CHF epoxy composites

 Table 1. Water absorption (%) of neat epoxy, treated and untreated epoxy composite

Composites	Water absorption (%)
Neat Epoxy	0.282
Untreated CHF Composites	3.120
Treated CHF Composites	1.154

Table 1 shows the water absorption (%) of neat epoxy, treated and untreated epoxy composite. In case of treated CHF composites there is improvement in moisture resistance compared to that of untreated CHF epoxy composites due to reduction in hydroxyl groups, which is representing improved interface between treated CHF and epoxy matrix.

Conclusion

The alkali treatment of CHF enhanced the interphase between CHF and epoxy as seen from the SEM images. XRD and FTIR spectra also reveal the partial removal of lignin and hemicellulose. Dynamic properties improve with addition of CHF in the composites and the best results are obtained at 6wt % CHF and 45^{0} angle of orientation of CHF. Moisture absorption of treated CHF epoxy composites is drastically reduced compared to untreated CHF epoxy composites. The improved interface between CHF and epoxy matrix widens its scope for applications in automobile and construction sector.

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Effect of Annealing on the Physical Properties of Absorber Cd0.95Zn0.05Te Thin Films for Solar Cells

Ritika Sharma^{1,*}, Himanshu¹, S.L. Patel¹, Anup Thakur² and M.S. Dhaka¹

¹Department of Physics, Mohanlal Sukhadia University, Udaipur-313001, India

²Department of Basic and Applied Sciences, Punjabi University, Patiala-147002, India

*Corresponding author: <u>ritikasharma2394@gmail.com</u>

Abstract

Annealing plays a crucial role in modifying the physical properties of thin films, hence, the present work deals with the effect of annealing on the physical properties of 800 nm thin $Cd_{0.95}Zn_{0.05}Te$ films deposited employing thermal evaporation technique. Structural analysis revealed that the pristine and annealed films are inclined towards (220) cubic plane and crystallite/grain size increased with annealing. The electrical analysis demonstrated the ohmic nature of the pristine and annealed films with decreasing conductivity. The optical analysis depicted variation in the optical absorbance where the band gap of the pristine and annealed films is found in the range 1.70-2.76 eV. The attained results indicate that the films annealed at 300°C are apt as absorber layer for the fabrication of high efficiency single junction and tandem solar cell devices concerned. **Keywords:** $Cd_{0.95}Zn_{0.05}Te$ thin films; Annealing; Physical properties; Thermal evaporation.

1. Introduction

Semiconducting thin films made up of II-VI compound semiconductors have paramount potential due to their desirable properties such as tunable band gap, lattice matching etc. The CdTe is a crucial II-VI compound semiconductor widely used as absorber layer in the thin films solar cells. Alloying ZnTe along with CdTe overcomes the large difference between the CdTe valence band and the work function of the metal contact. Hence, CdZnTe is used as a promising candidate for various optoelectronic devices such as room temperature radiation detectors, photodiodes, lasers etc. It is also used as an absorber layer in the single-junction and tandem solar cell devices concerned [1-2].

The surface qualities of the CdZnTe thin films such as surface defects, impurities etc. influence the solar cell device performance [3]. Therefore herein, the pristine CdZnTe thin films are subjected to annealing so that the surface qualities as well as the physical properties of these films can be enhanced.

The CdZnTe can be deposited using various physical and chemical route based deposition techniques wherein resistive heating based thermal evaporation technique is widely used due to control on deposition rate and good homogeneity of films. [1]. In the present work, the Cd_{0.95}Zn_{0.05}Te thin films having thickness 800 nm were deposited, annealed and the physical properties of these films were optimized for solar cell applications.

2. Experimental

The Cd, Zn and Te powders (purity more than 99%) were procured from Sigma Aldrich and Cd_{0.95}Zn_{0.05}Te alloy was developed using melt growth method. The Cd_{0.95}Zn_{0.05}Te thin films having thickness 800 nm were deposited using resistive heating based thermal evaporation unit (Hind High

Vacuum, SMART COAT 3.0). Before deposition, the glass and ITO substrates were cleaned using acetone and isopropanol. During the deposition, high vacuum of 1.8×10^{-5} mbar, current in the range of 45-52 Ampere and deposition rate of 7-9Å/sec were maintained. The obtained films were thermally annealed in air atmosphere at 200°C, 300°C and 400°C in Sonar muffle furnace for 60 minutes. The physical properties of these films were undertaken using various characterization tools.

3. Results and Discussion

3.1 Structural and electrical properties

The XRD patterns of pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ thin films are demonstrated in Fig. 1(a) which point towards the dominance of (220) diffraction peak in all the films. Apart from the dominant peak, some other peaks are also recognized corresponding to the (111), (200), (311) and (331) planes respectively, as confirmed by the JCPDS card number 53-0551. In comparison to the pristine films, the intensity of the dominant diffraction peak slightly increases for the annealing temperatures 200°C and 300°C and then slightly decreases at 400°C.



Fig. 1 (a) XRD patterns and (b) I-V characteristics curves for pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ films.

The increment in the intensity of the dominant peak (except for 400° C) with temperature indicates that the

annealing process provides freedom for the movement to the Cd, Zn and Te atoms within the lattice forming highly crystalline films [4-5]. The structural parameters are calculated corresponding to the dominant peak (220) using relations concerned [6] and are tabulated in Table 1.

Table 1: Structural parameters of pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ thin films.

Sample	20 (°)	FWHM	D(nm)	ε×10 ⁻³
Pristine	44.47	0.23	39	2.45
200 °C	44.47	0.22	40	2.37
300 °C	44.47	0.21	42	2.27
400 °C	44.47	0.22	42	2.30

The crystallite/grain size (D) of the films increases with annealing which is due to the corresponding decrement in the FWHM whereas the lattice strain (ϵ) decreases with annealing (except for 400°C) which might be attributed to the increment in grain size as a result of the strong interaction between the vapor atoms and substrate [5].

The I-V characteristics curves for pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ thin films are represented in Fig. 1(b) which indicate the Ohmic character of films. The conductivity decreases with annealing where the overlapped I-V characteristics curves of the films annealed at 300°C and 400°C are observed which showed less temperature impact. The diminution in conductivity or augmentation in resistivity is might be due to the potential barriers created by the grain boundaries [7].

3.2 Optical properties

The absorbance spectra of the pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ thin films are depicted in Fig. 2(a) wherein, as the annealing temperature increases, the variation in absorbance is observed upto 800 nm and maximum absorbance is observed for 300°C annealed films. Beyond 800 nm, the absorbance increases with annealing temperature and maximum absorbance is observed for 400°Cannealed films. Fig. 2(b) portrays the Tauc's plots for the pristine and annealed Cd_{0.95}Zn_{0.05}Te thin films where the optical energy band gap (E_g) is calculated by extrapolating a straight line on $(\alpha h \upsilon)^2$ vs. hu plots. As the annealing temperature increases, E_vis found to be varied within the range of 1.70-2.76 eV for pristine and annealed films. The variation in E_g is might be due to the disarray at the grain boundaries and the stoichiometric deviations [8]. The Cd_{0.95}Zn_{0.05}Te thin films annealed at 300°C showed band gap of 1.70 eV which is close to near optimum band gap for absorber layers.



Fig. 2 (a) Optical absorbance spectra and (b) Tauc's plots for pristine and annealed $Cd_{0.95}Zn_{0.05}Te$ thin films.

4. Conclusions

The present work deals with the impact of annealing on the physical properties of thermally evaporated $Cd_{0.95}Zn_{0.05}Te$ thin films. The XRD patterns revealed to the presence of (220) dominant diffraction peak and increment in grain size with annealing. The I-V characteristics curves depicted the ohmic nature of the developed films and diminution in conductivity with annealing. The optical absorbance spectra demonstrated fluctuating absorbance where the optical energy band gap is obtained in the range 1.70-2.76 eV. The obtained results signify that the films annealed at 300°C are suitable as absorber layer to the single junction and tandem solar cells.

Acknowledgement

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Spectroscopic Analysis of PVD Deposited Indium Selenide (In₂Se₃) Thin Films for Photodetector Applications

Sahana Nagappa Moger*, Mahesha M G

Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education 576104, India

*Corresponding author: sahananm96@gmail.com

Abstract

The manuscript presents spectroscopic studies of the Indium Selenide (In₂Se₃) films, which are grown via thermal evaporation technique. The deposited films are amorphous in nature and uniform throughout the substrate as confirmed by SEM/EDS results. The transmittance and absorbance spectrum were taken by spectrophotometer, and direct band gap was found to be 1.95 eV. The vibration mode was studied by Raman spectra and PL emission occurs in the UV and near IR region. The spectral response of the deposited films was high for 635 nm wavelength and suitable for visible range photodetector applications.

Introduction

development, In the current the III-VI chalcogenide thin films have shown enormous progress in the research point of view. The indium selenide films have attained much attention in the field of solar cell, photodetectors, and other optoelectronic devices [1][2]. The indium selenide can change its phase from amorphous to crystalline as function of temperature. It could play important role in the memory devices [3]. This paper reports spectroscopic analysis of indium selenide thin films for photodetector applications.

Experimental Details

In the present work, 300 thick thermally evaporated In₂Se₃ were deposited on pre-cleaned glass substrate. High purity (Alfa Aeser -99.999%) In₂Se₃ powder was taken in Mo boat (200 A) and 2×10^{-6} mbar base pressure was achieved. The substrate was kept at room temperature during deposition. The thickness of the films was measured by Dektak profilometer. Zeiss SEM EV018 with EDS was used for SEM/EDS results of the thin films. The XRD pattern of the films recorded by Ni-filtered Rigaku Miniflex-600 X-Ray Diffractometer with 20°-60° scanning range and 1°/min scanning rate. Shimadzu UV-1800 double beam spectrophotometer was used to record absorbance and transmittance spectra in the wavelength region 500-1100 nm. The PL and Raman spectra were measured by using LABRAM HR Horiba France model with excitation 532 nm. The electrical parameters and I-V characteristics were measured by computer interfaced Keithley 2450 Source Meter.

Results and Discussion



Fig. 1 a) SEM image, b) XRD pattern, c) Absorbance and Transmittance spectra, d) Tauc's Plot, e) PL spectra and f) Raman spectra of the In_2Se_3 film.

Fig 1.a) shows the SEM micrograph of the deposited In_2Se_3 thin films. From the micrograph it is cleared that films were homogeneous, dense, and crack free.

From the results of average areal scan of EDS spectra and elemental mapping shows that uniform distribution of the constituent elements. The films are selenium deficient (In – at. 45%; Se – at. 55%) than compared to source concentrations, which is common in the thermal evaporation technique due to difference in the vapour pressure of the constituent elements. **Fig 1.b**) shows the XRD patterns of deposited In₂Se₃ films and films exhibits the amorphous nature. These results are in line with the previous reported literature [3].

Fig 1.c) shows the transmittance and absorbance spectra of the deposited films. The absorbance edge of the films was found to be at 637 nm. The transmittance of the films increased at higher wavelength region and the optical uniformity of the films was confirmed by interference patterns. The band gap can be derived from Tauc's relation [4]. **Fig 1.d**) shows the Tauc's plot of the In₂Se₃ thin films and band gap was found to be 1.95 eV is matching with band gap of the γ - In₂Se₃ phase. From the Tauc's plot it is observed that tailing near the absorption edge. The disorder in the film system is responsible for tail which referred as Urbach energy. The Urbach energy was calculated by [4],

$$\alpha = \alpha_0 \exp\left(\frac{n\upsilon}{E_u}\right)$$
 [a]

The inverse slope of the plot $ln(\alpha)$ vs hv gives Urbach energy and found to be in the range of 141 meV. Higher Urbach energy is also due to localized state present within the band edge of the films.



Fig. 2 Typical I-V of the In₂Se₃ samples under dark and illumination at different wavelengths.

Fig 1.e) shows Gaussian fitted PL spectra of the films. The peak around 682 nm is corresponding to near band edge of the deposited In₂Se₃ films. The peak 751 nm arises due to different phase of the In₂Se₃ films, and 888 nm is corresponding to bandgap of InSe bulk [5].

Fig 1.f) shows the room temperature Raman spectra, peak was observed at 250 cm⁻¹ which supposed to be for γ - In₂Se₃ phase [6].

The electrical properties of the films were estimated by van der Pauw method at room temperature. Silver contact shows ohmic behavior of the deposited In_2Se_3 films. The films were n-type conductive in nature with 2.66×10^{15} cm⁻³ carrier density. The measured resistivity and mobility were in the order of 267.78 ohm-cm and 8 cm²V⁻¹s⁻¹. Low resistivity films were favorable for the photodetector applications.

The I-V characteristics of the films were measured in dark, and illumination of different wavelengths as shown in **Fig 2**. After illumination with different wavelengths, the considerable change in the electrical conductivity was observed. The higher sensitivity was observed at 635 nm wavelength region. The increase in the electrical conductivity is due to generation of electron-hole pair after illumination of the light. Higher photo-response was observed, if the incident photon energy is comparable with the band gap of the films and depend on the absorption coefficient of the sample [4]. Lower resistivity increased the electron hole pair creation appropriate for the photodetector applications.

Conclusion

The In₂Se₃ films were deposited by thermal evaporation method on glass substrate with a base pressure of 2×10^{-6} mbar. The films were amorphous in nature and band gap was found to be in the range of 1.95 eV. Higher Urbach energy found due to localized state present in the lower energy region and confirmed by PL measurements. Raman results gives chemical state of the sample. The film has shown high photo response at longer wavelength region of the visible spectrum and suitable for photodetector applications.

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Structural characterization of thermally annealed ZnO thin film grown on Si (111) by RF sputtering

Manu Bura¹, Divya Gupta¹, Nisha Malik¹, Gurvinder¹, Rahul Singhal², Sanjeev Aggrawal¹

¹Department of Physics, Kurukshetra University, Kurukshetra, 136119, ²Department of Physics, Malviya National Institute of Technology (MNIT), Jaipur, Rajasthan, 302017, India

*Corresponding author: manubura59@gmail.com

Abstract

This work presents the effect of thermal annealing on the structural properties ZnO thin film deposited on p-type Si (111) substrate using radio frequency sputtering technique. GIXRD pattern reveals the formation of polycrystalline ZnO thin film having hexagonal wurtzite structure with preferential growth along (002) plane. After annealing at 800°C, intensity of peak corresponding to another orientation i.e. (103) increases pointing towards the modification of surface chemistry due to heat treatment. Further increase in temperature to 900°C enhances the crystallinity of ZnO films. The hexagonal wurtzite structure of films is confirmed using FESEM.

Formation of a crystalline and magnetic alloy phase (Fe₃Ge) at the interfaces of Fe/Ge multilayers

C. L. Prajapat^{1,@}, Harsh Bhatt^{2,3}, Yogesh Kumar², and Surendra Singh^{2,3,*}

¹Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
²Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 40085Address, City, Code
³Homi Bhabha National Institute, Anushaktinager, Mumbai 400094, India

*Corresponding Author: surendra@barc.gov.in

@This paper is dedicated to the memory of Dr. C. L. Prajapat, who passed away on 10th September 2021

Abstract

Ferromagnet-semiconductor (FM-SC) alloy phase with room temperature ferromagnetic properties at the interfaces of FM/SC heterostructures are believed to improve the electron spin injection from the FM to the SC for the realization of spintronic devices. Here we report the formation of a crystalline alloy phase (Fe₃Ge) at the interfaces on growing ultrathin Fe/Ge multilayers at an elevated substrate temperature of ~ 523 K as well as on annealing the multilayer at a temperature > 523 K. The alloy phase formation at interfaces is achieved at a much lower temperature than the Fe₃Ge phase formation in bulk material (~ 973 K), mainly due to rapid interdiffusion of Fe and Ge at the interfaces.

Design of Non-periodic and periodic multilayer for high energy X-ray application and optimization of process parameters

A Biswas*, P Sarkar, Abharana N and D Bhattacharyya

Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India

*Corresponding author: arupb@barc.gov.in

Abstract

Systematic arrangement of non-periodic multilayer can reflect a band of high energy X-ray and periodic multilayer of ultra-low bilayer thickness can divert particular energy of X-ray in grazing angle geometry. Non-periodic W/Si multilayer has been designed for X-ray telescope application to cover up to 69.5 keV energy and WC/SiC periodic multilayer has been designed to divert 100 keV energy for direct measurement of U and Pu in spent fuel. The multilayer for X-ray telescope has been designed in two techniques and compared. In order to fabricate WC/SiC multilayer deposition power of in-house developed DC magnetron system has been optimized and a periodic multilayer of 10 bilayer has been fabricated.

Structure and Growth Mechanism of Thin Film of DNTT Molecules on SiO₂/Si Substrate

Subhankar Mandal*, Md Saifuddin, and Satyajit Hazra

Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata 700064, India

*Corresponding author: subhankar.mandal@saha.ac.in

Abstract

The structure, molecular orientation, and surface morphology of the dinaphtho[2,3-b:20,30-f]thieno[3,2-b]thiophene (DNTT) molecules on SiO₂/Si substrate, deposited by thermal evaporation, were investigated using X-ray reflectivity (XR) and atomic force microscopic (AFM) techniques to understand the growth mechanism of the thin film on dielectric SiO₂ surface, which has a strong influence on the charge transport properties of the DNTT based devices. The upright molecular orientation of the DNTT molecules and their crystallinity in thin film were realized by analyzing the XR profile and XRD maps in specular and off-specular directions, while the closely spaced domain-like structure of the DNTT thin film with high surface roughness was evident from AFM images.

Room Temperature Gas Sensing Properties of *H*-terminated Diamond

N. Mohasin Sulthana^{1,2}, K. Ganesan^{1,2,*} and P. K. Ajikumar²

¹Homi Bhabha National Institute, ²Surface and Nanoscience Division, Material Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603 102, Tamil Nadu, India.

*Corresponding author: kganesan@igcar.gov.in

Abstract

Hydrogen termination on diamond surface (HD) makes the surface conductivity to be very high with p-type doping through water adlayer mediated electrochemical charge transfer process. When the HD surface is exposed to chemical gases which undergo electrolytic dissociation, the surface conductivity changes greatly due to the disruption of charge equilibrium at the diamond/adlayer interface and this offers advantages for selectivity in gas sensor applications. Here, we report on the gas sensor response of HD towards H_2S at room temperature in ambient air. The HD sensor device exhibits a linear response from 5 to 70 % for H_2S in the concentration range of 10 to 90 ppm in ambient air. The gas sensing mechanism of HD is discussed in brief.

Amorphous Hydrogenated Germanium as Passivation coating on High Purity Germanium Detector: Optimization of film parameters

Shreyas Pitale^{*}, S.G.Singh, Manoranjan Ghosh, G.D. Patra and Shashwati Sen

Crystal Technology Section, Technical Physics Division, Bhabha Atomic Research Center, Mumbai, India 400 085

*Corresponding author: spitale@barc.gov.in

Abstract

Amorphous hydrogenated germanium (a-H-Ge) has emerged as a suitable passivant for HPGe detectors. The properties of the a-H-Ge affect the performance of the resultant detectors, and these properties substantially depend on and are controllable through the sputter deposition process parameters. The subject of this paper is this interconnection of fabrication process parameters, a-Ge film properties, and detector performance. Films deposited at high sputter pressure show high resistance and are capable of inhibiting surface leakage current of the fabricated HPGe detector considerably.

Ag₂O Decorated ZnO Nanorods Demonstrating Two-Step Visible-Light Photocatalytic Dye-Degradation Phenomena

Payel Sahu and Debajyoti Das*

Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata – 700 032, India.

*<u>Corresponding author: erdd@iacs.res.in</u>

Abstract

 ZnO/Ag_2O heterostructures, as the functional materials for photodegradation of MB dye under visible light irradiation, have been achieved using inexpensive hydrothermal and ultrasonic-assisted synthetic routes. The heterostructures had wurtzite ZnO peaks that were highly crystalline and hexagonal, as well as cubic Ag_2O peaks. The ZnO/Ag_2O photocatalyst demonstrated two dye degradation slopes, with the higher-slope arising later in the process, when metallic-Ag traps the valence electrons of Ag_2O nanoparticles and advances e⁻/h⁺ separation across ZnO/Ag⁰/Ag_2O heterojunction structures, making them readily accessible for superior dye degradation.

Diamond-Like Carbon Thin Films from Low-Pressure and High-Density CH₄ Plasma

Sucharita Saha and Debajyoti Das*

Energy Research Unit, School of Materials Sciences Indian Association for the Cultivation of Science, Jadavpur, Kolkata – 700 032, INDIA.

*E-mail: erdd@iacs.res.in

Abstract

DLC thin films were grown using a low-pressure high density CH₄/Ar plasma on glass substrates in a planar RF (13.56 MHz) Inductively Coupled Plasma CVD system. Using a plasma triggered by RF power to a mixture of 20 sccm CH₄ and 50 sccm Ar gas maintained at a low pressure of ~30 mTorr, a series of samples were prepared by varying the substrate temperature and then changing the RF power. The optimised DLC films, obtained at 500 °C and 900 W demonstrated high optical transmission of ~97 %,wideoptical band gap of ~3.58 eV and a minimum of I_D/I_G ~0.61 and a maximum of I_{Dia}/I_D ~1.32 in Raman analysis demonstrated the maximum sp³/sp² content in the carbon network.

Probing Carrier Traps by Photocurrent Transients in Sputtered ZnO Thin Films Grown Without and With O₂

Sourav Mondal and Durga Basak*

School of Physical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India

*Corresponding author: sspdb@iacs.res.in

Abstract

ZnO films have been deposited under various Ar and O_2 gas flow by RF sputtering method. The photoluminescence measurements suggest a decrease in the radiative defect levels. Huge decrease in the dark current and therefore highly enhanced ultraviolet photosensitivity with an increase in the O_2 flow during growth indicates a decrease in the donor defects. The photocurrent transient spectroscopy indicates majority carrier traps mainly lie within 2.06 eV for the film deposited with only Ar whereas within 2.06 to 2.48 eV below the conduction band for the films deposited with Ar and O_2 .

Effect of H₂-Dilution for Growing nc-SiGe Thin Films in PECVD

Amaresh Dey and Debajyoti Das*

Energy Research Unit, School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata – 700 032, INDIA *Corresponding author: erdd@iacs.res.in

Abstract

Hydrogen dilution facilitates for sustaining nanocrystallinity in SiGe thin films, simultaneously minimizing the difference in the decomposition rate of two source gases GeH₄ and SiH₄ in the plasma. At a H₂ dilution ratio $R(H_2) = [H_2]/[(SiH_4)+(GeH_4)] = 50$, nc-SiGe thin film with high crystallinity possessing dark conductivity $\sigma_D \sim 1.54 \times 10^{-2}$ S cm⁻¹ and optical band gap, E_g ~ 1.55 eV has been prepared at low substrate temperature, T_S ~220 °C. The narrow optical gap conducting material seems suitable for use in the bottom sub-cell of tandem-structured multi-junction nc-Si solar cell.

Tailoring the Performance of Phthalocyanine-Based Sensor: Side Chain Substitution and Nanofabrication

Rajan Saini^{1*}, Pooja Devi², Rajinder Singh³, Aman Mahajan³, R.K. Bedi³, D.K. Aswal⁴, A.K. Debnath⁵

¹Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, NJ, USA.
 ²Department of Physics, Maharaja Ranjit Singh Punjab Technical University, Bathinda-151001, India.
 ³Material Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143005, India.
 ⁴CSIR National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi-110012, India.
 ⁵Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India.

*Corresponding author: sainifizix@gmail.com

Abstract

Room temperature Cl₂ response kinetics of zinc phthalocyanine (ZnPc)-based sensor have been enhanced by peripheral substitution of alkoxy side chains functional groups on the ZnPc molecule (as Zn (II) 2,3,9,10,16,17, 23, 24-octakis(octyloxy)-29H, 31H-phthalocyanine (ZnPcOC₈)). ZnPcOC₈-based sensors have been fabricated by spin coating and solution-processed nanostructures, and Cl₂ response kinetics have been studied in the 5-1500 ppb Cl₂ concentration range. By making alkoxy substitutions at the peripheral sites of the ZnPc molecule, the detection limit of sensors is lowered from 50 ppb to 5 ppb with faster response and recovery time as compared to the ZnPc-based sensor. Among the three sensors, solution processed nanostructured sensor exhibits the best performance. The Cl₂ adsorption kinetics of sensors followed Elovich equation. The gas sensing mechanism of sensors has been investigated by XPS which suggest that the central metal ion (Zn⁺²) of the ZnPc molecule is the preferred site for Cl₂ interaction. The present studies suggest that alkoxy substitution leads to the fabrication of highly sensitive and Cl₂ selective low-cost solution-processed gas sensors.

Effect of Concentration on the Edge-on Oriented Ordering of Spin-coated Donor-Acceptor Type Copolymer Thin Films

Saugata Roy^{*}, Md Saifuddin, Subhankar Mandal and Satyajit Hazra

Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata 700064, India

*Corresponding author: saugata.roy@saha.ac.in

Abstract

The effect of concentration of polymer in solutions on the structures of spin coated poly-diketepyrrolopyrrole-thionothiophene [PDPP-2T-TT-OD] thin films were investigated using X-ray reflectivity (XR) technique. The edge-on oriented (EO) ordering near the film-substrate interface is found to be better for the film deposited with low concentration, which has of immense importance in the device properties, as such in-plane ordering near the film-substrate interface is known to play very crucial role to get better charge transport properties in organic thin film transistor (OFET).

Chemically Modified Successive Ion by Ion Synthesis of ZnO Thin Films for Optoelectronic Applications

Jayesh R. Pawar^{1, a}, Munjaji E. Dudhamal^{1, a} Nikhilesh S. Bajaj¹ and Rajesh A. Joshi^{1, *}

¹Thin Films and Sensor Laboratory,

Department of Physics,

Toshniwal Arts, Commerce and Science College, Sengaon Dist. Hingoli 431542 MS India

*Corresponding author: <u>urajoshi@gmail.com</u>

Abstract

Zinc oxide (ZnO) thin films are synthesized by using modified successive ionic layer adsorption and reaction techniques (SILAR) on glass substrate at room temperature. These as deposited thin films are characterized for structural, surface morphology and optical characterizations using X-ray diffraction (XRD), atomic force microscopy (AFM) and Uv-vis absorption spectroscopy. From XRD pattern; the low intensity peaks indicate that the films consist coarsely fine grains and/or amorphous in nature. The diffraction peaks observed at $2\theta = 31.71^{\circ}$, 36.27° and 56.29° are attributed to (100), (101) and (110) planes having hexagonal phase. Surface morphology observed from the AFM corresponds granular shape evenly distributed over substrate surface, while optical spectra attribute to exciton induced charge transportations.

Impact of 200 MeV Ag¹⁵⁺ Ion Irradiations on Structural and **Morphological Properties of Epitaxial Lanthanum Nickelate Thin** Films

Vishal Sharma¹, Sunidhi^{1, 2}*, S. K. Arora¹, Florencio Sánchez³, and Fouran Singh⁴

¹Centre for Nanoscience and Nanotechnology, Block-II, South Campus, Panjab University, Sector-25, Chandigarh-

160014. India

²Department of Physics, Panjab University, Chandigarh-160014, India

³Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus UAB, Bellaterra 08193, Spain

⁴Materials Science Group, Inter-University Accelerator Centre, New Delhi 110067, India

*Corresponding author: sunidhi3525@gmail.com

Abstract In this paper, we studied the influence of 200 MeV Ag^{15+} ion irradiations on the structural and morphological properties of epitaxial lanthanum nickelate (LNO) thin film on LaAlO₃ (001) substrate grown using PLD. The single phase and epitaxial nature of pristine as well as irradiated samples of different fluences i.e. 10^{11} , 5×10^{11} and 10^{12} ions/cm², were confirmed by large area 2D X-ray diffraction scans. We observed a decrease in the substrate induced lattice strain in LNO thin film with an increase in the ion dose through out-of-plane lattice constant variation using high resolution x-ray diffraction (HR-XRD). This decrease in an epitaxial strain is related to irradiation induced structural defects. Further surface roughness (rms value) was found to increase with an increase in an ion dose.

Introduction

Rare earth nickelates based oxide heterostructures form an intriguing and interesting class of materials due to their enriched tunable and controllable physical properties. Their heterostructures have attracted attention due to the presence of novel properties at the interfaces as compared to their bulk form [1]. Lanthanum nickelate (LaNiO₃, LNO) is a promising electrode candidate for various oxide based devices [2]. It has good lattice match with various ferroelectric perovskites. In epitaxial heterostructures, defects induced by the swift heavy ion (SHI) irradiation found to modify the structural properties of the thin films and alter lattice strain [3, 4]. In this paper, we report the impact of 200 MeV Ag¹⁵⁺ swift heavy ion irradiations on the mismatch strain in the epitaxial LNO thin film.

Experimental part

For this study, we used LNO thin film (27 nm) epitaxially grown on LaAlO₃ (LAO) substrate (1 x 1 cm²) by using Pulsed laser deposition (PLD). The detailed information about the growth of the film can be found elsewhere [5]. The irradiation of LNO film with 200 MeV Ag^{15+} ions (10¹¹ ions/cm², 5 x 10¹¹ ions/cm² and 10¹² ions/cm²) was performed at Inter University Accelerator Centre (IUAC), New Delhi. Detailed information related to ion irradiation experiment can be found elsewhere [4]. The general area detector diffraction system (GAADS) with HI-STAR large area detector was used to confirm the

epitaxial nature. Besides, further structural and morphological studies were carried out by HR-XRD and AFM, respectively.

Results and Discussion



Fig. 1. XRD 2θ - χ frame of the LNO (27 nm)/LAO(001) sample, showing (001) and (002) reflections of the LAO substrate, and (002) reflections of LNO layer for **a**. Pristine **b**. 10^{12} ions/cm², **c**. 5 x 10^{11} ions/cm² and **d**. 10^{11} ions/cm².

We performed large area X-ray diffraction scans of pristine as well as irradiated, LNO/LAO thin film based heterostructure with general area detector diffraction system (GADDS) in order to confirm the absence of polycrystallanity and parasitic crystalline phases. The XRD 2θ - χ map in Fig. 1(a-d) shows bright spots at $\chi = 0^{\circ}$ corresponding to (001) and (002) reflection of LAO substrate and (002) reflection of LNO layer. This confirms the epitaxial nature of LNO thin film in pristine as well as irradiated heterostructures. Figure 2 shows the variation of outof-plane epitaxial strain in the film with different ion doses. With increase in an ion dose there found decrease in the epitaxial strain from 2.08 % for pristine to 1.15 % for highest irradiation dose. We calculated these values from lattice constant, c determined from high resolution θ -2 θ scan performed using HR-XRD measurements on pristine and irradiated films (graph not shown here) [5].



Fig. 2. Variation of epitaxial strain in out of plane lattice parameter of LNO with irradiation

This decrease in the out-of-plane (c-axis) lattice constant with an increase in the ion dose is related to the formation of structural defects produced by high energy ions through large electronic energy loss. The impact of irradiations on mismatch strain in LNO epitaxial film has been studied earlier also [3]. They observed increase in mismatch strain with increase in ion dose. This different behaviour of epitaxial strain with irradiation can be explained due to different thickness of films used in the study. The impact of irradiations depends upon the initial strain state in pristine material. Figure 3. shows the variation of surface roughness with an ion dose as determined from 2µm x 2µm area AFM scan taken in semi contact mode at RT. The rms roughness for pristine, and irradiated samples were 0.55 nm, 1.67 nm, 1.96 nm and 3.69 nm for 10^{11} ions/cm², 5 x 10^{11} ions/cm² and 10^{12} ions/cm² respectively. We found an increase in the roughness with an increase in the ion dose. The increase in surface roughness is ascribed to irradiation induced defects in the thin film. These structural defects changes the [NiO₆]⁻ octahedral distortion angle in LNO and alters its epitaxial relationship with the LAO substrate by decreasing the lattice strain after irradiation. Thus, on the basis of this report we can say that ion irradiation can be used

as a leading tool to modify the structural and morphological properties of oxide thin films.



Fig. 3. Variation of surface roughness (rms) of LNO with irradiation.

Summary

Here, we studied the influence of swift heavy ion irradiations (200 MeV Ag^{15+}) on the structural and morphological properties of epitaxial LNO/LAO (001) heterostructure. From large area X-ray diffraction scans, single phase and epitaxial nature of film were confirmed. After irradiation, we observed the increase in surface roughness and decrease in out-of-plane epitaxial lattice strain due to induced structural defects after irradiation.

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Amine Functionalized Fe-MOF Membranes for Enhanced Flux and Rejection

K Vinothkumar, C Lavanya and R Geetha Balakrishna*

Centre for Nano and Material Sciences, Jain University, Bangalore 562112, Karnataka, India.

*Corresponding author: br.geetha@jainuniversity.ac.in

Abstract

Here in, we report the development of amine functionalized iron based (NH2-MIL-101(Fe)) metal organic frameworks (MOF) /polysulfone polymer-based membranes for removal of chromium, humic acid and chromium-humic acid complex by dead-end filtration method. The XRD, ATR-IR, BET and FESEM studies were carried out to confirm the formation of MOF and its embedment in membranes. The contact angle shows increased hydrophilicity of MOF membrane when compared to bare membrane and the removal of pollutants increased greatly for MOF membranes.

Introduction

Humic substances make up the natural organic matter consisting of humic acid (HA) and fulvic acid (FA). Humic acid reacts with chlorine to form dis-infection by products such as halo acetic acid, trihalomethane etc. These by-products are carcinogenic and mutagenic to living organisms. Also, hexavalent chromium (Cr^{+6}) is a hazard to human kind. Removal of these chromium ions using porous ultrafiltration (UF) membrane is highly impossible. However, Cr⁺⁶ forms complex with HA which makes the filtration of Cr^{+6} feasible via UF membranes [1]. Membranes are potential candidates towards a sustainable water treatment process with added benefits of lower energy and cost effectiveness. However, permeability and rejection ability is the major drawback for the membranes. Nevertheless, adding pore forming agents and hydrophilic nanoparticles (NPs) to make mixed matrix membranes (MMM) could be an alternative to address this challenge. Pore forming agents enhance the porosity during the phase inversion. But hydrophilic nanoparticles enhance the porosity as well as the rejection capacity of the membranes. In this direction, functionalized MOFs have been demonstrated as performance enhancers for MMM to achieve high permeability and separation efficiency [2]. MOFs are well structured crystalline organic-inorganic hybrid materials with high surface area and tunable property. Especially, Iron (Fe) containing MOFs are widely used in environmental applications [3]. In this study, we have developed Fe-MOF/PSf membranes for the removal of both HA, Cr⁺⁶ and HA-Cr⁺⁶ complex using a dead-end filtration method.

Experimental

Amine functionalized Fe-MOF (NH2-MIL-101(Fe)) nanoparticles were synthesized as per earlier report [4]. For MOF/PSf membrane synthesis maximum limit of 5 wt.% (according to polymer) in order to avoid agglomeration. Fine dispersion of Fe-MOF in NMP solvent via ultrasonication and 22 wt. % of the polysulfone was added to above solution and stirred for 24h at 60 °C. The homogenous mixture was casted on the glass plate and immersed in water and kept 24h for phase inversion. Obtained membrane was named as M5 and membrane without MOF particles are prepared in similar way and named as M0. For the water uptake (WU) studies prepared membranes were dried and taken weight and the same membrane were then soaked in water for 24h and final wet weight was taken. WU and flux study analysis were calculated as per literature [1]. Filtration experiments were conducted via customized dead-end filtration setup with active membrane surface area of 10.8 cm². HA-100 mg/L, Cr⁺⁶-10 mg/L and HA-Cr⁺⁶ (20-10 mg/L) mixture were used as model pollutants for testing the efficiency of membranes. For preparation of HA- Cr⁺⁶ mixture the solutions were mixed together and kept for shaking for 12h. All the testing experiments were conducted three times to get concordant value. Filtrate solution was collected at every 10 min interval for continuous 120 min and analyzed by UV-Vis spectroscopy. Rejection efficiency calculated by equation (1) shown below.

$$Rejection (\%) = \left(\frac{C_I - C_F}{C_I}\right) X \ 100 \tag{1}$$

where, C_I and C_F are initial and final concentration of feed solution.

Results and discussion

The XRD, ATR-IR, BET and FESEM, morphology analysis for Fe-MOF shown in Fig. 1(a)-(d). Synthesized Fe-MOF is in good agreement with the literature [4]. The BET N2 adsorption-desorption curves shows type-I isotherm proves the micropore nature of the material with highest surface area of 390 m2/g and pore diameter of 1.9 nm. FESEM reveals the synthesized Fe-MOF has micro-spindle morphology. Further characterization of M0 and M5 membranes by XRD and ATR-IR are shown in Fig. 2(a)-(b) which proves the successful incorporation of MOF particles into PSf membranes. FESEM images for the surface ((M0-S) and (M5-S)) and cross-section ((M0-C) and (M5-C)) of the membranes are given in Fig. 2(c) which confirms the presence of Fe-MOF. In addition to that, incorporation of particles increases the pore channels of the membrane. Contact angle (CA) and WU studies in Fig. 2(d) shows that CA decreased from 67.6° to 34.6° and WU ratio for M5 membrane is 5.6 times higher than M0 membrane, which confirms the drastic increment of hydrophilicity.



Fig. 1. Fe-MOF characteristic studies (a) XRD (b) ATR-IR (c) BET N₂- adsorption desorption isotherm (inset- pore diameter analysis) (d) FESEM



Fig. 2. MOF/membranes characteristic studies (a) XRD (b) ATR-IR (c) FESEM analysis of M0 and M5 (S-surface and C-cross-section) (d) water uptake and contact angle.

Flux and rejection studies of various feed solutions is given in Fig.3. Pure water flux of M5 was increased to 50.3 $L/m^2/h$ from 4.7 $L/m^2/h$ (M0)

because of increased permeability and hydrophilicity. Permeate (pure water + pollutant) flux for the M0 and M5 is less compared to pure water flux of the same membrane due to blockage of pores of the membranes by the pollutant present in the feed solution.

The rejection capacity for HA is 85.8% for M5 membrane which is 38.3% higher than M0 membrane. Similarly, the rejection capacity of the Cr^{+6} increased by 50% compared to M0 membrane. Compared to HA and Cr^{+6} solutions, the rejection of HA- Cr^{+6} mixture is higher for both M0 and M5 membranes. This is because of the complex formation which increases the size of the pollutant which leads to the higher rejection.



Fig. 3. Flux and rejection studies of M0 and M5 membrane Conclusion

The Fe-MOF, PSf and Fe-MOF/PSf membranes were successfully synthesized and characterized via various techniques. Filtration efficiency of the fabricated membranes were tested by dead-end filtration. Permeation ability and rejection efficiency is increased more than 50% for the Fe-MOF membranes compared to bare membrane.

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Vanadium Pentoxide Thin Film for NO₂ Gas Sensing Application B. M. Babar¹, K. B. Pisal¹, S. H. Sutar¹, S. H. Mujawar¹, V. L. Patil², P. S. Patil², L. D. Kadam³, U. T. Pawar⁴, P. M. Kadam^{4*}

¹Department of Physics, Yashwantrao Chavan Institute of Science, Satara, Maharashtra 415 001, India,

²Thin Film Materials Laboratory, Department of Physics, Shivaji University, Kolhapur, Maharashtra 416 004, India, ³Arts, Science and Commerce College, Ramanandnagar, Maharashtra 416 308, India,

⁴Smt. Kasturbai Walchand College Sangli, Maharashtra 416 416, India.

Corresponding Authors: kprakash5229@rediffmail.com

Abstract

Present work demonstrates a synthesis of vanadium pentoxide thin film by inexpensive hydrothermal method for hazardous NO₂ gas detection. Orthorhombic crystal structure of prepared calcinated product confirmed with the help of x-ray diffraction (XRD) technique. Functional group detection was done with the help of Fourier Transform Infra-Red spectroscopy (FT-IR) and nano stick-like morphology was confirmed with the help of scanning electron microscopy (SEM). Eventually, the gas sensing performance of vanadium pentoxide thin film was carried out for oxidizing gas NO₂. About 3.46% gas response observed towards NO₂ gas at 200°C, along with response/ recovery time 44 and 394 sec respectively.

The Effect of Electron Beam Treatment on the Third Order Nonlinear Optical Nature of the TPP Thin Film in Nano-Second Regime

Clavian L M¹, Rajesh Kumar P C^{1*}, Anil Kumar K V², Narayana Rao D³, Shihab N K³, and Ganesh Sanjeev²

¹Department of Physics, St Joseph Engineering College, Vamanjoor, Mangaluru- 575028
 ²Deptartment of Physics, Mangalore University, Mangalagangothri, Mangaluru- 574199
 ³Laser Lab, School of Physics, University of Hyderabad, Hyderabad- 500046

*Corresponding author: pcrajeshkumar@yahoo.com

Abstract. The impact of 8 MeV electron beam interaction on the third order nonlinear optical (NLO) properties of 5, 10, 15, 20 Tetraphenyl 21H, 23H- porphine (TPP) thin films were probed by means of z-scan technique with pulsed laser operating at 6 ns and 532 nm. The thin films of thickness 120 nm were fabricated using thermal vapor technique on an ultrasonically cleaned glass substrate. The irradiation sensitive UV-Visible absorption spectrum and the corresponding impact on its optical band gap were explored. The unirradiated thin film depicts reverse saturable absorption NLO property attributable to excited state absorption. A switch over to saturable absorption was observed due to the induced localized structural defects when subjected to 2.5 kGy and 10 kGy e-beam irradiation dose. The closed aperture z-scan studies illustrates self-defocusing optical nonlinearity in both pristine and irradiated thin film owing to electronic and thermal lensing effects. The strong nonlinear absorption (NLA) and nonlinear refraction (NLR) coefficient values (β and n_2) of TPP thin film provides prominence for device applications.

INTRODUCTION

Porphyrins and their derivatives are promising versatile molecules with large third order optical nonlinearity and potential applications in optical limiting, frequency conversion, optical switching, two photon fluorescence imaging etc. [1,2]. The practical employability of these compounds in the modern day photonic devices demands fabrication of high quality thin films and comprehensive understanding of its structure-property relationships [1]. The interaction of various radiations with matter can bring overwhelming and indispensable changes in material properties. Therefore, the knowledge of radiation interaction with materials are imperative in order to explore the positive contribution of this interaction to the non-linearity as well as the stability of the materials. This may also help when the materials are intended for device applications under extreme radiation conditions such as high radiation environment of nuclear plants, extra-terrestrial (i.e. space) applications etc. [1].

EXPERIMENTAL

The TPP (Sigma-Aldrich) thin films of thickness 120 nm were fabricated at room temperature (pressure of 10^{-5} Torr) on an ultrasonically cleaned glass substrate of dimension 37 x 12 x 1 mm using Hind-Hi vacuum thermal coating unit. The e-beam irradiation of thin films was carried out with the aid of an electron accelerator (RRCAT, Indore) having an output

energy of 8 MeV to deliver a dose of 2.5, 10, 20, 30, 40 and 50 kGy. The UV-Visible absorption spectrum was studied using shimadzu-1800 spectrophotometer. Pristine TPP, 2.5 kGy and 10 kGy electron irradiated (e-TPP) films were selected for NLO studies. Z-scan studies were carried out using nano-sec Q-switched Nd-YAG laser operating at 532 nm with an average power of 1.94 mW, repetition rate of 10 Hz and pulse width of 6 ns. The Rayleigh range (z_0) and beam waste (ω_0) of the z-scan set up were 3.641 mm and 2.484 x 10⁻⁵ m respectively.

RESULTS AND DISCUSSIONS

UV-VISIBLE SPECTROSCOPY



Fig. 1. (a) UV-Visible absorption spectrum (b) Tauc's plot of TPP and e-TPP thin film

UV-Visible absorption spectra (Fig. 1(a)) of pristine TPP and e-TPP thin films depicts bands attributable to $\pi \rightarrow \pi^*$ orbital transitions [1,2]. The soret absorption band in the e-TPP films is characterized by enhanced shoulder peaks. The decrease in the intensity of the

absorption peaks with the increase in dose indicates the degradation of the sample. The optical band gap is found to change inversely with irradiation dose (Fig. 1(b)).

THIRD ORDER NLO PROPERTIES

The effects of electron irradiation on the third order nonlinear optical properties of the thin film were probed by means of Z-scan technique described by Shiek Bahae et al. [3]. Figure 2(a-c) depicts normalized open aperture nonlinear transmittance curve. The pristine thin film illustrates characteristic RSA process, NLO property that is widely explored in optical limiters and bio-imaging [1]. The TPP thin film irradiated at 2.5 kGy and 10 kGy depicts SA process, which is widely applicable for pulse compression, Q-switching and mode-locking of ultrafast lasers [1]. The thin film irradiated at 20 kGy and above although depicts signature ground state absorption spectra, its NLO nature diminishes. The observed nonlinear RSA absorption behavior is attributed to strong excited state absorption (ESA) [3]. Whereas the SA observed is attributed to the depletion of the ground state due to the band filling effect. This effect emanates with the small increase in the localized defect states and disorders caused by irradiation [1].



Fig. 2. Open aperture Z-scan transmittance curve (a) Pristine TPP (b) 2.5 kGy e-TPP (c) 10 kGy e-TPP

The normalized closed aperture nonlinear transmission curve depicted in figure 3(a-c) indicates negative nonlinearity due to the self-defocusing nature of the thin films. The observed nonlinear refraction property is due to concurrence of electronic Kerr effect and thermal-lensing effect [1].



Fig. 3. Closed aperture Z-scan transmittance curve (a) Pristine TPP (b) 2.5 kGy e-TPP (c) 10 kGy e-TPP

Table 1. Third order nonlinear optical parameters of the pristine and irradiated TPP thin films

Sample name	Nonlinear Absorption Coefficient β (m/W)	Saturation Intensity I _s (W/m ²)	Nonlinear Refractive Index n ₂ (m ² /W)
Glass	-		-
Substrate			
TPP	1.28 x 10 ⁻⁵		-8.489 x 10 ⁻¹²
e-TPP (2.5	- 0.95 x 10 ⁻⁵	0.9 x 10 ⁹	-1.55 x 10 ⁻¹²
kGy)			
e-TPP (10	-0.44 x 10 ⁻⁵	0.9 x 10 ⁹	-6.630 x 10 ⁻¹³
kGy)			

CONCLUSIONS

In summary, the z-scan analysis show that the NLA mechanism shifts from RSA to SA due to band gap changes introduced when irradiated with e-beam. The CA Z-scan results demonstrated that the thin films exhibit strong self-defocusing type optical nonlinearity. The third order nonlinear coefficients (β and n_2) are found to decrease with irradiation dose.

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Effect of dc Self-bias on Residual Stress of PECVD Deposited ^{nat}B_xC Thin Films

Arundhati Bute¹, Shuvendu Jena², Naresh Chand¹, D. V. Udupa², and Namita Maiti¹

¹Plasma Processing Section, L&PTD, BARC, Mumbai-400085

²Optics & Analytical Spectroscopy, A&MPD, BARC, Mumbai-400085

*Corresponding author: butearundhati@gmail.com

Abstract

The substrate self-bias plays a significant role in determining the nature and magnitude of the residual stress in the ^{nat}boron carbide thin films deposited by Radio Frequency Plasma Enhanced Chemical Vapour Deposition (RF-PECVD) technique. The residual stress in films was calculated with the help of surface curvature method. Films were deposited as a function of substrate dc "self-bias". The stress profile in the films was found to change from tensile with a magnitude of 25 MPa to compressive with a magnitude of -150 MPa with increase of substrate self-bias from -100V to -150V.

Introduction

Stress in thin films is an important factor as it can affect the physical properties of the thin film or multilayer like conductivity, dielectric permittivity, charge carrier mobility etc. In addition, the residual stress can significantly affect the adhesion and fracture toughness of the films which can affect the performance of functional films [1]. Stresses in thin films can be divided in three main categories: intrinsic, thermal and mechanical stress. Out of which the intrinsic and thermal stresses are referred together as residual stress. The intrinsic stress arises during the thin film deposition and dependent on the deposition process. Thermal stresses arise due to difference in thermal expansion co-efficient of the thin films and the substrate. When the thin film is kept at a temperature different than deposition temperature, the total residual stress comprises of both thermal and intrinsic stress. Nearly all films contain residual stress which significantly affect their performance.

In our work we have measured the residual stress in PECVD (Plasma Enhanced Chemical Vapor Deposition) deposited ^{nat}boron carbide thin films via surface curvature method. Stresses in the films have been measured as a function of substrate dc "selfbias". The substrate self -bias was found to be a deterministic factor in determining the nature and magnitude of stress in the deposited thin films.

Experimental

In this study two ^{nat}boron carbide thin films have been deposited using a capacitively coupled RF-PECVD system [2] at different substrate self-bias value. One film was deposited at -100V and other was deposited at -150V dc self-bias value. For ease of discussion, we will henceforth refer to the sample deposited as -100V and -150V as Film A and Film B respectively.

For the residual stress measurements, the surface profiles were extracted by analysing the interference patterns formed between the thin film sample and an optical flat disc placed in a laser Fizeau interferometer [3]. Using the Zernike polynomial, the spherical shape component was extracted from the surface profile data. The different co-efficient of this polynomial represent different surface aberrations. One of the coefficients is called defocus term that represents the length of the sagitta (s) of the spherical shape component, which is used for calculating the radius of curvature. This sagitta of a circular arc is defined as the distance from the centre of the arc to the centre of its base. The radius of curvature (R) of the surface is calculated from the following equation [4]:

$$R = \frac{r^2}{2s} + \frac{s}{2}$$
(1)

Where, $r \ (\sim 8.75 \text{ mm})$ is the radius of circular-shaped surface under consideration, and s is the sag in the curvature profile. Subsequently, residual stress (σ) in the films has been derived from the measured curvatures using the Stoney's equation [5]:

$$\sigma = \frac{1}{6} \left(\frac{E_s}{1 - v_s} \right) \left(\frac{1}{R_a} - \frac{1}{R_b} \right) \left(\frac{d_s^2}{d} \right)$$
(2)

where, R_a and R_b are the radius of curvature of the substrate before and after deposition, respectively, E_s is the young's modulus, v_s is the Poisson's ratio of the substrate, d_s and d are the thicknesses of the substrate and the film, respectively where $d \ll ds$.

Results AND Discussion

The 2D surface profiles of the substrates, Film A and Film B before and after deposition are shown in

Fig. 1. The change in the surface curvature profile is clearly visible in the figure. Equation (2) is valid for isotropic and homogeneous stress distribution in the film, when deformations due to internal stress are very small compared to the film thickness. Following



Fig. 1. 2D surface contour map of substrates before and after deposition of Film A and Film B.

standard convention, tensile stress has been considered positive and compressive stress has been considered negative. The parameters of Si (100) substrates used in Equation (2) are E_s = 130 GPa, v_s = 0.26, and d_s = 0.5 mm. Thicknesses of the films were calculated from the optical reflection spectra and were found to be 1242 nm and 1503 nm, respectively. These thicknesses were used in equation (2). Utilizing equations (1) and (2), residual stresses in the films were calculated. It was found that the stress is tensile in nature for Film A with a magnitude of 25 MPa and compressive for Film B with a magnitude of -150 MPa. Fig. 2 shows the variation of residual stresses in the deposited films.



Fig. 2. Residual stress in Film A and Film B.

The compressive or tensile nature of residual stress in thin films depends upon the deposition techniques and film growth mechanisms. Various kinetic processes, for example defect annihilation, grain growth, grain boundary formation, diffusion of atoms through grain boundary, and phase transition are the mechanisms that promote intrinsic stresses. In RF-PECVD processes, the deposition parameters like input power, gas flow, deposition temperature, ion bombardment energy etc. can affect the nature and magnitude of the stresses. In our study the stress in the films is dependent on the "self-bias" which in turn determined the energy of the incoming ions. The nature of the stress changes from tensile for Film A to compressive for film B on account of higher ion bombardment energy. During the initial phases of thin film growth, island formation takes place followed by grain growth, then coalescence of grains and grain boundary formation. When these grain coalesce, tensile stress is generated [6]. With increasing ion energy, the adatoms on the growing film surface are provided with more energy to diffuse across the grain boundaries. This diffusion and accumulation of atoms near grain boundaries gives rise to compressive stresses in the films deposited at a higher energetic process.

Conclusion

The residual stress profile in RF-PECVD deposited ^{nat}boron carbide film changes from tensile to compressive for with increase in substrate self-bias. The magnitude of the stress also increases from 25MPa to -150MPa with impinging ion bombardment energy.

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Thermal Behaviour of Au@SiO₂ Core-shell Nanoparticles Under Nitrogen Atmosphere

Susheel Kumar Gundanna¹ and Umananda M Bhatta^{1,*}

¹Centre for Incubation, Innovation, Research and Consultancy, Jyothy Institute of Technology, Visvesvaraya Technological University, Bengaluru - 560082, India

*Email: nandasringeri@gmail.com

Abstract

In this work, solvothermally prepared Au@SiO₂ core shell nanoparticles have been subjected to Thermo Gravimetric Analysis up to 900 °C under nitrogen atmosphere. The resulting physicochemical behavior has been explained using Transmission Electron Microscopy analysis of the specimen before and after thermal treatment. Further, as prepared nanoparticles have also been dispersed on Si(100) substrate and subjected to high temperature annealing under nitrogen atmosphere. Interaction among Au core, SiO₂ shell, native SiO₂ and the Si substrate at high temperatures, and the resulting inter diffusion across these interfaces have been studied using Scanning Electron Microscopy.

Introduction

Gold, like any other noble metal, is chemically inert even in humid and oxygen rich environment. It is also one of the most thermally and electrically conductive metals. However, the atoms on the surface are unbound in one direction thus even such noble metal nanoparticles are highly reactive and have potential applications in various field like catalysis, optoelectronics, photovoltaics etc.¹⁻⁴. For example, during thermal treatment of any material, least stable surface atoms experience the external heat energy which leads to breaking of surface atoms, and exposing the inner core of the material. This leads to instability of the nanoparticles at high So, encapsulation temperatures. of such nanoparticles in an insulating shell with relatively higher melting point, not only protects the embedded nanostructure from melting at lower temperatures, but also the resulting interface throws up a lot of interesting properties. Au@SiO₂ core shell nanostructures is one such system, when dispersed on Si(100) substrate results in 3 different interfaces namely, $Au - SiO_2$ (Shell), SiO_2 (shell) - SiO_2 (native), and the usual SiO_2 (native) – Si(100).

In this work, chemically synthesized core shell nanoparticles are subjected to thermo gravimetry analysis (TGA) under nitrogen atmosphere up to 900 °C, in order to understand the thermal stability of the specimen. Further, as prepared core shell nanoparticles have been dispersed on Si(100) substrate and subjected to ex-situ thermal annealing to mimic the TGA conditions. Morphological changes post annealing has been studied by using Scanning Electron Microscopy (SEM) and the results have been used to explain the degradational behavior observed during TGA.

Experimental details

Au@SiO₂ core shell nanoparticles were synthesized using modified method reported in our earlier work^{5,6}. Cetrimonium bromide (CTAB) is used as a surfactant for the synthesis of core shell nanoparticles, which plays an important role during the high temperature study, as will be explained later. The thermal behaviour of Au@SiO₂ was investigated by thermogravimetric analyzer using Shimadzu, DTG-60. The sample was subjected to heating up to 900 °C under nitrogen atmosphere. The effect of heating on the shape, size and distribution of nanoparticles were studied using Transmission electron microscopy (TEM) technique (200 *kV* JEM-2010, JEOL machine at Institute of Physics (IOP), Bhubaneswar). Further, the sample was drop cast over Si(100) substrate and characterized using FESEM (Tescan-Mira 3 LMH) before and after annealing, by mimicking the TGA conditions.

Results and Discussion



Fig. 1. (a) TEM image of Au@SiO₂ core shell particles before TGA (b) TGA curve (c) TEM image of Au@SiO₂ core shell particles after TGA. *Powder Technol.* 381, (2021).

formation of Au@SiO₂ The core-shell nanoparticles is confirmed using TEM analysis as shown in Fig 1(a). Average Au core size was found to be around 40 nm and that of SiO₂ shell is about 18-20 nm. The thermal stability of the particles is studied using TGA. This shows a multi-step weight loss of about 40%, as shown in Fig 1(b). Initial 5% of weight loss can be attributed to removal of moisture, as the temperature reaches 120 °C. Upon increase in temperature, further weight loss of about 35% is observed in the range of 120 - 750 °C, in three steps. This could be due to the thermal decomposition of CTAB molecules situated in between the Au core and the SiO₂ shell and also residual CTAB molecules in the system. Initially,

the removal of residual CTAB molecules takes place, as it requires lesser energy as compared to the removal of CTAB present in between the core and shell. The detailed explanation of decomposition of CTAB molecule has been reported in our previous work⁶. Decomposition of SiO₂ and evaporation of gold might only occur above 700 $^{\circ}C$ which accounts for only about 1% of total weight loss. This is further corroborated from the TEM analysis, as shown in Fig 1(c). Here, the clusters of nanoparticles are randomly distributed, resulting agglomeration of Au nanoparticles at high temperatures. This occurs when either Au diffuses through SiO₂ shell and make contact with neighbouring Au particles or SiO₂ shell itself decomposes and makes way for agglomeration. The diffusion of Au clusters as a whole resulted in the partial breaking of SiO₂ shells. However, most of the shell content remains in the specimen in the form of large encapsulation of nonuniform thickness, covering the clusters of agglomerated gold nanoparticles7.



Fig. 2. Au@SiO₂ dispersed over Si(100) substrate (a) asprepared (b) ex-situ annealed at 900 °C under nitrogen atmosphere. *Nano-Structures & Nano-Objects* 23, 100521 (2020).

It has also been well reported that the process of decomposition of SiO₂ gets faster when it comes in contact with pure Si atoms. Such a reaction gives rise to gaseous SiO and the presence of gold atoms further catalyzes this reaction⁸. So, we have prepared a system by drop casting the as-prepared nanoparticles over Si(100) substrate and annealed at 900 °C under nitrogen atmosphere. Exact location was imaged before and after annealing using SEM in order to ascertain the effect of thermal treatment. Fig 2(a) shows the SEM image of as-prepared nanoparticles over Si(100) substrate, where we can observe more than 100's of Au@SiO2 isolated coreshell nanoparticles. After thermal treatment, number of particles have significantly reduced and average particle size has increased, as shown in Fig 2(b). In this case, there are two entirely different interfaces, namely Au - SiO₂ and SiO₂ - Si, which play important roles during agglomeration⁵.

Summary

 $Au@SiO_2 \quad core-shell \quad nanoparticles \quad were \\ prepared \ using \ a \ solvothermal \ method \ and \ as-$

prepared specimen was subjected to Thermo Gravimetry Analysis under Nitrogen atmosphere up to a temperature of 900 °C. Structural changes using TEM images before and after thermal treatment were explained. Further, role of Si(100) substrate was also studied.

1. TGA curve shows a multi-step weight loss of about 40%.

2. Post annealing, agglomeration of gold nanoparticles could be seen resulting from breaking up of individual SiO_2 shells.

3. Presence of Si substrate further helps in agglomeration and degradation of individual SiO_2 shells, resulting from inter diffusion across the $Si(100) - SiO_2 - Au$ interfaces.

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Demonstration of strong coupling between Tamm plasmon polariton and cavity mode in metal/micro-cavity thin film multilayer

S. Jena^{*1}, R. B. Tokas¹, Sourav Bhakta², Pratap K. Sahoo², S. Thakur¹, and D. V. Udupa¹

¹Atomic & Molecular Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085 ²School of Physical Sciences, National Institute of Science Education and Research, Bhubaneswar, 752050

*Corresponding author: shujena@barc.gov.in; shuvendujena9@gmail.com

Abstract

Strong coupling between Tamm plasmon polariton (TPP) and cavity modes has been experimentally demonstrated in a metal/micro-cavity thin film multilayer. Both the TPP and cavity mode are detected as a resonant dip in the optical reflectivity spectrum. The reflectivity of the multilayer has been numerically computed using transfer matrix method. The metal/micro-cavity multilayer made of $Ag/TiO_2/(SiO_2/TiO_2)^3/SiO_2/(SiO_2/TiO_2)^4/BK7$ glass has been prepared using physical vapor deposition method. The cross-section imaging and reflectivity spectrum of the multilayer have been measured using FESEM and spectrophotometer, respectively. The measured reflectivity spectrum exhibits two resonant dips at the wavelengths of 558 nm and 584 nm, which corresponds to the coupled TPP-cavity modes resulted due to their strong coupling as predicted by the theoretical simulation. The dual resonant modes have applications in light emitting diodes, photodetectors, and optical sensors.

Growth and Structural Characterization of Copper Phthalocyanine Molecules in Thin Films

Sabyasachi Karmakar^{*} and Mrinmay K. Mukhopadhyay

SPMS Division, Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata-700064, India

*Corresponding author: sabyasachi.karmakar@saha.ac.in

Abstract

Semiconductor organic thin films are one of the key components for modern flexible electronic devices. We have developed a thin film evaporator to deposit the organic thin films. Copper phthalocyanine (CuPc) on silicon substrate and also on cobalt thin films was deposited using this evaporator. The structural characterization of these films was done using x-ray reflectivity, and atomic force microscopy (AFM) techniques. The results show a uniform film of vertically stacked but tilted CuPc molecules on both the Si substrate and on Co/Si substrate which can be used for the study of organic spin valve systems.

Introduction

Organic semiconductor (OSC) thin films have received the interest to the material science researchers due to their physical, optical and electronic properties similar to the Si based semiconductors with some more advantages than Si in some cases and also some disadvantages too. These materials are very light weight, mechanically flexible and also inexpensive which makes them eligible for low-cost, large scale device fabrication process. OSCs are successfully used in various electronic devices like organic light emitting diodes (OLEDs), organic solar cells and organic field effect transistors (OFETs) [1, 2] etc. Nowadays, spindependent devices such as organic spin valves (OSVs), OLED-based magnetic sensors, and spin-OLEDs are under intensive investigation to achieve their new pathways as spintronic devices [3]. Functionality of these devices highly depends on charge carrier mobility through the OSCs which is directly related to the crystallinity having larger domain sizes of the OSCs. So, the better performance of these devices requires a homogeneous wellordered organic film with sufficiently large domains. Here we are presenting the growth and structural characterization of Copper phthalocyanine (CuPc) on Si and also on the Co film to demonstrate its potential application for its use as OSV systems.

Evaporation system design

Thermal evaporation is one of the very common methods of physical vapor deposition (PVD) for producing thin films. We have developed a very simplified thermal evaporation system to deposit thin films of organic materials. The system uses a tungsten basket of 700W rating as the evaporation element. This heating filament is powered using a LT transformer. A PID controller with thermocouple (TC) sensor is used to control the power of the primary winding of the LT transformer to maintain a constant temperature during evaporation. We have used a circular copper block with a PTFE casing and a clipping mechanism to hold substrate. Two cartridge heaters of 40W rating and a TC sensor have been mounted inside the substrate holder to provide substrate temperature during deposition or post deposition heat treatment. A second PID controller is used to control substrate temperature.



Fig. 1. Schematic diagram of vacuum evaporator system

Experiment

Films were deposited on freshly cleaned Si substrates by sonication with acetone and isopropanol successively. Co has been deposited on Si substrate using dc magnetron sputtering in Ar environment. CuPc (purchased from Sigma Aldrich - 99.9% pure) were deposited using the thermal evaporator at 5.0×10^{-5} mbar pressure and at a rate of 0.15 Å/s. Substrate temperature 373K and filament temperature 790K was maintained during evaporation. X-ray reflectivity was performed using a Rigaku SmartLab instrument with Cu K α source. AFM was performed using a Multi-Mode 8-HR BRUKER instrument.

Results and Discussion

The XRR profiles are fitted with Parrat recursive formalism (Fig. 2) and corresponding electron density profile (EDP) is shown in the inset [4]. The EDP shows that the CuPc molecules have been stacked vertically in layer-by-layer growth mechanism as shown in the inset - the gaps between the two stacked layers appear as the low-density region in the EDP as schematically modeled in the inset. This kind of periodic orientation of the molecules along the perpendicular growth direction on the substrate leads to the observed Bragg peaks which correspond to a bilayer thickness of about 13Å. The length of CuPc molecule strand is ~14Å but from our fitted parameters we got high-density region of length 8.5Å. So, the molecules are tilted from the vertical by an angle of ~ 37° . From our XRR data only, we cannot conclude about the tilt direction, it may be symmetric tilt for all layers or may have vertical stack of alternate tilting layers. The surface layer of the film has more disordered orientation with respect to the surface normal due to less surface coverage.



Fig. 2. XRR profile of CuPc film on Si substrate: Experimental data (open circles) and fitted curve (red line). Inset: Fitted EDP and a cartoon of CuPc molecules on Si.

Fig. 3 shows the XRR profiles of Co film and CuPc/Co film on Si substrates. The XRR profile of Co/Si indicates the film thickness of about 31 nm as shown in the EDP. The EDP for the CuPc/Co/Si film shows a CuPc layer of thickness about 20 nm on the Co film (~31 nm). The vertical stacking variation of the CuPc film on the Co film is also visible in the EDP. In addition, a hump at $q_z = 0.48 \text{\AA}^{-1}$ in the XRR profile is also visible which is a signature of CuPc as observed for the XRR profile of CuPc/Si [5, 6]. The GIXD pattern (not shown here) of the CuPc/Co/Si

also gives a peak at $q_z = 0.48 \text{\AA}^{-1}$. The surface morphology as found from the AFM image (Fig. 3 lower inset) of the CuPc film shows a rod-like domain of the molecules. From these observations, we can infer that the CuPc molecules assemble in vertically stacked tilted layer structure with in-plane morphology as rod like domains.



Fig. 3. XRR profile of Co film (red) and Co/CuPc bi-layer (wine): Experimental data (open circles), fitted curve (solid lines) and corresponding EDP profiles (upper inset). Lower inset: AFM image of the CuPc film on Co/Si.

Conclusion

We have successfully developed a vacuum evaporation thin film deposition system with precise temperature control in our laboratory. The XRR results from the CuPc films deposited on Si and Co/Si substrates show very good quality thin films of about 20nm thickness. The CuPc molecules stack vertically in a standing-up orientation and found it to be tilted by about 37° with respect to the normal. The successful fabrication of Co/CuPc bilayer structure on Si can be used for further development of spin-valve devices.

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ZnO Nanowires based Electronic Nose for Toxic Gas Determination

K. R. Sinju,^{1,2*}, N. S. Ramgir^{1*}, B. Bhangare¹, A. K. Debnath,^{1,2} ¹Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India

²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400 085, India

*Corresponding author: k.r.sinju@gmail.com / niranjanpr@yahoo.com

Abstract. Development of an electronic nose (EN) based on ZnO nanowires (NW) with a machine learning models namely hierarchical cluster analysis (HCA) and principal component analysis (PCA) has been demonstrated. The developed EN could successfully detect and/or discriminate toxic gases namely H2S and NO2 in the lower detection range from 1 to 10 ppm. The studies revealed that the EN could qualitatively as well as quantitatively discriminate both the toxic gases under investigation.

Synthesis of Superhydrophobic/Superoleophilic Polyaniline and its Application for Oil-Water Separation

Purushottam Jha^{1,2}, S.P. Koiry^{1,2}, C. Sridevi¹, Bhupendra Singh¹, Deeksha Gupta^{1,2}, P. Veerender¹ and A. K. Chauhan^{1,2}

¹Technical Physics Division, Bhabha Atomic Research Centre, Mumbai,400085, ²Homi Bhabha National Institute, Mumbai, India, 400094

*Corresponding author: akc.barc@gmail.com

Abstract

Superhydrophobic/superoleophilic materials have attracted much attention for applications in oil/water separation owing to an extremely high water contact angle and very low oil contact angle. However, wide applications of these materials are constrained due to complex, expensive, and non-eco-friendly fabrication procedures. Here, we have successfully introduced superhydrophobic/superoleophilic properties in polyaniline using easy, simple, cost-effective, and environmentally friendly solution processible method. For this purpose, nano structured polyaniline co-doped with sodium dodecylbenzenesulfonate, are synthesized by chemical polyemerization method in aqueous solution. These polymer exhibit water contact angle >150⁰ and oil contact angle ~0⁰ and thus explored for oil/water separation.

Effect of O₂ Partial Pressure on Valence Band Maxima of HfO₂ Thin Film

Mangla Nand^{1,2*}, Y. Kumar^{1,2}, S. Tripathi¹, Babita¹, S. K. Rai³, S. N. Jha^{1,2}

¹Beamline Development & Application Section, Bhabha Atomic Research Centre, Mumbai, India - 400085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, India - 400 094 ³Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore, India – 452013

Corresponding email: <u>mnand@rrcat.gov.in</u>

Abstract

The effect of the oxygen (O₂) partial pressure on the valence band maxima (VBM) of pulsed laser deposited HfO₂/Si(100) thin films were investigated by photoelectron spectroscopic (PES) technique. GIXRD measurements suggest that the deposited films were in polycrystalline monoclinic phase. The VBM was determined using PES measurements. It was observed that the VBM shifted towards the higher binding energy from 2.79 eV to 3.24 eV in the film deposited in O₂ environment as compared to that deposited without O₂ environment. The O 1s core level spectra showed that oxygen vacancy reduces as O₂ was introduced during deposition of film. The films were found stoichiometric.

Wemple – Di Domenico Single Oscillator Analysis of Zr Doped **TiO₂ Thin film**

Dr. Mava Devi¹

¹School of Applied Sciences, KIIT Deemed to be University, Bhubaneswar, 751024

*Corresponding author: mdevifpy@kiit.ac.in

Abstract

The Zr doped TiO₂ thin films are deposited on FTO glass slide by unconventional sol-gel method. The optical properties of the thin film annealed at 350°C was studied by UV-Visible spectroscopy in the wavelength range of 300-900nm. Refractive index dispersion data is fitted with Wemple -Di Domenico single oscillator model and the various dispersion parameters are calculated. The carrier concentration to effective mass ratio and electric free carrier susceptibility was calculated by Spitzer -Fan analysis.

Introduction

In recent years the transition metal doped TiO₂ has drawn much interest of researchers as they find several applications starting from solar cell to photocatalysis [1]. Out of all the transition metals as Zr has the same valence cell $(n-1) d^2ns^2$ structure as that of Ti, it has been studied very frequently [2]. The optical parameters play a significant role for various applications. In this paper an attempt has been made to study the various optical features like dispersion energy parameters, carrier concentration to effective mass number (N/m*), and carrier susceptibility (χ) by Wemple-Di Domenico and Spitzer-Fan model.

Experimental Detail

The Zr (0.01% atomic weight percent) doped TiO_2 thin films were deposited on FTO glass slides by doctor blade technique from the gel obtained by unconventional method and annealed at different temperatures. Here the film annealed at 350° C is chosen for study because of its better optical properties. The transmission and reflectance data of the films were taken in the wavelength range 300-900nm by UV-Visible photo-spectrometer (Cary 5000) and the refractive index was calculated by Kubeka-Monk method which is reported some-where else[3].

From the variation of refractive index it is observed that it increases initially up to 400nm and then decreases, which shows the dispersion in refractive index. The Wemple Di Domenico single oscillator model is useful to study the spectral dependence in the inter band absorption region [4].

Results and Discussion

A straight line fitting is done to $(n^2-1)^{-1}$ versus $(hv)^2$ plot as shown in Fig.1 and from the slope and intercept of the graph $-(1/E_oE_d)$ and E_o/E_d values are obtained respectively [4], where E_o represent the oscillation energy and E_d represent the dispersion energy. The oscillation energy is found to be 9.76 eV which is nearly equal to 3.18 times the calculated direct bandgap for the film annealed at 350°C [3] which is in good approximation to the empirical relation as reported by B.Yous [5] These parameters are related to the moments of imaginary part of complex dielectric constant (ε_2) [6]. The calculated values of M₋₁ and M₋₃ moments are found to be 2.29 and $0.024 (eV)^{-2}$, respectively.

The static dielectric constant of the film is also obtained from the optical parameters by using the relation $\varepsilon_r(0) = \eta_0^2 = 1 + \frac{E_d}{r}$(1)

The nd to be 3.29 and hence the value of zero frequency refractive index (n_0) is found to be 1.81.



Fig. 1. Plot of $(n^2-1)^{-1}$ vs $(hv)^2$ of Zr doped TiO₂ thin film

From Spitzer Fan model fitting to the optical data, contribution of free carrier electric susceptibility (χ) to the real dielectric constant is obtained [7]. According to this model

A straight line is fitted to the graph between real dielectric constant value and square of wavelength as shown in Fig. 2 whose slope and intercept gave the values of N/m* (carrier concentration to effective mass) and $-4\pi\chi$ respectively [7]



Fig.2. Plot of (ε_r) vs $(\lambda)^2$ of Zr doped TiO₂ thin film

From the slope the value of N/m* is calculated which is found to be 108.18×10^{44} m⁻³ and from the intercept the high frequency dielectric constant is found to be 1.37.



Fig.3. Plot of (-4 $\pi\chi$) vs $(\lambda)^2$ of Zr doped TiO_2 thin film

Fig.3.shows the variation of $-4\pi\chi$ with $(\lambda)^2$ which indicates that the electric susceptibility value increases with squared value of wavelength which is responsible for decrease in refractive index at higher wavelengths.

The calculated optical parameters obtained from both the models are presented in table 1

Table 1. Values of calculated optical properties of Zrdoped TiO2 thin film from Wemple Di Domenicomodel and Spitzer – Fan model.

Eo in in eV	Ed in eV	E ₀	n ₀	(N/m*)* 10^44 in m ⁻³
7.76	22.4	3.29	1.81	108.18

Conclusion

In this paper the detail optical properties study of the Zr doped TiO_2 thin film is studied by single oscillator model fitting proposed by Wemple Di Domenico and the dispersion in the refractive index and variation of real value of dielectric constant with wavelength is found to be well agreement with the variation of electric susceptibility obtained from Spitzer –Fan model. Based on this study the application of his film for solar cell application can be studied.

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Electrical Characterization of CH₃NH₃PbI₃ Based Planar Perovskite Solar Cells

Ashok Vishwakarma, M.S. Patel and Lokendra Kumar

Department of Physics, University of Allahabad, Prayagraj-211002

**Corresponding author: lokendrakr@allduniv.ac.in*

Abstract

Interface engineering between charge selective layers and photoactive metal halide perovskite absorbing layer is crucial to optimize the performance and stability of planar perovskite solar cells (PSCs). Here, we have fabricated perovskite solar cells with device architecture FTO/c-TiO₂/CH₃NH₃PbI₃/hole transport layer (HTL)/Ag by two step sequential spin coating method in nitrogen environment and used different conjugated polymers Poly[2,1,3-benzothiadiazole-4,7-diyl[4,4-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b'] dithiophene-2,6-diyl]] (PCPDTBT), Poly (3-octylthiophene-2,5diyl) (P3OT) and Poly (3-hexylthiophene-2,5diyl) (P3HT), as HTL. Highest power conversion efficiency, 6.68% has been obtained owing to better perovskite/HTL interface for P3HT as HTL in CH₃NH₃PbI₃ based planar PSCs. Electrical characterization is performed under 100 mW/cm² incident solar irradiation.

Introduction

Scientific community and industrial research paid more attention to fulfill the energy crisis in upcoming future due to limited fossil fuels. Metal halide PSCs have been obtained tremendous attention owing to its easy fabrication process and outstanding photovoltaic performance. PSCs have great potential to replace high cost processed commercialized silicon solar cells. Intensive research is devoted to commercialize planar PSCs due to its low-cost solution processibility on rigid as well as on flexible substrates. Outstanding power conversion efficiency (PCE) and environmental stability of planar PSCs make it a reasonable candidate for next generation solar cells. Methylammonium lead tri-iodide (CH₃NH₃PbI₃) based planar perovskite solar cells have great promise for low cost, stable and large area solar cells.

Understanding of charge transfer mechanism and efficient hole extraction from photo-active perovskite layer is necessary to optimize the photovoltaic performance of planar PSCs. Both organic (small molecules and conjugated polymers) as well as inorganic (CuSCN, CuI etc.) hole extracting layers are in application to produce efficient planar PSCs.

Seok *et al.* demonstrate that interface engineering of hole conducting polymers are key to realizing high photovoltaic performance of CH₃NH₃PbI₃ based PSCs. Poly (bis{4-phenyl} {2,4,6-trimethylphenyl} amine) (PTAA) produces high performance planar PSCs in normal as well as in inverted device architecture. Spiro-OMeTAD produces high performance PSCs but the dopants used in it restricts its application due to depression of perovskite/HTL interface. Therefore, there is need of a hole transport layer forming stable interface and efficient hole extraction for high photovoltaic performance and environmental stability to commercialize planar PSCs.

Here we have fabricated CH₃NH₃PbI₃ based planar PSCs with different hole transport layers like PCPDTBT, P3OT and P3HT in N₂ filled glove box and studied the effect of these conjugated polymers on J-V characteristics of planar PSCs.

EXPERIMENT AND OUTCOMES:

Experimental Section

Fluorene doped Tin Oxide (FTO) coated glass substrates were cleaned as standard method. A c-TiO₂ layer has been deposited using spin coating method at 2000 rpm for 30 sec in open air. The c-TiO₂ film first dried at 100°C for 10 minutes in open air on hot plate then calcined at 500°C for 1 hour in furnace. After that, 1M PbI2 solution in Dimethylformamide (DMF) has been spun on FTO/TiO₂ substrates at 3000 rpm for 30 sec and annealed at 90° C for 60 sec in N₂ filled glove box. After cool down to room temperature, Methylammonium Iodide of 40mg/ml concentration has been spun on rotating FTO/TiO₂/PbI₂ substrates at 3000 rpm for 30 sec. Color of substrates get changed after 10 sec of spinning indicating the formation of CH₃NH₃PbI₃ perovskite and after annealing the film at 90°C for 1 hour well crystallized black perovskite thin film obtained. Thin film of about 30 nm of different HTL deposited using spin coating method after cooling down to room temperature of perovskite film at 2000 rpm for 60 sec. Finally, 80 nm silver thin film as counter electrode is deposited using thermal evaporator.

Results and Discussion

Structural, optical and morphological properties of fabricated perovskite thin film have been analyzed

through X-Ray Diffraction (XRD) pattern, UV visible spectroscopy and scanning electron microscopy (SEM). Figure 1(a) represents XRD pattern of perovskite thin film with characteristic peaks well matched with the literature. An additional peak at 12.7° of PbI₂ has been observed. Optoelectronic characteristics, absorbance and band gap (1.5eV) were determined from UV-visible spectroscopy presented in figure 1(b).



Fig. 1. (a) XRD pattern, (b) UV-visible Spectra of $CH_3NH_3PbI_3$ perovskite thin film, (c) and (d) SEM of $CH_3NH_3PbI_3$ perovskite thin film at different resolutions.



Fig.2. (a) Energy level diagram and (b) J-V characteristics of CH₃NH₃PbI₃ based planar PSCs

Photovoltaic parameters of CH₃NH₃PbI₃ based planar PSCs with different HTL obtained from J-V curve have been presented in Table 1.

Solar cells	$\mathbf{J_{sc}}$	Voc	FF	PCE
with different	(mA/cm ²)	(Volt)	(%)	(%)
HTLs				
With	18.9	0.72	40	5.52
PCPDTBT				
With P3OT	14.2	0.70	45	4.50
With P3HT	15.9	0.70	60	6.68

Table 1. Parameters obtained from J-V curve

From J-V characteristics and energy level diagram of solar cells, a high series resistance (25.0 Ω -cm²) has been observed for PCPDTBT as HTL in planar PSCs. resulting low fill factor 40% and PCE (5.52%). Highest photocurrent density 18.9mA/cm² of PSCs with PCPDTBT as HTL is due high mobility of PCPDTBT (10⁻² cm²V⁻¹sec⁻¹) in comparison to P3HT and P3OT (10⁻³ cm²V⁻¹sec⁻¹). For P3HT as HTL, a low series resistance (17.7 Ω -cm²), highest fill factor 60% and PCE of 6.68% have been obtained for CH₃NH₃PbI₃ based planar PSC. The highest performance of planar PSCs, P3HT as HTL, is a result of better interface and efficient hole transfer to electrode. Thus, P3HT is better candidate among these polymers having great promise to produce efficient planar PSCs.

In conclusion, we have applied interface engineering and fabricated CH₃NH₃PbI₃ based planar PSCs to study the effect of different polymeric HTL on electrical characteristics via solution process. The central conclusion of our experiment is that P3HT form better interface for efficient hole transfer in CH₃NH₃PbI₃ based planar PSCs. Thus, interface engineering can be employed to find out other superior HTL candidate through tailoring the HOMO levels for high performing and stable planar PSCs in future.

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Effect Of Modifier On Spectroscopic Properties Of Lead Bismuth Phosphate Glass System Mixed With Neodymium (III) Oxide

G. Chinna Ram^{1*}, T. Narendrudu¹, A.Suneel Kumar² and D. Krishna Rao³

¹Department of Physics, Aditya Engineering College, Surampalem-533437, A.P., India. ²Department of Physics, Vivekananda Degree and PG College, Hyderabad-500072,India. ³Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar - 522510, A.P.,India. **Corresponding author:rangirajala@gmail.com*

Abstract

PbO–P₂O₅– Bi₂O₃–R₂O₃ (R = Al, Ga, In, Tl) glasses doped with Nd₂O₃ were prepared by melt quenching technique. The prepared glasses were characterized by the XRD patterns. Conventional spectroscopic studies viz., optical absorption bands around 351,431,473,514,526,581,628,683,747,804 and 874 nm wavelength corresponding to the transitions ${}^{4}I_{9/2} \rightarrow {}^{4}D_{1/2}$, ${}^{2}P_{1/2}$, ${}^{2}G_{9/2}$, ${}^{4}G_{7/2}$, ${}^{4}G_{7/2}$, ${}^{4}G_{5/2}$, ${}^{2}H_{11/2}$, ${}^{4}F_{9/2}$, ${}^{4}F_{7/2}$, ${}^{4}F_{7/2}$, ${}^{4}F_{7/2}$, ${}^{4}F_{7/2}$ and ${}^{4}F_{3/2}$ respectively. Judd-Ofelt(J-O)parameters have been evaluated for the prepared glasses using optical absorption spectra and these J-O intensity parameters have exhibited three prominent peaks at about 885, 1054, 1323 nm wavelength corresponding to the ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$, ${}^{4}I_{11/2}$, ${}^{4}I_{13/2}$ transitions levels respectively in the near infrared region. By using the J-O parameters various radiative parameters for the excited luminescent levels of Nd³⁺ ions are evaluated. Emission cross section and branching ratio values are observed to be high for ${}^{4}I_{11/2}$ level of Nd³⁺ ions The above investigations indicate that the glass system mixed with Ga₂O₃ could be a suitable candidate for 1.06 µm laser source in the near IRregion

Effect of substrate temperature on growth of Ti sub-oxide thin films deposited by DC Magnetron sputtering

Swapan Jana¹, Jitendra Bahadur^{1,2} and Debarati Bhattacharya^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085 India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094 India **Corresponding author:* <u>swapanj@barc.gov.in</u>

Abstract

Amorphous titanium sub-oxide (a-TiO_x) thin films have been deposited on Si substrates by DC magnetron sputtering technique with sputter power of 50 W at room temperature (RT) and 200 °C substrate temperature (T_s). The effects of substrate temperature on the structural and morphological properties of the thin films have been investigated. All films are smooth and uniform, their density increases and thickness and roughness decrease when deposited at T_s. This work gives some idea about the growth of a-TiO_x thin films from this technique without introducing external O₂ sources.

Analysis of Varied Atmospheric Annealing Effects on the Optical Properties of an Alternative SERS Platform.

Risa Marium Philip¹ and D. Bharathi Mohan^{1*}

1 Department of Physics, School of Physical, Chemical and Applied Sciences, Pondicherry University, R.V. Nagar, Kalapet, Puducherry 605014, India. *Corresponding author: d.bharathimohan@gmail.com

Abstract

Bismuth (Bi) thin films were fabricated on quartz substrates using DC magnetron sputtering and the post deposition annealing at 200° C were done on these films by varying atmospheric conditions such as high vacuum, nitrogen (N₂) and air. The optical responses supporting the plasmonic enhancements were studied. Color changes noticed support the plasmonic responses of the fabricated Bi films and the effect of different annealing's on the Surface Plasmon Resonance's (SPR's) can aid in optimizing a better film in future. As an application part, Surface Enhanced Raman Scattering (SERS) using Rhodamine 6G (RH6G) on initial film has resulted in an excellent upshot with Enhancement Factor (EF) of 10^{5} and Limit of Detection (LOD) of 10^{-7} molar concentration. This confirms the potential application of the films fabricated, for developing multifunctional, wide range SERS based plasmonic biosensors from Bi.

Study On In Doped ZnO Thin Film As Electron Transport Layer For Lead Free Perovskite Solar Cells And Its Simulation

Ebin Joseph, John Paul, Devika Mahesh and M.C. Santhosh Kumar*

Optoelectronic Materials and Devices Lab, Department of Physics, National Institute of Technology Tiruchirappalli, Tamil Nadu – 620 015

*Corresponding author: santhoshmc@nitt.edu

Abstract.

Perovskite solar cells are new generation solar cells which show efficiency more than 20%. A perovskite solar cell consists of an electron transport layer (ETL) or a hole transport layer (HTL) between the active layer and the cathode (or the anode) in order to reduce the recombination of the free charge carriers. Indium doped Zinc Oxide (In:ZnO) thin film is a potential ETL for perovskite solar cells. In:ZnO thin film is deposited on glass substrate by chemical spray pyrolysis technique at 425 °C. Structural studies carried out using X-Ray diffractometer showed crystalline structure and the optical band gap has been calculated using UV-Visible spectroscopic technique. Hall Effect measurement of the as-deposited film showed n-type conductivity. Further, simulation using SCAPS 1D software was carried out to study the possibility of utilizing this layer as an ETL of a perovskite solar cell. The obtained solar cell structure with 3 at% indium doped ZnO as ETL has a conversion efficiency of 5.65 %.

Introduction

A solar cell is a device that can convert light energy into electrical energy by the photovoltaic effect. The reasons for choosing perovskite materials for the application of solar cells are the high efficiency, tuneability of bandgap, easy and repeatable synthesis methods, facile low temperature solution-based fabrication, high absorption coefficient, very high values of open circuit voltage (V_{oc}), high diffusion length, high charge carrier mobilities etc [1].

The large-scale commercial production and photovoltaic field application of lead halide perovskites is hindered by the toxicity of lead. For development of environmental friendly lead-free perovskite solar cells (PSCs) some novel non- or low-toxic perovskite materials have been explored so far.

SCAPS is a one-dimensional solar cell simulation software developed at the Department of Electronics and Information Systems (ELIS) of the University of Gent, Belgium.

Experimental Methods

3 at% In doped ZnO thin film was deposited on cleaned glass substrate by spray pyrolysis technique as reported elsewhere [2] and named as I3ZO. Structural characterization has done by Rigaku Ultima IV. Transmittance spectra recorded using JASCO V670 and Hall Effect measurement has done with Ecopia HMS5000. Simulation of the proposed solar cell is done using SCAPS 1D solar cell simulation software.

Results and Discussion

Structural Characterization

The XRD pattern shown in Fig.1 is in well agreement with ICDD card number 36-1451 and thus confirmed the formation of crystalline film. The crystallite size (D) of the film was calculated using Debye Scherrer formula.

$$D = k\lambda/\beta cos\theta$$
 a)

where k is shape factor (0.94), β is full width at half maximum (FWHM) of major peaks of I3ZO, λ is the wavelength of X-rays (1.54 Å) and θ is the corresponding diffraction angle. The crystallite size is found to be ~ 24 nm.



Fig. 1. The XRD pattern of I3ZO

Optical Characterization

The smoothness and uniformity of the asdeposited thin film was confirmed from the interference observed in the transmittance spectrum (Fig. 2). The film thickness calculated from transmittance spectra using the Swanepoel's envelop method [3] is 731 nm.



Fig. 2. The transmittance spectra of I3ZO

The band gap of the thin film was calculated by extrapolating $(\alpha hv)^2 v/s$ (hv) curve to the energy axis (Tauc's plot) and estimated to be 3.25 eV, which is an admissible value for an ETL.

Electrical Characterization

The electrical properties of the sample were calculated using Hall Effect measurement at room temperature and the thin film was found to have n- type conductivity and the properties are shown in Table 1.

Table 1. Electrical properties of Indium doped ZnO

Carrier Concentration (cm ⁻³)	Resistivity (Ωcm)	Mobility (cm ² V ⁻¹ s ⁻¹)	
1.76x10 ¹⁸	1.52×10^{1}	2.69x10 ⁻¹	

Solar Cell Simulation with I3ZO as ETL

Three sets of simulations were carried out as reported [4-6]. The structure of each perovskite solar cell is assumed to be TCO/ETL/perovskite/HTL/metal. The perovskite materials chosen were $CH_3NH_3SnI_3$, CH_3NH_3SnBr and $CsSn_{0.5}Ge_{0.5}I_3$. The ETL and HTL for each of the solar cell is fixed (TiO₂ and CuI respectively) and the perovskite layer is varied. For each of such perovskite solar cell, the first simulation sequence conducted was by fixing the thickness of both ETL and HTL.

When the thickness of the perovskite layer is varied there was a corresponding variation in the efficiency of the solar cell. So, the thickness of perovskite layer is fixed for the highest efficiency observed. Then for the second sequence of simulation, the thickness of both perovskite layer and HTL were fixed and the thickness of ETL was varied to find the efficiency variation and the thickness of ETL for highest efficiency is optimized. For the last sequence of simulation, the thickness of both perovskite layer and ETL were fixed, in order to find the thickness of HTL for which the solar cell has optimum efficiency.

Among the reported solar cells, of which we have simulated, $CH_3NH_3SnI_3$ has the highest efficiency and was estimated to be 29.39%. So, the ETL of this solar cell (TiO₂) was replaced with Indium doped ZnO and found that the new proposed solar cell has an efficiency of 5.65 % which is actually less than the previous case. The reduction in efficiency may be attributed to the smaller film thickness (731 nm) in comparison to TiO₂ layer (1.5 µm). Various defects present in the ZnO film may act as traps for photogenerated carriers, which may also play a major role in governing the efficiency of the solar cells.

Conclusion

Indium doped zinc oxide thin film was prepared by spray pyrolysis method and its structural, optical and electrical properties were studied. Indium doped ZnO thin film was proposed as an ETL for perovskite solar cell and the simulation studies have done. From the simulated data, it can be concluded that In doped ZnO thin film can be used as a potential ETL for perovskite solar cells. The proposed solar cell has an efficiency of 5.65 %.

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Electrical Characterization of Nickel-Oxide Based Thin Films Obtained By Chemical Bath Deposition

Abhishek K J¹ and Umananda M Bhatta^{1,*}

¹Centre for Incubation, Innovation, Research and Consultancy, Jyothy Institute of Technology, Visvesvaraya Technological University, Bengaluru - 560082, India *Email: nandasringeri@gmail.com

Abstract

In this work, Nickel Oxide (NiO) based thin film has been grown on silicon (111) substrate by chemical bath deposition method, followed by annealing at 400°C under air atmosphere. X-ray diffractometry has been used to ascertain the formation of NiO and its crystallinity. Current-Voltage (IV) characteristics have been performed at different temperatures (from 30°C to 180°C) under natural light conditions. At a constant voltage, current increases with respect to increase in temperature confirming the semiconductor nature of the NiO thin film. Further, at room temperature, the thin film shows a better current response under natural light as compared to dark conditions.

Introduction

Attention towards Nickel Oxide based films has been increasing due to their potential applications as electro-chromic devices, gas and moisture sensing devices, alkaline batteries, p-type transparent conducting films¹⁻³ among others.

Several methods of deposition have been employed to obtain NiO thin films, such assputtering technique, sol-gel method, pulsed laser deposition, spray pyrolysis, evaporation, chemical bath deposition, colloidal deposition etc. All these depositional techniques offer varied advantages depending on the application of interest. Among these various deposition methods, chemical bath deposition (CBD) offers unique advantages in terms of larger area deposition and relative simplicity. Thus, CBD method has been successfully employed to obtain, sulphide, selenide and other semiconductor compounds⁴. There are a few reports where CBD method has been employed to obtain NiO and/or Ni (OH)2 thin films5-7

In this work, NiO thin films have been deposited by chemical bath deposition method on Si (111) substrate. The specimen was then characterized using XRD. IV measurements under dark and natural light conditions have been performed. Further, temperature dependent IV measurements have also been performed under natural light.

Experimental details

Growth of NiO film is based on the thermal treatment of an aqueous solution containing Ni2+ and urea. 1 mole of nickel nitrate hexahydrate was dissolved in 50ml DI water to which 1 mole of urea solution (in 50ml DI water) was mixed at RT to create 100 ml chemical bath solution. This chemical bath solution was heated to a temperature between $95^{\circ}C - 100^{\circ}C$ in an oil bath^{5,6}.

RCA cleaned Si (111) substrate was introduced vertically into the chemical bath solution and kept undisturbed for 2 hours. A greenish precipitation was observed at the bottom of the bath solution. The substrate was then withdrawn from the bath solution, washed in DI water, and is immediately annealed at 400°C in air for an hour to obtain black/grey film. Subsequently, X-ray diffraction (XRD) was performed on the annealed specimen in a Bruker D8-Advanced ecosystem equipped with 1KW Cu-K $_{\alpha}$ source of wavelength 0.154nm. Later, temperature dependent IV measurements were done using homemade 2 probe instrument in a temperature ranging from 30°C to 180°C, under natural light. IV measurements were also done under dark and natural light conditions at RT.

Results and Discussion



Fig. 1. XRD pattern of the NiO thin film

Figure 1 shows the XRD pattern of the annealed specimen. The pattern confirms the formation of NiO thin film with 32% crystallinity. Peaks corresponding to NiO was observed at (111), (200) and (220) corresponding to FCC (PCPDF no: 00-004-0835). The substrate Si (111) peak at 28.3° is subdued, indicating the uniformity of the deposited NiO film. Further, Scherrer equation was applied to

calculate the average crystallite size which comes out to be 7.8 nm.

Electrical characterization of NiO thin films has been done by IV measurements for which two gold electrodes were deposited on NiO film, 0.8 cm apart.



Fig. 2. IV measurement of NiO thin film under natural light and dark conditions at RT

Figure 2 shows the IV measurements performed under dark and natural light conditions at RT. It reveals an almost linear response of current and the current response under natural light conditions is better as compared to dark condition. This is because, under natural light conditions, the incident photon is able to create electron-hole pairs in the film which results in an elevated current response.



Fig. 3. (a): current response to voltage at various temperature; (b) : Current response to temperature at various applied voltages.

Figure 3(a) shows the temperature dependent IV response of NiO thin films which reveals a departure from the linear behavior at higher temperatures. Figure 3(b) further reiterates this observation. As the temperature increases, at any given applied voltage, an increase in current thereby, an increase in conductivity is seen. Further, the rate of increase in conductivity increases at higher temperatures, which reflects a typical semiconductor behavior of the NiO thin films⁷. As the temperature is increased, more and more charge carriers will make it to the

conduction band from the valence band, thus increasing conductivity. Further, at elevated temperatures, the crystallinity of the thin film is improved, which results in an increase in grain size, thus leading to a reduction in the grain boundaries, thereby enhancing the mobility of the charge carriers. This further contributes to the increase in the electrical conductivity of the specimen⁸.

Summary

NiO thin films were successfully grown on Si (111) substrate via chemical bath deposition method. Nickel nitrate hexahydrate is used as the source of nickel and urea as the precipitating reagent. XRD analysis confirmed the formation of NiO thin films with an average crystallite size of 7.8nm. IV measurements were done in the temperature range 30°C to 180°C under natural light conditions which revealed a nonlinear current response, especially at higher temperatures. An increase in current, thereby conductivity, with increasing temperature was also observed, which indicated the semiconductor behavior of the NiO thin film. IV measurements under dark and natural light conditions at RT revealed a better photoresponse of the NiO thin film under natural light conditions.

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Studies on CH₃NH₃PbI_{3-x}Cl_x Mixed Halide Perovskite Thin Films for Photovoltaic Application. Preeti Shukla¹, P. Kumar² and Lokendra Kumar¹

^{1.} Molecular Electronics Research Laboratory, Physics Department, Faculty of Science, University of Allahabad, Prayagraj-211 002, India

²CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi-110012, India.

*Corresponding author: lkumarau@gmail.com

Abstract

Mixed halide perovskite thin films have proved to be a successful attempt to fabricate stable solar cells. We have fabricated and characterized the CH₃NH₃PbI_{3-x}Cl_x mixed halide perovskite thin films for photovoltaic applications. Here, a device architecture FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/P3OT/Ag was fabricated with TiO₂ as electron transport layer (ETL) and P3OT as hole transport layer (HTL). Structural and optical properties were investigated using X-ray diffraction, UV-vis absorption spectroscopy, and photoluminescence spectroscopy. The fabricated solar cells have been explored for P3OT as a promising hole transport material in mixed halide perovskite solar cell.

Introduction

The mixed halide perovskite has attracted immense attention due to its fascinating properties: high absorption coefficient, long-range diffusion length, and low-cost fabrication, which is significantly attributed to increased current density [1-3]. The degradation and stability of perovskite solar cells depend on various parameters, among which layers composition plays an important role. It decomposes to the orthorhombic phase at low temperatures, which is not preferable for solar cell application. Increasing the efficiency of solar cells is one of the most challenging and vital tasks in the photovoltaic domain, which needs an understanding of the fundamental photo-physics and optoelectronic properties of these halide perovskites. The single halide CH₃NH₃PbI₃ perovskite solar cells showed high power conversion efficiency (PCE) but low stability. Recently, several works have been reported on mixed halide perovskite due to its stability, photoconductivity, and tunable bandgap [4-6]. It was reported that chlorine ions boost the mobility of excitons and charge transport in perovskite and stabilize the CH₃NH₃PbI₃ lattice [7-8].

In the present study, we have studied the properties of mixed halide perovskite thin films fabricated via the solution process method. The structural and optical properties were analyzed by X-ray diffraction, UV-vis. absorption spectroscopy, and Photoluminescence (PL) spectroscopy. Further, solar cells in FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/P3OT/Ag configuration were fabricated to investigate photovoltaic properties.

Experimental details

FTO coated glass substrates were patterned and then cleaned with soap solution, acetone, and isopropanol. Then hole blocking layer TiO_2 was deposited at 2000 rpm for 30 seconds, annealed at

100 °C for 10 min, and then sintered at 450 °C for 60 min. After that, the active layer of CH₃NH₃PbI_{3-x}Cl_x was spin coating on the substrate at 3000 rpm for 30 seconds from the solution containing PbI₂, PbCl₂, and CH₃NH₃I in an optimized appropriate molar ratio under a nitrogen-filled glove box and then annealed for 60 minutes at 100 °C. Furthermore, the HTL of P3OT 16mg/ml in chlorobenzene was spin-coated at 2000 rpm for 60 seconds. A thermal evaporator is used to deposit the Ag electrode (85nm) at a base pressure of 1×10^{-6} Torr.

Optical characteristics were carried out by Motras Double Beam UV-vis. spectrophotometer (Model: UV Plus). The steady-state PL spectra were recorded using Horiba Florolog spectrometer equipped with a 450W xenon lamp. X-ray diffractometer (Proto A-XRD) equipped with CuK α (λ = 1.54 Å) radiation was used to analyze the structural properties. The current density and voltage (J-V) curve were recorded using Photo Emission Technology, USA (PET-SS50AAA-EM), class AAA solar simulator attached with a Keithley 2400 source meter.

Results and discussion A. Optical Properties

Figure 1 shows the UV-vis. absorption spectrum and photoluminescence spectrum of CH₃NH₃PbI₃. _xCl_x mixed halide perovskite thin film on glass substrate. The absorption spectrum of the perovskite layer shows an excellent coverage of the solar spectrum. The experimental value of the bandgap calculated from tauc plot is 1.58 eV. The steadystate PL emission spectra of the perovskite layer shows emission peak at 770 nm recorded with excitation wavelength 667 nm. The bandgap of perovskite film has also been estimated from PL spectra (~ 1.61 eV) which is approximately equal to that calculated from tauc plot (~1.58 eV).



Fig. 1. UV-vis. Absorption and PL emission spectra of CH₃NH₃PbI_{3-x}Cl_x perovskite thin film.

B. Structural Properties



Fig. 2. XRD pattern of CH₃NH₃PbI_{3-x}Cl_x perovskite thin film.

Figure 2 shows the XRD pattern of as-deposited perovskite thin film on the glass substrate. The diffraction peaks at 14.1° , 28.4° , and 43.2° correspond to (110), (220), and (330) planes of the tetragonal phase of CH₃NH₃PbI₃ perovskite film, which indicate the high crystallinity of perovskite film [9]. Williamson-Hall plot was used to calculate the micro strain from XRD data, and it is found approximately equal to 4.25×10^{-4} .

C. Photovoltaic Properties

Further to investigate the photovoltaic characteristics, solar cells are fabricated using TiO₂ as ETL and P3OT as HTL. A photoactive perovskite layer is sandwiched between ETL and HTL, and then Ag is deposited as the top electrode resulting in FTO/TiO₂/CH₃NH₃PbI_{3-x}Cl_x/P3OT/Ag structure. Figure 3 shows the dark and illuminated current density versus voltage (J-V) characteristic curve of devices. The photovoltaic parameter was found to be: short circuit current density (J_{SC}) of 12 mA/cm², open-circuit voltage (V_{OC}) of 0.7V, and fill factor (FF) of 0.58, which leads to a power conversion efficiency of 4.83%.



Fig. 3. The J-V characteristics of CH₃NH₃PbI_{3-x}Cl_x based solar cell.

D. Conclusion

We have investigated the optical, structural, and photovoltaic properties of mixed halide perovskite for solar cell application. The UV-vis. and PL emission spectra reveal bandgap of 1.58 eV and 1.61 eV, respectively, which is in good agreement with previously reported results. XRD pattern shows highly crystalline tetragonal phases of perovskite. The fabricated solar cell exhibited $J_{SC} = 12 \text{ mA/cm}^2$, $V_{OC} = 0.7 \text{ V}$, FF = 0.58 and PCE of 4.83%.

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Surface modifications study of Si substrate in Ar/O₂ RF plasma for semiconductor device applications

First Yogendra Kumar*, Vrushank Mehta, Chetan Jariwala, and Rajesh Kumar

Institute for Plasma Research, Gandhinagar, 382428

*Corresponding author: yogendra.kumar@ipr.res.in

Abstract

Plasma etching/modifications is critical in the development of silicon based electronic devices such as solar cell, integrated circuits (ICs), and transistors. In this study, we report the surface modifications of single crystalline silicon induced by RF plasma formed using argon and oxygen gases. Field emission scanning electron microscopy (FE-SEM), Atomic force microscopy (AFM) and Raman spectroscopy techniques have been utilized to examine the surface modifications. Raman spectra results reveal the enhancement in longitudinal optical phonon mode (~520.5 cm⁻¹) due to the nanostructures formation by plasma treatment. FE-SEM results analysis of the pristine and plasma treated samples indicate the surface modifications upon plasma treatment. AFM results exhibit that the surface roughness significantly increases for plasma treated samples and corroborated with FE-SEM results.

INTRODUCTION

Semiconductor materials have drawn an immense attention due to wide range of technological applications such as light-emitting diodes (LEDs), transistors, solar cells, photodetector, thermistor, thermoelectric, field emission, biosensors, and so on [1]. In particular, the silicon (Si) is a widely explored semiconductor materials in scientific community and industries because remarkable electronics and optoelectronics properties. [1-2]. Nowadays, plasma etching/modifications of Si are crucial for the improvement of several critical parameters, i.e., stoichiometry, morphology, and process rates, which are a key feature in the various emerging fields such as nanotechnology, microelectronics, optics, medical engineering and so on [3]. Moreover, monitoring and controlling the constitutional parameters (e.g., gas pressure, power, composition, substrate temperature, etc.) are essential for designing the surface texture for the particular applications [1-2].

In addition, the Si surface texturing process has drawn more attention to reducing the surface reflectance and enhancing the light trapping to achieve the higher conversion efficiency. In order to improve the solar cell device performance, plasma etching/surface modifications have been investigated as alternative approach to develop the large area surface texturing in short processing time [4]. Hence, surface roughness plays a crucial role in determining the optical properties (e.g., absorbance and reflectance) [1].

In view of this, we have investigated the surface modifications of crystalline silicon induced by RF plasma formed using argon and oxygen gases. Surface texturing of crystalline silicon are examined using FE-SEM, AFM, and Raman spectroscopy. FE- SEM and AFM results provide the evidence of surface modifications, while Raman spectroscopy results bolster the FE-SEM and AFM studies.

EXPERIMENTAL DETAILS

Plasma etching/surface modifications were conducted using in house developed system in which plate electrode was connected to 13.56 MHz RF generator. Gas flows (Ar:O₂, 20:80) are controlled by a standard mass flow regulator. P-type c-Si substrates with thickness of 270 μ m has been used. The pristine and surface modification of plasma treated c-Si sample (10 min.) were characterized using FE-SEM, AFM, and Raman spectroscopy.



Fig. 1. FE-SEM image of pristine (a) and (b) plasm treated Si sample at 150 KX. (c) and (d) represent the magnified view of pristine and plasma treated Si sample.

EXPERIMENTAL DETAILS

Fig. 1. Exhibits the FE-SEM image of pristine and plasm treated Si samples. Pristine Si sample shows the smooth structure surface, i.e., no signature of surface modifications/texturing is present. However, crystalline Si sample treated with the Ar/O_2 plasma indicates the surface modifications, i.e., the evolution of nanostructures. Moreover, the magnified view of pristine and plasma treated Si samples [Fig.1 (c-d)], apparently confirms plasma induced the surface modifications. The AFM micrographs of pristine and plasma treated Si samples are shown in fig. 2 (a-b). The root mean square (RMS) value of pristine and plasma treated samples is found to be 0.302 nm and 0.509 nm, respectively.



Fig. 2. AFM images of pristine (a) and (b) plasma treated Si samples.

Here, it is should be noted that plasma treated sample exhibits the formation of asperities on the surface. The enhancement in the RMS value of plasma treated sample as compared to pristine sample seems attribute to the emergence of asperities; and eventually enhances the surface roughness [5]. These results are in well corroborated with the FE-SEM results. Raman spectra of pristine and plasma treated c-Si are shown in fig. 3 (a-b). The very intense and narrow peak at ~520.5 cm⁻¹ is observed for pristine and plasma treated Si sample, which arises due to the first-order longitudinal (LO) optical phonon mode.



Fig. 3. Raman spectra of pristine and plasma treated Si sample (a) and (b) magnified view of first order optical phonon mode (\sim 520.5 cm⁻¹). Inset [Fig. 3 (a)] shows the second order mode.

A broad structure appears in the Raman spectrum in the range ~ 925 to 1000 cm⁻¹. It is found that this broaden band in c-Si attributes to second order optical (2TO) phonon modes. Further, Raman spectra demonstrates that Raman band intensity is not similar for pristine and plasma treated samples, i.e., there is a relatively enhancement in the intensity of Raman modes of plasms treated c-Si sample. It is noteworthy that the intensity of the Raman band is sensitive to the crystal structure, defects, and anomalies in the materials due to strong sensitivity towards phonon characteristics and provide the significant information about the materials [6]. The one or two orders of enhancement in the Raman intensity attributed to formation of photonic nanojet have been observed earlier [7]. In the present study, the relative enhancement in the peak intensity may be unlikely to occur from this phenomenon. Further, we wish to stress that we did not observe the any signature of oxide and amamorphous phase formation in Raman spectroscopy results. Previous studies reported that the peak intensity of the Raman scattering signal enhanced from etched silicon due to increase of the interaction area [8]. Here, FE-SEM and AFM results demonstrate the formation of nanostructures in plasma treated c-Si sample. The enhancement in the intensity of the Raman mode of plasma treated sample in comparison of pristine sample attributed to the different absorptions of probe light scattered and reflected due to enhancement of surface roughness and formation of asperities in the plasma treated sample. Therefore, the enhancement in the intensity of Raman modes of plasma treated Si sample may attribute to increase of surface area. Here, we assume that induce surface roughness and asperities would be suitable to enhance the absorption of incident light.

CONCLUSION

In the present study, we have investigated the surface modifications of c-Si sample using the FE-SEM, AFM, and Raman spectroscopy techniques. FE-SEM micrographs analysis confirm the formation of nanostructures. AFM analysis shows that the RMS value and surface roughness are higher in plasma treated sample. The relatively higher Raman band signal of plasma treated sample is attributed to the enhancement of the interaction area due to surface modifications.

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The Study of Hydrophilicity, Structural and Optical Properties of Zn and N-doped TiO₂ Thin Films

Manish K Vishwakarma^{*1}, Manjeet¹, and Puneet Jain¹

¹Department of Physics, Indian Institute of Technology Roorkee, Roorkee, Uttarakhand, India, 247667

*Corresponding author: mvishwakarma@ph.iitr.ac.in

Abstract

Among the wide bandgap semiconductors, TiO_2 is the highly stable and cost-efficient semiconductor used for the different photocatalysis processes like water splitting, chemical waste degradation, anti-micro bacterial activities, and more. Materials showing high hydrophilicity (surface phenomenon) with low bandgap are required to improve photocatalysis efficiency. We report the synthesis of Zn (4 wt.%) and N (4 wt.%) doped TiO₂ thin films using the spin coating technique to improve surface wettability. The XRD pattern shows the growth of the pure anatase phase of TiO₂. UV absorption spectra show a minor increment in the bandgap of the Zn and N doped TiO₂ thin films. The water contact angle with pure TiO₂ is 33.45° and reduces to 17.94° after 4 wt.% doping of Zn and N. The results show the enhanced hydrophilicity in the Zn and N doped TiO₂ thin films.

Introduction

The hydrophilicity of the surface is an essential property of a photocatalyst. Metal oxides (TiO₂¹, ZnO, NiO, and more) were always popular among researchers in wide bandgap semiconductors. TiO₂ is a chemically stable, cost-efficient metal oxide that shows high photocatalytic property². In this paper, we proclaim the synthesis of Zn and N-doped TiO₂ using the spin coating technique. Our focus is to study the change in the surface wettability and optical properties of the TiO₂ after the transition metal (Zn) and nonmetal (N) doping. The water contact angle measurement is performed to check the surfaces hydrophilic property, and UV-absorption spectroscopy is done to study the change in optical properties. Crystallinity and compactness of the surface are studied with the help of XRD measurement and FE-SEM images, respectively.

Thin Film Fabrication

Pristine and doped TiO₂ thin films are prepared using the spin coating technique. Precursor solutions were prepared for the p-TiO₂ thin films by dissolving 1 ml of titanium tetra-isopropoxide (TTIP) in 5 ml of isopropyl alcohol (IPA) and stirred on a magnetic stirrer for 5 min. Then after 0.5 ml of acetic acid is mixed with the solution dropwise to prevent the precipitation of the TiO₂ and stirred vigorously for 1 hour. A solution is prepared for the Zn and N doping by dissolving 4 wt.% (CH3COO)₂Zn in methanol and 4 wt.% Urea in IPA, respectively. The prepared dopant solution is mixed accordingly with the precursor and coated on the glass substrate (1 cm x 1 cm x 1.34 cm) with the help of the spin coater at 3000 rpm for 60 sec. Coated films were dried on the hot plate at 100°*C* for 1H and then annealed in a muffle furnace at $450^{\circ}C$ in air for 1H to achieve the crystallinity and remove the organic solvents.

Results and Discussion

Figure 1 represents the XRD pattern of p-TiO₂ and Zn, N-doped TiO₂. The Pure anatase phase of TiO₂ is formed with the two peaks at $2\theta = 25.3^{\circ}$ and $2\theta = 47.9^{\circ}$. The crystallite size is calculated using Scherrer's equation,

$$D = \frac{0.9\lambda}{\beta Cos\theta}$$

Where D is the crystallite size, λ is the wavelength of the X-Ray, β is the FWHM of the peak, and θ is the angle. We found that the crystallite size got increased with the doping. Crystallite size of p-TiO₂ and Zn, N-TiO₂ at peak positions $2\theta = 25.3^{\circ}$ are 0.2558 nm, 0.2957 nm.



Figure 1 XRD pattern of p-TiO₂ and Zn, N-doped TiO₂

Figure 2 represents the FE-SEM micrographs of p- TiO_2 (Figure 2(a)) and Zn, N- TiO_2 (Figure 2(b)) which shows the flat and compact surface morphology. The lattice distortion and the change in the grain size of the crystallite are not obvious from the micrographs.



Figure 2(a) p-TiO₂





Figure 2 FESEM micrographs of TiO₂ Thin Films

Figure 3 shows the UV visible absorption spectra of p-TiO₂ and Zn, N-TiO₂ thin films. We calculated the optical bandgap of the p-TiO2 and Zn, N-TiO₂ thin films 3.19 eV and 3.48 eV, respectively using the tauc plot method. The absorption spectra of Zn, N-TiO₂ show the blue shift with respect to p-TiO₂. Figure 4 shows the water contact angle (WCA) with the Zn, N-TiO₂ thin film. WCA with p-TiO₂, and Zn, N-TiO₂ are 31.45° and 17.94°, respectively, which shows the doping of Zn and N increased the surface hydrophilicity impressively.



Figure 3 UV-Vis absorption spectra and tauc plot



Figure 4 WCA of Zn, N-TiO₂

Conclusion and Acknowledgement

In this paper, we synthesized the undoped TiO_2 and Zn (4 wt.%) and N (4 wt.%) doped TiO_2 thin films and characterized it systematically. We found an impressive increment in hydrophilicity. We also reported the observed blue shift in the absorption spectra of the Zn, N-TiO_2. Finally, I would like to thank my colleague Mr. Ramesh Kumar for his support and discussions regarding the work.

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Enhanced UV Photodetection of NiO Thin Film With Au Decoration

Athira M^{1,2}, S Angappane¹

¹Centre for Nano and Soft Matter Sciences (CeNS), Shivanapura, Bangalore-562162, India, ²Manipal Academy of Higher Education (MAHE), Manipal-576104, India

*Corresponding author: angappane@cens.res.in

Abstract

Nickel oxide is a p-type semiconductor having wide bandgapwhich makes it a desirable candidate for visible-transparent UV detection applications. In this study we have chosen the NiO thin film optimized using RF magnetron sputtering. A highly crystalline NiO thin film was achieved and tested for 365 nm UV detection. Further, when the NiO thin film was subjected to Au decoration, the responsivity and the response time areimproved by about six times.

Introduction

Nickel oxide is p-type semiconductor having particular electrical and optical properties, which makes it an excellent candidate for transparent conducting film, solar cells, photodetectors and electrochromic device applications [1]. NiO thin films are synthesized using chemical methods like, sol-gel synthesis and spin coating, as well as using physical vapor deposition methods. The RF magnetron sputtering is a feasible method to produce high quality crystalline thin films with good thickness control and uniformity [2]. Nickel oxide has reportedly shown bandgap in the range 3.2-3.7 eV. It is the presence of Ni^{3+} ions in the NiO matrix that gives p-type conductivity [1, 2]. RF sputtered NiO thin films were used as HTL in solar cells, and as the p-type material in p-n heterojunction diodes and plasmonic photoelectric conversion devices [3, 4].

NiO film responds to UV illumination through photo conduction. The incorporation of noble metal nanoparticles in the metal oxide matrix improves the photoresponse and associated parameters like photodetectivity and response time. Notably, Au nanoparticles can act as a catalyst for light absorption by acting as charge separation and recombination centers [5].

Device fabrication and characterization

Firstly, we have fabricated gap electrode of Au on quartz substrate. Over the gap electrode, with a shadow mask of area 4 mm², the NiO thin film was deposited by RF sputtering using Ni target at 60 W and at 30 % oxygen flow. The deposition temperature was 100 °C followed by annealing at 350 °C. The process resulted in a barely conducting NiO thin film. Further, with shadow mask, Au was sputtered on the NiO device for 5 seconds followed by heating at 150 °C to get nanoparticulated Au film. The fabricated

devices were tested for UV photodetection using UV source of wavelength 365 nm with an incident light intensity of 78 mW/cm². The *I-V* characteristics were measured using Keithley 4200 SCS.



Fig.1. UV-Visible absorption spectra of NiO and Au/NiO thin films. Inset shows the XRD data of cubic crystalline NiO and FESEM image of Au decorated NiO surface.

Results and Discussion

The UV-visible absorption spectrum of pure NiO and Au/NiO in Fig. 1 shows that Au/NiO has better light absorption. The annealed NiO thin film was characterized using X-ray diffraction showing the formation of cubic crystalline NiO with (200) dominant plane (Fig. 1 inset). NiO is known to exhibit electrical aging when exposed to ambient atmosphere which means it becomes more resistive with time. Typical growth of sputtered NiO is along (111) and (200) planes. However, when the dominant plane is (200), the film is electrically more stable. The I-V characteristics of the devices, NiO and Au/NiO films deposited on the gap electrodes, without (dark) and with 365 nm light illumination are shown in Fig. 2. Notably, the dark current of NiO has increased from tens of nanoamperes to hundreds of nanoamperes with incorporation of Au. This implies that the sputtered Au has not formed a Schottky junction with NiO, in case of which the dark current would have been lower than that of pure NiO film. When illuminated with UV light, the photocurrent generated, which shows that NiO, with or without Au, is photoconducting. The photocurrent is higher for Au/NiO than NiO device.

Inset of Fig. 2 shows the temporal response of NiO and Au/NiO photodetectors. The measurements were carried out at an interval of 100 s. The responsivity (R) was calculated using the following equation:

$$R = \frac{I_{ph} - I_d}{r}$$

 $P_{in}A$

where I_{ph} , I_d , P_{in} and A are the photocurrent, dark current, incident power density and area of the device, respectively.



Fig. 2. *I-V* characteristics of NiO and Au/NiO devices. Insets show the cross-sectional schematic diagram of the device (top-left) and the temporal response of NiO and Au/NiO photodetectors on illumination with 365 nm light (bottom-right) at 5 V bias.

Table 1 shows the calculated photodetector parameters of NiO and Au/NiO devices. The responsivity, detectivity and rise and decay times are better for Au/NiO device. The rise time is longer than decay for pure NiO device possibly due to the presence of adsorbed O2 molecules on the metal oxide surface which slows down the charge transfer. The Au/NiO device has higher photocurrent and much faster rise and decay times which can be attributed to the presence of Au on NiO surface. The Au on NiO surface prevents the adsorption of O_2 molecules and thereby improves the response time. Also, the decoration of Au on NiO film (Au/NiO) has shifted the UV absorption peak to 530 nm. The redshift of the plasmonics absorption with the increase in gold thickness is not uncommon [6, 7].

Moreover, the peak broadens due to the irregular shape and size of the gold agglomeration which creates the plasmonic resonances at different wavelengths having most at 530 nm.

Table 1. UV photodetector parameters compared

Sample	R (µA/W)	Detectivity (Jones)	Rise time (s)	Decay time(s)
NiO	3.5	1×10 ⁷	71.8	54.9
Au/NiO	22.7	1.8×10 ⁷	11.6	11.6

Conclusion

Highly crystalline NiO thin film was deposited using RF magnetron sputtering. The photodetector of NiO was fabricated on gap electrode and tested for UV detection. The device performance was compared with the nanoparticulated Au deposited NiO photodetector. The Au/NiO device has achieved a responsivity of 22.7 µA/W while the pure NiO device shows responsivity of 3.5 µA/W. The response time of Au/NiO device is six times higher than that of pure NiO. The improvement in performance of Au/NiO device is attributed to the presence of noble metal nanoparticles which enhanced the UV absorption and limited the oxygen adsorption on metal oxide surface. The UV response and photodetector parameters can be further improved by optimizing the Au nanoparticle size and the processing temperatures.

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Magnetic Ground State of Iron Mononitride

Niti¹, Yogesh Kumar¹, Thomas Prokscha² and Mukul Gupta^{1*}

¹UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India ²Laboratory for Muon Spin Spectroscopy, PSI, CH-5232 Villigen PSI, Switzerland

*Corresponding author: mgupta@csr.res.in

Abstract

In the quest to understand the magnetic ground state of iron mononitride (FeN), we performed low energy muon spin-rotation (LE- μ SR) measurements in the temperature range of 5-320 K. Instead of a rock salt (RS) type structure prevalent in transition metal nitrides, FeN crystallizes in a zinc-blende (ZB) type structure. Theoretical works suggest a non-magnetic ground state for ZB-FeN while a magnetic component has been recently observed in ultrathin (< 5 nm) FeN films. On the contrary, thicker FeN films always exhibited a nonmagnetic ground state. To further clarify, we studied 3 and 30 nm thick epitaxial FeN thin films. LE- μ SR measurements confirmed the presence of a ferromagnetic component, irrespective of the thickness of FeN thin film.

Surface Morphological Study of Swift Heavy Ion Irradiated CdZnTe Thin Films

Praveen Dhangada^{1, 2}, *Madhavi Thakurdesai², Smita Survase³, Arvind R. Singh⁴

¹A.Vartak College, Vasai Rd. (W), Dist. Palghar, Vasai, 401 202,

² Thin Film Research Laboratory, B.K. Birla College (Autonomous), Kalyan, 421 304,

³ K.J. Somaiya College of Arts, Commerce and Science (Autonomous) Mumbai, 400 077,

⁴GNK Nano Research Group, Department of Physics, G. N. Khalsa College, Matunga, Mumbai 400 017,

*Corresponding author: madhavi.thakurdesai@bkbirlacollegekalyan.com

Abstract

Swift Heavy Ion (SHI) irradiation is an effective technique to induce surface modifications in thin films. In the present investigation, CdZnTe films deposited by vacuum evaporation method are irradiated by 100 MeV Ag ions at a fluence of 1×10^{12} ions/cm² and 5×10^{12} ions/cm². Atomic Force Microscopy (AFM) is employed to investigate Ag ion induced surface modifications. Effect of Ag ion irradiation on grain size, grain distribution, surface roughness, etc is studied.

1. Introduction

Polycrystalline CdZnTe (CZT) has gained much attention due to its widespread applications in nuclear radiation detectors, solar cells and other optoelectronic devices [1]. The performance efficiency of these devices is strongly dependent on reactions occurring at the surface. These surface reactions are sensitive to surface topography e.g. the surface roughness value strongly influences the charge transport properties of CZT thin films [2].

Irradiation by Swift Heavy Ions (SHI), having energies more than 1 MeV/nucleon is an efficient tool for modifying the surfaces of these films in the controlled way [3]. Therefore in the present work 100 nm thick CZT thin films are irradiated by 100 MeV Ag ions beam at various fluences.

2. Experimental Method:

The thermal evaporation method is used to deposit CZT thin films over cleaned glass substrates with commercially available 99.999% pure stiochiometric CZT powder. Pressure was maintained approximately at 10⁻⁶ mbar throughout the process of evaporation. The thickness of the films was monitored in-situ by quartz crystal thickness monitor and was kept around 100 nm for all the films. All irradiations were carried out in an extended beam-time at Inter University Accelerator Center (IUAC), New Delhi, using the 15 UD Pelletron facilities.

The surface morphology of as-deposited and irradiated films is studied by Atomic Force Microscopy (AFM) using Nanoscope IIIa from Digital Instruments, Veeco.

3. Results and discussion: 3.1 Atomic Force Microscopy (AFM) study:

The surface morphology of the as-deposited and Ag ion beam irradiated CZT thin films is studied using Atomic force Microscopy (AFM) in the contact mode. Fig. 1 shows the three-dimensional (3D) AFM pictures of as-deposited and Ag ion beam irradiated CZT thin films. The AFM image of as-deposited films shows large grains of uneven sizes. Hence image J software is used to determine the average size of the grains. The average size of the grains in case of as-deposited films is ~ 7.3 nm. After irradiation at fluence of 1x 1012 ions/cm2, grain distribution changes and uneven grains seen in the asdeposited film are found to be more circular in shape. The average grain size is changes to 5.8 nm. When irradiated at a fluence of 5×10^{12} ions/cm², the average grain size changes to 3.6 nm and the flattening of surface is observed which might be due to ion assisted enhancement of surface diffusion. Further, if the value of electronic energy loss (Se) reaches beyond a threshold value (Seth) then latent tracks having cylindrical geometry and radius of a few nanometers are formed in the wake of ion beam. If the latent track temperature exceeds the melting temperature of target material then transient melting of the target material occurs. With increasing ion fluence, numbers of such modified zones increase and tend to overlap. This track overlapping leads to surface flattening [4, 5]. RMS roughness and average roughness of as-deposited sample is 11 nm and 8.5 nm, respectively. The RMS roughness and average roughness values for the CZT thin films after Ag ion irradiation decreases, as listed in Table 1.



Fig.1. 3D AFM images of CZT films (a) as-deposited; (b) irradiated by Ag ions with fluence $1 \times 10^{12} \text{ ions/cm}^2$ (c) irradiated by Ag ions with fluence $5 \times 10^{12} \text{ ions/cm}^2$



Fig.2. PSD analysis of CZT films (a) as-deposited; (b) irradiated by Ag ions with fluence 1×10^{12} ions/cm² (c) irradiated by Ag ions with fluence 5×10^{12} ions/cm²

 Table 1: AFM roughness and PSD data obtained from AFM images.

Sample Name	As- deposited	Ag ion irradiated 1x10 ¹² ions/cm ²	Ag ion irradiated 5x10 ¹² ions/cm ²
RMS (nm)	11	9.0	4.7
Ra (nm)	8.5	7.3	3.6
PSD roughness (nm ⁴)	2 x 10 ⁻⁵	4 x 10 ⁻⁵	2 x 10 ⁻⁶

This decrease in surface roughness could be attributed to diffusion of bombarded ions into the matrix after irradiation. To get more information

about surface roughness, we plotted power spectral density (PSD) plot of data obtained from AFM images. Power spectral density (PSD) is a technique that calculates power (roughness amplitude squared) as a function of spatial wavelengths of the features that are contributing to the surface image. PSD utilizes a Fourier decomposition of an image into spatial frequencies. PSD surface roughness accounts for lateral as well as vertical roughness. As see from the data the PSD roughness values for as-deposited sample is $2 \times 10^{-5} \text{ nm}^4$, whereas for Ag ion irradiated samples with 1×10^{12} ions/cm² and 5×10^{12} ions/cm² are 4×10^{-5} nm⁴ and 2×10^{-6} nm⁴ respectively. This shows that although RMS roughness of as-deposited sample is more as compared to irradiated sample with 1×10^{12} ions/cm², the PSD roughness value for irradiated sample with 1×10^{12} ions/cm² is more as compared to as-deposited sample. This shows that sample with 1×10^{12} ions/cm² has flattened a bit after irradiation but the width of globular structures has increased. The PSD roughness value for irradiated sample with 5×10^{12} ions/cm² is 2 x 10⁻⁶ nm⁴.

4. Conclusion:

In this paper, Cadmium Zinc Telluride (CZT) thin films are irradiated with 100 MeV Ag ion-beams at a fluence of 1×10^{12} ions/cm² and 5×10^{12} ions/cm². Atomic force microscopy (AFM) study reveals that the grains of the size ~7.3 nm in the as-deposited film are fragmented into smaller grains of size 5.8 nm and 3.6 nm at a fluence of 1×10^{12} ions/cm² and 5×10^{12} ions/cm² respectively. The surface roughness is found to decrease after irradiation. The decrease in value of average roughness indicates the surface smoothening due to latent track overlapping and surface diffusion process.

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Single and double layer Al and Al/Al₂O₃ passive film coatings on AZ31 alloy by PVD technique for corrosion inhibition

Hema Palani¹, Sundeep Kumar Marndi¹, and Thangadurai Paramasivam^{1,*}

¹Centre for Nanoscience and Technology, Pondicherry University, Kalapet, Puducherry- 605014, India

 $* Corresponding \ author: \ thangaduraip.nst@pondiuni.edu.in \ / \ thangadurai.p@gmail.com$

Abstract

This paper deals with single and dual layer coating of aluminium metal and its oxide in nanometer thicknesses on Mg alloy AZ31 to prevent the alloy from corrosion. Aluminium metal was coated on AZ31 by thermal evaporation method. On the top of that Al_2O_3 film was coated by RF Sputtering technique. Microstructure and electrochemical studies were done. Structural morphology analyzed by field emission scanning electron microscopy showed smooth, pore free and uniform film coating on AZ31. The corrosion behaviour was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy carried out in wet environment of 0.6M NaCl solution. The study revealed that the corrosion resistance was higher for AZ31 coated with 100 nm thick Al film. This work provided a fascinating coating to passivate the surface of the AZ31 Mg alloy against corrosion.

Introduction

In recent years, industries are focusing on introducing light-weight materials in the field of automobiles and aerospace. Light-weight materials have high strengthto-weight ratio excluding corrosion resistance and greater design flexibility^[1]. Magnesium and its alloys are the lightest structural materials having low (1.74g/cm^3) density compared with other conventional materials such as steel (7.79 g/cm^3) and aluminium alloys (2.7g/cm³). The Mg alloys have high thermal conductivity, elastic modulus, specific strength, good antishock resistance and electromagnetic shielding effect. However, they have some undesirable properties such as poor corrosion, creep and wear resistance. To enhance the corrosion resistance of Mg alloys, their surface was protected by coating various materials using different deposition techniques^[2]. In this work, Physical Vapour Deposition (PVD) technique is used to passivate the surface of AZ31 alloy by coating with Al and Al₂O₃ thin films to protect them from corrosion.

Experimental methods

The commercially available AZ31 Mg alloy plates of 6 mm thick were cut into a smaller dimension of 1.5 cm \times 1.5 cm using a low speed, high precision cutting machine (Baincut LSS, Chennai Metco) that is equipped with diamond wafer blade. The AZ31 substrates were polished (Bainpol SA, Chennai Metco) using silicon carbide sheets of different grit sizes up to P4000 and finally with diamond slurry of size 0.5-1.0 µm. The polished AZ31 substrates were cleaned in 2-propanol under ultrasonic agitation for 10 min and dried under warm air using dryer.

Aluminium (Al) metal film of 100 nm thickness was coated on AZ31 substrate by thermal evaporation method (Model:12A4D, Hind High Vacuum), where metal aluminium pieces were kept inside tungsten helical coil. On the top of the Al film, 50 nm thick Al_2O_3 layer was coated by RF Sputtering (Advanced Process Technology, India). The uncoated, single layer of 100 nm Al coated and dual layer of 100 nm Al and 50 nm Al_2O_3 coated AZ31 are labelled as bare, AZA1-100, and AZAO-50, respectively for easy referencing in this manuscript.

Surface morphology was studied by scanning electron microscopy (SEM). Electrochemical measurements (polarization and impedance) were carried out using three electrode configuration in 0.6M NaCl electrolyte (Solartron SI1260 and SI1287). The coated AZ31 samples (1 cm^2 area) were used as a working electrode, Ag/AgCl and Pt mesh were used as reference and counter electrodes respectively. The Tafel profiles were recorded in the potential scan range of ±0.5 V at a scan rate of 0.1667 mV/s.

Results and Discussion

Microstructure analysis

The SEM images of bare alloy and AZAO-50 samples taken before and after corrosion measurements are shown in Fig. 1. Surface of the bare and coated AZ31 (Fig. 1a and 1c) is found to be smooth and uniform before corrosion measurements. However, after corrosion measurements, their surface (Fig. 1b and 1d) show a region of corrosion very well through a rough morphology. After corrosion occurs, some cracks are also seen on the surface due to breakdown of the coated Al-Al₂O₃ passive films.



Fig.1. FESEM images acquired before and after corrosion for (a, b) bare and (c, d) AZAO-50 samples.

Potentiodynamic polarization

The Tafel profiles obtained for bare, AZAI-100 and AZAO-50 are presented in Fig. 2; they were fitted with traditional method^[3] and the fitted corrosion parameters are given in Table 1. Fig. 2 shows that the coated AZ31 shifts its corrosion potential (E_0) more towards the noble potential. The current density for AZAI-100 ($0.35 \times 10^{-5} \text{A/cm}^2$) is the lowest among all, and this signifies that the pure metal aluminium film coating is more passive and inhibits the corrosion reaction better.



Fig. 2. Tafel profiles for (a) bare (b) AZAI-100, and (c) AZAO-50.

Electrochemical impedance spectroscopy

The impedance Nyquist plots for bare, AZAI-100 and AZAO-50 are shown in Fig. 3. The Nyquist plots exhibit two capacitive and an inductive loop at high and mid-frequency ranges. A depressed semicircle in the high and mid frequency ranges represents the properties of coatings like film, charge transfer resistance and double layer capacitance ^[4]. The low-frequency inductive loops are attributed to Faradic process and also related to relaxation of adsorbed anions on the surface ^[4].

For bare AZ31, the diameter of the semicircle is larger before polarization indicating that the double layer capacitance (C_{dl}) and resistance (R_2) are higher but they decrease after corrosion. The AZAI-100 and AZAO-50



Fig. 3. Nyquist plots obtained for (a) bare, (b) AZAI-100, and (c) AZAO-50.

show the reverse trend, that is, the C_{dl} and R_2 are increased after corrosion measurements. This could be due to the formation of additional oxide layer of Al during corrosion. Many experiments are required to have a complete understanding and they are in progress.

Table 1: Traditional and EIS fit parameters values.						
Code	$E_0(V)$	$I_0(10^{-5})$	CR	C _{dl}	R ₂	
		A/cm^2)	(mmpy)	$(\mu F/cm^2)$	(Ω.c	
)	m ²)	
AZ31	-1.34	24.90	5.78	48.1	57.03	
				79.0	79.92	
AZAI-100	-1.12	0.35	0.07	3.97	74.6	
				4.60	139.5	
AZAO-50	-1.12	2.90	0.66	27.9	67.41	
				3.33	235.9	

Conclusion

Single and dual layer coated AZ31 alloy was prepared by thermal evaporation and RF sputtering methods. Microstructure showed a smooth and uniform coating of the films. Their corrosion behaviour was studied using potentiodynamic and EIS. It was observed that the corrosion resistance was higher for AZAI-100 sample, which could be attributed to the oxide layer formation of Al metal during exposure to the wet environment.

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Optical Characterization of CZTS Layer for solar cell application

Devendra Bhale^{1, 3}, Arup Biswas², Dibyendu Bhattacharyya^{2, 3}, and Namita Maiti^{1, 3}

¹Laser and Plasma Technology Division, ²Atomic and Molecular Physics Division, BARC, Mumbai, 400085, ³Homi Bhabha National Institute, Mumbai 400094

*Corresponding author: dbhale@barc.gov.in

Abstract

Copper Zinc Tin Sulphide (Cu₂ZnSnS₄) i.e., CZTS is an important quaternary semiconductor material for the thirdgeneration solar cells. In this work, the influence of substrate temperature on the optical properties of CZTS thin films has been investigated. The fabrication route was radio frequency physical vapor deposition RF-PVD for these thin films. Spectrophotometric characterization of the films has been performed to establish a correlation between deposition parameters and optical properties of the thin film. A composite thin film of CZTS was deposited using the single target sputtering from a stoichiometric sputtering target on soda lime glass substrate. The refractive index, absorption co-efficient, band gap and thickness of thin films were calculated from measured transmission spectrum. It was found that the change in deposition temperature causes reduction of band gap from 2.05 eV to 1.9eV.

Studies on composition and mechanical properties of Ni-W coatings electrodeposited using citrate ammonia bath

Satish C. Mishra¹, R.K.Chowdhary¹, Vishal Singh², P Mishra¹

¹Materials Processing and Corrosion Engineering Division, ²Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400085

*Corresponding author: scmishra.barc@gmail.com

Abstract

Ni–W alloy coatings were electrodeposited on copper and SS304L substrates using citrate bath by direct current (DC) method. The effect of bath temperature on composition, morphology and hardness of Ni–W coatings were investigated. With increase in the bath temperature from 27° C (room temperature, RT) to 90°C, the tungsten (W) concentration in the coating increased from 5.25% to 35.82 wt% and the corresponding nano hardness of the coated film also increased from 3.86GPa to 7.85GPa. Incorporation of Al₂O₃ nanoparticles in Ni–W alloy coating resulted in further increase in the hardness to 8.68GPa. The root mean square (RMS) roughness of the Ni-W-alloy film coated at RT was 128.3nm and for the film deposited at 90°C was 59.6nm. FESEM of the coated film revealed that film morphology markedly changed with deposition temperature. Ni-W alloy deposited at RT showed large grained, well faceted pyramidal microstructure and a nodular morphology for the alloy deposited at 60°C.

Introduction

electrodeposited Ni-based alloys The containing refractory metals, such as tungsten or molybdenum, has gained more interest in recent years as an alternative to conventional hard chromium plating as it requires the use of carcinogenic Cr⁶⁺ ions and restrictions put on its disposal due to adverse environmental and toxicological concerns. It also has limitations for high temperature application as the hardness and corrosion resistance of hard chromium plating deteriorates as the operating temperature increases beyond 200°C [1]. Ni-W and Ni-Mo alloys exhibit distinguished wear properties which provide enhanced surface performance for engineering applications. In the recent years lots of effort has been dedicated towards the research and development of such coatings [2]. Ni-W and Ni-Mo coating has also been considered as the most promising catalysts for HER [3]. In the present work the effect of bath temperature has been studied on the microstructure and hardness of the deposited Ni-W alloy films.

Experimental:

The electrodeposition of Ni-W coatings have been carried out on copper foil $(20 \times 30 \times 0.2 \text{ mm}^3)$ and on metallographically mirror polished SS304L substrates $(15 \times 15 \times 2 \text{ mm}^3)$ using a citrate bath containing NiSO4.6H₂O (0.1M), Na₂WO₄. 2H₂O (0.2M), C₆H₉Na₃O₉ (0.5M), NH₄Cl (0.5M) and NaCl (0.1M). In some of the deposition experiments, Al₂O₃ powder (50nm, Linde Trademark USA) was suspended in the above bath (10g/L). The total volume of the deposition bath used was 250ml. The deposition experiments were conducted at a constant current density of 30mA/cm² using DC power source (Elektro Automatik GmbH & company). During experiments the pH was maintained in the range 8.5-9.0 and total deposition time was fixed for 30 minutes. In one set of experiments, the stirring speed was kept constant at 250 rpm and the bath temperature was varied from RT to 90°C in steps of 15°C. In another set of experiments, the bath temperature was fixed at 60°C and stirring speed was varied at 0/250/500/750 rpm. The thickness and surface roughness of deposited films were measured using stylus based surface profilometer, NanoMap 500LS. The composition and the surface morphology of the coated films were analysed using FESEM (Carl Zeiss Auriga Cross Beam FESEM installed with Oxford X-Mas EDS detector). The mechanical properties of the coated film were measured by nano hardness equipment SEMILAB IND 1000 using Berkovich nano indenter in depth control mode where maximum depth was fixed for 1000nm for all coated samples.

Results and Discussion:



Fig. 1. FESEM image of the Ni-W film deposited at different bath temperature of (a) RT (b) 60° C, (c) 90° C

FESEM of Ni-W coated films on copper substrates showed uniform, crack free and dense morphology.

It can be seen from the figure 1a that the surface morphology of the film deposited at R.T. and stirring speed of 250rpm consists of well faceted pyramidal shaped crystallites and as the temperature increases to 60° C the microstructure changes to nodular morphology (figure 1b). Further increase in the bath temperature to 90°C leads to the refinement of grains and showing irregular flakey microstructure (figure 1c), with average grain size in the range of \approx 100-200nm [4].

EDS analysis confirmed that the coatings consisted of solid solution of tungsten in nickel and concentration of W in the deposited Ni-W alloy changes from 5.25wt% to 35.82wt% as we increase the bath temperature from R.T. to 90°C, and is shown in fig. 2.



Fig. 2. Variation of Ni and W concentration in the deposited Ni-W alloy as a function of bath temperature.

It was also observed that W concentration changes from 25.46 wt% to 29.53 wt% as the stirring speed was increased from 0rpm to 750rpm at bath temperature of 60° C.

The thicknesses of the Ni-W films deposited on SS304L substrates were measured using NanoMap-500LS Profilometer and were in the range of 15- $20\mu m$.



Fig 3. The step height and surface topography of the Ni-W alloy deposited at 90°C and 250rpm for 30 minutes.

Table 1 shows the RMS surface roughness (measured over $200\mu m \times 200 \mu m$ area) of Ni-W films deposited at different bath temperatures and at constant stirring speed of 250rpm.

Table 1	. RMS	surface	roughness	for	the	Ni-W
coating de	eposited	l at const	ant pH 8.5,	$J_d 3$	0mA	.cm ⁻²

	F 0.0, 0 u 0 0		
bath	RMS surface		
temperature (°C)	roughness (nm)		
RT	128.3		
60	37.6		
90	59.6		

The plots of nanohardness measurement on Ni-W films deposited under three conditions are shown in figure 4.



Fig. 4. Comparison of load *vs* depth profile of three different types of coating.

The nanohardness value of 7.85GPa was obtained for the film deposited at 90°C and 3.86GPa for film deposited at RT. It can be also concluded from the EDS and Nanohardness analysis that the films with highest W concentration showed maximum hardness [5]. Figure 5 shows that the nanohardness can be further increased to 8.68GPa for Ni-W alloy film deposited at 90°C and 250rpm having alumina powder suspended in the bath during electro-deposition process.

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Understanding the structural and morphological changes in pulsed laser deposited TiO₂ thin films on soda lime glass substrates

Steffi Antony¹, Vijay Pedhasingh¹, Diksha Mishal¹, Mukul Gupta², R.S. Hyam¹

¹SPAS, Physics Department, Goa University, Taleigao, Goa 403206

² UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001

*Corresponding author: rajesh.hyam@unigoa.ac.in

Abstract

In the present investigation, commercially available P25 TiO_2 powder pellet is used as target for growing nanocrystalline TiO_2 thin films on heated soda lime glass substrates by using pulsed laser deposition technique (in constant EG and HV mode). XRD and FTIR characterization were studied before deposition to understand the presence of different phases and vibration modes. Two different thicknesses of the films were studied by controlling time for deposition (10 min and 30min) and keeping all other PLD parameters constant. GI-XRD of these deposited TiO_2 films were studied to understand structural/phase changes occurring in these films due to large lattice mismatch at the interface of the substrate and deposited thin film material. UV-Visible absorption was studied to understand the band edge position and to determine the band gap of these samples using Kubelka-Munk function. Surface morphological studies were carried out by using SEM to understand the growth mechanisms occurring in these films due to two different modes of depositions.

Introduction

Pulsed laser deposition technique is widely used to grow highly epitaxial device quality thin films of different materials on highly oriented single crystal substrates for diverse applications which includes, resistive switching, solar cells, sensors etc. However the single crystal substrates are very costly. In order to optimize the parameters of PLD for the growth of metal oxide thin films, cost effective soda lime glass substrates were used which have rough surfaces. Metal oxide thin films (TiO₂) on rough surfaces also has wide range of applications as SERS substrates (Surface Enhanced Raman Scattering), Li ion battery, electrochromism (smart windows) etc.

Experimental

In the present investigation Coherent Compex Pro 102F excimer laser (KrF 248 nm wavelength) is used to grow TiO₂ thin films on soda lime glass substrates heated at 500°C. The deposition was carried out in high vacuum range of the order of 10^{-5} mBar and substrate to target distance of 3.8 cm. PLD of TiO₂ thin film on soda lime glass substrates was carried out using P25 TiO₂ powder pellet target by using two different modes, i.e. constant energy mode (165mJ) and constant HV mode (20kV). In order to understand the growth mechanism, all other parameters like repetition rate (Rep rate 8 Hz), substrate temperatures (500°C), pressure inside the chamber (order of 10^{-5} mBar) etc. are kept constant. The crystalline phases of the target TiO2 pellet were

characterized by X ray diffractometer using a Cu-K_a source and Fourier transform infra-red spectroscopy (Schimadzu FTIR-8900). GI XRD studies on TiO₂ thin films were carried out at IUC Indore at Bruker D8 Advance - Powder XRD instrument. Optical transmittance and reflectance measurements were carried out using UV-visible spectrophotometer (Schimadzu UV-2401). The nanostructured film morphology was characterized using scanning electron microscope (Carl-Zeiss).

Results and discussion

Fig. 1 (a) shows the XRD data of the commercially available P25 TiO_2 powder (70% anatase and 30% rutile) which was later used as target for PLD to grow TiO₂ thin films. From the XRD data it was observed that the broad anatase (101), (112), (200), (105), (204), (116), (220), (201), rutile (111) and brookite (121) phases are present in the nanopowder pellet sample.

The FT-IR spectrum of TiO_2 showed various characteristic peaks as shown in Fig. 1(b). In this spectrum, the intensive and broad band at low wavenumber range between 400 and 800 cm⁻¹ were ascribed to the strong stretching vibrations of Ti–O and Ti–O–Ti bonds. The absorption band at 3300cm⁻¹ is related to stretching and 1630 cm⁻¹ to bending vibration of O-H, representing the water as moisture adsorbed on the pellet surface. UV visible absorption spectroscopic data i.e % T of the EG mode thin films and HV mode films are as shown in Fig. 1 (c) and



Fig.1. (a) XRD and (b) FTIR plot of P25 TiO_2 nanopowder sed as target for PLD. UV-Visible absorption i.e. % Transmission data for (c) EG mode and (d) HV mode of deposition.

1(d), which clearly shows that for 10 min and 30 min. samples there is not much difference in the band edge positions and % transmittance for EG mode with incident wavelength variation, which in turn implies uniformity as well as compact nature of the grown films with respect to time variation. In case of HV mode films, it can be clearly seen that the % Transmittance difference in 10 min and 30 min samples for the wavelengths varying from 800 nm to 350 nm which was later confirmed by SEM, implies non uniform and not so compact depositions with respect to time. Fig. 2(a) and (b) shows that the GI-XRD data for constant EG and HV mode samples for which deposition were carried out for 10 min and 30 min. From the Fig. 2(a) for constant EG mode, it is clearly observed that 10 min sample has one rutile (110) peak at angle 27.8° along with another small anatase (112) peak at 38.5°. The rutile peak vanishes for the samples deposited for 30 min and anatase peak remained as it is. This implies that the initial island type growth of the PLD TiO₂ film takes place which causes rutile phase from target to germinate initially on the substrate surfaces, which transforms into antase phase with subsequent growth of the thin film with respect to time as laser energy is constant in EG mode. Thus there is no rutile peak being observed for HV mode 10 min or 30 min. samples as the laser energy drops very fastly in HV mode of PLD. Only anatase phase with preferential orientation along

(112) direction is being observed in thin film even though the parent TiO_2 pellet has anatase (101) as the dominant peak as compared to small anatase (112) peak. No rutile peak is observed with HV mode.UV-Visible absorption data plot for band gap measurement also shows that there is small variation in band gap values due to EG mode and HV mode and slight variation due to increase in the film thickness. Subsequent SEM images of the samples show large overgrwoth on EG mode sample as compared to HV mode samples due to continuous ablation of the target with high energy.



Fig. 2. GI-XRD data of TiO_2 thin films deposited for 10 min and 30min. on glass substrates (a) EG mode (b) HV mode

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Study of Strain Relaxation in Epitaxial CrN Thin-film

Shailesh Kalal, Suman Karmakar, Rajeev Rawat and Mukul Gupta*

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India *Corresponding author: mgupta@csr.res.in

Abstract

We studied the real time in-situ growth of the epitaxial CrN (001) thin-film on MgO (001) substrate using refection high energy electron diffraction (RHEED). The in –plane lattice parameter (LP) calculated from the RHEED shows rapid strain relaxation after the 5 nm of the film growth. However, the film possesses in-plane tensile strain up 30 nm which can be attributed to the very small miss-match ($\approx 1\%$) between the LP of CrN and MgO. Strain in the film can be further visualized by the out of plane LP calculated from the x-ray diffraction exhibiting a compressive strain in out of plane direction. Further, the x-ray absorption spectra confirms +3 charge state of Cr and the structural transition ≈ 230 K as evidenced by the electrical resistivity measurements.

Introduction

CrN shows magnetostructural transition cubic (Fmparamagnetic to orthorhombic *3m*) (pnma) antiferromagnetic below the Néel temperature (T_N) of 280 K [1]. It produces zero magnetization and zero parasitic stray field and is robust against magnetic perturbations. These characteristics make CrN an ideal for secure data storage and memory devices. Compared to other well-established metallic antiferromagnets, such as MnPt, IrMn, and Mn₂Au, CrN does not consist of noble elements [2]. In contrast, CrN is an inexpensive, chemically stable, and corrosion resistive, which are the central requirements for developing functional devices. Therefore, understanding of thickness, strain, and orientation effects on the structural and electronic properties of CrN films are indispensable for their practical applications [2].

In view of this, we have grown epitaxial CrN thin films on MgO (001) substrate. The strain relaxation was studied by real time monitoring of in-situ reflection high energy electron diffraction (RHEED) measurement. After the deposition samples were thoroughly characterized using complementary techniques.

Experimental Details:

Epitaxial CrN (001) thin film was deposited on MgO (001) substrates using a reactive direct current magnetron sputtering at a power of 100 W. A ϕ 3-inch Cr target (99.95 % purity) was sputtered in a mixture of 33 sccm Ar (99.9995% pure) and 17 sccm N₂ (99.9995% pure) gases. With a base pressure of about 1×10^{-7} Torr or lower, the pressure during deposition was 2.8 mTorr due to the flow of process gases. During the film deposition, the substrate temperature was maintained at 400 °C. Structural characterization was done using in-situ RHEED and x-ray diffraction (XRD) measurement. Electronic structure was

analysed using x-ray absorption spectroscopy (XAS) measurements collected at $Cr-L_{3,2}$ in total electron yield (TEY) mode at soft x-ray beam line (BL-01) of Indus-2, synchrotron radiation source at RRCAT, Indore [3]. Temperature dependent resistance measurement was performed using home-made four probe resistivity setup.

Results and Discussion:

The in-plane lattice parameter (LP) obtained from insitu RHEED measurements as a function the film thickness (t) is shown in the Fig. 1 (a). On the basis of strain relaxation, it divided into three regions: Region (i) t = 0 to 5 nm: In this region at very early stages of film growth, deposited CrN film is fully strained and the in-plane LP of CrN is ≈ 4.20 Å (nearly equal to the LP of MgO substrate ≈ 4.21 Å). The respective RHEED image taken along (110) direction after 4 nm deposition of the film is shown the Fig. 1 (b). The intense streaky pattern suggests that film follows the symmetry of the substrate with the 2D layer-by-layer growth. Region (ii) t = 6 to 15 nm: In this region strain relaxation takes place and the in-plane LP of the film is decreasing rapidly and approaching the LP of the bulk CrN \approx 4.16 Å [1, 2]. RHEED image taken from this region (\approx 12 nm) was shown in the Fig. 1 (c) shows the streaky pattern suggesting, the film is still growing in layer-by-layer manner. Region (iii) t = 15 to 30 nm: In this region the LP is nearly constant and comes out to be 4.17 Å which is slightly larger than bulk value indicating that even 30 nm thick film is not fully relaxed but possess some in-plane tensile strain. This can be attributed to the low LP mismatch of about 1% between CrN and MgO. The streaky RHEED pattern with some intense spots (see Fig. 1 (d)) like pattern suggests the transition from 2D layer-by-layer to 3D island type growth which can be attributed to increase in surface roughness due to the increase in the thickness of film. The XRD pattern shown in the Fig. 1 (b) taken after the film deposition possess only (002)
and (004) reflections. The LP calculated from the (002) reflection comes out to be 4.14 Å which is smaller than the bulk-CrN (4.16 Å) indicating the out of plane compressive strain and supports RHEED data. Hence, by combining RHEED and XRD we observed that 30 nm thick CrN film possess in-plane (out of plane) tensile (compressive) strain.



Fig. 1 (a). In- plane lattice parameter as a function of CrN film thickness. RHEED images taken at a thickness of **(b)** 4 nm **(c)** 12 nm and **(d)** 30 nm. **(e)** XRD pattern of the 30 nm thick CrN film taken after the deposition.

Further, the local and electronic structure has been analyzed using the XAS measurements performed at $\operatorname{Cr} L_{3,2}$ edges was shown in the Fig. 2. The $\operatorname{Cr} L$ -edge spectra correspond to transitions from a well -defined ground state $2p^63d^3$ the final state $2p^53d^4$ followed by the dipole selection rule. Fig. 2 reveals two broad peaks centred at the position of around 576 and 585 eV assigned to L_3 (Cr $2p_{3/2}-3d$) and L_2 (Cr $2p_{1/2}-3d$) transitions respectively, owing to the spin-orbit coupling. The overall shape of the spin-orbit spitted Cr $L_{3,2}$ absorption peak is determined by the crystal-field effects along with the multiplet effects, which originated by 3d-3d Coulomb interaction, the 2p-3dCoulomb interaction and exchange interactions. The Cr $2p_{1/2}$ peak is more broadened than that of Cr $2p_{3/2}$ due to Coster- Kronig Auger process. These spectra agrees well with the previous XAS measurements of the CrN [1, 2, 4]. Here, we compared the L-edge spectra of the CrN film and bulk Cr₂O₃ which confirms the +3-charge state of Cr in the grown CrN film and suggests very few numbers of vacancies in the film.

Further the inset of Fig. 2 shows the variation of resistance as a function of temperature of the grown CrN film. The anomaly around 230 K (clearly visible in the derivative plot shown in the inset) is due to magnetostructure transition from the high temperature paramagnetic cubic to the low temperature antiferromagnetic orthorhombic phase [1, 2].



Fig. 2. XAS measurements taken at $Cr L_3$ and L_2 edges with insets show temperature dependent resistance and derivative of resistance.

In the summery, the real time strain relaxation phenomena in the epitaxial CrN (001) thin film was studied using RHEED and XRD. In the grown CrN film charge state of +3 confirmed using the XAS and structure transition ≈ 230 K is evidenced by the RT measurements.

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PVDF@ZnO Membrane For Their Potential Application In Oil/water Separation

Fayez U Ahmed¹ and Debarun Dhar Purkayastha¹

¹Department of Physics, National Institute of Technology Nagaland, Dimapur, P.O.: Chumukedima, 797103, Nagaland, India

*Corresponding author: ddebarun@yahoo.com

Abstract

A facile synthesis of PVDF@ZnO composite membrane by cost-effective phase inversion method is reported. The samples are well characterized by XRD, FESEM and contact angle meter. XRD confirms the poly-crystalline nature of PVDF, hexagonal wurtzite structure of ZnO. Contact angle studies showed the membranes were hydrophobic-oleophilic in nature. Oil/water separation study showed that the membrane could effectively separate 96% of oily wastewater. The membranes could significantly degrade methylene blue under UV-light. Such dual functional membrane which could separate oily waste water and photocatalytically degrade organic pollutants will have potential application in sustainable cleaning of environmental pollutants in aqueous systems.

Optical and Electrical Studies on Nebulized Spray Pyrolysis coated Antimony doped Tin Oxide thin films

Karuppasamy Balasubramanian and Gayathri Venkatachari

Nanomaterials Laboratory, Department of Physics, Thiagarajar College of Engineering, Madurai, 625015

*Corresponding author: drvg2004@rediffmail.com

Abstract

Transparent conducting nanoporous thin films based on the tin oxide materials are the promising candidates for the application of electrodes, catalysts, photovoltaic devices and energy-storage devices. Antimony is a penta valance element which gives n type conductivity while doping with SnO₂. Antimony doped tin oxide (ATO) thin films have been prepared by nebulized spray pyrolysis method. Electrical and optical properties were studied for the as deposited and annealed at 500°C thin films. Resistivity of the as deposited and annealed at 500°C ATO thin films were varied from 60.72 X $10^{-3} \Omega$ m to 24 X $10^{-2} \Omega$ m. Annealed film shows lower resistivity than the as deposited film. Both films had shown the n type conductivity which was found through the hot probe method.

Introduction

Metal oxide semiconductors are in use since five decades for the application of thin film transistor, sensors, as transparent conducting oxide (TCO) electrodes in light emitting diodes, flat panel displays and window materials in solar cells [1]. The metal oxides are having the wide band gap which leads them have good optoelectronic properties [2]. There is several number of metal oxide compounds has been studied earlier. The semiconductors used in the form of binary compounds like, SnO₂, ZnO, In₂O₃, Ga₂O₃, and CdO [3], [4]. Among these, transparent conductive oxides (TCO), based on wide band gap, degenerate semiconductors are mechanically hard and can withstand high temperatures. As wide band gap semiconductors, doped SnO₂ and undoped SnO₂ are known to have a wide range of applications, such as transparent conducting electrodes in dye-sensitized solar cells (DSSCs), sensors and they seem to be more attractive for their luminescence properties [5]. ATO (Sb:SnO₂) thin films are prepared by various Physical and chemical methods [6], [7]. Spray pyrolysis is a simple, single step technique for producing good conductive and adherent Sb:SnO₂ thin films in a cost-effective way [8]. In the present investigation, we have studied the electrical and optical properties of Sb:SnO₂ thin films prepared by spin coated and nebulized spray pyrolysis.

Materials Methods

Tin II chloride dihydrate from Merck and antimony III chloride extra pure from Loba Chemie were used as the precursors. The solution was prepared using SbCl₃ and SnCl₂.2H₂O with the concentrations of 1:2 with the molar ratio of 2, solved in propanol and de-ionized water. Microscopic glass slides were used as the substrates. Before depositing the film, the substrate was cleaned with chromic acid, high power soap water, distilled water and then with acetone. Substrate temperature while depositing the films was maintained at 350°C throughout the deposition. After the deposition films were cooled to the ambient temperature. The deposited thin films were subjected to the structural, optical, electrical and morphological studies. Before that one film was annealed at 500°C for 2 hours.

Results and discussion

Structural analysis (XRD)

The XRD patterns of the ATO thin films deposited through nebulized spray pyrolysis were given in the Fig.1a) & c). The XRD data have been matched with JCPDS - ICDD files. As deposited thin film has 3 peaks corresponds to the SbSnO₂ (Tetragonal) along the directions (1 1 0), (1 0 1) and (2 1 1) matched with (JCPDS: 882348) and Only 1 peak Sb_2O_3 (Cubic) along the direction (4 0 0) matched with (JCPDS: 710365). Annealed film highly crystalline nature and has grown (Tetragonal) along the directions (1 1 0), (1 0 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 1 0) and (3 0 1) matched with SbSnO₂ (JCPDS: 882348). The grain size was calculated using the Scherer's formula and the average size comes out to be ~ 42 nm and ~ 60 nm for the thin films as deposited & annealed respectively.

Surface analysis (SEM)

Scanning electron microscopic images are shown in the Fig.1a) &1b) (insert). From the micrograph grains on the surface of the spray coated thin films were closely packed and the size more or less equal to the calculated value. Both nebulized spray coated thin films show the grains on the surface and the texture of the surface are like pyramidal structure. The pyramidal like surface is the best for light harvesting on the surface.



Fig.1.XRD pattern for the Nebulized Spray coated thin films. a) as deposited b) annealed at 500°C, SEM micrographs were inserted for the corresponding thin film.

Optical Properties (UV-Vis Spectrum)

The optical transmittance spectrums of the films were recorded for the range of wavelength 300 to 800 nm. Transmittance spectrums of the films are shown in the Fig.2. From the figure we could observe the maximum of 59% of transmittance in the visible region for as deposited thin film. And after annealing at 500°C it reduces to 30%. This reduction is due to a charge transfer between the two oxidation states of antimony, (Sb³⁺ and Sb⁵⁺)while annealing [9]. From the transition probability calculations the band gap of the as deposited and annealed ATO thin films are found to be direct allowed band gaps are 3.64 eV and 3.72 eV, which are deduced from the plots of (α hu)² Vs photon energy (hu) shown in the insert in Fig.2.



Fig. 2. UV-Vis transmittance spectra for the as deposited and annealed ATO thin films and plots of $(\alpha h\nu)^2$ Vs photon energy (hv) (insert).

Electrical properties

Electrical resistivity of the thin films was measured by the four point probe with Keithley 2000 digital multi meter and the values are obtained for the dark and light conditions. Electrical properties of the thin films were given in the Table.1. The films show the n type conductivity while doing the simple hotprobe experiment and it is confirmed by the Hall Effect studies which gives negative hall coefficient values. Through the hall experiment majority charge carrier concentration and the mobility were obtained. From the table annealed film having the higher carrier concentration and mobility than the as deposited thin film.

Table 1. Properties of the ATO thin films

Sample	ρ(x10 Light	⁻² Ω.m) Dark	n 10 ⁻²⁰ cm ⁻³	$\mu x10^{-2} cm^2 V^{-1}s^{-1}$	Т %	Eg (eV)
As deposited	24.1	22.23	5.94	4.74	59	3.64
An. At 500	6.07	5.544	9.66	11.7	30	3.72

Conclusion

Nebulized spray deposited ATO thin films both as deposited and annealed film shown the n type conductivity while they subjected to the hot probe method. Annealed thin film shows more crystalline properties than that of the as deposited thin film. Annealed thin film shows that it having the good absorption in the visible region. Its conductivity increases while measuring under light illumination. Overall annealed thin film shows the better electrical and optical Properties and, it can be used as the Photo anode for the Photovoltaic applications.

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Poole-Frenkel Conduction Mechanism Observed in Sputter Grown Silicon Carbide Thin Film

Alisha¹, Parvesh Chander², V. K. Malik^{2,*}, and Ramesh Chandra¹

¹Institute Instrumentation Centre, ²Dept. of Physics, Indian Institute of Technology, Roorkee, 247667

*Corresponding author: vivek.malik@ph.iitr.ac.in

Abstract

SiC thin film based devices are in great demand because of their better performance at high temperature, high frequency and high power applications. Here, SiC films are fabricated by a cost-effective and simple approach of RF magnetron sputtering. Metal-Semiconductor-Metal (MSM) junction is fabricated using gold electrodes by shadow sputtering. The Current-Voltage (I-V) characteristic of this fabricated device reveals the presence of Poole-Frenkel mechanism at Gold-SiC MSM junction indicating defect states and trap centers, which can be advantageously used to design some specialized electronic devices for application such as optical detection, power electronics, memory and energy-efficient devices.

Study of Intense Ion Beam Interaction Effects on Post-Experimental Nuclear Reaction Thin Film by SEM Investigation.

G.R.Umapathy ¹* Akashrup Banerjee ^{2†} Rudra N.Sahoo³, A. Sharma⁴, Meenakshi¹, Honey Arora⁵, Arshiya Sood³, Pankaj K Giri⁶, M.M. Hosmani⁷, Pankaj Kumar¹, Sunil Ojha¹, Sundeep Chopra¹, and Dinakar Kanjilal¹

¹Inter University Accelerator Center, Aruna Asaf Ali Marg, New Delhi 110067.
 ²GSI Helmholtzzentrum fur Schwerionenforschung, Darmstadt, 64291 Germany.
 ³Department of Physics, Indian Institute of Technology Ropar, Rupnagar 140001.
 ⁴Department of Physics, Himachal Pradesh University, Shimla. 171005.
 ⁵Department of Physics, Panjab University, Chandigarh 160014.
 ⁶Department of Physics, Central University of Jharkhand, Ranchi 835205.
 ⁷Department of Physics, Karnataka University, Dharwad, 580004.

*[†] Corresponding author: umagrphysics@gmail.com, arb169.banerjee@gmail.com

Abstract

It has been observed that material properties tend to undergo changes due to bombardment by energetic ion beams. The MeV-range energetic ions beyond Coulomb's barrier of a target-beam combination lead to nuclear reactions and, subsequently the modification of target materials. This can also be understood as consumption or high burn up, yielding reaction fragments to the surrounding. For example, the lanthanide Erbium (Er) is used as burnable neutron absorbers with nuclear fuel. In this study we have reported the surface morphology of selected targets: Te, Er, Tm, Sn and Zn exposed to MeV ion in order to have local high burn up conditions. The permanent morphological structures are observed: (1)Elongated and vermicular inter-granular bubbles in Te; (2)Clustered spherical inter-granular bubbles and fuel cracks in Er and Tm; (3)Carbonaceous deposits on Sn and Zn.

Introduction

An energetic ion beam on reaction with target subjects it to physical and chemical changes, by creating high burn-up conditions. A detailed investigation of structural, morphological and compositional changes reflects the burn-up environment. Er is used as solid burnable poison directly incorporated in to the zirconium based cladding tubes. Besides it is also effective as alternative metal for radiation wall shielding. The oxide form of Er has different properties than that of enriched or isotopically pure ¹⁶⁷Er. Extreme radiation condition via reaction with heavy ion at burn up environment and high energy will provide multidimensional results. Te is semiconducting material explored for production of ¹³¹I by neutron activation.

In fission, gases from the fuel target are subjected to release during and post burn up. Most of fission/fusion products escape from the surface leaving behind traces. These traces refer to permanent defamation of the target and are observed under microscope in post irradiation status. In one such interesting experiment [1], elongated and vermicular inter-granular bubbles were observed. The clustered spherical inter-granular bubbles and fuel cracks are observed in Er, Tm and other targets where material abundance is high. The vermicular inter-granular bubbles in a target help to build sequence of events from reaction initial buildup to permanent deformation structure.



Fig. 1. The sequence of events (from top to bottom) target preparation, ion irradiation, fission process, post experiment deformed target.

Burn up condition

The burn-up refers to consumption of the material in the reaction process. This condition is made possible by providing MeV beam above Coulomb barrier. The energetic MeV ion has sufficient energy to interact with target nucleus and hence form unstable compound nuclei, known as fusion process. Subsequent decay into daughter nuclei is called fission. In the present work, different target-beam combinations were considered, as mentioned in Table 1. The ¹³⁰Te was bombarded with 93-103MeV ³⁷Cl beam, ¹⁶⁴Er was bombarded with 185MeV ²⁸Si beam, ¹⁶⁹Th was bombarded with 94 MeV ¹⁶O beam, ^{116,118}Sn was bombarded with 15-29MeV ⁷Li beam, and ⁶⁴Zn was bombarded with 45-89MeV ¹⁶O beam. All the experiments were carried using 15UD Pelletron accelerator at IUAC, New Delhi.

The scope of experimental understanding includes (a)Fission gas swelling and release during irradiation and interim storage, (b)Radioactive fission products released during irradiation and interim storage, (c)Behaviour of fission product actinides, rare earths, alkaline earth and zirconium in oxygen free fuels, (d)Nobel metals and fission gases metallic inclusion structural and phase formation in the fuel target matrix, (e)Observation of phase shift or traps of volatile products.

Table 1. Nuclear experiment target, Projected beam , Δ T-Target thickness, and Preparation method

Target	Beam	Energy	ΔT	Meth ⁺	Ref ^{\$}
		(MeV)	nm		
Te	Cl	150	50	А	1
Er	Si	150	1K	В	2
Th	0	94	6K	В	3
Sn	Li	29	200	А	4
Zn	0	84	500	А	5
*Preparation Method, A-Thermal evaporation, B-Cold Rolling, \$-References					

Observations and Discussion

Fission generates gas atoms and during the continuous process those with sufficient energy close to the grain come out. The remaining settle down in the matrix. Once the reaction process stops and temperature of molten stage starts falling down, these gas atoms trapped in intra granular fission bubbles nucleate to the permanent structure. The SEM images shown are of this stage. The mechanism for high burn up bubble structure formation is described: targetbeam fusion occurs near the surface and eventually decays into fission products, this results in a high local fission density and burn up. The fission damage is not annealed as temperature of surface is low but accumulated damage results in local recrystallisation at grain boundaries. This causes fission products like Xe, Ke, and other gases to precipitate into small, isolated bubbles. The bubbles are initially circular and uniform in the local defect grain, then they tend to migrate and in the path gain addition bubble or lose to another. These type of bubbles are seen in Er [2] and Th where the targets were thick and material burnt is only on the surface. The trapped gas atoms like H tend to form molecules in H₂ or H₃. To compensate the size of newly entered atom, stable molecules may be ejected leaving behind cracks. In case of Te, the target

is very thin and along the full length there is fission hot regime and the escape boundary is also very close. Trapping probability is thus reduced and can be explained by this mechanism. The gas atoms and vacancies are also ejected from the bubbles by energetic fission fragments in a process known as irradiation-induced re-solution. The intra-granular and grain face bubbles grow as fission gas atoms and vacancies diffuse in them. The size of the bubbles is governed by the net result between these two competing processes. In steady-state conditions, the radius of the (spherical) intra-granular bubbles tends towards an equilibrium value, while the grain face bubbles tend to grow. The inter-granular bubbles are initially lenticular, but as they grow and coalesce, they become first elongated and then vermicular. The black surface observed on the beam spot is examined and this is observed to be carbon rich. This was noted in shine surface of Sn, Zn, Er and Th [3,4]. The building of carbonaceous is due to locally developed heat and trapping carbon and other gases from the surrounding. As evidence of this, Sn- black spot and pristine sample were compared in EDS analysis



Fig. 2. The SEM images of Te target at beam interacted boundary(top-right), and centre (bottom-right). The SEM image of Tm target after experiment(top-left). EDS spectra of Sn target at beam-black spot compared with pristine.

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Synthesis of High-end Piezoelectric and Electroactive Polymer Nanocomposite Thin Films based on PVDF/CNTs for Ultrasound Transducer Application.

Nur Amin Hoque, Samir Kumar Biswas*

IISER Mohali, Physical Science, Punjab- 140306

*Corresponding author: skbiswas@iisermohali.ac.in

Abstract

A suitable PVDF/CNTs nanocomposite based high-end piezoelectric and colossal dielectric material is developed through simple low-cost drop casting and high voltage electro poling methods. The transformation of nonpolar α -phase to polar and electroactive electroactive β -phase was observed and quantified by FTIR spectra and, XRD diffraction pattern. Highest piezoelectric β – phase exhibited 85.2 % in PVDF/CNTs nanocomposite thin film. This enhancement of polymer composites thin film's β -phase also shows the high dielectric constant ~ 64 at 20 Hz. Same piezoelectric thin film is used to fabricate a high frequency, low pressure sensitive ultrasound senor which converts ultrasound pulsing waves generated by 10 MHz ultrasound transducer to an electrical output (~70 mV).

Introduction

Electroactive polymers, specially poly(vinylidene difluoride) (PVDF) show potential piezoelectric properties which leads to suitable materials for designing force sensor, energy harvesting, bio-medical sensor and Ultrasound transducer applications. PVDF, a cost-effective material that show at least five different phases like α , β , γ , δ , and ε under various engineering conditions. Most electroactive phase is β – phase that consists of all trans conformations (TTTT) and shows highest electroactive properties among any other phases.^{1,2}

Several strategies have been followed to engineer and enhance the polar β -phase through electrospinning, spin coating, drop casting through nanofillers additions (*in-situ* and *ex-situ*), melting quenching, and high electro poling etc. In this study, a simple ex-situ drop-casting methods followed to synthesize thin films fallowed by high voltage electro poling and ice quenching. To enhance the β -phase polymorph, dielectric constant and resonance impedance matching, PVDF/CNTs composite would be a suitable candidate .^{1,3}

In the recent past, extensive research works have been conducted on PVDF polymer nanocomposite-based tactile sensor, force sensor, energy harvesting, *etc* applications. Some research studies have been conducted on PVDF nanocomposite thin film-based ultrasound transducer.⁴ Piezoelectric thin films can generate mechanical vibration from electrical signal and vis versa.⁵ The aim of this studies is to engineer the PVDF/CNTs composition for obtaining the best sets of β -phase, dielectric constant and frequency resonance impedance match in the developed PVDF/CNTs nanocomposite thin film and thereafter develop aimed ultrasound transducer. To avoid adhesive issues, PVDF/CNTs nanocomposite directly casted on the backing layer(aluminium).⁴⁻⁶ A non-radiative and non-invasive technology is ultrasonography for real time medical imaging applications. Real time photoacoustic imaging, noninvasive temperature monitoring, ultrasound based diagnostic imaging, etc are the immediate application can be done with the developed ultrasound sensor.

Experimental

Poly(vinylidene difluoride) (sigma Aldrich, MW), N,N dimethyl formamide (Merck, India) and Multi walled Carbon nanotubes (CNTs)(Merck, India) are used in this study. To prepare PVDF/CNTs nanocomposite thin films, 5 ml DMF, 10% PVDF and 1% CNT of PVDF poured into a 15 ml clean glass tube. And stirred for overnight (~14 hours) at 60^oC followed by 30 min bath sonication. Then uniform solutions were drop casted on 0.5 mm aluminum substrates and dried at 80 °C for 2 hours. For the confirmation of phase formation, X-ray diffraction (XRD; Model-D8, Bruker AXS Inc., Madison, WI) at atmospheric pressure and room temperature is carried out using nickel-filtered Cu-Ka radiation with operating voltage of 40 kV and, later Fourier Transform Infrared Spectroscopy (FTIR) (FTIR-8400S, Shimadzu) is performed for the developed thin film deposited on glass petri plate. Top electrode (1.2 cm X 1 cm) deposited on nanocomposite thin film via silver sputtering unit and connected through a copper wire for further electrical characterizations such as dielectric constant, impedance, phase, capacitance. For high voltage electro poling, sample thin film (~143 µm) was sandwiched by two electrode and applied 32 kV electric field.

Results and discussion

Figure 1(a) represents FTIR spectra from the range of 400 to 1300 cm⁻¹ for the line 1 PVDF/CNT nanocomposites (PCNT) thin film after electro poling and 2 is FTIR spectra of the PVDF/CNT before electro poling. FTIR results indicates α -phase peaks (488 cm⁻¹ (CF₂ waging) 532 cm⁻¹ (CF₂ bending), 615 and 764 cm⁻¹ (CF₂ bending and skeletal bending), and 796 and 976 cm⁻¹ (CH₂ rocking)) are disappear and all β -phase peaks at 510 and 840 cm⁻¹, 445 and 1274 cm⁻¹ shows in line 1 and 2.^{1,2} To quantify the β -phase contain, we are using Lambert–Beer law, i.e., F (β) = $\frac{A_{\beta}}{(\frac{K_{\beta}}{K_{\alpha}})A_{\alpha}+A_{\beta}}$

100%, line 1 shows 85.2% and line 2 shows 73% β – phase presents to the corresponding film.¹ Though after electro poling, FTIR shows the highest β –phase results, we have further characterized it with X-ray diffraction (XRD) after electro poling PCNT sample. XRD pattern of PCNT depicted in figure 1(b) which also confirm the β –phase (peaks at 2 θ = 20.4° and 36.6° corresponding to the (110,200) and (020,101) plane) formation of PCNT. Peak at 42.9 due to CNT presence in PVDF matrix only. FESEM image shows the spherulites size ~10 µm which also confirm the β – phase presence in PVDF/CNT composite thin film.²



Fig. 1. (a) FTIR spectra of PCNT after electro poling (red line) and before electro poling (green line), (b) XRD diffraction pattern of PCNT, and (b) inset FESEM images of PCNT thin films.

The dielectric constant (k) is calculated by the equation, $k = C.d / \varepsilon_0 A$. Dielectric constant k is 64 at 20 Hz frequency and decreasing this value with increasing frequency has shown in figure 2(a). This phenomenon may occur due to Maxwell–Wagner–Sillars (MWS) interfacial polarization.¹

Two planer device is design by drop casted on aluminum substrate which also act as backing layer and top electrode formed by deposited silver. Piezoelectric resonance behavior of ~143 μ m PCNT thin film-based device has shown in figure 2(b).

Fabricated device is also capable to receiving signal from 10 MHz commercial sensor which is depicted in figure 2(c). The resulting voltage is traced from the ultrasound excitation by Digital Storage Oscilloscope (DSO, Agilent). Peak to peak generated piezoelectric voltage is ~ 74 mV induced by ultrasound wave.



Fig. 2. (a) Dielectric constant with frequencies, (b) Impedance and phase with frequencies from 5MHz to 25 MHz range for prepared PCNT sensor, and (c) Ultrasound pulse receiving signal by the developed PCNT thin film based ultrasound sensor.

Conclusion

PVDF/CNT nanocomposite thin films show the high piezoelectric β -phase formation that is 85.2% confirmed by the FTIR spectra. XRD pattern and FESEM images also confirm the β -phase formation. The dielectric properties of PCNT thin film is also observed high *i.e* k= 64 at 20 Hz. Impedance spectrum of the prepared enginnered piezoelectric thin film shows the resonance around 10 MHz. Fabricated ultrasound device also responses and generated piezoelectric voltage ~74 mV from the ultrasound wave of 10 MHz ultrasound device. So, the PCNT thin film may be used as piezoelectric layer for developing ultrasound transducer.

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Study of thermal oxidation behavior of N⁺ ion implanted zirconium thin film

Ranjini Menon^{1*}, Sujoy Sen³, S Amirthapandian^{3, 4}, P Jegadeesan³, P Gangopadhyay³ and P Y Nabhiraj^{1, 2}

¹Accelerator Physics Group, Variable Energy Cyclotron Centre, ²HBNI-Kolkata, Saltlake, Kolkata-700064 India ³Materials Science Group, Indira Gandhi Centre for Atomic Research, ⁴HBNI-Kalpakkam, Kalpakkam-602103 India

*Corresponding author: ranjini@vecc.gov.in

Abstract

Zirconium thin films were deposited on sapphire substrate using DC magnetron sputtering at room temperature and in argon atmosphere. These thin films were implanted with nitrogen ion beam and further annealed to study the oxidation behavior. As expected, XRD reveals that the samples completely turned to ZrO₂. The band gap of the film is found to be 3.15 eV from diffused reflectance spectroscopy. SEM analysis shows a peculiar nature of the N⁺ ion implanted and annealed thin film where blisters are formed and also there are cracks developed on the blisters for the release of implanted nitrogen. The Zr film which was annealed at nitrogen atmosphere retained the metallic luster and SEM shows a smooth film with large grain boundaries without any blisters.

Magnetic Proximity Effect In La_{0.67}Sr_{0.33}MnO₃ /SrTiO₃/YBa₂Cu₃O_{7-δ} Heterostructures

Harsh Bhatt^{1,2,*}, Yogesh Kumar¹, C. L. Prajapat^{2,3}, C. J. Kinane⁴, S. Langridge⁴, S. Basu^{1,2} and Surendra Singh^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085 India
 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094 India
 ³Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085 India
 ⁴ ISIS-Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot, Oxon OX11 0QX, United Kingdom

*Corresponding author: harshbhatt@barc.gov.in

Abstract

Magnetic proximity effect (MPE) in La_{0.67}Sr_{0.33}MnO₃(LSMO)/SrTiO₃(STO)/YBa₂Cu₃O_{7- δ}(YBCO) heterostructures has been investigated using spin-polarized neutron reflectivity experiments. We find modulation in magnetization in the ferromagnetic LSMO layer at the interface in the form of an emergent layer of thickness ~ 20 Å with depleted magnetism. This emergent layer is found only below the superconducting transition temperature of YBCO, indicating that superconductivity is essential for the phenomenon of MPE which is attributed to tunnelling of electron cooper pairs from YBCO to LSMO through the STO layer.

Highly Sensitive Room Temperature NO₂ Gas Sensor Based on MgO Functionalized ZnO Nanowires

Ankita Pathak^{*}, Soumen Samanta, N.S.Ramgir, Manmeet Kaur and A.K.Debnath

Technical Physics Division, Bhabha Atomic Research Centre, Mumbai, 400085

*Corresponding author: ankitap@barc.gov.in

Abstract

Abstract. Surface modification of Metal oxide semiconductors have been found to significantly improve the gas sensing characteristics. In the present study hydrothermally grown ZnO NWs were functionalized with MgO and sensing measurements were carried out. Sensors are found to be highly sensitive and selective towards NO₂ gas with sensor response of ~310 for 10ppm concentration at room temperature. Minimum detection limit of 400ppb is achieved with highly repeatable and stable response for more than two months. Compare to pristine ZnO films, composite films shows remarkable 25 fold increment in sensor response at room temperature.

Thickness dependent crystallinity variation in ZnO thin films synthesized by pulsed laser deposition method

Hrudya Radhakrishnan¹, Ramanathaswamy Pandian¹, R. Krishnan¹, R.M. Sarguna², G. Mangamma¹, S. Dhara¹

¹Surface and Nanoscience Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam, Tamil Nadu, 603102

²Condensed Matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam, Tamil Nadu, 603102

*Corresponding author: rpandian@igcar.gov.in

Abstract

ZnO thinfilms were synthesized by pulsed laser deposition technique on Silicon substrates at various thicknesses. The influence of film thickness on crystallinity of the film was analyzed via fracture cross-sectional SEM and GI-XRD techniques. SEM observation revealed the columnar grain structure with orientation vertical to the substrate. XRD analysis revealed the preferential orientation along c-axis of the films. The preferential orientation improved with the thickness. RMS roughness of the films measured by AFM technique initially increased with thickness and decreased afterwards for higher thickness.

Hydrogen-induced modification of opto-electronic properties of ZnO(10-10)/graphene interface

Tanmay Das, Sesha Vempati

¹Department of Physics, Indian Institute of Technology Bhilai, GEC Campus, Raipur, 492015

*Corresponding author: tanmayd@iitbhilai.ac.in

Abstract

Organic and inorganic interfaces are known to offer hybrid functionalities which are superior to that of individual materials. However, the unavoidable adsorption of gas molecules/atoms can further modify the opto-electronic properties of the materials. In this work, we have studied the modification of opto-electronic properties of ZnO/graphene system due hydrogen adsorption at ZnO mixed terminated nonpolar (10-10) surface.

Tuning of electronic and magnetic properties SrRuO₃ thin film via electric field assisted growth

Anita Bagri*, Sophia Sahoo, Anupam Jana, R. J. Choudhary, D.M. Phase

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, India

*annybagri15@gmail.com

Abstract

Electric field assisted and unassisted SrRuO₃ thin films have been grown on the (00l) Si substrate using pulsed laser deposition technique. An applied electric field during film growth enhances the nuclei coalescence, resulting a better crystallinity of film. X-ray absorption study suggests that in electric field assisted film, the crystal field splitting is found higher as compared to unassisted SRO film, resulting the enhanced Ru 4*d*- O 2*p* hybridization. Enhanced magnetic anisotropy is observed in electric field assisted SrRuO₃ thin film.

Study of Interfaces in Metal/ C₆₀ Bilayer under X-ray Standing Wave Condition; Theoretical Simulations

Sonia Kaushik, Md. Shahid Jamal, Avinash G. Khanderao and Dileep Kumar^{a)}

(UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore - 452001, India) a) Corresponding author: dkumar@csr.res.in

Abstract

In the present work, we demonstrated the depth selectivity of the FeCoB/C₆₀ interface on the basis of theoretical simulations by generating x-ray standing wave (XSW) using a waveguide structure Si/Pt/C₆₀/FeCoB (interface)/FeCoB (bulk)/C₆₀/Pt. Fek_{α} fluorescence (XRF) spectra were simulated theoretically for increasing angle of incidence for the different values of electron density and thickness of interface FeCoB layer. It is found that the fluorescence peaks corresponding to the XSW antinodes crossing the interface layer are highly sensitive to the electron density and thickness of interface FeCoB layers. The present study demonstrates that by measuring electron density profiles through XRF measurement under XSW, interface resolved structural information can be achieved by moving the antinode region and selecting an appropriate incident angle.

Introduction

Fullerene (C₆₀) based ferromagnetic (FM) multilayered (ML) nanostructures are the imperative candidates for organic spintronics (OS) devices because of the low spin-orbit coupling due to lower atomic weight, longer spin lifetime, and reasonably good mobility[1,2]. In such devices, organic semiconductor (OSC) such as C_{60} , Alg₃ etc, sandwiched between two ferromagnetic (FM) layers are used to mediate or control a spin-polarized electron transport, but the mechanical softness of OSC create challenges owing to penetration and possible chemical reaction of metal atoms at the interfaces, which creates complicated magnetism and transport in these structures. Recently, the combination of different FM layers such as FeCoB, Co have been grown on C_{60} , and unusual magnetic properties at the interfaces[1-3], significantly different from their constituent layers, were obtained. In view of this, a clear picture of how an effective organic spin valve (OSV) could be achieved for an efficient spin injection has not been experimentally realized till date[3,4]. The main difficulty is to get genuine and depth-resolved interface structure using conventional lab-based characterization techniques such as x-ray reflectivity (XRR), secondary ion mass spectroscopy (SIMS) etc., either do not have enough depth resolution so as to resolve the interfaces or may not be probing the real interfaces. Furthermore, techniques like XRR is sensitive to all the individual parameters of the layers (thickness, roughness, and electron density etc.).

In the present work, understanding of interface diffusion and deep penetration of FeCoB atom into C_{60} is understood through theoretical simulation, where the use of XRF under XSW will be demonstrated to be a suitable method for FM-C₆₀ systems otherwise, it is difficult in the systems where deep penetration of the FM atom and spread over up to hundreds of angstroms in OSC layer. Present simulation has been used to demonstrate increased sensitivity from the interface by generating x-ray standing wave (XSW) using a waveguide structure (WGS). Interface selectivity could be used to follow the evolution of the interfaces with thermal annealing to get insight into the interface structure and diffusion. Reported XRF simulations under XSW condition seems to be promising in order to develop better understanding at FM/C_{60} interface and to tune the properties for the desired functionality.

Formation of XSW in Waveguide Structure

In the case of the waveguide structure, the XSW can be generated by total reflection of x-rays from an underlayer of high Z element (e.g., Au, Pt). Interference between the incident and the reflected wave-fronts form a standing wave above the surface of the reflecting layer, with separation between the successive antinodes given by D=1/q, where q is the scattering vector. Figure 1(a) provides a waveguide with structure, where a lowdensity layer (Fullerene- C₆₀) is sandwiched between two dense layers (say Pt). Simulated electric field intensity (EFI) profile inside the cavity (along the depth), as shown in fig. 1(b). It may be noted that when the angle of incidence changes, the position of antinode shifts and the formation of different standing wave modes (TE01, TE02, TE03 etc.,) takes place along the depth of the cavity. X-ray measurements such as XRF under XSW conditions would provide selective information from the region of antinodes when it crosses the layer inside the cavity. In the case of XRF measurement, fluorescence intensity at any given value of q is obtained by integrating the concentration profile $\rho(z)$ of the FeCoB layer weighted with the x-ray

intensity I(q, z) at that depth [5,6]:

 $F(q) \propto \int I(q,z)\rho(z) dz$ -(1).



Fig 1. (a) Schematic of waveguide structure: where one low-density layer is sandwiched between two high density layers, (b) Rearrangement of x-ray field intensity (EFI) inside the C_{60} cavity as function of the scattering vector q; simulated for Si substrate /Pt(30nm)/C₆₀/(35nm)/Pt (2nm) structure.

Fluorescence under XSW; Results and Discussion

Fe_{Kα} fluorescence patterns are calculated by taking an incident x-ray of energy 8.045 keV, where the sensitivity of the XRF peaks on interfaces of the FeCoB layer is demonstrated for (**a**) different combinations for densities of the bulk and interface FeCoB layer by keeping $\rho_{bulk} = 7.45$ g/cc and varying ρ_{int} For this purpose, FeCoB layer is divided in two sections; one with FeCoB_{bulk} (d_{bulk} = 40Å) and FeCoB_{interface} (d_{int} = 120Å), (**b**) increasing thickness of interface layer but keeping bulk FeCoB layer fixed (d_{bulk} = 40 Å). From the contour plots of EFI 2D profile, as shown in Fig. 2a &2b, the position of the FeCoB bulk and interface layer is marked in the presence of XSW modes inside the waveguide cavity.



Fig 2. (a)shows simulated contour plot for the Si/Pt/ C_{60} / FeCoB (interface)/ FeCoB(bulk)/ C_{60} /Pt. The shaded region represents the bulk and interface FeCoB layers. (c)

Simulated XRF for $\rho_{\text{bulk}} = 7.45$ g/cc and different values of $\rho_{\text{int.}}(i) \rho_{\text{int}} = 3.19$ g/cc (ii) $\rho_{\text{int}} = 2.11$ g/cc (iii) $\rho_{\text{int}} = 6.35$ g/cc (iv) $\rho_{\text{int}} = 5.63$ g/cc (v) $\rho_{\text{int}} = 3.72$ g/cc d) Simulated XRF for varying thickness of interface layer (i) $t_{\text{int}} = 80$ Å (ii) $t_{\text{int}} = 60$ Å (iii) $t_{\text{int}} = 40$ Å (iv) $t_{\text{int}} = 30$ Å (v) $t_{\text{int}} = 20$ Å

In the case of Fig. 3(c)&(d), XRF curves clearly show a drastic change in the relative peak intensities corresponding to TE1, TE2 and TE3 modes. The intensity of the second peak mainly depends upon the FeCoB bulk layer, while the shape and intensity of the third peak depend upon the concentration profile of the FeCoB interface layer and is sensitive to the subtle change in the interface layer. In the case of Fig.3d, where $Fe_{K\alpha}$ fluorescence from FeCoB layer is plotted for increasing thickness of interface layer. It is clear from the contour plot that the interface layer is near to the bottom side of TE1 mode, therefore XRF second peak is sensitive to the interface. In view of the fact, the fluorescence intensities peaks corresponding to FeCoB_{bulk} and FeCoB_{interface} layer are very sensitive to the subtle change in the concentration, thickness, and roughness of FeCoB_{bulk} and FeCoB_{interface} layer.

Conclusions

Fe- Ka fluorescence (XRF) patterns are calculated with an aim to demonstrate the generation of node and antinodes inside the waveguide structure and to make them useful for the precise study of interfaces in metal-organic systems. It is made possible through XRF data simulated under XSW from the FeCoB/C₆₀ system by taking different electron densities and thicknesses of the interface FeCoB (diffused) layer. It is found that high resolution with depth selectivity of XSW based xray fluorescence (XRF) makes it possible to measure subtle change at the interface. Detail theoretical simulations have demonstrated the usefulness of the XSW method to study the interfaces of Metal /organic layered structures.

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Morphological Evolution and Surface/Interface Fe-oxide formation in Epitaxial Fe(001)/MgO(001) Thin Film

Md. Shahid Jamal and Dileep Kumar*

UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore-452001, India *Corresponding author: dkumar@csr.res.in

Abstract

Epitaxial Fe film has been grown on ion beam sputtered MgO(001) substrate by electron beam evaporation. Reflection high energy electron diffraction (RHEED) and transport measurements (TM) were performed simultaneously during the growth of the film. While TM provided information about film morphology, RHEED provided information about the structure of the film. The film grows via Volmer–Weber mechanism, where epitaxial islands grow larger to impinge with other islands and eventually coalesce into a continuous film at around 1.8 nm thickness. In contrast to the literature, no evidence of the formation of the iron oxide layer is observed at Fe/MgO interface even up to 300° C. High quality epitaxial Fe₃O₄ layer is found to develop on Fe surface when the sample is annealed under a moderate oxygen partial pressure.

Introduction

Over a decade Fe/MgO system has been a subject of extensive investigations due to numerous interesting phenomenon such as tunnel magnetoresistance [1], perpendicular magnetic anisotropy [2], interlayer coupling [3], and the exchange bias [4]. Here, interface oxidation is well known for drastically alter the behaviour of the system. The oxide layer formation at the Fe/MgO interface and its clear role in modifying magnetic and transport properties is still missing in the literature..

Present work deals with the growth of an epitaxial Fe film on MgO(001) substrate, where real-time characterization was done simultaneously using reflection high energy electron diffraction (RHEED) and transport measurements (TM) measurements during and after the film growth. TM provided information about the different stages of the film growth, whereas RHEED gave information about the structure and morphology of the film surface.

Experimental

Fe film of ~3.0 nm thickness is grown on MgO(001) substrate using e-beam evaporation and characterized in-situ using RHEED and TM during growth. Au contact pad has been deposited (~ 30 nm) on the substrate for TM. Before Fe deposition, the substrate was cleaned by annealing at 500 °C for 30 min followed by Ar+ ion etching at 1 KeV for 20 min. Insitu RHEED measurements were also performed after annealing Fe film upto 300 °C. All the RHEED images collected along [100] direction of Fe. For magnetic properties, magneto-optic Kerr effect (MOKE) measurements were performed before and after annealing at 300 °C (with and without oxygen partial pressure).

Results and Discussion

Fig. 1(a) shows a schematic, where the direction of RHEED, deposition, ion gun, and TM are mentioned. Total sheet resistance (R_{Fe}) vs Fe film thickness (d_{Fe}) is plotted in Fig. 1(b) and divided into three different regions (A, B, and C) to understand different stages of growth. R_{Fe} in region "A" is large (~19 k/ \Box) and remains almost the same up-to film thickness of ~0.8 nm due to the small island state of Fe film. In this state, island to island hopping probability of electron is negligible and therefore, resistance is large and resistance is mainly coming from the substrate. With increasing d_{Fe} , beyond ~0.8 nm (region B), isolated islands start to connect and hence, resistance decreases drastically.



Fig. 1.(a) Schematic of the in-situ measurements.(b) Sheet resistance (R_{Fe}) Vs Fe thickness on MgO(001) substrate and morphological evolution; A- isolated islands, B-connecting islands, and C- continuous film. Insets shows Au contacts for TM measurement. RHEED images at Fe layer thickness; (c) 0.53 nm, (d) 0.92 nm, and (e) 3.0 nm.

After ~1.8 nm thickness (region C), it decreases slowly due to the formation of a continuous layer.

RHEED images 1(c-e) correspond to 0.53 nm, 0.92 nm, and 3.0 nm thick Fe films. The spotty and streaky pattern in all images indicate epitaxial growth of Fe (001) on MgO(001) substrate. As RHEED is a surface-sensitive technique up to ~ 3 nm, therefore all three images are expected to have structural information throughout the Fe thickness (including interface). It may be noted that the absence of any other additional line (other than Fe) clearly shows the absence of an oxide layer at the surface and interface of the Fe/MgO layer.



Fig. 2(a,) & (b, c) show hysteresis loops and RHEED images of 3 nm thick Fe film before and after annealing (300 $^{\circ}$ C), respectively. Loop (inset of Fig. 2a) and RHEED (Fig. 2d) taken after annealing at 300 $^{\circ}$ C in oxygen partial pressure. (e) Intensity profile of all RHEED images.

To further study the effect of annealing, Fe film is heated at 300 °C temperature for 20 min. RHEED and MOKE measurements, before and after annealing, are shown in Fig. 2. Hysteresis loops Fig. 2(a) and RHEED (Fig. 2b & c) patterns are hardly affected by the annealing. A slight difference in the loop signal (height) and coercivity (Hc), is mainly due to the structural relaxation after heating. The same has also been confirmed by the shaping of the RHEED lines after annealing (Fig. 2c). On the other hand, when the oxygen partial pressure of 5×10^{-7} mbar is created in the chamber for 5 min during heating at 300 °C, a drastic change in the loop signal (inset of Fig. 2a) and presence of additional lines between Fe lines in RHEED image (Fig. 2d) can be understood in term of the surface oxidation of the Fe film. The intensity line profile (along the marked rectangular line in Fig. 2c & 2d) of all three images are extracted and shown in Fig. 2e. The appearance of three additional lines in between two intense high lines corresponds to the Fe_3O_4 [5].

Drastic reduction in Kerr signal after the formation of the Fe_3O_4 layer on Fe surface can be understood by

the expression of Kerr intensity in Longitudinal geometry of MOKE, where Kerr signal is linearly related to the thickness (d_{Fe}) of magnetic film in the ultrathin regime and given by the relation [6]-

$$\varphi_{long} = \frac{4 \pi n_{sub} Q d_{Fe} \theta}{\lambda (1 - n_{sub}^2)}$$

Q being the magneto-optical constant and θ is the angle (~45°) of incidence measured from surface normal. As the oxide formation took place at the cost of the Fe layer on the surface, therefore the reduction in the Kerr signal could be attributed to the decrease in d_{Fe}. On the other hand, an increase in the Hc is may be due to the increase in domain wall pinning at the Fe₃O₄/Fe interface.

Conclusion

Fe film is grown epitaxially on MgO(001) substrate to study morphological evolution and surface/interface Fe-oxide formation. Systematic studies of epitaxial Fe film were done in-situ during different stages of the Fe growth using RHEED, MOKE, and TM. Fe film is found to grow via Volmer-Weber mechanism, where epitaxial islands grow larger to impinge with other islands and eventually coalesce into a continuous film at around 1.8 nm thickness. Unlike the literature [7], no evidence of the formation of an iron oxide layer is observed at Fe/MgO interface even up to thermal annealing at temperature 300 °C. A well-defined epitaxial Fe₃O₄ layer is found to form on Fe(001)/MgO(001) surface when the sample is annealed at 300 °C for 5 min in the presence of oxygen partial pressure.

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Optical Properties of La_{0.7}Sr_{0.3}MnO₃/ZnO Heterostructures

S. Dash¹, B. Das¹, S. N. Achary² and P. Padhan¹

¹Department of Physics, Indian Institute of Technology Madras, Chennai, 600036 ²Chemistry Division, Bhabha Atomic Research Center, Mumbai, 400085

*Corresponding author: ph19d005@smail.iitm.ac.in

Abstract

La_{0.7}Sr_{0.3}MnO₃/ZnO heterostructures of various ZnO thicknesses have been grown on (001) oriented Si substrate using RF magnetron sputtering. The growth conditions of the La_{0.7}Sr_{0.3}MnO₃ and ZnO were chosen to achieve the stoichiometry and the preferential growth along the (001) direction. The variation of band gap of ZnO with thickness has been determined using diffuse reflectance spectroscopy. The band gap of ZnO grown on Si/LSMO increases with decrease in the thickness of the ZnO films. The band structure of bulk ZnO, hence, the band gap was studied using the first-principle density functional theory. This LSMO/ZnO heterostructures can be utilized for a wide range of spintronics and optoelectronics applications.

Introduction

Over the last decades, artificially tailored vertical heterointerfaces, superlattices, and multilayers of La₁. $_xA_xMnO_3$ with A = Ca, Sr, Ba, etc. are being heavily studied due to its colossal magnetoresistance [1] and promising applications in the field of spintronics [2], magnetic field sensing, non-volatile memory [3], etc. ZnO has a wide direct band gap of ~3.37 eV and high exciton binding energy of ~60 meV [4].

The interface of two materials in reduced dimensions offers various novel properties different from the bulk phase of parent materials. The interface behaves as a two-dimensional system and can be altered by external magnetic field, stress, strain, and electrical field. LSMO is p-type and its growth on ntype as grown ZnO shows photocarrier injection effect [5]. In this work, the ZnO films of various thicknesses have been grown on (001)Si/La_{0.3}Sr_{0.3}MnO₃, and their band gaps have been determined using diffuse reflectance spectroscopy. The electronic band structure calculation of bulk ZnO was also carried out using the density functional theory.

Experimental Methods

The targets were synthesized by the solid-state reaction method. High-quality polycrystalline powders of La₂O₃ (99.99 %), SrCO₃ (99.99 %), Mn_2O_3 (99.99 %) were mixed in proper stoichiometric ratio, ground, and then calcinated at 900 °C in the air for 24h. The pellets of 50 mm diameter were made and sintered in the atmosphere for 12h at 1200 °C to improve the thermodynamic stability of the target. Similarly, highly pure polycrystalline ZnO powders were ground and

calcinated at 900 °C. Then, the calcinated ZnO powder was pelleted and sintered at 1200 °C for 24hr. Respective targets were mounted inside the sputtering chamber and the cleaned silicon substrate was mounted on the heater for pulsed plasma deposition. The chamber pressure was reduced to 10^{-6} mbar and then, the substrate was heated to 700 °C followed by filling the chamber with Argon as the sputtering gas and oxygen as the reactive gas with the ratio of 20:80 for the growth of LSMO. At first, the LSMO film was grown on (001) oriented Si at 700 °C and 9×10⁻³ mbar pressure. Then, the ZnO was grown on LSMO with Ar:O₂ (60:40) ratio keeping same temperature and pressure. Different thicknesses of ZnO were achieved by controlling the growth durations.

The diffuse reflectance spectroscopy was carried out in wavelength range of 200-900 nm. The oriented growth of the films was confirmed by the X-ray diffraction spectra and thickness was determined from low angle X-ray reflectivity [6]. Further, we have used the first principle calculation to simulate the bulk band structure of ZnO using the Quantum Espresso package [7]. The projector-augmented wave potentials in a plane wave basis are used. The generalized gradient approximation exchangecorrelation function is applied according to Perdew-Burke-Ernzerhof prescription. Monkhorst-Pack grid of $8 \times 8 \times 6$ and kinetic energy cutoff of 50 Ry are used for the respective simulation.

Results and Discussion

Figures 1(a)-(d) shows the diffuse reflectance spectra of the Si/LSMO/ZnO heterostructures with different ZnO thicknesses. The reflectance is related to the band gap of the ZnO films through the Kubelka-Munk function, which is defined as F(R).

$$F(R) = \frac{(1-R)}{2R} \tag{i}$$

$$(F(R)h\nu)^2 = h\nu - E_g \qquad (ii)$$

The R is reflectance and hv is the photon energy. Eq. (*i*) explains the relation of F(R) and R, while Eq. (*ii*) explains the explicit relation of F(R) with the direct optical band gap of the heterostructure [8]. The linear part of the graph is extrapolated, and its intercept with the x-axis gives the band gap.



Fig. 1. Diffuse reflectance spectra (a)-(d), the photograph of the films (e)-(h) and $(F(R)hv)^2vs.hv$ plots (i)-(l).

Table 1. Band gap of (001)Si/La_{0.3}Sr_{0.3}MnO₃/(t Å)ZnO.

t (ZnO thickness) (Å)	Band gap (eV)
930	2.829
744	3.089
558	3.184
372	



Fig. 2. Electronic band structure of bulk ZnO.

The ZnO thickness of 558 Å of the LSMO/ZnO heterostructure shows a band gap \sim 3.18 eV, which is close to that of the bulk ZnO [Fig. 1(j)]. With the increase in ZnO film thickness in the heterostructure,

the band gap decreases as listed in the table-1 and the contribution from LSMO to the absorption spectra decreases. However, for the heterostructure with 372 Å thick ZnO, the contribution of LSMO to the absorption spectrum suppresses the contribution of ZnO. Thus, the actual band gap of the heterostructure with 372 Å thick ZnO is not possible to determine [Fig. 1(i)]. The unique change in heterostructure surface color was witnessed with the change in ZnO film thickness [Figs. 1(e)-(h)]. Fig. 2 shows the simulated electronic band structure of bulk ZnO where the valence band maximum and conduction band minimum occur at Γ point gives rise to the direct band gap ~3.3 eV. The band gap obtained from simulations consistent with the experimental bulk band gap ($\sim 3.37 \text{ eV}$) and close to the band gap of the 558 Å ZnO thin film (~3.18 eV).

Conclusion

Highly oriented film of ZnO was grown on (001) Si/LSMO. The optical band gap was analyzed using diffuse reflectance spectroscopy and first-principle density functional theory. The optical spectra confirmed that with the decrease in thickness of ZnO, the band gap increases.

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Fabrication Of CuO Coated Mesh For Efficient Oil/Water Separation

Mihir Paul^{1*}, Debarun Dhar Purkayastha²

¹Department of Physics, National Institute of Technology Nagaland, Chumukedima-797103, Dimapur, India

*Corresponding author: g.paulmihir13@gmail.com

Abstract

In this work, we fabricated CuO coated superhydrophobic mesh by simple immersion method. The coated mesh showed excellent superhydrophobic-superoleophilic mesh with water and oil contact angle of 156° and 0° respectively. The as deposited mesh meets the current need for the separation of oil-water mixtures owing to its high separation efficiency (~98%) and stability.

X-ray absorption study of manganese mononitride thin films

Yogesh Kumar¹, Akhil Tayal² and Mukul Gupta^{1*}

¹UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 001, India ²Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, D-22607 Hamburg, Germany

*Corresponding author: mgupta@csr.res.in

Abstract

We report a comprehensive study to resolve the debate about the crystal structure of manganese mononitride (MnN). Single phase MnN thin film was obtained by varying the partial pressure of N_2 in the sputtering process. The optimized film was studied in detail using x-ray absorption near edge spectroscopy at Mn and N *K*-edges and Mn *L*-edge. Pre-edge peak intensity of XANES at metal *K*-edge is very sensitive to the local coordination symmetry of the central atom and was used to confirm the crystal structure of MnN thin film.

DFT+U Study on the Half-Metallic Ferromagnetic Behavior in CoRuVAl Quaternary Heusler Alloy

V. Aravindan, V. Vijayanarayanan, and M. Mahendran*

Smart Materials Lab, Department of Physics, Thiagarajar College of Engineering, Madurai, 625015

*Corresponding author: manickam-mahendran@tce.edu

Abstract

In the framework of density functional theory, the physical characteristics of the quaternary Heusler alloy CoRuVAl have been estimated using the Full Potential and Linearized Augmented plane wave (FP-LAPW) approach. We employed a Coulomb interaction (U) within the GGA method to get accurate results. The electronic structure has half-metallic behavior, and a minority band gap of 0.278 eV is formed at Fermi level. By satisfying the Slater - Pauling rule of 24 ($M_t=Z_t-24$), we estimated a total magnetic moment of 1 μ_B . The calculated results show that CoRuVAl quaternary Heusler alloy is a good spintronics material.

Introduction

Spintronics is a novel technology that makes use of spin as a data carrier. Compared to conventional semiconductor devices, they have a significant advantage, including being non-volatile, consuming low power, and high data processing speed [1]. Halfmetallic materials can be used as electrode materials in spintronic devices such as spin diodes, spin valves, spin filters, MRAM, etc., [2]. The primary distinctive feature of half-metallic ferromagnets is their unique electronic structure which shows semiconductor or insulator nature in the spin down channel and metallic nature in the spin up channel. Due to the presence of half metallic band gap around Fermi level, the spin polarization is 100%. Heusler alloys have attracted numerous scientists due to their halfmetallic nature. Since the first half-metallic Heusler alloy NiMnSb was predicted, these materials have piqued research interest [3]. Heusler alloys are classified into four groups based on their structures: half-Heusler (XYZ), full-Heusler (X₂YZ), inverse-Heusler (Y₂XZ), and quaternary Heusler (XX'YZ). Compared to other Heusler alloys, Co-based Quaternary Heusler Alloys (QHA) have a high spinpolarization, a high Curie temperature, and a stable half-metallicity due to the minor disorder in the crystal structure [4].

Computational Methods

We computed the physical properties using Full Potential and Linearized Augmented Plane Wave (FP-LAPW) method implemented in the quantum mechanical code package WIEN2k [5]. The exchange-correlation (V_{XC}) potentials were approximated using a Generalized Gradient Approximation (GGA) with onsite Coulomb interaction (U). U_{eff} = U - J in this case, with J denoting the onsite exchange interaction and U_{eff} denoting the Coulomb potential. Assuming J = 0, the optimized U_{eff} values for Co, Ru, and V are 1.92 eV, 2.24 eV, and 2.34 eV, respectively. With a value of 6.0 Ry, the states of valence and core electrons are detached. The radii of the muffin tins (R_{MT}) were chosen to avoid charge leakage through interstitial regions. The R_{MT} × K_{max} value for the present alloy has been set at 8. We used a mesh of 400 special k-points. Tolerances for charge and energy convergence were 10⁻⁵ Ry and 10⁻⁴ e, respectively.

Results and Discussions.

The CoRuVAl QHA crystallized in LiMgPdSntype structure with a Fm-3m space group. We calculated the total energies of CoRuVAl in nonmagnetic (NM) and ferromagnetic (FM) states which are depicted in Fig. 1. As can be observed, the ferromagnetic state has the lowest energy of the two states, indicating that it is the most stable magnetic state. By expanding the Birch-Murnaghan equation of state, the ground state properties were determined. To investigate the potential of experimentally synthesizing CoRuVAl QHA, we calculated the formation energy of the alloy using the formula,

 $E_f = E_{Tot} - (E_{Co} + E_{Ru} + E_V + E_{Al})$ (1)

Where E_{Tot} denotes the total energy of the CoRuVAl QHA and E_{Co} , E_{Ru} , E_V , and E_{Al} denote the total energies of the Co, Ru, V, and Al atoms, respectively. The formation energy obtained is -0. 2135 eV, indicating that this alloy is energetically stable and capable of being fabricated experimentally. The derived mechanical properties of CoRuVAl are defined by three elastic constants, C₁₁, C₁₂, C₄₄, which are listed in Table 1. This alloy satisfied Born and Huang's mechanical stability criteria, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$ [6]. Additionally, we estimated the band structure for GGA+U, as

illustrated in Fig. 2. It exhibits metallic behavior in the spin up channel and a spin down channel indirect bang gap (Γ - X) of 0.278 eV around the Fermi level. The total magnetic moment obtained is 0.99 μ_B , with the majority of the contribution coming from the Co atom, and it is satisfied the Slater – Pauling rule (M_t=Z_t-24).



Fig. 1. Volume optimization curves of NM and FM states



Fig. 2. Band structure and Total density of states (TDOS) of GGA+U.

Another critical factor in the utilization of halfmetallic magnetic materials in spintronics is their high Curie temperature. The mean field approximation is frequently used to predict the Curie temperature (T_c) of materials theoretically by following equation [6];

$$T_C = \frac{2\Delta E_{NM-FM}}{3CK_B} \tag{2}$$

Where ΔE_{NM-FM} denotes the total energy difference between NM and FM states. C is the

number of magnetic atom, while K_B is the Boltzmann constant. The Curie temperature is derived using formula (2) is 190 K.

Table 1. Calculated physical properties ofCoRuVAl QHA.

Physical Parameter	CoRuVAl
Lattice parameter	5.898 Å
Ground state energy	-14235.10 Ry
Formation energy	-0.2135 eV
C ₁₁ , C ₁₂ , C ₄₄ (GPa)	283, 182, 104
Bulk modulus (B)	108.13 GPa
Shear modulus (G)	173.67 GPa
Young's modulus (Y)	339.35 GPa
Poisson ratio (v)	161.85
Elastic anisotropy (A)	2.06
Caushy's pressure (Cp)	78.41 GPa
Pugh's ratio (B/G)	2.77
Frantsevich's ratio (G/B)	0.36
$T_m \pm 300 \ (K)$	2229 K
Band gap	0.278 eV
Fermi energy	0.781 eV
Total magnetic moment	0.99 μ _B
Spin polarization	100%
Curie temperature (T_C)	190 K

Conclusion

The structural, mechanical, electronic and magnetic properties were studied using DFT+U method. CoRuVAl QHA in FM phase is the most magnetically stable phase. This QHA is stable mechanically. The band gap of 0.278 eV in spin down channel confirms its half-metallicity. The whole spin magnetic moment is 0.99 μ_B at the equilibrium lattice constant. On average, 190 K is the Curie temperature. CoRuVAl QHA has 100% spin polarisation, making it a good candidate for spintronic applications.

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Ab initio investigation of the electronic structure and magnetic properties of cubic spinel Fe₃O₄

Riyajul Islam,* and J. P. Borah

Department of Physics, National Institute of Technology Nagaland, Dimapur, Nagaland 797103, India

*Corresponding author: riyajul80@gmail.com

Abstract

We present the results of *ab initio* calculations of cubic Fe_3O_4 , investigated by using density functional theory (DFT). The computed density of states (DOS) shows the distribution of cations in the octahedral sites give rise to half-metallic behavior. The magnetocrystalline anisotropy energy (MAE) computed by both the total energy calculations and magnetic force theorem are equal to -2.92×10^4 J/m³ and -2.02×10^4 J/m³ respectively comparable to the experimentally observed value of -2.0×10^4 J/m³.

Importance Of The Type Of Coulomb Interaction In DFT+DMFT Method To Study Magnetic And Electronic Properties Of Nickel

Shivani Bhardwaj^{1, *}, Antik Sihi¹ and Sudhir K. Pandey²

¹School of Basic Sciences, Indian Institute of Technology Mandi, Kamand - 175075, India ²School of Engineering, Indian Institute of Technology Mandi, Kamand - 175075, India

*Corresponding author: spacetimeuniverse369@gmail.com

Abstract.

Here, the effect of different Coulomb interactions is investigated within DFT+DMFT method for exploring the magnetic and electronic structure properties of Nickel (Ni). The value of U = 7.2 eV (J=1.2 eV) is used for this study, which is computed by cRPA (Yukawa screening). The results of the comparative study of estimations by Coulomb interactions show that Full type of Coulomb interaction gives T_c (~600K) in close approximation with experimental value (631K). The value of saturation magnetization using Ising (Full) comes out to be ~0.50 (~0.44) μ_B /Ni. Momentum-resolved spectral function using both Coulomb interactions is also studied and the results suggest considerable dependence of the physical properties on the type of Coulomb interaction used. Thus, using the appropriate Coulomb interaction to examine the physical properties of materials becomes crucial in the DFT +DMFT framework.

Introduction

Strongly correlated materials pose complications in being treated by first-principle methods. However, currently there are various combined approaches being proposed and developed for probing these materials. Such as, use of first-principle approaches combined with model Hamiltonian. One such theoretical approach which is being exploited widely for these types of materials, is density functional theory (DFT) and dynamical mean field theory (DMFT), (DFT+DMFT). In this case, we generally use different types of Coulomb interactions, such as "density-density" type of Coulomb interaction (Ising), rotationally invariant Coulomb interaction (Full) etc¹. Most of the work within DFT+DMFT method utilizes Ising type for studying different physical properties of materials, where this Coulomb interaction typically shows overestimation² of observables e.g., magnetic moment. Moreover, the model Hamiltonian approach requires interaction parameters as input quantities for calculations, namely on-site Coulomb interaction energy (U) and Hund's coupling energy (J). Thus, proper estimation of these material specific parameters becomes essential. One of the widely used first-principle based methods to calculate U and J is, constrained random phase approximation (cRPA). A clear distinct study on a strongly correlated magnetic material as simple as an elemental transition Ni metal for different types of Coulomb interactions, lies unexplored with detailed study on magnetic and electronic properties. In this work, a comparative study of magnetic and electronic properties, between the results obtained from Ising and Full, are carried out for Ni. It is wellknown transition metal with partially filled 3d

orbitals. The work includes estimation of temperature dependent magnetization, magnetic transition temperature and consequently momentum-resolved spectral function, obtained for Ising and Full.

Computational Details

Ni crystallizes in face-centered cubic crystal lattice, the lattice parameter of value 3.52 Å is used with space group number 225³. The spin-polarized calculation is performed using WIEN2k⁴. The values of Coulomb interaction parameters are calculated using cRPA by GAP2^{5,6} code. The calculations of DFT+DMFT are done by eDMFT⁷ code for different temperatures, where WEIN2k performs the DFT calculation throughout DMFT iterations. Continuous-time quantum monte carlo impurity solver is used with 'exactd' double-counting method^{8,9}.

Results and Discussion



Fig. 1. Coulomb interaction parameters as a function of ω .

Fig. 1 shows the variations of U and J with frequency (ω). The values of U_{full} (U_{diag}) are calculated by taking average of all (diagonal) matrix elements of Coulomb interaction at particular ω . In low frequency region (below ~20 eV) the values of both U_{diag} (~7.2 eV) and U_{full} (~5.97 eV) remain almost constant whereas, in the higher frequency region (above ~23 eV) there is

abrupt increase in their values. The value of J (~0.76 eV) remains almost same throughout the studied frequency range. This behaviour indicates the importance of excluding the 3d-3d electron transition for finding U. Moreover, accurate estimation of U(J), becomes critical, as it is seen that the magnetic transition temperature (T_c) depends on the values of these material specific parameters. Here, the values of U(J), calculated using cRPA for Ni, are found to be ~7.2 (~0.76) eV. Generally, when J's value obtained from cRPA is used for DFT+DMFT calculation, it does not give proper estimation of different physical properties. Moreover, the value of J (1.2 eV) corresponding to the value of U (7.2 eV) obtained using Yukawa screening is preferable for performing this calculation. Further, the temperature dependent magnetization for both Coulomb interactions, is computed. The values of reduced magnetization obtained for the studied temperatures are plotted in Fig. 2 along with the experimental data¹⁰. The reduced magnetization for the corresponding temperature is obtained by dividing the value of magnetization at that temperature by the saturation magnetization for that type of Coulomb interaction. Saturation magnetizations for Ising (Full) interaction comes out to be ~0.50 (~0.44) μ_B /Ni at 200K. whereas experimental data¹¹ suggest the value ~0.49 μ_B /Ni at 200K



Fig. 2. Reduced magnetization as function of temperature for Coulomb Interactions along with experimental curve 10 .

Ising can be seen to overestimate the values of magnetization than Full. Although, Full seems to be underestimating the values of magnetization as compared to experimental curve till ~600K. The value of T_c can be inferred for the respective Coulomb interactions from the figure. T_c is the temperature at which magnetization value drops to zero. As per the experimental data curve¹⁰, T_c is found to be 631K. The variation trend of Ising shows the overestimation of T_c . However, the value of T_c obtained from Full *i.e.*, 600K comes out to be in good agreement with the experimental value¹⁰. Now after having looked at the effect of Coulomb interactions on magnetic properties of Ni, it would be interesting to observe whether these Coulomb interactions give significant differences in estimating the electronic structure properties. Thus, the momentum-resolved

spectral functions are calculated for these two Coulomb interactions at 300K as shown in Fig. 3. On colour gradient scale as one goes from "min" to "max" on scale, the degree of coherency of states increases. Both the plots show almost similar behaviour along the observed high-symmetric kdirections. However, in case of Full, near the Fermi level (~-2.5 eV) appearance of incoherent states seems prominent along L-X direction, whereas, these incoherent states are not present in case of Ising. The presence of incoherent states using Full, might be the cause of obtaining close estimation of T_c with experimental T_c .



Fig. 3. Momentum-resolved spectral function of Ni metal using (a) Ising & (b) Full, at 300K.

Conclusions

The effect of different Coulomb interactions (i.e., Ising & Full) in DFT+DMFT framework is studied for magnetic and electronic properties of Ni metal. Here, Ising is seen to overestimate T_c . The value of saturation magnetization using Ising (Full) comes out to be ~0.50 (~0.44) μ_B /Ni. The estimation of temperature dependent magnetization & T_c (~600K), by Full come out to be in good agreement with the experimental value $(631K)^{10}$. This might be attributed to the presence of incoherent states at ~-2.5 eV, seen in the momentum-resolved spectral function using Full. Thus, the proper estimation of physical properties using appropriate choice of Coulomb interaction becomes essential to understand the phenomena exhibited by correlated magnetic materials even for the simple elemental transition metal.

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First-Principles Calculations of Structural, Elastic, Electronic, and Magnetic Properties of Ru₂TiMn Heusler Alloy

CH. Prashanth and J Krishnamurthy

Department of Physics, School of Sciences, National Institute of Technology, Andhra Pradesh -534101, India

*Corresponding author: prashanth.c159@gmail.com

Abstract

Structural, elastic, electronic and magnetic properties of novel Ru_2TiMn (RTM) Heusler alloy have been investigated by using the first principles calculations based on the framework of density functional theory (DFT). The elastic constants, Cij, elastic moduli, mechanical stabilities and the Raman spectrum of RTM have been estimated. The metallic ferromagnetic behavior of RTM has predicted with the approach of GGA-PBE and GGA+U-PBE and a comparative study of electronic density of states (DOS), projected density of states (PDOS), band structures have been analyzed. To the best our knowledge, physical properties of RTM have neither measured experimentally nor calculated theoretically leads to the scope of future experimental study on Ru_2TiMn .

Introduction

With the expansion of research in material science, the research interest in spintronic application materials has intensified. Full Heusler alloys are one of those prime research important materials because of their diverse applications, like spintronics, optoelectronic, superconductivity, shape memory and thermoelectrics ^[1]. Heusler alloys are with three intermetallic compounds, usually consists of two transition metals (X; Y) and one main group element (Z). The chemical formula of compounds with X2YZ having four fcc sub lattices and compounds with formula XYZ consisting of three fcc sub lattices are the two groups of Heusler alloys^[2]. Recently, renewed research interest about the experimental and theoretical studies on X₂YZ type full Heusler alloy is foucused, mainly to the ones containing Co/Mn as Y and Z compounds. Very few theoretical studies exist on Heusler compounds containing Ru. In the present work, we have evaluated systematically about the structural, elastic, electronic and magnetic properties of Ru₂TiMn. The comparative study of electronic and magnetic properties of RTM alloy using GGA-PBE and GGA+U-PBE are presented.

Computational methods:

The structural, elastic, electronic and magnetic properties of RTM alloy were calculated using the first-principles calculations with projected augmented plane wave (PAW) method as implemented in the quantum-espresso ^[3] (qe) code within generalized gradient approximation (GGA) in the scheme of Perdew–Burke–Ernzerhof (PBE). BFGS quasi-newton algorithm and all cell parameters were moved to find the optimized unit cell and Wyckoff positions. The optimized unit cell was self consistently converged with Marzari-Vanderbilt-

DeVita-Payne cold smearing, with 400 Ry as kinetic energy cutoff, 10^{-8} convergence limit and with 5*5*5 dense K-mesh and 10-IBZ k-points convergence is achieved. Phonon calculations were done to find Raman spectrum with convergence as 10^{-10} . With higher dense k-mesh the nscf calculations were calculated to find electronic DOS, PDOS and band structures in ferromagnetic state. For DFT+U calculations, rotationally invariant scheme of Liechtenstein et al., were employed for Ru, Ti, Mn with U parameters as 4ev, 3.5ev, 3.9ev and J parameters were chosen as 0.8ev, 0.6ev, 0.7ev respectively and corresponding electronic and magnetic calculations were done.

Results and Discussion:

(i) Structural properties: Full Heusler intermetallic alloys with the stoichiometric composition of Ru₂TiMn with face-centred cubic structure of space group Fm3m was predicted, where Ru atoms occupy the Wyckoff position 8c (1/4, 1/4, 1/4), Ti and Mn atoms are located at 4a (0, 0, 0) and 4b (1/2, 1/2, 1/2), respectively similar to reported X₂YZ compounds ^[2]. The ground state structure of RTM was obtained by volume and cell relaxation up to a total force of 0.000007 Ry/au. The optimized lattice parameters are used for elastic, electronic and magnetic properties.

(ii) Elastic properties: Elastic properties play a key role in understanding the binding properties of compound. The stress tensor was obtained from the self-consistent calculation of six different deformed unit cell. Strain tensor was obtained from Bilbo server for those deformed lattice parameters. From stress = C_{ii} *strain relation, the elastic constant vectors C_{11} , C_{12}

and C44 are calculated and presented as shown in Table. 1(a). From which poisons ratio youngs modulus shear modulus and anisotropic ratio and bulk modulus are calculated^[2] and tabulated in table(II)-left. Based on these results, we find that the stability criteria ^[4] C₁₁-C₁₂>0, C₁₁>0, C₄₄>0 (C₁₁+2C₁₂)>0 are satisfied for these compounds, and are elastically stable. It can be seen that the C₁₁ constant for RTM much higher than C₄₄ constant and with Cauchy pressure positive (C_p) positive and B/G >1.7 prove RTM as a ductile.

Table 1(a	Table 1(b)			
C ₁₁	1507.91		GG	GG
C ₁₂	1396.43	Energy (Ry)	A 707.	A+0 706
C ₄₄	124.41		35	48
bulk modulus (B)	1433.59	Fermi	20.0	19.8
Shear modulus(G)	317.97	Magnetic	3.20	3.92
Young's modulus E(GPa)	888.24	Table 1(a) E	lastic n	arameter
B/G	4.51	Table 1(b) e	lectron	ic and
Cauchy pressure (C)	1272.02	magnetic res	sults	
(C_p) Poisons ratio (9)	0 39673	4		

(iii) Electronic and magnetic properties: The calculated eelectronic properties of RTM, including total energy and fermi energy, in both GGA and GGA+U are tabulated in Table 1(b).





It can be infererred from ground state total energy that without hubbard parameter $(U)^{[5]}$ the system is more stable than with U correction. The calculated DOS (Fig.2(a)) and PDOS (fig.2(b) of RTM in spin up and spin down modes were plotted for both GGA and GGA+U (with $U_{Ru}=4$ eV, $U_{Ti}=3.5$ eV and $U_{Mn}=3.9$ eV). Here, it can be seen in both cases that RTM is mettalic with majority conduction electrons contribution from Ti. Further, band structure was plotted for RTM in GGA+U calculations as shown in Fig.2(a) and magnetic moment of RTM is calculated in both GGA and GGA+U and are tabulated in Table. 2(b). The zero band gap of RTM with magnetic moment ranging from 3.2 μ_B to 3.92 μ_B in GGA and

GGA+U cases respectively, and is yet to be verified experimentally.

(iv) Optical properties: Raman spectrum of RTM was obtained from phonon calculations using quantum-espresso package and is shown in Fig.2(b) and observed the absence of IR active modes in RTM.



Figure: 2(a) Band structure of RTM with GGA+U 2(b) Raman spectrum of RTM

Conclusion:

In summary, structural, elastic, electronic, magnetic and optical properties of RTM are studied using projected augmented wave method (PAW) based on density functional theory (DFT). From the elastic constants, it can be inferred that RTM is elastically stable alloy. From the spin polarized DOS and band structure calculations, it is clear that conduction and valency electron contributions are from Ti and Ru, respectively. Magnetic moment of RTM with GGA approach is $3.2 \ \mu_B$ and from GGA+U it is $3.9 \ \mu_B$. The properties of stable RTM serve as reference for experimental verification and for suitability to spintronic applications.

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Modelling of Shock-Hugoniot for single crystal Ni using Molecular Dynamics : Comparison with ab-initio and Experimental results.

S, Madhavan¹, V. Mishra^{1,2}, P.V. Lakshminarayana³ and Manoj Warrier^{1,2}

¹Computational Analysis Division, BARC, Visakhapatnam, 531011 ²Homi Bhabha National Institute, Anushakti Nagar, Mumbai, 400094 ³Dept. of Nuclear Physics, Andhra University, Visakhapatnam, 530003

*Corresponding author: madhavan@barc.gov.in

Abstract

Molecular Dynamics (MD) simulations and ab-initio calculations have been carried out to obtain the coefficients of the linear relation between the shock velocity (U_s) and particle velocity (U_p) for single crystal, Nickel (Ni). Foiles embedded Atom Method (EAM) potential is used in the MD simulations. In order to confirm the effectiveness of Foiles EAM potential for high strain rate and high pressure shock simulations, the results from MD are compared with both, the ab-initio calculations and published experimental results. Our simulations yields a better match with experiments, compared to earlier published MD results.

Introduction

Classical Molecular Dynamics with validated interatomic potentials has the advantage over ab-initio simulations in the fact that it can simulate several hundred million atoms. Therefore, MD simulations can be carried out for hundreds of picosec to nanosec to study high strain rate deformation mechanisms of materials. In this work, we use the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS)¹ for our MD Simulations of flyer impact to target at high velocities (500-3000 m/s). Jarmakani², Hai³, Choi⁴ have used different EAM potentials of Ni to obtain the Us-UP relationship. Their results show large deviations from experimental data. In this work we have verified the suitability of the Foiles⁵ EAM potential for MD simulations at a very high strain rates (above 10^6 / sec).

Computational Methods

(a) MD method using LAMMPS : The simulations are carried out on a region consisting of 99x20x20 unit cells with a total of 158400 Ni atoms. MD simulations using an isothermal-isobaric (NPT) ensemble are carried out, using the Foiles⁵ EAM potential to relax the system. Periodic boundary conditions (PBC) were used along all the three axes and the simulations are carried out for 10 ps. For the 1D planar shock simulations, the computational domain is divided into two blocks. One block (referred to as flyer) is given an initial velocity in one direction such that it makes a planar impact on the other stationary block of atoms (referred to as target) using a micro-canonical (NVE) ensemble. Free boundary conditions are implemented along the axis lying along the direction of impact, whereas PBCs are implemented along the axes perpendicular to the direction of impact. A time step of 0.1 femtosec was used in these simulations after verifying that there is no change in the results using a shorter time-step. These simulations are repeated with different impact velocities (500-3000 m/s). The particle velocity (U_P) is given by half of the impact velocity since the flyer and the target are of same material. The impact creates a planar shock which travels through the flyer and target in a direction perpendicular to the plane of impact. From the MD simulations, the location of propagating pressure wave at different instant of time is obtained. The time and locations of the pressure wave are used to find the shock velocity (U_s). Hence we obtain the U_{s} - U_{P} relationship using MD.

(b) First Principle or ab-initio Method : We have used the VASP code to generate cold-curve (EOS contributions at zero kelvin, which is the major contribution) of Ni and a locally developed QEOS code for calculating the ion-thermal and electron thermal contributions of EOS. The EOS data so generated was combined with the Rankine-Hugoniot Jump conditions to obtain U_s-U_P Hugoniot. In the VASP calculations, Perdew, Burke, and Ernzerhof form of the Generalized Gradient Approximation (GGA) is employed to describe electron exchange and correlation. For the plane-wave set, a cut off energy of 300 eV was used. The Brillouin zone of face cantered unit cells were sampled by 15x15x15 kpoint meshes generated in accordance with the Monkhorst-Pack scheme. The total energy was minimized until the energy convergence became less than $1 \ge 10^{-6}$ eV. Using these parameters, cold energy $E(\rho)$ of the crystal is calculated for several volumes

(V) or density(ρ). Cold pressure is calculated from the first derivative of this 'EV' data (P = -dE/dV).

Results and Discussion

Results from our simulations are presented in figures 1-2. Figure 1 gives the relation between U_P and U_S obtained from MD and ab-initio (First Principle) calculations. Experimental results^{6,7} are also included.

MD results are presented in fig.1, with error bars to account for the inaccuracy involved in the shock velocity calculations. From fig.1, we see that for a particle velocity (U_P) range of 500 to 2500 m/s, MD results are matching well with the experimental and ab-inito calculations. For higher U_P the deviation is found to increase. The values of the straight line fitting for MD data is shown in figure 1. Comparison of the coefficients obtained between MD simulation with experiment indicate that the deviation is 16%.



Fig.1: Comparison of U_s - U_P obtained from MD and first principles calculations with experimental results for Ni.

Figure 2 shows the comparison of U_S - U_P relation, obtained from different EAM potentials²⁻⁵ along with experimental results⁶. The potentials used by Jarmakani² and Choi⁴ both have resulted with large deviation. Shock velocity (U_S) calculated, are higher than the experiments even at lower range of particle velocity (U_P). Shock velocity (U_S) calculated from Hai³ are on the higher side for the entire range. Two of the potentials demonstrated by Choi⁴ mostly yielded lower values for the shock velocity (U_S), compared to the experimental values. However the Foiles⁵ EAM potential used in this work, gives better result than other potentials as can be seen in figure 2.



Fig-2: MD result : U_s - U_P Hugoniot relations for single crystal Ni with various EAM potentials. For a better comparison, results from experiments⁶ is also shown.

Conclusions

For single crystal Ni, the shock-hugoniot is obtained from MD and ab-initio methods. In the plot of U_{S} - U_{P} , the MD results are found to be reasonably close for U_{P} range of 500-2500 m/s. But for higher U_{P} , MD results are found to deviate up to 16% in comparison to the experimental results. The ab-initio simulations show a good match with experiments. Comparison of shock-hugoniot obtained from MD simulations using other EAM potentials, published by different teams, indicate that the Foiles EAM potential is better than others for high strain rate shock simulations.

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Applicability of Oseltamivir Drug against SARS-CoV-2:A **Computational Study**

Pooja Yadav¹ and Papia Chowdhury^{1*}

Department of Physics and Materials Science & Engineering, Jaypee Institute of Information Technology, Noida 201309, Uttar Pradesh, India.

*Corresponding author: papia.chowdhury@jiit.ac.in

Abstract

The virus SARS-CoV-2 has created an epidemic situation all over the world from the last year. In the present study, we have tested the efficacy of oseltamivir (O) drug against COVID-19. The strong binding affinity, hydrogen bond interaction and lower inhibition constant validated the better complexation possibility of O:3CL^{pro} structure. Various thermodynamical parameters from Molecular dynamics (MD) simulations like RMSD, RMSF, radius of gyration (R_g), solvent Accessible Surface area(SASA) energy, interaction energies, Gibbs free energy (ΔG_{bind}) etc. also favoured effectivity of Oseltamivir(O) against CoV-2 protease.

Introduction

Recently, SARS-CoV-2 has created an epidemic situation in the World. Presently, the researcher and expert groups have suggested a number of variants of COVID-19 and they labelled them as α , β , γ , δ , and δ +. δ + variation appears to spread more quickly and easily than other variants, which potentially leading to an increase in COVID-19 cases, which is suggested as the most devastating variant [1].

To overcome with this deadly disease, various vaccines, alternative medicines and repurposed drugs are introduced by worldwide [2,3]. Some generally repurposed drugs are used to treat COVID-19 infection: Ivermectin, Doxycycline, Oseltamivir, Favipiravir, Lopinavir/ritonavir etc [4,5]. Oseltamivir is one the mostly used repurposed antiviral drug nowdays against CoV-2 infections. Originally, Oseltamivir was used as an anti-MERS-CoV therapy in Korea and an anti-SARSCoV-2 therapy in China [6]. Now it is being tested as anti COVID drug. Clinical trials have been done on adult patients with the symptom of fever from March 2020 to June 2020. It was observed that Oseltamivir helps to decrease the temperature. The fever disappeared in all patients at 4 days after the initial administration of Oseltamivir [6]. Now, reports of more 20 clinical trials have been registered which include Oseltamivir in the treatment for COVID-19. It is the goal of our present study to check the effectiveness of antiviral: Oseltamivir against SARS-CoV-2 to treat COVID patients.

Materials and Methods

Protease and Ligand preparations

A 3CL^{pro} (6LU7) proteases was used as main target protease. The structure of the 3CL^{pro} and O were downloaded from the Protein Data Bank website and PubChem (National Library of Medicine) shown in table 1.

Computational details

MD simulations calculations have been computed in a single system using HP Intel Core i5 - 1035G1 CPU and 8 GB of RAM with Intel UHD Graphics and a 512 GB SSD.



Molecular docking and MD simulation

Molecular docking was used to study the proteinligand interaction with the help of Autodock Vina [7]. By using Autodock Vina and Discovery studio visualizer, docking based studies of the inhibitors against protease of SARS-CoV-2 have been performed. After the docking, there were nine different poses for complex structure obtained. Among all of 9 poses, the best pose was chosen as such in which, shows maximum non bonded interaction, minimum binding affinity, dreiding energy, dipole moment and also minimum inhibition constant.

MD simulation was used for calculating thermodynamics parameters of the O:3CL^{pro} complex structure the LINUX based platform "GROMACS 5.1 Package" with GROMOS43A2 force field was used[8]. In the MD simulation process many thermodynamic parameters for the complex system were computed. These thermodynamic parameters are used to know the stability and to observe possible configuration changes of receptor protein and complex structure at time resolved simulation trajectory. Some important parameters are RMSD, RMSF, Rg, inter-molecular H-bonds, SASA for O:3CL^{pro} complex structure.

Analysis of molecular docking and MD simulation results

For pose 1 we obtained the best O:3CL^{pro} complex structure having binding energy (-6.2 Kcal/mol), dreiding energy (91.62), dipole moment(4.039 Debye) and inhibition constant $(2.8 \times 10^{-5} \text{M})$ at 300K depending upon the maximum number of intermolecular hydrogen bonding between protein and ligand which is 3 (Fig.1).

Fig 1: a) Binding energy **b)** Possible types of interaction in pose obtained from O: 3CL^{pro}.



Lowest dreiding energy and high dipole moment [9] means the most stable and favourable structure of O:3CL^{pro} complex structure. Appearance of H-bonded interactions between O and 3CL^{pro} protein residues also validated the possibility of complex formation between O and 3CL^{pro}. To analyse the stability of the studied structure, MD simulation of complex structure have been studied for the period of 0 to 10000 ps. With the use of MD simulation, H-bonds, R_g, RMSD, RMSF, SASA and ΔG_{bind} are thoroughly studied to check the potentiality and stability of considered inhibitor.

Parameter	protease (3CL ^{pro})		0: 3CL	oro	
	Mean	Range	Mean	Range	
MD Simulation Result					
Coul-SR	NA	NA	-2.6	040	
Energy					
SR-LJ Energy	NA	NA	-20.4	040	
RMSD (nm)	0.22	0.13-	0.23	0.09-0.48	
		0.32			
Inter H-Bonds	NA	NA	2	0-3	
Radius of	2.18	2.13-	2.18	2.16-2.4	
gyration(nm)		2.24			
SASA (nm ²)	33	30-35	8	6.5-9	

Table 2: Data obtained by MD simulations for 3CL^{pro} and for the O: 3CL^{pro}. Energy in Kcal/mol.

RMSD is used to check the stability of complex structure with respect to the reference carbon backbone structures of $3CL^{pro}$. Less fluctuation in RMSD value (0.22 nm) shows the better stability of O: $3CL^{pro}$ complex structure. Perfect similarity in RMSF values also confirmed that the complex structure does not affected the protein backbone. Perfect matching of protein backbone and ligand: protein complex of R_g (2.18 nm) also shows that the O: $3CL^{pro}$ complex structure is quite stable and it is a compressed complex structure. SASA tells about the area of receptor contact to the solvents. Lower value for SASA for O: $3CL^{pro}$ (8 nm²) than $3CL^{pro}$ (33 nm²) confirms the best complexation possibility in time

trajectory 0-10000ps. Stability of O:3CL^{pro} complex structure is mainly depend on the contribution of nonbonded interactions. The obtained numbers of intermolecular H-bonded interactions from MD simulation for O:3CL^{pro} complex were perfectly matched with the molecular docking results (Fig. 1b, Fig 2a).

Fig 2: For O: 3CL^{pro} structure **a**) Intermolecular H-bond numbers **b**) Variation of Coulombic interaction energy and Lenard Jones interaction energy with respect to time.



In Figure 2b, a 3D graph of Coul-SR energy and LJ-SR energy with respect to time shows a larger decrement LJ-SR energy than Coul-SR after time interval ~4000ps which confirms the better binding capability for O:3CL^{pro} complex structure. The average binding energy ΔG_{bind} of O:3CL^{pro} complex structure of -6.2 Kcal/mol over the time scale of 10000 ps also validates the better stability of the said structure.

Conclusion

For the present study we have tried to identify the mechanism of action of Oseltamivir antiviral drug against COVID-19. By analysing all the in-silico results obtained from molecular docking and MD simulations we can definitely conclude that Oseltamivir has established its strong candidature as a promising potential inhibitor drugs for targeting SARS-CoV-2 virus. We are definite that our in-silico results on the drug Oseltamivir against CoV-2 infections will help the current clinical research to identify the perfect cure for COVID -19 treatments.

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Energy Loss Rate in Bilayer Graphene on GaAs Substrate due to Piezoelectric Phonon Scattering

Meenhaz Ansari¹* and SSZ Ashraf²

¹Interdisciplinary Nanotechnology Centre, Aligarh Muslim University, Aligarh, 202002 ²Department of Physics, Aligarh Muslim University, Aligarh, 202002

*Corresponding author: meenhazphysics@gmail.com

Abstract

Electron excitation and subsequent electron energy loss rate by scattering through piezoelectric acoustic phonon modes in bilayer graphene from piezoelectric GaAs substrate at a distance apart have been studied as a function of elevated temperature, substrate distance, and the electron density in the Equipartition regime. A recent study has reported the energy loss rate in the conditions mentioned above in the Bloch-Gruneisen regime which corresponds to the low-temperature region depicting T^3 dependency on temperature and $n^{-3/2}$ on electron density. The electron-phonon interaction at high temperatures is vital in determining the novel thermoelectric properties of low-dimensional materials. Motivated by this, we investigated electron-piezoelectric acoustic phonon scattering and obtained analytical results for the electron energy loss rate at high temperatures. We find the electron energy loss rate to vary linearly with temperature, d^{-2} with substrate distance and as $n^{-3/2}$ with electron density.

Keywords: Bilayer Graphene, Energy Loss rate, Piezoelectric Substrate.

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Introduction

Bilayer graphene (BLG) is a coupled double-layer graphene sheet in which chiral quasiparticles charge carriers show parabolic energy dispersion relation and Berry's phase 2π . Recently BLG has come out as a subject of intense research due to the possibility of a tunable energy band-gap that can be manipulated externally by an applied electric field [1-2].

As BLG is a 2D material, these samples are experimentally deposited on various piezoelectric substrates for better fundamental studies and engineering applications in device formations [3-6]. The higher dielectric constant and lower surface roughness of gallium arsenide (GaAs) material make it the first choice. The greater hydrophilic nature of GaAs substrate also prevents the folding of BLG and provides a better stickiness of the samples [3]. The electron transport in cleaner BLG samples is limited by lattice, i.e., phonons that cannot be eliminated and get populated with the increase in lattice temperature [2]. The underlying piezoelectric substrate provides an additional electron-phonon scattering channel due to piezoelectric deformation coupling, which strongly affects the electronic/thermal/optical/thermoelectric properties of the BLG samples and acts as one of the significant sources of resistivity at room temperature [2-4]. The investigation of scattering by electronpiezoelectric phonon mode is of practical importance in developing and controlling the operating performance of high-speed electronic/optoelectronic devices [6].

Therefore in the light of the above arguments, we calculate the electron energy loss rate in bilayer graphene taking piezoelectric acoustic phonon modes into account in the Boltzmann transport formalism and determine the energy loss rate exponents as a function of electron temperature and density.

Formalism

The cooling of the excited electrons is mainly achieved through the interaction with acoustic phonons. An important property for describing this cooling is the electron energy loss rate, the time on which the energy is lost by electrons as a whole and is given as [2,4]

$$F_{pz}(T_e) = -\frac{1}{n} \sum_{q} \hbar \omega_p \frac{dP_q}{dt}$$
(1)

where *n* is the total number of electrons, $\hbar \omega_p$ is the piezoelectric acoustic phonon energy and dP_q/dt gives the rate of change of phonon distribution due to electron-phonon interaction. Using the value of the piezoelectric matrix element, $|Z_{pz}|^2 G(\theta) = [c_p^2 D_0^2 \hbar/2\pi \rho A v_p] \left[1 - 2\left(\frac{q}{2k}\right)^2\right]^2$, where $G(\theta)$ is the chiral function and the collision integral as given in [4], we may obtain $F_{pz}(T_e)$

$$= -\frac{c_p^2 D_0^2 m^2}{8\pi^3 \hbar^4 \rho n v_p} \int_0^\infty (\hbar \omega_p)^2 \frac{E_0}{\sqrt{E_k - E_q}} P_q e^{-2qd} dq (2)$$

where D_0 is the piezoelectric deformation potential, v_p is the velocity of phonons on a GaAs substrate,

and ρ is the mass density of GaAs substrate. Though the matrix element does not have the phonon wave vector dependence itself but the dependence comes through the chirality function and exponential term of equation (2). In a high-temperature region characterized by $\hbar \omega_q \ll k_B T$, after making suitable approximations, we get the simplified expression for the energy loss rate as

$$F_{pz} = -\frac{c_p^2 D_0^2 m^2 k_B T}{2^5 \pi^3 \hbar^3 \rho n d^2 k_F} \quad (3)$$

The above equation (3) represents the analytical result of electron energy loss rate due to piezoelectric acoustic phonons present in the piezoelectric substrate lying at a distance, d apart from the BLG sample. The analytical calculations have been performed assuming BLG on GaAs substrate and using the values of the parameters as given in reference [4].

Results



Fig. 1. Electron energy loss rate due to piezoelectric acoustic phonons, F_{pz} as a function of temperature for different values of electron density.

Figure 1 depicts the variation of the analytically calculated F_{pz} as a function of electron temperature from 50K to 300K for different values of electron density. Curves A, B and C correspond to the three different values of the electron density as n = 0.5, 1 and $5 \times 10^{12} cm^{-2}$. As F_{pz} varies $n^{-3/2}$ with the electron density, it is clear that increasing *n* will decrease the magnitude of F_{pz} that's why curve C corresponding to the higher value of *n* lies deeper. It is found from equation (3) that the magnitude of F_{pz} increase linearly with an increase in electron

temperature. The higher the electron temperature, the greater will be the magnitude of electron energy loss rate. It is also evident from equation (3) that the magnitude of F_{pz} is inversely proportional to the square of the distance, d between the BLG sample and the underlying piezoelectric substrate. Thus for the smaller distances ($d \leq 5A^0$), it may provide a parameter for controlling the magnitude of F_{nz} . For the longer distances, we can exclude the piezoelectric distance factor, as $e^{-2qd} \approx 1$ in this case. Also, it is observed that the chirality function appearing in the matrix element of the electron-phonon interaction, which is more effective in the BLG sample than the monolayer graphene in the Bloch-Gruneisen regime [2] has no effect in the higher temperature range. If the temperature is raised further than the room temperature, the other scattering mechanisms such as electron-optical phonon interaction start to contribute and dominate.

The electron temperature and density dependence of energy loss rate provide deep insight into the thermal relationship between chiral quasiparticles and phonons and also provides a method to determine the quality of electron-phonon coupling in mono/bilayer graphene and other low dimensional materials.

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Computational analysis of Ethyl N-acetyl-L-Tyrosinate (ENALT) by DFT calculations for NLO applications

N. Balagowtham*, T. Kamalesh, P. Karuppasamy, Muthu Senthil Pandian and P. Ramasamy

SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai – 603110, Tamilnadu.

*Corresponding author: <u>balagowtham16@gmail.com</u>

Abstract

The theoretical investigation on the Ethyl N-acetyl-L-Tyrosinate (ENALT) molecule was studied for nonlinear optical (NLO) applications by quantum chemical calculations. The geometrical structure optimization and Mulliken charge distribution were obtained through DFT-B3LYP/6-31G (d,p). The theoretical IR spectra was analyzed for fundamental vibrations and fingerprint of the molecule. The frontier molecular orbitals and hyperpolarizability value are computed and confirm that the ENALT molecules have higher NLO property.

1. Introduction

Amino acids form proteins, which in the crystalline form constitute very special systems where N⁺ and ⁻H•••O hydrogen bonds play a vital role in the stability of the structure. Amino acid based derivatives were explored for its peculiar NLO property used in photonics based applications (1). Ethyl N-acetyl-L-Tyrosinate (ENALT) is one of the derivative of L-Tyrosine amino acid, which is hydrophobic and non-essential amino acid.

Quantum chemical calculation was used for analyzing the NLO property of the present molecule. The optimization of ENALT molecule was done using B3LYP/6-31G (d,p) basic set as in ground state. B3LYP function has proven as the most popular and effective computational method. The vibrational spectra for each functional group was investigated and also studied hyperpolarizability.

We have not seen any literature report on DFT calculations of ENALT molecule. In our present work we have done DFT calculations for analyzing the NLO application of ENALT molecule.

2. Geometrical Optimization and Mulliken Charge distribution



Fig. 1. Optimized molecular structure of ENALT

The molecular structure of ENALT ($C_{13}H_{17}NO_4$) was constructed and optimized using Gaussian09 software.

The ENALT molecule (Fig.1) was optimized using keyword #opt B3LYP/6-31G (d,p) in ground state and its atoms are labeled. The optimization process alters the bond length, bond angle and dihedral angles, so that optimized structure (minimum energy state) can be used for further computations.

The Mulliken charge depicts the distribution of electron and relates with vibrational properties (2). It also makes impact in the values of dipole moment, polarizability, electronic structure and properties of molecular system. The charge distribution of atoms in ENALT molecule is given in Fig. 2.



Fig. 2. Atomic charge distribution of ENALT molecule.

3. Spectroscopic Analysis of ENALT

The vibrational IR spectra was computed using keyword: #freq B3LYP/6-31G (d,p). The scaling factors for fundamental frequency is 0.966 for density

functional (B3LYP) level of theory with 6-31G basis set.

The IR spectrum gives the clear picture about the functional groups and their various mode of vibrations. The sharp and less intense single peak at 3657 cm^{-1} indicates the stretching of N-H amine group attached with the acetyl compound (3).



Fig. 3. Theoretical IR spectra of ENALT.

A broad and less intense peak in 3000-3200 cm⁻¹ is caused by asymmetric bending of CH₂ bond like wag. Two high intense peaks in 1730 cm⁻¹ region correspond to C=O stretching and C=C stretches in aromatic ring is observed at 1557 cm⁻¹. In the fingerprint region, peak at 1056 cm⁻¹ is due to C-O stretching between the linkage of C-34 and C-19 with O-18.

4. Frontier Molecular Orbital analysis

The highest occupied molecular orbital (HOMO) represents the ability to denote an electron, lowest unoccupied molecular orbital (LUMO) as an electron acceptor represents the ability to obtain an electron (3). For ENALT the HOMO lying at -0.21795 a.u, is a delocalized π orbital and LUMO lying at -0.00586 a.u, is localized π orbital. The energy gap and other calculated data are listed in the Table 1. The HOMO-LUMO gap energy makes impact in the molecular electrical transport properties.

Parameters(B3LYP/6-31G(d,p)	Values
Eg : Еномо (a.u) - Ецимо (a.u)	0.21305
Ionization energy(eV) = - E_{HOMO}	0.21891
Electron Affinity(eV)= - E_{LUMO}	0.00586
η: Hardness(eV) =Energy gap/2	0.10652
μ: Electronic chemical potential(eV)	0.11239
$= (E_{HOMO} + E_{LUMO})/2$	
ω: Electrophilicity index= $\mu^2/2\eta$	0.05929
S: softness = $(1/\eta)$	9.38791
χ : Electro negativity = - μ	-0.11239
$\Delta N_{max} = -\mu/\eta$	-1.05512

5. NLO calculations

The interaction of electromagnetic fields with contrasting media causes change in characteristics like frequency, phase, amplitude and other properties, thereby the incident fields resulting nonlinear optical (NLO) properties. The total hyperpolarizability (β_{tot}) which estimate the NLO susceptibility (4). The compound with large value of β_{tot} is predicted to be a potential NLO active molecule (5). It is a wise tool to suggest the possibilities to design or synthesize novel NLO materials.

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} a)$$

For B3LYP/6-31G, the calculated first order hyperpolarizability (β_{tot}) for the ENALT molecule is 1.590×10^{-30} esu which is four times greater than urea ($\beta_{tot} = 0.372 \times 10^{-30}$ esu) calculated using equation (a). This shows the ENALT compound will be an effective choice for NLO materials.

Table 2. Polarizability values.	
Parameters	B3LYP/6-31G
	(d,p) polar
Dipole moment	2.2458×10 ⁻²³ esu
First-order hyperpolarizability	1.5902×10 ⁻³⁰ esu
(β_{tot})	
Anisotropic polarizability	72.598 a.u

6. Conclusions

ENALT molecule was examined for its NLO properties by quantum chemical calculation (DFT). Various parameters like Mulliken charge distribution, vibrational spectra, HOMO-LUMO energy gap and hyperpolarizability was calculated. The hyperpolarizability value was 1.5902*10⁻³⁰ esu, which is four times greater than urea. The above calculations leads to conclude that the ENALT molecule is suitable for NLO applications.

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HAXPES Study of a Kondo Lattice System CeCuAs₂

Sawani Datta¹, Ram Prakash Pandeya¹, Arka Bikash Dey², Christoph Schlueter³, Andrei Gloskovskii³, Thiago Peixoto³, Arumugam Thamizhavel¹, Kalobaran Maiti^{1,*}

¹Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, India, 400005

²Photon Science Division, Deutsches Elektronen-Synchrotron DESY, Notkestraße 85, 22607 Hamburg, Germany ³Deutsches Elektronen-Synchrotron DESY, 22607 Hamburg, Germany.

*Corresponding author: kbmaiti@tifr.res.in

Abstract

We investigate the electronic properties of a Ce-based Kondo material, CeCuAs₂. To probe the surface bulk differences of the electronic structure, high-resolution hard *x*-ray photoemission spectroscopy measurements were done with photon energies having varying probing depth. We observe significant difference in the hybridization physics for the surface and bulk electronic structure leading to different Ce valencies. Surface termination appears to play an important role in the correlation physics of this system. Spectra show signature of electron-plasmon coupling induced loss features. These results bring out complexity of a novel Kondo material having no magnetic order down to the lowest temperature studied and have significantly different surface-bulk properties.

First-principles study of Co and Ho co-doped ZnO

K. Mukhopadhyay^{1*} and Priyanka Banerjee²

¹Department of Physics, City College, Kolkata-700009, India, ²Department of Physics, Kazi Nazrul University, Asansol, W.B. 713340, India

*Corresponding author: kausik_city@yahoo.com

Abstract

In this work from first-principles simulations, we investigate the structural, electronic, and magnetic properties of transition metal cobalt (Co) and rare-earth holmium (Ho) co-doped zinc oxide (ZnO) using Quantum-Espresso. A lot of interesting results were found from the analysis of energy band structure and density of states. From spin-polarized calculations within the framework of density functional theory, we have noticed that the value of total magnetization of co-doped ZnO is substantially enhanced compared to that of pure ZnO.

Introduction

Dilute magnetic semiconductors (DMSs) are nowa-days of great interest due to their spintronics applications, alongside the charge and spin of the carriers can be simultaneously controlled [1]. DMS materials are ideal sources of spin-polarized carriers and they can be easily integrated with semiconductor devices for both semiconducting and magnetic properties. It has been theoretically predicted that wide-band-gap oxide semiconductors doped with transition metal elements are the most promising candidates for DMSs with high Curie temperatures [2]. Wide studies have been carried out on zinc oxide (ZnO) based DMSs and there have been many reports of room temperature ferromagnetism (RTFM) in 3d transition metal (TM) doped DMSs [3]. However, the 3d electrons in 3d TMs are exterior and delocalized, therefore the orbital momentum is often zero and gives a small total magnetic moment per atom. On the other hand, rare earth (RE) atoms have partially filled f-orbitals which carry high magnetic moments that can be born on a single ion and may take part in the magnetic coupling as in the case of TMs with partially filled d-orbitals.

Here in this current work, Co (TM, 3d orbital electrons) and Ho (RE, 4f orbital electrons) co-doped ZnO was explored using the first-principles method calculation. For better understanding the changes in structural, electronic and magnetic properties, as well as to clarify the origin of the observed ferromagnetic ordering, here DFT plays an important role.

Results and Discussion

To examine the electronic and magnetic properties of TM (Co) and RE (Ho) co-doped ZnO (ZnCHO), we have used DFT in the pseudopotential formalism as implemented in Quantum-Espresso (QE) [4,5]. Interactions between valence electrons and nuclei are modeled using ultrasoft pseudopotentials. The generalized gradient approximation (GGA) is employed to approximate the exchange-correlation potential with the Perdew– Burke–Ernzerhof (PBE) exchange correlation functional.



Fig. 1. Calculated electron band structure along the high symmetry K points in the Brillouin zone in (a) ZnO and (b) ZnCHO.

All results are obtained by explicitly treating the valence band wave functions of different atoms (Zn: $[Ar]3d^{10}4s^2$ O: $[He]2s^22p^4$, Co: $[Ar]3d^74s^2$, Ho: $[Xe]4f^{11}6s^2$) as a linear combination of atomic orbitals. Both ZnO and ZnCHO structures were optimized having a wurtzite type hexagonal structure with P6₃mc space group. Based on the unit cell, a (2 $\times 2 \times 2$) supercell containing total 32 atoms of ZnO were first obtained by minimizing the ground state energy.

Table 1 presents the Fermi energy, total magnetic moment and energy band gap of the optimized structural parameters of pristine ZnO and (Co, Ho) co-doped ZnO. It is found that the volume of the supercell slightly increases [198.62 Å³ (for ZnO) and 210.45 Å³ (for ZnCHO)] but the overall crystal

systems remain unchanged. The change of volume may be attributed to the different ionic radii of Co (0.65\AA) , and Ho (0.90\AA) atoms which substituted two Zn (0.74\AA) atoms.

Our calculations for band structures along the high symmetry direction in the Brillouin zone are shown in Figs.1 (a) and (b). As shown in Table 1, the band gap (E_g) of ZnO has a value of 1.86 eV, and that of ZnCHO is 0.83 eV. We have noticed that the value of band gap has been reduced, i.e., the gap between valence and conduction bands shows a rather slow decrease due to substituting of TM as well as RE element in pristine ZnO. The observed changes in the bonding environment due to Co and Ho co-doping, which ultimately results in the lowering of lattice symmetry.



Fig. 2. Calculated density of states (DOS) of (a) ZnO and (b) ZnCHO.

The spin-polarized Density of States (DOS) for ZnO and ZnCHO are shown in Figs. 2 (a) and (b). DOS are reported for spin-up and spin-down electrons above and below the central horizontal line, respectively. The asymmetrical DOS between the up and downspin channels near the Fermi level suggests the magnetic properties. Therefore, ZnO has no such magnetism. However, DOS for Co and Ho co-doped ZnO produces magnetization behavior significantly different from pure ZnO. The DOS of up-spin and down-spin has an excursion, which indicates that the system exhibits magnetic ordering. The spin polarized calculation demonstrates that the electronnumber of down-spin is more than that of up-spin in case of ZnCHO. It is suggested that ZnCHO is ferromagnetic in nature. The ferromagnetism originates from two main perspectives, firstly due to the hybridization between Co-3d and O-2p electrons in the vicinity of the Fermi level and the second due to the strong hybridization of the local Ho-4f electrons with the d conduction electrons.

Table 1. Fermi energy, total magnetic moment, and band	
gap of (a) ZnO and (b) ZnCHO.	

Samples	Fermi	Total magnetic	Band
	energy, EF	moment, M _{total}	gap, Eg
	(eV)	(μΒ)	(eV)
(a) ZnO	6.66	0.00	1.86
(b) ZnCHO	10.62	2.80	0.83

Conclusions

In summary, we have performed a detailed DFT analysis of pure and (Co-Ho) co-doped ZnO. The DOS calculations of the optimized structures suggest a P6₃mc hexagonal symmetry in both samples and there are no drastic changes in the structures except the lattice parameters and cell volumes. Theoretical verification using DFT was carried out to understand the underlying mechanism behind the magnetic behaviour of co-doped ZnO. It was done by optimizing the structural parameters comparable to the room temperature values. The spin-polarized oxygen atoms (O-2p), TM (Co-3d), and RE (Ho-4f) contributes to the total magnetic moments in ZnCHO.

Therefore, such a theoretical analysis within DFT framework by using QE might be helpful in the future experimental prospect of DMS and suggesting a possible great improvement of magnetic properties in co-doped DMS systems.

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Electronic and Optical Properties of Single Benzene Ring Graphene Quantum Dot

Priya Rani¹, Ranjeet Dalal¹, and Sunita Srivastava^{1,2*}

¹Department of Physics, Guru Jambheshwar University of Science and Technology, Hisar- 125001, India ²Department of Physics, Panjab University, Chandigarh- 160014, India

*Corresponding author: sunita@pu.ac.in, priyaphd1996@gmail.com

Abstract

In the present work, we have investigated the structural, electronic and optical properties of Graphene Quantum Dot (GQD) containing single benzene ring in strong confinement regime using Density Functional Theory. HOMO and LUMO energy gap of this single benzene ring GQD is found to be equal to 7.23eV which is very close to the band gap predicted by Goki Eda et al. The Density of States (DOS) of this QD are found to be discrete which is very well known property of QDs. Further, the absorption coefficient and imaginary part of dielectric function for this single benzene ring GQD is calculated for parallel and perpendicular polarizations. The plasma frequency (Ω) emerges at position 5eV for parallel polarization. However, for perpendicular polarization there is occurrence of two plasma frequencies nearly at 13.7 eV and 17.6 eV.

Introduction

In recent years, quantum dots (OD) have attracted the attention of researchers because of their size and shape dependent electronic and optical properties. The physical domain of ODs lies between atoms and the bulk materials. As the size of QD becomes comparable to the Bohr Radius, the quantum confinement effect plays very important role. The electronic and optical properties of QDs vary with their size and become significantly different from that of the bulk materials. Because of these size tunable properties, the ODs are very useful in various opto-electronic applications [1,2]. Owing to its very interesting properties, Graphene has become a very intensive topic of research. Graphene's ability to absorb 2.3% of white light is unique property. The charge carriers inside the graphene act like massless particles resulting in high mobility and conductivity. These exciting properties of Graphene lead to its use in many applications including solar cells [3], in energy storage [4], chemical sensing [5] and many others. However, its widespread use in electronic devices is hindered by the absence of band gap in graphene material. Inducing a suitable band gap in graphene is the main requirement for its successful use in electronic devices. This objective could be achieved by synthesizing quantum dots of graphene which could open the possibilities of additional applications specific for QDs.

Here, we have investigated the electronic and optical properties of smallest unit of Graphene Quantum Dot (GQD) i.e. single benzene ring. This work finds some application in electronic devices where the band gap in Graphene sheet may be induced by cutting it into the small quantum dots. This work is part of our ongoing research in which electronic and optical properties of graphene QDs of different sizes are investigated.

Computational Details

The present investigation of the structural, electronic and optical properties of single benzene ring GQD has been carried out using SIESTA code [6]. The Density Functional Theory (DFT) calculations are performed using Generalized Gradient Approximation (GGA) [7] according to Perdew, Burke, Ernzerhof (PBE) parametrization for double zeta plus polarized basis set. The Brillouin zone sampling has been done by 11x11x1 k-points Monkhorst-Pack (MP) [8]. The interaction between the adjacent layers produced from the boundary conditions has been prevented by taking 20 Å height of super cell which provide sufficient vacuum in all the three directions. A mesh cut off of 400 Ry is used and the sufficient number of SCF iteration has been given for the convergence of energy. The optical calculation has been carried out by using 10x10x1 optical mesh and 0.02 optical broadening.

Result and Discussion

The optimized structure and density of states of Single Benzene Ring GQD are shown in fig.1 and fig. 2 respectively. The C-C bond length in the optimized structure is 1.40 Å which is in agreement with the experimental value [9]. The energy gap between the LUMO and HOMO has been calculated and is equal to 7.23 eV. This is in consonance with the predicted value by Goki Eda et. al. [10].



Fig. 1. Optimized Structure of single benzene ring graphene quantum dot (SBRGQD).



Fig. 2. Density of States of single benzene ring graphene quantum dot.

The band gap of graphene could be increased from 0eV to 7eV by cutting it into smallest graphene quantum dot. This increase in band gap is due to the strong confinement of charge carriers in all the three directions. The fig. 2 shows the discrete nature of density of states which verifies the confinement effects in quantum dot. The absorption coefficient and imaginary part of dielectric function are depicted in fig. 3 and fig. 4 respectively. It is clear that the absorption spectra of SBRGQD is in UV-visible region. The appearance of multiple peaks in case of parallel polarization may be attributed to the edge states. It is clear from the figure that absorption peaks are sharp in nature and are not broadened which is due to the high confinement in SBRGQD. In perpendicular polarization, the most prominent peak occurs at 17.8eV and this excitation may be due to $\pi + \sigma$ plasmon. Also the occurrence of peak at 13.7eV may be attributed to π plasmon.

Conclusions

The optimized geometric structure, electronic and optical properties of single benzene ring QD has been computed by using GGA/PBE method implemented in SIESTA code. The calculated band gap, E_g and C-C bond length values are very near to experimental observed values. The density of states, absorption

coefficient and dielectric function have been evaluated.



Fig. 3. Absorption coefficient for parallel and perpendicular polarization.



Fig. 4. Imaginary part of Dielectric Function for different polarization.

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Silver adsorption on monolayer MoS₂ and WS₂: A first principles study

S Reshmi¹, Mihir Ranjan Sahoo², K Bhattacharjee^{1,3*}

¹ Institute of Physics, Sachivalyala Marg, Gajpati Nagar, Bhubaneswar 751005 Odisha, India

2 Harish-Chandra Research Institute, Prayagraj, 211019 Uttarpradesh, India

3 Indian Institute of Space Science and Technology, Valiyamala P O, Thiruvanantapuram 695547, Kerala,

India

*Corresponding email: <u>kbhattacharjee@iopb.res.in; kuntala.iopb@gmail.com</u>

Abstract. First principles calculations based on periodic boundary conditions were carried out using density functional theory (DFT) to obtain the structural and electronic properties of Ag adsorbed MoS_2 and WS_2 monolayers. The results demonstrate emergence of in-gap states due to Ag adsorption on the monolayers of MoS_2 and WS_2 , thus, proposing a simple method of modification of the electronic properties and tuning the bandgap of these monolayers. The appearance of additional states within the bandgap can be observed near the Fermi energy as a result of the contribution from Ag s and Mo d orbitals.

Introduction

Two-dimensional transition metal dichalcogenides (TMDs) have been on extensive investigation due to their exotic properties and diversified applications in the field of nanoelectronics, spintronics etc.^{1,2}. The metal atom is staked between two chalcogen atoms with individual layers bonded by van der Waal's force³. These materials possess a direct bandgap in the monolayer regime which makes them highly useful in low dimensional electronics. Various techniques like creation of vacancies via defects⁴, addition of impurities by adsorption⁵, doping⁶ etc. have been in use to modify the physical and chemical properties of 2D monolayers. Metal adsorption on TMDs has shown promising applications in the field of catalysis, photo sensing, gas sending etc. Ag doped monolayer of WS₂ is reported to show magnetic behavior with a half metallic nature which can be further modified by the application of tensile strain⁶. Even after a lot of experimental realization of these properties, the knowledge of atomic level interaction between metal atoms and TMD layers is still limited. Here, we investigate the atomic level interaction between Ag adatom on monolayer MoS₂ and WS₂ and the structural and electronic modifications happening in the system.

Calculation details

All calculations are performed using the Vienna Abinitio Simulation Package (VASP)7 within the projector augmented wave (PAW) approach. The ground state of the electronic structure is described within the density functional theory (DFT) using the generalized gradient approximation (GGA) with PBE exchange correlation functional. All calculations are spin-polarized with the D3 van der Waals (vdW) correction. The cutoff energy for expansion of the wave functions is 500 eV. The Monkhorst- Pack scheme k-points sampling method is used for the integration in the first Brillouin zone and $2 \times 2 \times 1$ k-mesh is used in this study. The atomic positions are fully relaxed until the force on each atom is less than 0.02 eV.Å⁻¹. A 3x3x1 slab surface is used for all the calculations with a vacuum slab of 15 Å along Z direction.

Results and discussion



Figure 1. Supercell for monolayer MoS_2 . (a) side view and (b) top view.

Figure 1 shows supercell of a monolayer MoS_2 or WS_2 surface [Figure 1 (a) & (b) side view and top view respectively]. The band structure [Figure 2(a)] plotted for monolayer MoS_2 along the Γ -M-K- Γ path displays a direct bandgap of ~1.62 eV at K point, whereas, WS_2 exhibits a bandgap of ~1.76 eV (not shown here) at K point.



Figure 2. (a) Band structure, (b) DOS of monolayer MoS_2

The density of states (DOS) plots of monolayer MoS_2 [Figure 2(b)] or WS_2 (not shown here) reveal that the conduction band (CB) edge is composed mainly of Mo or W d orbitals and valence band (VB) is composed of hybridized Mo or W d and S p orbitals.

Next, we investigate the modification of these monolayers upon adsorption of Ag atom. To find out the most stable adsorption position, we have considered different configurations with single Ag atom on four different positions labelled as T_S (at the top of S atom), T_M (at the top of metal atom), H (above the center of the hexagonal ring of MoS₂/WS₂) and B_{S-S} (bridge site between two S atoms). The favorable adsorption site was obtained by calculation of adsorption energies using the formula,

$$E_{ads} = E_{TMD} + E_{Ag} - E_{M-TMD}$$

Where E_{M-TMD} is the total energies of TMDs monolayer with Ag atom adsorbed (M-TMD), and E_{Ag} and E_{TMD} denote the energy of isolated Ag atom and the pristine TMD monolayer, respectively.



Figure 3. Structural configuration of stable Ag adsorbed MoS₂ monolayer.

Our calculations reveal the most stable position for adsorption of Ag atom on MoS_2 or WS_2 monolayer which is the H site with lowest adsorption energy [Figure 3]. The initial S-Ag plane distance was set to be 3.4 Å which reduced to 1.9 and 2 Å respectively for MoS_2 and WS_2 . After the structural relaxation, Ag-S bond length reduces to 2.65 for MoS_2 and 2.68 Å for WS_2 . The band structure of the Ag adsorbed MoS_2 is shown in Figure 4(a) and the DOS plots [Figure 4(b) and Figure 5(a, b)] show an additional state appearing (shown by arrow) near the Fermi energy (E_F) which is composed of mainly hybridized Ag s and Mo or W d orbitals.



Figure 4. Band structure of Ag adsorbed MoS₂



Figure 5. (a) Comparison of MoS₂ monolayer and Ag adsorbed surface and (b) DOS of Ag adsorbed MoS₂ monolayer

On comparison of the Ag adsorbed monolayer MoS_2 DOS to the monolayer MoS_2 [Figure 5(a)], we observe an overall shift in the bands by 0.5 eV. Another additional feature related to Ag adsorption can be observed in the deep VB around ~ -4 eV (spread between -6.2 eV to -1.9 eV) [Figure 5(b)]. The appearance of in gap states reduces the bandgap considerably and can be seen in the band structure. For the Ag-WS₂ system, most of the contribution is from the Ag d orbitals for the deep VB state and is spread between -6.6 eV to -2.3 eV.

Conclusion

We have investigated the adsorption of single Ag atom on monolayer MoS_2 and WS_2 using DFT calculations. For Ag adatoms, the most favourable position is at the hollow site. The calculations reveal emergence of an additional energy state near the E_F reducing the bandgap drastically. The signature of Ag atom is mainly observed at two energies, one near E_F , other in the deep VB.

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Optical Properties Of Two-Dimensional Pentagonal Tellurene

Jaspreet Singh¹, Mukesh Jakhar¹, and Ashok Kumar^{1,*}

¹Department of Physics, Central University of Punjab, Bathinda, 151001, India

*Corresponding author: ashokphy@cup.edu.in

Abstract

Motivated by the simple structures and astonishing properties of mono-elemental monolayers of group VI-b elements, the electronic and optical properties of newly predicted pentagonal tellurene (penta-Te) have been studied with the help of density functional theory. It has a pentagonal structure constituting six tellurium atoms with a square unit cell. The indirect band gap of 0.89 eV has been obtained with PBE functional. The absorbance peaks of optical spectra lie in the UV-visible region imply its optoelectronic applications. Comprising the semiconductor nature, previously examined mechanical and thermoelectric (TE) properties, and optoelectronic (OE) properties, this material has potential applications in flexible OE-TE multifunctional devices.

Introduction

Mono-elemental two-dimensional (2D) materials are of great interest because of their simple structural constituency and remarkable physical and chemical properties. Many mono-elemental 2D materials of groups III, IV and V are predicted and experimentally synthesized such as graphene, silicene, borophene, phosphorene, etc. All these materials have potential applications in different fields such as spintronics, optoelectronics, etc [1]. Because of their excellent properties, there is a lot of research going on the mono-elemental 2D materials. In recent years, the multivalent nature of group VI-b elements (mainly tellurium (Te) and selenium (Se)) results in many 2D allotropic forms. These materials have moderate band gap value, high carrier mobilities, and good air stability that overcome the limitations in previous existing 2D materials such as graphene, MoS₂, and phosphorene [2]. Thus, these materials have a wide range of applications in different fields. Additionally, the experimental synthesis of a thin film of Te and Se has attracted great attention among researchers [3, 4].

A very recently, mono-elemental 2D pentagonal layer of Te (penta-Te) is predicted. Its structure is similar to that of pentagonal PdSe₂ [5]. The electronic, mechanical and thermoelectric (TE) properties of this 2D layer have been very recently studied [6], however, the optical properties of penta-Te remain unexplored. In this paper, we have evaluated the optical properties of the monolayer penta-Te in terms of optical absorbance and electron energy loss spectra (EELS).

Computational Details

We have used the Quantum Espresso package [7] to perform first-principles calculations based on the density functional theory. The plane augmented wave (PAW) pseudopotentials with generalized gradient

approximations (GGA) are used in which exchangecorrelation energies are contributed through Perdew-Burke-Ernzerhof (PBE) functional. The energy cutoff of 60 Ry is used. The k-point mesh of 8x8x1 and 12x12x1 is used for structural relaxation and electronic structure calculations, respectively. The convergence criteria of 10^{-4} eV and 10^{-3} eV/Å in energy and force have been employed in structural optimizations, respectively. The vacuum layer of ~20 Å is used to restrict the interactions between the neighboring layers. The random phase approximation (RPA) method is employed for a qualitative study of the optical properties. A very dense mesh of 40x40x1and optical broadening of 0.1 eV is used for optical calculations.

Results and Discussion

Structural and Electronic Properties

The stability of the penta-Te has been confirmed already in the literature by phonon and molecular dynamics simulations [6]. We have obtained here the relaxed structure of penta-Te with a lattice constant of a = b = 6.94 Å and thickness (d) equal to 2.03 Å (Fig. 1). Here, the square unit cell has a total of six Te atoms of which four have the coordination number of 3 (Te₃) and two have the coordination number 4(Te₄). The bond lengths of 3.05 Å and 2.76 Å have been obtained between Te₃-Te₄ and Te₃-Te₃ atoms, respectively. All the relaxed lattice parameters are in good agreement with the existing literature [6]. The calculated cohesive energy value of 3.01 eV/atom is comparable to the existing 2D allotropes of Te describes the stability of penta-Te. Furthermore, we have obtained the indirect band gap value of 0.89 eV (0.91 eV) [6]) with PBE functional implying its semiconducting nature (Fig. 1(c)). The PDOS of penta-Te shows that there is merely a contribution of p orbitals of Te_3 atoms near the valence band maximum and conduction band minimum (Fig. 1(d)).



Fig. 1(a) Top view, **(b)** Side view, **(c)** Electronic band structure and **(d)** PDOS of the penta-Te, respectively. Irreducible Brillouin zone is shown inset of **Fig.1(c)**.

Optical Properties

For practical purposes, the TE properties of this 2D monolayer are discussed in the literature [6]. It comes out to be a very good thermoelectric material with a ZT value of ~2.84 for n-type doping at 300K. We have discussed here the optical properties of penta-Te for its applications in multifunctional optoelectronic (OE) and TE devices. We have obtained here the optical absorbance and electron energy loss spectra. The optical absorbance has been obtained from the imaginary part of the dielectric constant (ε_2) as:

$$A(\omega) = \frac{\omega}{c} L \varepsilon_2(\omega) \qquad a)$$

where L is the vacuum distance across the z-direction.



Fig. 2 (a) Optical absorbance and (b) Electron energy loss spectra of the penta-Te, respectively.

The absorption peaks around 1.4 eV and 2.1 eV along X and Y-directions, respectively lie in the UVvisible region (Fig. 2(a)) imply its application in optoelectronic devices. The absorption edge at ~0.9 eV and structural peaks in absorption spectra are consistent with the band gap value and inter-band transitions in the band structure, respectively. The calculated static dielectric constant values are 4.8 and 5.8 along with X and Y directions, respectively, which are lower than that of α -Te (13.9) and α -Se (11.6) [8] because of its higher band gap value than α -Te and α -Se following two band model for semiconductors. To understand the plasmonic features of penta-Te, we have evaluated the EELS using real (ε_1) and imaginary (ε_2) parts of dielectric constants (Fig. 2(b)) as:

$$Im\left\{\frac{-1}{\varepsilon(\omega)}\right\} = \frac{\varepsilon_2(\omega)}{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}$$
b)

The lower energy peaks around 5 eV correspond to the excitation of π -electrons and higher energy peaks around 7.5 eV corresponds to the excitations of both σ and π -electrons.

CONCLUSIONS

We have studied here the electronic and optical properties of very recently predicted stable penta-Te. It has a square unit cell with six Te atoms bonded to form a pentagonal structure. The indirect electronic band gap value of 0.89 eV with PBE functional is consistent with the previously reported value of 0.91 eV. The cohesive energy value of -3.01 eV is analogous to existing 2D monolayers of group VI elements indicates its energetical stability. The optical absorbance peaks around 1.4 eV and 2.1 eV lies in the UV-visible describes its optoelectronic properties. Combining its OE properties with previously reported TE and mechanical properties, this monolayer has potential applications in multifunctional flexible OE-TE devices. The stability and its properties will motivate the researchers to synthesize this monolayer in the future.

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Collinear Magnetic Coupling of *3d* Transition Metal Atoms on Ni₂MnGa (001) Surface

Joydipto Bhattacharya^{1,2}, Aparna Chakrabarti^{1,2}

¹Theory and Simulations Laboratory, Raja Ramanna Centre for Advanced Technology, Indore 452013, Madhya Pradesh, India ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India

*Corresponding author: joydipto@rrcat.gov.in

Abstract

In this paper, we focus on magnetic 3d atoms, used as an adatom on the Ni₂MnGa (001) surface. We investigate the orientation of the magnetic atoms and stabilization of collinear magnetic solutions of these composite systems. It is found that early transition metals (Ti,V,Cr,Mn) couple antiferromagnetically to the substrate, while (Fe,Co,Ni) couple ferromagnetically (FM). Further, surface and termination dependent magnetic coupling of lattice matched Fe have been studied and it is observed that Fe has FM coupling to the substrate as well as within themselves irrespective of Fe layer thickness and surface termination.

INTRODUCTION

Magnetic coupling at the surfaces and interfaces of 3d transition metals (TM) have significant attentions, where drawn the magnetic properties can be largely influenced by its local environment and adlayer thickness. From density functional theory (DFT) based ab initio calculations, various researchers have investigated enhancement of magnetic moments of 3d TM atoms on mono-elemental magnetic and nonmagnetic metal surfaces [1,2]. The magnetic coupling for few of these TM adlayers are found to be significantly different from what is observed in bulk.

In this article we have investigated the magnetic coupling of 3d TM (Ti to Ni) adlayers on the (001) surface of multi-component ferromagnetic Heusler alloy Ni₂MnGa, which shows large magnetic moment for Mn atom. Further, as Fe has lattice constant (2.86 Å), which is almost double of Ni₂MnGa (5.82 Å), it is particularly worthwhile to investigate whether it shows any dependence of adlayer thickness and surface termination on the magnetic coupling, as observed for lattice matched Cr [3].

COMPUTATIONAL DETAILS

We have used Vienna Ab-initio Simulation Package [4] and the exchange correlation functional is approximated under the generalized gradient approximation as given by Perdew-Burke-Ernzerhof[5]. We have used the energy cut-off of 370 eV for the planwave expansion. For The Brillouin zone sampling we have used a K mesh of 9×9×3 with Monkhorst-Pack scheme . We have performed the crystal orbital Hamilton population (COHP) analysis using the electronic structure construction (LOBSTER) programme [6].

RESULTS AND DISCUSSION

Here we have considered two cases of collinear magnetic states of adatoms (Ti to Ni) on the ferromagnetic Mn-Ga atom terminated surface. In one case they are FM coupled to the substrate and in another case, they are AFM coupled.



Figure.1. *3d* adatoms on the Mn-Ga terminated surface of Ni₂MnGa. Top and bottom panels show the energy difference between the AFM and FM coupling and magnetic moments of these adatoms in two different possible configurations, respectively.

In Figure.1 we show the energy difference between the AFM and FM solutions for the 1monolayer (ML) of adatoms on the Mn-Ga surface. This clearly indicates the difference in magnetic couplings for the early TM as compared to the late TM atoms, where the transition from AFM to FM coupling occurring between Z=25 to Z=26.Further, due to the half field d bands Mn atom carries the highest magnetic moment followed by Cr and Fe atoms.

As discussed in the previous section due to the lattice matching between the Fe bulk and Ni₂MnGa substrate, we have investigated in detail the magnetic coupling of the Fe adtoms on both the Mn-Ga and Ni terminated surfaces for adlayer thicknesses of 1 and 2 ML. In both these cases, it is found that the Fe adatoms are FM coupled with the substrate as well as with each other, unlike the Cr case [3]. In Table.1, we have shown the exchange coupling constants for 1ML on Ni and Mn-Ga surfaces, which is calculated by fitting the DFT energies with the Heisenberg Hamiltonian [2]. We can see stronger intra-layer exchange coupling (higher values of JFe-Fe) between the Fe atoms as compared to that of adatom and substrate (JFe-Mn and JFe-Ni), which drives the system to be FM coupled. Further, we have used the COHP technique in order to understand the observed magnetic behaviour, from the chemical point of view (Figure.2), which clearly shows the presence of anti-bonding states (positive value of COHP) at the Fermi energy in the NM framework, which got reduced significantly in the spin-polarized calculation and hence suggests ferromagnetic stability.



Figure.2. COHP bonding analysis between the Fe adatoms on the Mn-Ga surface. NM, Up and Down represent nonmagnetic, majority and minority spin states, respectively.

Table1. ICOHP values and magnetic coupling constants for 1ML of Fe adatoms on Mn-Ga and Ni terminated Ni₂MnGa (001) surface.

ICOHP values (eV/bond)			Exchange coupling constants (meV)
Mn-Ga	Fe-Fe	-0.43	J _{Fe-Fe} = 114.87
termination	Fe-Mn	-0.80	$J_{Fe-Mn} = 57.92$
Ni	Fe-Fe	-0.78	JFe-Fe = 101.12
termination	Fe-Ni	-0.60	J _{Fe-Ni} = 23.63

CONCLUSIONS

Using spin-polarized density functional theory based electronic structure calculations, we have investigated the magnetic coupling of 3d TM adlayers on Ni₂MnGa (001) surface. From our present study, it is found that, the early TM atoms (Ti,V,Cr,Mn), try to couple anti ferromagnetically(AFM) to the substrate, whereas the coupling of Fe, Co, Ni atoms are rather ferromagnetic (FM). We also do not observe any surface or termination dependence on the magnetic coupling of Fe atoms. It always couples FM to the substrate as well as with the other Fe atoms. This is unlike the case of Cr adlayers [3]. Our work is expected to give useful insight into the magnetism of composite systems of thin adlayer on surface of Heusler alloys for understanding different aspects of twodimensional magnetism.

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Correlation Effects In Finite Width One-Dimensional Electron Wire

Ankush Girdhar^{1,*} and Vinod Ashokan²

^{1,2}Department of Physics, Dr. B. R. Ambedkar National Institute of Technology, Jalandhar (Punjab) 144 011, India

*Corresponding author: ankushgirdhar@hotmail.com

Abstract. We study the ground state properties of the electron fluid in one-dimension at high density. The regularization of the Coulomb potential in one-dimension is achieved by confining the electron in one-dimension through a harmonic potential. The dependence of the ground state energy on the wire width is studied for electron fluid at high density confined in a Harmonic potential using the variational quantum Monte Carlo simulation. The low energy physics of Tomonaga-Luttinger liquid are characterized by Tomonaga-Luttinger parameter or exponents. We have extracted the Tomonaga-Luttinger liquid exponent from the momentum density data by fitting the data around k_F for different confinement of harmonic wire widths. The Tomonaga-Luttinger liquid exponent is than extrapolated to the infinitely thin wire. The extrapolated Tomonaga-Luttinger liquid parameter is in agreement with the infinitely thin wire simulation data.

Introduction

The study of the one-dimensional (1D) electron fluids has attracted a lot of attention over past years due to the distinct and fascinating features of 1D electron systems. The conventional Landau-Fermi liquid theory is not applicable in 1D due to Peierls instability [1]. The failure of existing theory has paved way for extensive theoretical and experimental research of the field. The correlation effects in 1D electron systems bring forth the collective behavior of electrons and a whole new set of physical properties. The theory of Tomonaga-Luttinger (TL) liquid explains the physical properties of 1D interacting systems. The 1D electron systems are known to be strongly correlated systems at all densities. There are several intriguing phenomena in 1D fluid that clearly establish the uniqueness of the system. Some of them are Wigner crystallization, spin-charge separation, charge fractionalization, etc.

The 1D quantum fluid model is easier to anticipate but the experimental verification is complicated. However, the advancements in material fabrication technology has made realization of quasi 1D systems possible. Some of the features of TL model have been observed in carbon nanotubes, organic conductors (Bechgaard salts), confined cold atomic gases, semiconductor nanowires, and edge states in quantum Hall liquids.

In this work, we perform a detailed study of 1D electron fluid at high density using variational Quantum Monte Carlo techniques for electrons interacting via long range Coulomb potential. The ground state properties including the ground state energy, momentum density (MD) are calculated as a function of wire widths. From the simulated MD, we extract exponent α by fitting it to appropriate fit function. The exponent is plotted as a function of

wire width showing the regularization of Coulomb potential.

Theoretical Formalism

The Hamiltonian for an N-electron 1D homogenous electron gas is

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^{N} \frac{\partial^2}{\partial x_i^2} + \sum_{i < j} V(x_{ij}) + \frac{N}{2} V_{\text{Mad}}, \quad a)$$

where $V(x_{ij})$ and V_{Mad} are the Ewald interaction and Madelung energy, respectively. The Ewald interaction term for harmonic wire is given as,

$$V(x_{ij}) = \sum_{m=-\infty}^{\infty} \left[\frac{\pi}{2b} e^{(x_{ij} - mL)^2 / (4b)^2} \operatorname{erfc}\left(\frac{|x_{ij} - mL}{2b}\right) - \frac{1}{|x_{ij} - mL|} \operatorname{erf}\left(\frac{|x_{ij} - mL}{2b}\right) \right] + \frac{2}{L} \sum_{n=1}^{\infty} \operatorname{E}_{1}[(bGn)^2] \cos(Gnx_{ij})$$
b)

where *b* is the width of the wire, $G = 2\pi / L$, and E₁ is the exponential integral function. The corresponding Madelung energy is defined as:

$$V_{Mad} = \lim_{x \to 0} \left\{ V(x) - \frac{\sqrt{\pi}}{2b} \right\}$$
 c)

Computational Method

We compute the ground-state properties of the 1D electron system using the variational Monte Carlo (VMC) technique. In the VMC method, the expectation value of the Hamiltonian is calculated using a trial wave function via importance-sampled

Monte Carlo integration. The optimization techniques are used to optimize a number of variable parameters of wave function. A Slater-Jastrow-backflow trial wave function with plane wave orbitals up to $k_F = \pi / 2r_s$ was used in the calculations. We have used CASINO [2] codes for VMC calculations. The details of the calculations were discussed by Lee and Drummond [3,4]. In our current study, we focus on fully polarized ferromagnetic systems at high density.

Results and Discussion

The VMC ground state energy per electron was calculated for $r_s = 0.5$. The calculations were performed for simulation cell of length $L = 2Nr_s$ subject to periodic boundary conditions, where N is the total number of electrons in wire. The ground state energy was extrapolated to the thermodynamic limit taking N = 37, 55, 77, 99 using the fit function of the form $E(N) = E_{\infty} + AN^{-2}$ where E_{∞} , and A are fitting parameters. The ground state energies extrapolated to thermodynamic limit for different wire widths are plotted in Fig. 1.



Fig. 1. Ground state energy as a function of b for the Harmonic wire for $r_s = 0.5$.

The MD is calculated using the trial wave function as,

$$n(k) = \frac{1}{2\pi} \left\langle \int \frac{\psi_T(r)}{\psi_T(x_1)} \exp[ik(x_1 - r)] dr \right\rangle \qquad \text{d}$$

where the trial wave function $\psi_T(r)$ is evaluated at $(r, x_2, ..., x_N)$. The angular brackets denote the average taken over electron configurations.

In 1D, the interaction leads to power law behavior in MD, which has a continuous behavior around $k = k_F$. However, the first order derivative is found singular at $k = k_F$. It is known from TL theory that MD has the following form around $k = k_F$,

$$n(k) = n(k_F) + A[sign(k - k_F)] | k - k_F |^{\alpha} \qquad e)$$

where $n(k_F)$, A, and α are taken as fitting parameters. Here, the exponent α is related to TL parameter as,

$$\alpha = \frac{1}{4} \left(K_{\rho} + \frac{1}{K_{\rho}} - 2 \right).$$
 f)

The range of MD data used for fitting is described by $|k-k_F| < \epsilon k_F$. Ideally $\epsilon \rightarrow 0$, as Eq. e) is only valid for $k \rightarrow k_F$. We have taken the points where $\epsilon > 0.035$. The parameter is plotted as function of wire width in Fig. 2. The exponent obtained on extrapolating to b = 0 is 0.0539(5) which is in agreement with the value known for infinitely thin wire (0.0505(2)) given in Ref. [4]. In this work we have performed the VMC simulation study of electrons wire interacting via a long range Coulomb potential at high density for different confinement widths. Further, the study of TL parameters will motivate the experimental work in 1D electron systems at high density.



Fig. 2. Exponent α as a function of *b* for the Harmonic wire for $r_s = 0.5$.

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Structural and Electronic Properties of WS₂-MoS₂ Van Der Waals Heterostructures

Vaishali Nimbewal¹, Ramesh Kumar¹, and Sunita Srivastava²

¹Department of Physics, Guru Jambheshwar University of Science & Technology, Hisar-125001, India ²Department of Physics, Panjab University, Chandigarh-160014, India

**Email:* ramesh85@gjust.org, nimbewalvaishali@gmail.com

Abstract

Van der Waals heterostructures, which are created by stacking monolayers vertically, have a wide range of optoelectronic applications. The structural and electrical properties of heterobilayer WS_2 -MoS₂ Transition Metal Dichalcogenide are explored using first principle calculations. According to our calculations, the monolayers MoS₂ and WS₂ have direct bandgaps. However, when these monolayers are stacked vertically to form a heterobilayer with van der Waals interaction, we get indirect bandgaps with bandgaps smaller than those of the monolayers WS₂ and MoS₂.

Electronic and Optical Properties of Novel Double Perovskite Compound Cs₂RbInI₆

Yashaswi Soni¹, Varsha Yadav¹, and Ajay Singh Verma^{2*}

¹Department of physical sciences, Banasthali Vidyapith, Banasthali, Rajasthan, India, 304022 ²Department of Natural and Applied Sciences, Glocal University, Saharanpur, India, 247232

*Corresponding author: ajay_phy@rediffmail.com

Abstract

Novel energy materials grab the much attention of researchers because of the huge demand for green energy sources. Double perovskites of $A_2BB'X_6$ framework has been conspicuous by the dint of their magnificent electronic and optical properties. We have computed the physical properties of $C_{s2}RbInI_6$ double perovskite compound using first principle method along with density functional theory (DFT). Complete computational analysis has been done within wien2k code. $C_{s2}RbInI_6$ demonstrates the low band gap, high absorption and high dielectric constant which are preferable for various optoelectronic applications.

Introduction of Defects in 2D α-SiN for Improvement in Hydrogen Evolution Reaction Activity: A DFT Study

Darshil Chodvadiya^{1,*}, Prafulla K. Jha¹ and Brahmananda Chakraborty^{2,3}

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat,

India-390002,

²High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India-400008, and ³Homi Bhabha National Institute, Mumbai, India-400094

*Corresponding author: darshil9000@gmail.com

Abstract

In this work, we have studied the potential of pristine and defected 2D α -SiN for HER catalyst. The defect enhances HER activity by 90% as compared to pristine α -SiN and makes it comparable to one of the best Pt metal alloys. The enhanced performance of HER is attributed to the redistribution of charges after vacancy defect creation. Defect makes α -SiN metallic which serves as an electrocatalyst. This work could open up an avenue for the fabrication of earth abundant non-nobel metal based electrocatalyst.

Introduction

To solve energy crisis, the hydrogen (H_2) can be a potential alternative of non-renewable fossil fuels because of its unique properties such as non-toxicity, abundant on earth, high energy density per unit mass and cleanness [1]. To produce H₂ from water needs highly efficient catalysts. Noble metal Pt based catalysts hold excellent hydrogen evolution reaction (HER), but they are less abundant and expensive, which limits their large-scale practical implementation. Hence, design of largely available and cheap catalysts with excellent HER performance is highly demanded [1-2].

After successful exploration of two-dimensional (2D) graphene, 2D materials get huge attention in the field of the catalyst due to its tremendous physical, chemical and mechanical properties [1-4]. Pristine form of most studied materials such graphene, h-BN, MoS_2 is not suitable for the HER activity. For enhancement of it's HER activity researchers try creation of defect on material and found huge success. [3-4]. In DFT study of Yixin et al. they studied 16 types of structural defect and found desirable enhancement in the HER activity of MoS_2 [3]. Similarly, functionalized defected graphene and h-BN monolayer also give HER activity comparable to Pt metal [4].

Most recently, Burak et al. predicted dynamically stale 2D α -SiN similar to graphene, h-BN and MoS₂. 2D α -SiN has P $\overline{6}$ m2 space group and 1.74 eV band gap [5]. Till date, α -SiN is not investigated for its use as catalyst. In present work, we have investigated the catalytic activity for HER of pristine and defected α -SiN using dispersion corrected density functional theory.

Computational methodology

All calculations were performed using first principles based density functional theory (DFT) in Quantum Espresso code [6]. The exchange correlation interaction was considered within the generalised gradient approximation (GGA) given by Perdew-Burke-Ernzerhof (PBE). The kinetic energy cut-off and a k-point taken as 70 Ry and 7x7x1 respectively which were sufficient enough to converge the total energy within the specified threshold criterion. Vacuum of 20 Å is kept in z direction to avoid the inter-layer interaction.

Results and discussion

To investigate the HER activity of α -SiN, we systematically optimized its 3x3 size of supercell (see Fig. 1(a)) and studied its structural and electronic properties. The optimal Si-Si, N-N, Si-N bond lengths are 2.40 Å, 3.51 Å, and 1.75 Å, respectively and exhibiting 1.75 eV band gap which is in good agreement with previous study [5].

Gibbs free energy (ΔG) is crucial parameter for the evaluation of HER activity and for an ideal catalyst ΔG should be close to zero. ΔG is given by equation; $\Delta G = \Delta E_{ad} + 0.24$ eV, where ΔE_{ad} is adsorption energy of H atom [1-2]. To study the HER activity; we have kept H atom at all possible site of the α -SiN such as Si site, N site, and hollow site etc. The Si site is found to be minimum energetic. Calculated ΔE_{ad} and ΔG are 0.56 eV and 0.80 eV, respectively. Very high value of ΔG indicates that non-suitability of α -SiN for HER activity.

For enhancement of HER activity, we have created vacancy defect such as Si atom vacancy and N atom vacancy. After vacancy of Si and N atom both system become metallic in nature that means conductivity of the system increases. To examine the HER activity of defected α -SiN, we have explored all possible sites such as N site, Si site, hollow site and defected site for both cases. For Si defected α -SiN. outcome of the all four cases is same i.e. near N atom. Calculated ΔE_{ad} and ΔG are -2.61 eV and -2.37 eV, respectively and suggest non-suitability of Si defected α -SiN for the HER activity because desorption process became very difficult for this case. For N defected α -SiN (see Fig. 1(b)), out of four possibilities only N and Si site are found to be active for HER activity (see Fig. 1(c, d)). E_{ad} (and ΔG) is -0.16 eV (0.08 eV) and -0.12 eV (0.12 eV) for N and Si site of N defected α -SiN, respectively. Due to creation of N defect, HER activity at N site increases by 90% as compared to pristine α -SiN. Here, $\Delta G \approx 0$ eV and comparable of Pt metal.



Fig. 1. Top view of α -SiN (a), N defected α -SiN (b), H adsorbed at N site (c) and Si site (d) of N defected α -SiN.



Fig. 2. PDOS of α -SiN (a), N defected α -SiN (b), H adsorbed at N site (c) and Si site (d) of N defected α -SiN.

To understand the effect of N defect and H adsorption, we have calculated the partial density of state (PDOS) and presented in Fig. 2. Band gap of 1.75 eV for α -SiN is confirmed from Fig. 2(a) and presences of Si-3p and N-2p orbitals on Fermi level (see Fig. 2(a)) responsible for metallic behaviour after creation of N defect. Presence of additional Si-3p and N-2p orbitals (see Fig. 2(c)) near both sides of the Fermi level leads to charge gaining behaviour from H-1s orbitals in case of H adsorbed at N site of defected (at N) α -SiN as compared to non-adsorbed case (see Fig 2(b)). Depletion of Si-3p and N-2p orbitals (see Fig. 2(d)) near Fermi level as compared to non-adsorbed case (see Fig 2(b)) leads to charge losing behaviour to H-1s orbitals in case of H adsorbed at Si site of defected (at N) α-SiN. Splitting of the H-1s orbitals (see Fig. 2(c and d)) in bonding and non-bonding states validate interaction with N defected α -SiN. Löwdin charge analysis confirms that the H atom losing 0.01e charge to N site and gaining 0.14e charge form Si site of defected (N) α-SiN, respectively. Here, PDOS and charge analysis are consistent with each other and confirming optimal interaction of H atom with N defected α -SiN.

Conclusions

In present work, we have studied structural, electronic and HER activity of pristine and defected α -SiN. After creation of the defect, system becomes metallic in nature which leads to increment in the conductivity of the α -SiN. ΔG of N site of defected (N defect) α -SiN is 0.08 eV which is comparable to nobel Pt metal. After creation of N defect performance of the HER activity increases by 90% as compared to pristine α -SiN.

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The Magnetic Order And Electronic Structure Of Gd Doped EuCd₂As₂

Amarjyoti Choudhury and T. Maitra

Department of Physics, Indian Institute of Technology, Roorkee, Roorkee 247667, Uttarakhand, India

*Corresponding author: achoudhury@ph.iitr.ac.in

Abstract

In this work, we have theoretically investigated the magnetic order and electronic structure of $Eu_{2/3}Gd_{1/3}Cd_2As_2$ compound. The chemical substitution at 1/3rd of Eu sites in EuCd₂As₂ by Gd is observed to affect significantly its physical properties. Our density functional theory (DFT) calculations reveal that Gd substitution leads to a transition from semi metallic antiferromagnetic (A-AFM) ground state of the parent compound to metallic ferromagnetic ground state, where the energy difference between FM and A-AFM configuration is quite close, which can be tuned easily with externally applied magnetic field.

Introduction

The europium-based 122 pnictides with a general formula AM₂X₂ have been studied extensively in recent decades. These compounds have generated a lot of interests among the researchers because of their intriguing physical properties such as a strong interplay between magnetism, transport and optical properties. These properties also make these layered materials favorable for device application in areas of spintronics, thermoelectrics, etc.

The recent experimental investigation on the compound EuCd₂As₂ shows that Eu²⁺ (4f⁷) moments form a long range antiferromagnetic (AFM) order at 9.5K and offers scattering to conducting carriers from Cd and As [1]. An A-type AFM ground state with spin moments residing in the ab-plane is also confirmed by both DFT calculations as well as resonant X- ray scattering measurements [2, 3]. In this work we have investigated the effect of Gd doping on electronic structure and magnetic properties of EuCd₂As₂.

Methodology

The electronic structure calculations were performed within the framework of ab initio density functional theory (DFT) with Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [4] exchange-correlation functional within the full potential linearized augmented plane-wave method (FPLAPW) as implemented in WIEN2K [5]. In the 'Gd' and 'Eu' due to presence localized felectrons both coulomb correlation and spin-orbit interaction were considered in our calculations GGA+U and through the GGA+U+SO approximations. The cut-off energy was set to -6.0 Ry for the separation of core and valance electrons. The plane wave cut-off parameter $R_{mt} \times K_{max} = 7.0 \text{ Ry}$ (where K_{max} is the largest reciprocal lattice vector and R_{mt} is the muffin-tin sphere radii) were used to control the convergence of basis set. In irreducible Brillouin zone (BZ) 165 k- points were taken for self-

optimization we used 2Doptimization package as implemented in WIEN2K.



Fig. 1. Hexagonal crystal structure of Eu_{2/3}Gd_{1/3}Cd₂As₂ (space groupP3m1). As (green) and Cd (yellow) form a double-corrugated hexagonal layer sandwiched between Eu (blue) and Gd (red) atoms

Results and discussion

The parent compound EuCd₂As₂ has a known structure with space group P3m1. The Wyckoff positions in EuCd₂As₂ are 1a (0,0,0), 2d (1/3, 2/3, 0.6331(3)), and 2d (1/3, 2/3, 0.2466(5)) for the Eu, Cd, and As atoms, respectively [5]. We have taken the structural data of $EuCd_2As_2$ from experiment [5] and doped 1/3rd of Eu sites by Gd to form the compound Eu_{2/3}Gd_{1/3}Cd₂As₂. To optimize the structure we first performed volume optimization.In order to obtain the equilibrium lattice parameters corresponding to optimized volume, we have also optimized the c/a ratio. Finally we optimized the atomic positions. The optimized lattice constants and atomic positions are then used for further calculation in this work.

consistent calculations. For the volume and c/a ratioAE SSPS 2021

The electronic structure and the magnetic order were explored by spin polarized calculations with **GGA-PBE** exchange correlation potential as implemented in Wien2k. To find the magnetic ground state we calculated the total energy under various approximation for different magnetic configurations, i.e, A-type antiferromagnetic (A-AFM), ferromagnetic (FM), C-AFM, and G-AFM in addition to the nonmagnetic (NM) case (where Eu spin moments are set to zero). For the NM, C-AFM and G-AFM magnetic configurations, total energies are found to be much higher than FM & A-AFM states. Therefore, we only listed the total energies calculated for FM & A-AFM in Table I. In GGA, the FM state is the ground state even if the energy difference between FM and A-AFM configuration is very small. When we apply 'U' in GGA+U calculation, we see that the FM state is favored by 4.60 meV for U_{eff}=U-J=3eV (where U is the Coulomb correlation and J is Hund's exchange). By increasing Ueff to 5eV, FM stabilizes more as the ground state magnetic configuration. We note that the parent compound EuCd₂As₂ shows A-type AFM ground state with Ueff=5eV [2]. Our GGA+U+SO calculations further show that the spin moments lie in the ab-plane in the FM state.

TABLE I. V between A-A respect to U	TABLE I. Variation of the energy difference between A-AFM and FM ($\Delta E=E_{AFM}-E_{FM}$) with respect to U _{eff}				
$U_{eff}(eV) = 0$ 3 5					
$\Delta E (meV)$	+0.78	+4.60	+4.64		

To study the electronic structure, we have calculated the partial density of states (PDOS). In Figure 2(a) and 2(b), we present the PDOS for the ground state FM within GGA and GGA+U respectively. In GGA, we see that highly delocalized Gd d-states are present at the Fermi level (FL) in the spin up channel whereas highly localized Gd-f states are present in the spin down channel. Since f electrons of Eu and Gd are strongly correlated we have performed GGA+U calculations. On the application U, the f states of Eu and Gd are pushed away from the FL. The itinerant states of the Gd d, Cd s, As p, characters crossing the Fermi level giving rise to a metallic character with high spin polarization.

Conclusions

In summary, we have used the DFT calculations to study the electronic structure and magnetic order in $Eu_{2/3}Gd_{1/3}Cd_2As_2$. We observe that on doping Gd, the ground state magnetic order changes from A-AFM to FM with spin moments residing in the ab-plane. Further the electronic structure calculations indicate a metallic character with highly spin polarized carriers.



FIG. 2. Partial DOS for FM in (a) GGA (b) GGA+U with spin up dos (upper panel) and spin down dos (lower panel) shown.

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In-situ STS studies and first principles calculations on the mechanically exfoliated WS₂ layers

Manu Mohan¹, Vipin Kumar Singh², Mihir Ranjan Sahoo³, Reshmi S⁴, Sudipta Roy Barman², K Bhattacharjee^{1,4*}

¹Department of Physics, Indian Institute of Space Science and Technology, Valiyamala, Trivandrum, 695547 ²UGC-DAE Consortium for Scientific Research, University campus, Khandwa Road, Indore,452001, M.P, India ³Harishchandra Research Institute, Prayagraj, 211019, Uttarpradesh, India

⁴ Institute of Physics, Sachivalaya Marg, Sainik School (PO), Bhubaneswar, 751005, Odisha, India *Corresponding email: <u>kbhattacharjee@iopb.res.in;</u> kuntala.iopb@gmail.com

Abstarct. Transition metal dichalcogenides (TMDs) have received immense research interest in the past few years due to their promising applications in nano- and opto- electronic devices. In the present work, we report mechanical exfoliation of few layers of ultra pure WS₂ crystal under ultra-high vacuum (UHV) conditions and investigation of the local electronic structure by in-situ scanning tunneling spectroscopy (STS) measurements and first principle calculations. STS investigations reveal the local density of states of the WS₂ surface with a bandgap of approximately 1.34 eV. First principles calculations performed on the bulk WS₂ crystal corroborate the experimental STS results with an indirect bandgap of the order of 1.38 eV and evidence of S p and W d states at both sides of the Fermi level.

Introduction

Isolation of graphene from graphite [1,2] has given a new dimension to materials research with emergence of two dimensional (2D) quantum materials that exhibit superior properties and applications. Transition metal dichalcogenides (TMDs) [3,4] like MoS_2 or WS_2 with honey comb lattice [5] structure seem to be promising materials candidates for superior device applications. Here, we report our scanning tunneling spectroscopy (STS) studies carried out on the bare WS₂ surfaces which exhibit a bandgap of approximately 1.34 eV. Density functional theory (DFT) calculations performed using Vienna Ab-initio Simulation Package (VASP) to understand the experimental STS results reveal a band gap of around 1.38 eV for the bulk WS₂, very close to the experimentally observed bandgap value. In this paper, we discuss our experimental STS results probing the local density of states (LDOS) of the bare WS₂ surface and the related DFT calculations which have been carried out to quantify the observed value of the bandgap.

Experimental and Calculation Details

WS₂ crystal of 99.99% purity was procured from 2D Semiconductors, USA and was mechanically exfoliated under ultra-high vacuum (UHV) conditions in a load-lock chamber of pressure around low 10^{-9} mbar. The load lock chamber is attached with a sample preparation and growth chamber which has the in-situ low energy electron diffraction (LEED) and Auger electron spectroscopy (AES) characterization facilities. The whole system was procured from Omicron Nanotechnology, Germany. Mechanically cleaved WS₂ crystal was insitu transferred from the load lock to the STM chamber via a magnetic transfer rod. STM and STS measurements were performed at RT under UHV conditions with a base pressure of the order of low 10⁻¹⁰ mbar. DFT calculations were carried out using Vienna Ab-initio Simulation Package (VASP) [6] within the projector augmented wave (PAW) approach to describe the ion-electron interactions and the ground state of the electronic structure is described using the generalized gradient approximation (GGA) with PBE exchange correlation functional. The cut off energy for expansion of the wave functions is 500 eV The Monkhorst- Pack scheme of k-points sampling method is used for the integration in the first Brillouin zone and 12x12x1 k mesh is employed. The atomic positions are fully relaxed until the force on each atom is less than 0.02 eV.Å⁻¹.

Results and Discussion

Atomically resolved constant current STM micrograph acquired at RT on the bare WS_2 surface is shown in Fig.1. Fig.1(a) shows a large scale STM image of the UHV cleaved WS_2 surface, whereas, Fig.1(b) shows an atomically resolved surface of the WS_2 crystal. Fig. 1(a) shows flat surface with few dark spots, a typical signature of the TMD crystal surface. We do not find any signature of contaminants or foreign adsorbed species in the STM micrographs shown in Fig.1. Bare WS_2 in the atomic scale exhibits clear honeycomb lattice structure with lattice constant of approximately 0.34 nm [5] as can be seen in Fig.1(b). We assign the bright protrusions in the STM micrograph [Fig.1(b)] as the S atoms [5].



Fig.1. STM images of (a) large scale bare WS_2 , (b) atomically resolved WS_2 surface with a lattice constant of 0.34 nm.

The constant current STS measurement carried out on the WS₂ surface is shown in Fig. 2. Fig.2 shows an average dI/dV spectrum which was obtained by averaging around 10 individual dI/dV spectra obtained at different points on the bare WS₂ surface with the feedback loop off and at constant height mode by ramping the bias voltage from -1.5 V to +1.5 V. The dI/dV measurements were carried out using a lock-in amplifier with modulation voltage 4 mv. STS investigations reveal signature of many states (shown by arrows in Fig.2) at the two sides of the Fermi energy and a bandgap of around 1.34 eV [Fig.2]. DFT calculations were carried out considering the bulk unit cell for bare WS₂.



Fig. 2. Typical dI/dV vs. voltage (V) spectrum obtained from bare WS₂ surface.

The relaxed bulk WS₂ (lattice parameter a=3.18 Å) structure is shown in Fig.3 [Fig.3 (a) and (b) side and top view respectively]. Fig.4 depicts the band structure and DOS of bulk WS₂. We get an indirect bandgap of ~1.38 eV with valence band (VB) maxima at the Γ point and conduction band (CB) minima between the K- Γ line [Fig.4(a)]. Partial density of states (PDOS) calculations [Fig.4(b)] reveal mainly the S *p* and W *d* states which spread over in the VB and CB.



(a) 3 (b) 3 (c) 3 (c) 4 (c

Fig.4. Band structure and density of states of WS₂

Conclusion

In-situ STS studies and DFT calculations carried out on the mechanically exfoliated WS₂ under UHV conditions reveal the bulk bandgap which is 1.34 eV according to the STS measurements and 1.38 eV as per DFT calculations. The calculations reveal a bulk indirect bandgap with VB maxima at the Γ point and CB minima between the K- Γ points. PDOS calculations show various S *p* and W *d* states within the VB and CB that can be correlated with the STS data shown in Fig.2.

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Fig. 3. Relaxed structure of bulk WS₂.

(ZnO)₆₀: An UV active magic nanocluster under DFT study

Bijal R. Mehta¹, Esha V. Shah¹, and Debesh R. Roy¹

¹Materials and Biophysics Group, Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat 395007, India

*Corresponding author: drr@phy.svnit.ac.in

Abstract

The minimized energy geometries of $(ZnO)_{6n}$ (n= 8 to 11) clusters were optimized using a systematic density functional theory. In addition to our previously identified magic nanocluster ($(ZnO)_{42}$, the present work reports a novel ultraviolet active magic nanocluster ($(ZnO)_{60}$. ($ZnO)_{60}$) identify as exceptionally stable 'magic' nanocluster upon investigation on the electronic properties of ($ZnO)_{6n}$ nanoclusters in terms of the HOMO-LUMO gap (HLG), ionization potential (IP), electron affinity (EA), chemical hardness (η), electrophilicity index (ω) and energy gain (ΔE). Interestingly, as the n value increases in the multiple of six, the electronic properties energy gain (ΔE) of ZnO clusters demonstrate a zigzag pattern, identifying 'magic' ($ZnO)_{60}$. Furthermore, the optical absorption spectra analysis show ($ZnO)_{60}$ is active in the UV-A region. The developed magic nanocluster in the present work is expected to find useful applications as quantum dots and cluster assembled materials in semiconductor and optoelectronics domains.

Prediction of Intrinsic Spin Half-Metallicity and Ferromagnetism of Co-based Full Heusler Alloys: Hunt for Spintronic Applicability

Ashwani Kumar^{1,*}, Shakeel Ahmad Sofi², Tarun Chandel³ and Naveen Thakur¹

¹Department of Physics, Career Point University, Hamirpur -176041, INDIA ²Condensed Matter Theory Group, School of Studies in Physics, Jiwaji University, Gwalior – 474011, INDIA

³Department of Physics, Abhilashi PG Institute of Sciences, Mandi-175008, INDIA

*Corresponding author: ashwani.bits05@gmail.com

Abstract

The computational methods are reliable in predicting the ground state as well as other properties of a material. There have been abundant endeavors to configure the high spin-polarized materials for controlling the spin electron to renovate conventional electronics. In the light of current investigation, the structural stability as well as magneto-electronic properties of Co-based Heusler alloys has been examined. The structural optimization signifies that both the materials are most stable in the ferromagnetic phase. The present Heusler alloys deliver half metallic performance conveys 100% spin polarization at Femi level. The source of carrying magnetism generates predominantly from half-filled *d*-orbitals of the present set of Co-based Heusler compounds. The present set of Co-based Heusler materials reflects good performance in spintronics applications.

Introduction

The Full Heusler materials illustrate by chemical configuration X₂YZ in their respective stoichiometric ratios delivering L21 and C1b structures. These alloys are predicted with their competence of exhibiting high Curie temperature demonstrating robust ferromagnetic nature [1]. Half-metallic ferromagnetic materials deliver a momentous intuition predominately for the researchers and industrialists due to recent advancements in numerous fields including robust spin-polarization, outstanding band occupations, thermophysical electronic properties, and shape-memory effects established in various bids comprising of spin filters, GMR, shape memory effects [2]. Therefore, electronics based on spin system are anticipated to deliver active and dynamic developments mostly in the fields comprising of information technology. HMF materials exhibits 100% spin polarization assumed the proficiency of instruments based on spin content [3]. Using this momentous approach, we present the magneto-electronic as well as structural properties of Co-based Heusler materials by DFT calculations.

Computational Details

The Density functional theory is treated as the characteristic and successful tool predominately used for the examination of numerous properties in solid state materials. The effect of exchange and correlation for electronic band profile were executed within the framework Wien2k simulation code of vital techniques like the PBE-GGA approximation. The separation in between core as well as valence states is approx. 7.0 Ry. A dense mesh of 1500 *k*-points is being caste-off for the Brillouin zone integration through the tetrahedron framework.

Results and Discussion

The structural property for а material demonstrates the momentous characteristic clarification of the atomic alignment at their respective locations. The settlement in unit cell of atoms for Co-based alloys in both configuration structures via Hg₂CuTi (space group #216) and Cu₂MnAl holding space group (#225) and is illustrated in Fig. 1. In the present set of materials, the Co atoms exhibits the Cu₂MnAl prototype structure.



Fig. 1. Unit cell configuration of Co_2YZ in (b) the Cu_2MnAl and (a) the Hg₂CuTi prototype structure Co_2YZ Heusler materials, as Co occupies X position.

To figure out the interpretations on structural stability, we precisely estimate the ground state for the present set of alloys using Murnaghan's equation. The optimization of structural unit cell is executed in numerous optimization structures to configure its stability criteria. The Co-based alloys reveal the minimum energy in Fm-3m symmetry possessing ferromagnetic performance as clarified in optimized curves and are presented in Fig. 2. The various

typical properties linked with these materials are placed in Table 1.



Fig. 2. The optimization plots of Co₂YZ Heusler materials.

Table 1. The calculated equilibrium lattice constant a_0 (Å), bulk modulus B_0 (GPa), its pressure derivative B' and energy E_0 (Ry) for Co₂YZ Heusler alloys in both ferromagnetic and paramagnetic phases.

Alloys	Magnetic	a ₀ (Å)	B _o (GPa)	B	E _o (Ry)
	Phases				
Co VCh	PM State	6.43	126.55	4.84	-25311.6748
$C0_2 I S0$	FM State	6.47	119.83	4.65	-25311.6981
Ca.VD:	PM State	6.56	106.27	4.65	-55508.4366
C02 I B1	FM State	6.61	99.69	4.61	-55508.4622

The electronic band occupation of a typical material is tremendously necessary for the application-based perception. In the present work we have explored the band profile of Co-based materials through numerous functionals to elucidate the typical electronic performance. The band gap appearance of halfmetallicity in these alloys typically instigated from dd hybridization of atoms. The energy difference on different states is lifted typically from Fermi level promotes a wide range band gap there. The band occupation of half-metallic Co-based materials is illustrated in Fig. 3. Half metallic materials deliver metallic performance in one spin and rest other spin exhibits semiconducting performance conveys 100% spin polarization at Femi level. These typical materials demonstrate significant properties predominately in spintronics etc. The graphical interpretation of density of states exhibited in Fig. 4 delivers the unevenness in spin down configuration and spin up alignment i.e., asymmetric performance on Co-states, that demonstrates the origin of magnetism. Furthermore, the analysis of DOS demonstrated the hybridization between *d*-orbitals typically for group III as well as IV elements of Co and Y that presents prominent performance. From the interpretations of DOS plots the peaks get intensifying and give rise to magnetism of the materials. The difference in energy in between hybrid as well as non-hybrid functionals becomes the ground breakthrough of making energy gaps in both alignments. Therefore, the inclusive band profile as well as DOS reflects that *d-d* hybridization is maintained in these materials. Materials magnetism is momentous based on application perception. The distinct role of atom as well as total magnetic moment is displayed in Table 2 of Co_2 -based Heusler materials. The source of carrying high magnetism generates predominantly from half-filled *d*-orbitals of the present set of Co-based Heusler compounds.



Fig. 3. Band profile of Co₂YZ Heuslers materials along high-symmetry Brillion zone.



Fig. 4. DOS plots for Co₂YX Heuslers compounds.

Table 2. Total magnetic moment (M_{tot} in μ_B) per unit cell, local magnetic moment, magnetic moment in the interstitial region, and of each atom for Co₂YZ Heusler materials

Alloys	Magnetic moment (µB)				
	Co	Y	Ζ	Interstitial	Total
Co ₂ YSb	1.16	-0.10	0.00	-0.23	1.99
Co ₂ YBi	1.14	-0.09	0.00	0.19	1.99

Conclusions

By successful forecasts from *ab-inito* calculations we deliver a reliable investigation which precisely forecasts the magnet-electronic and structural stability of Co₂YZ Heusler materials. The unit cell configuration of Co2YZ exhibits the Cu2MnAl prototype structure rather than the Hg₂CuTi-type. The depiction of band occupation as well as density of states illustrates the half-metallic performance of the present set of materials. The source of carrying magnetism generates predominantly from half-filled d-orbitals of the present set of Co-based Heusler compounds. The present set of Co-based Heusler materials reflect good performance in GMR, spintronics as well as spin injection-based applications.

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Modelling the reactivity of Entrectinib and evaluation of its potential anticancer activity using Molecular Docking approach

Shradha Lakhera^{1*}, Meenakshi Rana¹, Kamal Devlal¹

¹Department of Physics, School of Sciences, Uttarakhand Open University,

Haldwani, 263139, Uttarakhand, India

*Corresponding author: shradhalakhera6025@gmail.com

Abstract

Hepatocellular carcinoma (HCC) leads to approximately 80% deaths due to cancer worldwide. Hence a proper drug is necessary to fight against it in initial stages. In this paper, we have reported the spectral reactivity and stability of the Entrectinib (ENC) molecule with the help of Density functional theory. Molecular docking is also performed for ENC with vascular endothelial growth factor (VEGF-2) to report the mechanism of ENC as an anticancer candidate. Chemical reactivity and good docking scores are obtained for ENC system, which suggests that the molecule is chemically stable and can be used as a potent druglike molecule against various HCC drug receptors.

Keywords: Entrectinib; Mulliken charges; Density functional theory; Molecular docking

1. Introduction

Hepatocellular carcinoma (HCC) is the most common type of primary liver cancer which is often developed among the people with liver disorders or suffering from hepatitis [1]. Several signaling pathways involved with HCC have become a major source of targets [2]. In the present work, we had taken vascular endothelial growth factor receptor (VEGFR-2) that is an important signaling protein [3]. VEGFR-2 is an essential tyrosine kinase propagating receptor protein that contributes in angiogenesis [3]. Due to its involvement in formation of new blood vessels, VEGFR-2 has attained a position in the field of novel drug discovery [4].

Entrectinib (ENC) is a known drug for ROS1positive non-small cell lung cancer and NTRK fusion-positive solid tumors [5]. In the present study, we had done a drug repurposing for reporting the complex stability of ENC with VEGFR.

2. Computational tools and methods

The molecule of ENC was optimized to the ground state with the help of software "Gaussian 09" and analyzed by "Gauss view 5.0.8". We had downloaded the structure of ENC from online database "PubChem". The crystal structure of VEGFR-2 (PDB ID- 2OH4) with a benzimidazoleurea inhibitor (Resolution: 2.05 Å) had been downloaded from "Protein data bank". The FMO parameters like ionization potential (IP), electron affinity (EA), chemical potential (CP). electronegativity (χ), hardness (η), and softness (S) were calculated with the help of Koopmans' theorem to explain the chemical reactivity and stability of the molecule [6,7]. The software "AutoDock Vina" was used for performing the molecular docking. The results obtained from docking of the ENC with

20H4 were analyzed with the help of software "Biovia Discovery Studio Visualizer"

3. Results and Discussion

3.1 Structure and charge analysis

The molecule of ENC has huge four membered structure consisting of three benzene rings and fluorine atoms bonded with benzene ring, and nitrogen atoms associated to amino group. The optimized structure of ENC has 2.35Debye dipole moment and -51165.9eV electrostatic potential energy that shows the molecule possesses intramolecular interactions.



Fig.1. (a) Mulliken charge distribution graph of ENC. Inset of Fig. 1 represents Mulliken charge distribution of C atoms of ENC molecule, **(b)** Molecular electrostatic potential surface of ENC.

However, the charge distribution of the compound shows the positive charge impact of H atoms and negative charge impact of N, O and F atoms. The Mulliken charge graph (Fig.1. (a)) show the possibility of charge transfer within the molecule. The C atoms present in the molecule shows rapid change in the polarity of the charge (Fig.1. (b)). The 33C atom show the highest negative charge of -0.561e and 28C atom possesses the highest positive charge of 0.551e. This variation in the polarity of the charges shows the high reactivity of the molecule.

3.2 Chemical reactivity

The Highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) energies are reported as -5.392eV and -1.262eV. The gap between the LUMO and HOMO energies is 4.130eV which is quite low. This shows the high charge transfer between the orbitals. The IP (5.392eV) and EA (1.262eV) values describes the high reactivity of the molecule. CP gives the value -3.32eV that represent the stability of the probe molecule. The value of χ (3.327eV) is computed as average of IP and EA. It shows the interaction of the electrons and functional group. The value of *S* (0.484eV) and η (2.065eV) shows that the compound has high hardness.

3.3 Molecular electrostatic potential (MEP) analysis

The molecule's capability to possess intramolecular charge transfer is reported by MEP analysis (Fig 1. (b)). The red part of the MEP indicated the electrophilic sites of the molecule caused by O atom. The blue region indicates the nucleophilic part caused by the N atoms. The free electrons from the nitrogen atoms are accepted by oxygen atoms. This shows the possibility of charge sharing from nucleophilic to electrophilic part of the molecule.

3.4 UV-Vis analysis

The UV-Vis spectra of the ENC molecule was represented by a broad absorption band between 250 to 450nm (Fig.2. (a)). The peak shows the availability of the π - π^* and n- π^* electronic transitions within the molecule. The transitions with maximum wavelength are shown by the transitions from S_0 state to excited states S_1 , S_2 , and S_3 . The transition $S_0 \rightarrow S_1$ occurs with the maximum wavelength of 333.95nm and oscillator strength (f) 0.1675. The wavelength of 301.51nm s observed for transition $S_0 \rightarrow S_2$ in which the *f* is 0.2491. The value of f for transition $S_0 \rightarrow S_3$ is observed as 0.0018 at 295.51nm wavelength. These types of transitions assure that the molecule possesses the intramolecular transitions between the lone pair (n) electrons and the π electrons. The more the intramolecular interactions, more will be the stability of the molecule.

3.5 Molecular Docking results analysis

Molecular docking of the ENC molecule with VEGFR-2 protein give nine sites where ligand get bonded with the protein. The number of H-bonds enhances the protein-ligand interactions and shows the best binding between the protein and ligand. Thus, more the number of H-bonds in the complex, more stable will be the binding between the receptor and inhibitor. The fourth pose have six H-bonds associated that is the maximum among all the other poses, therefore the fourth pose with binding affinity -9kcal/mol is selected as the best pose of the protein-

ligand complex. The binding mode of fourth pose of protein-ligand complex of the ENC with VEGFR-2 is shown in Fig. 2(b).



Fig.2. (a) UV-Vis absorption spectra of ENC molecule with transition levels and oscillator strength. **(b)** Donor-acceptor interactions obtained by docking of ENC with VEGFR-2. Inset of Figure 1 represent 2D view of protein-ligand interaction showing conventional (dark green), and carbon (light green) H-bonds.

4. Conclusion

The high values of dipole moment and electrostatic potential energy of the molecule shows the good molecular stability. The values of FMO orbital energies shows the low energy gap by that shows the stability of the molecule. The optimized structure of ENC gives high values for EA and IP that shows the high chemical reactivity of the molecule. The chemical potentiality of the molecule is justified by the high value of its CP. The high value of η denotes the high rigidness or hardness of the molecule. The availability of the electrophilic and nucleophilic part suggests that the molecule is reactive towards the protein. The UV-Vis spectra of the molecule shows that the molecule shows electronic stability. This also shows that the molecule of ENC is a highly conjugated and stable molecule. The potentiality of the ENC molecule is better justified with the help of docking. The binding score obtained by docking ENC with VEGFR-2 is -9kcal/mol which shows that the molecule of ENC binds finely with VEGFR-2 giving a stable complex. The present work validates the possibility of ENC being chemically active and possesses strong candidature to be used as a druglike molecule against different HCC diseases.

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Investigation of Nonlinear Optical Response of Organic Compound Pyrrolidine-2,5-dione Shradha Lakhera¹, Meenakshi Rana^{1*}, Kamal Devlal¹

¹Department of Physics, School of Sciences, Uttarakhand Open University,

Haldwani, 263139, Uttarakhand, India

*Corresponding author: mrana@uou.ac.in

Abstract

In the present work, the computational investigation has been done for detecting NLO responses of Pyrrolidine-2,5-dione (P2D). The structure of P2D is optimized to ground state energy level by B3LYP/6-311G basis set using density functional theory (DFT). Optimized geometry is used for determining the Mulliken charges, and molecular electrostatic potential (MEP) surface. Frontier molecular orbitals (FMO), spectral behavior and the high value of dipole moment (μ_{total}), polarizability (α) and first order hyperpolarizability (β) shows the high polarizabile nature of P2D.

Keywords: Nonlinear optical material; Pyrrolidine-2,5-dione; Mulliken charges; Polarizability density functional theory

1. Introduction

The nonlinear optical (NLO) materials are the materials that show the modified behavior of the field under the externally applied field [1]. These materials show π -conjugation in alternate single and double bonds in aromatic rings present in their structures [2,3]. NLO materials are in high demand due to their wide multidisciplinary applications in engineering in the mechanical field as well as in chemical and biological sciences [4].

Pyrrolidine is one such organic compound having conjugation between the bonds hence, it might show the NLO response [5]. Pyrrolidine-2,5-dione (P2D) is a five-membered compound having four carbon and one nitrogen atom [6]. It is a heteromonocyclic derivative of Pyrrolidine having wide applications in pharmaceutical raw material, preparation of drugs, rubber accelerators and inhibitors, and epoxy resin curing agents [7]. The computational analysis of NLO properties of P2D have been reported in this work. Mulliken charge analysis, frontier molecular orbitals (FMO), molecular electrostatic potential (MEP), and spectral analysis (UV-Vis, FTIR, Raman), dipole moment (μ_{total}), polarizability (α) and hyperpolarizabilities (β) are computed to get idea about NLO responses of the compound.

2. Computational tools and methods

The structure is optimized to the ground state with the help of software "Gaussian 09" and analyzed by "Gauss view 5.0.8" [8]. Spectral calculations like a Raman, FTIR and FMO are further calculated with the help of optimized geometry. These energies are used to calculate ionization potential (IP), energy gap (ΔE), electron affinity (EA), chemical potential (CP), and electronegativity (χ). These parameters are calculated with the help of Koopman's equations [9,10]. Polarizability parameters α and β are also calculated to check the NLO response of P2D.

3. Results and Discussion 3.1 Structure and charge analysis

Optimized structure (Inset of Figure 1) of P2D have an aromatic ring having two carbonyl (C=O) group and one nitro (NO₂) group. P2D have electrostatic potential energy equal to 15376.01 eV, which is the representation of intramolecular interactions of the molecule [10]. High value of dipole moment (5.97Debye) suggests that compound have high intramolecular interactions. These intramolecular interactions lead to high polarizability of the probe molecule. More the molecule is polarizable, more it will respond to NLO properties.

The mulliken charge distribution of the P2D (Figure 1) shows the positive charge contribution of hydrogen (H) atoms and negative charge contribution of oxygen (O), nitrogen (N) and carbon (C) atoms. Charge analysis of P2D suggests that 9C and 10C are the carbon atoms associated to C=O group shows maximum positive charge of 0.593e and 0.592e respectively.



Fig. 1. Mulliken charge distribution graph of P2D. Inset of Figure 1 represent Optimized structure of P2D.

The oxygen atoms associated to C=O groups (10 and 20) shows negative charge (-0.30 each) impact on the functional group. However, the 6N atoms of NO₂ group shows 0.318e positive charge (Figure 1). A huge charge variation between the functional groups within the compound shows the possibility of

intramolecular charge transfer (ICT) in the system. **3.2 Chemical reactivity**

Chemical reactivity of the molecule is determined by FMO energies. For P2D, values of HOMO and LUMO energies are -8.38eV and -3.48eV respectively and the value of energy gap (ΔE) is 4.90eV. Lower the ΔE , higher will be chances of ICT interactions. Lower ΔE valued compounds are considered chemically reactive and optically polarizable. Negative of HOMO and LUMO energies gives us values of IP (8.38eV) and EA (3.48eV) respectively. CP is the average of E_{LUMO} and E_{HOMO} , value of CP is calculated as -5.93eV. χ is calculated as average of IP and EA and for our molecule, value of χ is reported as 5.93eV. It represents the interaction of electron cloud present towards the functional groups present in the molecule. All these parameters are considered as global reactivity descriptors and helps us to get idea about reactivity and stability of the molecule.

3.4 Molecular electrostatic potential (MEP) analysis

MEP analysis helps in identifying the reactive sites and charge transfer within the molecule. The blue region shown in MEP indicates electrophilic attack site that is caused due to presence of carbon atoms (Figure 2 a). Red region indicates the nucleophilic site and charge cloud (Figure 2 a). These regions show the charge transfer within the molecule. In MEP of P2D green color is not present. This conclude that, the major part of the molecule participates in charge transfer. The more the charge transfer is, more will be the ICT within the molecule.



Fig. 2. a) MEP surface of P2D. b) UV-Vis absorption spectra of P2D molecule.

3.5 Vibrational analysis

High value of Raman intensity leads to high polarizability and vibrational stability of the molecule [10]. The peak at wavelength 1539 nm correspond to v_{N-O} and v_{C-O} mode is found at 1728cm⁻¹ (Table 1). v_{C-H} possesses maximum value of Raman intensity (786.03cm⁻¹). The high values of Raman intensity shows the high extend of the bond conjugation within the molecule and hence, high NLO behaviour.

Table 1: Computed Raman and FTIR data fo	r P2D.
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Modes	Frequency	IR	Raman	Raman
			activity	intensity
VNO	1539.38	180.63	3.7048	126.20
v _{co}	1728.93	578.84	0.4468	91.28
V _{CH}	3069.65	0.0112	210.147	786.03
V _{CH}	3118.23	2.648	93.0489	326.40

3.6 UV-Vis analysis

For the probe system, the transition $S_0 \rightarrow S_1$ is observed at the highest wavelength 347.05nm with oscillator frequency 0.0018. The transition $S_0 \rightarrow S_2$ have oscillator strength (*f*) 0.0125 at wavelength 314.46nm (Figure 2 b). The value of *f* for transition $S_0 \rightarrow S_3$ is observed as 0.0018 at 305.80nm wavelength (Figure 2 b). These transitions show the high intramolecular interactions between the lone pair (n) electrons and the π electron. These type of interaction makes the system unstable and hence enhances the possibility of ICT.

3.7 NLO analysis

For the detection of NLO response of P2D, we have computed μ_{total} , α , and β and compared the results with known organic NLO material urea. The value of μ_{total} for P2D is computed as 2.35Debye that is higher than that of Urea (1.52 Debye). The polarizability parameters like mean isotropic polarizability (α) and anisotropy of polarizability ($\Delta \alpha$) can be calculated as 9.88×10^{-24} esu and 19.94×10^{-24} esu respectively. These values for P2D are much higher than α (5.66×10^{-24} esu) and $\Delta \alpha$ (6.30×10^{-24} esu) values of Urea. The value of β for P2D is 1.536×10^{-30} esu, which is more than β value of Urea (0.781×10^{-30} esu). These values indicate the high polarizability of P2D and validates the NLO behavior of P2D.

4. Conclusion

High value of dipole moment, chemical reactivity parameters show the better chemical reactivity of the probe molecule. The obtained high values of Raman intensity and availability of π - π * and n- π * electronic transitions in P2D shows its reactive nature. Along this, the observed high value of α and β represent the polarizable nature of the molecule. All these observations validate the strong potential candidature of P2D as an NLO material.

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Structural and Electronics properties of the RhFeSi Compound under different Approaches

Dipangkar Kalita^{*}, Nihal Limbu, Mahesh Ram and Atul Saxena

Department of Physics, North-Eastern Hill University, Shillong, 793022, India

*Corresponding author: dipangkarnehu@gmail.com

Abstract

Investigation of the structural and electronic properties of the RuFeSi has been performed using the first principle calculations. The optimized lattice parameters of the system corresponding to the ground state has been determined using the Murnaghan's equation of states. The positive phonon dispersion predicts the dynamical stability of the alloy. To account for the highly correlated valence electrons, an onsite Coulomb interaction (U) is included in local density approximation (LDA) and generalized gradient approximation (GGA) as LDA+U and GGA+U, respectively. Within LDA+U and GGA+U schemes, the title material reflects half-metallic behavior with a band gap of 0.81 eV under both the schemes.

Introduction

Spintronics is an area that is developed from the half-metals which use the spin of the electron. In 1983, de. Groot et al. were the first to predict the half metallicity in half Heusler MnNiSb compound using the first principle calculations which later find applications in the field of spintronics, especially in spin-transfer torque, giant magnetoresistance (GMR), magnetic random access memory (MRAM), etc. [1]. After that, researchers were fascinated to explore these Heusler compounds using the first principle calculations. Ma et al. [2] investigated around 378 half-Heusler alloys, including RhFeSi compound using the generalized gradient approximation (GGA) for the possibility of application in spintronics, where the RhFeSi compound in particular reflected the near half-metallic behavior. A similar approach has been used by Meenakshi et al. [3] to study the RhFeZ (Z=P, As, Sb, Sn, Si, Ge, Ga, In, Al) compounds using FP-LAPW method. The title material possesses highly correlated d orbitals and hence exchange correlation like LDA and GGA falls to predict the ground state and other physical properties accurately.

Hence, in this paper, we have explored the structural and electronic properties of the sample material incorporating the U value along with LDA and GGA schemes.

Computational details

The structural and electronic properties of the title material were explored using the plane-wave pseudopotential method as implemented in the Quantum ESPRESSO package [4]. Two different correlation functionals like LDA, and GGA, along with incorporation of Hubbard correction term (U), LDA+U and GGA+U were used. The cutoff energy for

the expansion of wave function was chosen to be 75 Ry and for the charge density cutoff 750 Ry. A Monkhorst-Pack grid of $10 \times 10 \times 10$ k-points sampling were taken for the integration in the first Brillouin Zone (BZ). *U* for the Rh and Fe compounds were found to be 2.00 eV and 2.50 eV, respectively. The convergence thresholds for the self-consistent field calculation were set at 10^{-10} Ry.



Fig. 1. Phonon dispersion curve of RhFeSi.

Results and discussion

The RhFeSi compound condensed in C1_b-type FCC cubic crystal ($F\bar{4}3m$, Group No. 216) with the Ru, Fe and Si atoms located at 4c (1/4, 1/4, 1/4), 4b (1/2, 1/2, 1/2) and 4a (0, 0, 0) sites respectively. The estimated equilibrium lattice parameter (a_0) of the studied compounds were found to be 5.564 Å, 5.586 Å, 5.680 Å and 5.706 Å with LDA, LDA+U, GGA and GGA+U respectively. Our result is in close agreement with the theoretical results [2,3] under GGA approach. Since the studied compound is a hypothetical material, we investigated the phonon dispersion curve for determining the stability of the material. The positive

Phonon frequency indicates the dynamical stability of the compound in cubic phase. Title material consists of three acoustics and six optical branches in the phonon dispersion curve. A clear optical phonon gap of 79.6 cm⁻¹ was observed at *K*-*W* direction. No phonon band gap was noticed, since the upper acoustic and lower optical modes overlaps with each other.

The electronic structure of a specimen is a fundamental property that determines the potential of a compound as a material in spintronic devices. In LDA and GGA, the material under investigation reveals a metallic and nearly half-metallic character respectively. Whereas under the LDA+U and GGA+U approaches, E_F shifts towards the valence region which results in the HM character of the studied compound. The inclusion of the U value in the LDA and GGA scheme mainly affects the Fe element near the E_F .



Fig. 2. Energy Bands structure (a) LDA+U (insert LDA) and (b) GGA+U (insert GGA).



Fig. 3. Total and partial density of states (a) LDA+U (insert LDA) and (b) GGA+U (insert GGA).

To better understand the mechanism behind the formation of bands, we studied the total and partial density of states (DOS) in Fig 3. Both DOS and bands reveal a similar profile. In DOS, the observed peaks are due to the flat bands of the corresponding energy bands (Fig. 2). In the Partial DOS, it is noticed that the gap is mainly due to the *d*-*d* hybridization between Rh and Fe atoms. The band gaps are found to be 0.81 eV from both LDA+U and GGA+U, respectively which gives the semiconducting nature in the minority channel. The GGA+U scheme gives more accurate

results as compared to the LDA+U scheme. Under the LDA+U and GGA+U approximations, the material shows 100% spin polarization due to the presence of a spin-up channel at E_F . The total magnetic moment (M_{T}) of the sample material can be calculated using the 18 Slater Pauling (SP) rule. The valence electron of the sample material is 21; thus, the expected value of M_T is $3\mu_B$. In table 1, we show that the material follows this rule under the inclusion of U value under both the approximations where the partial magnetic moment of Fe atom contributes more towards the M_T value. The individual magnetic moment of the Rh and Fe are aligned in the same direction which reflects the ferromagnetic behavior of the studied compound. It is also noticed that the magnetic behavior marks out in the total and partial DOS of the studied materials.

Table 1. Total and individual magnetic moment per formula unit (in μ_B) of the studied compound.

Scheme	M_T	Rh	Fe	Si
LDA	2.82	0.268	2.557	-0.035
LDA+U	3.00	0.243	2.858	-0.077
GGA	3.00	0.257	2.878	-0.07
GGA+U	3.00	0.198	3.058	-0.122

Conclusion

We presented the material's structural, dynamical, electronic and magnetic properties, which were investigated by the different approaches. The effect of the inclusion of Hubbard correction term (U) on the LDA and GGA formalisms was also investigated. The positive phonon dispersion curve gives the structural stability of the sample material in the cubic phase. In the LDA+U and GGA+U formalisms, the material reveals half-metallic behavior with band gap of 0.81 eV. The half-metallicity is further demonstrated by an integral value of total magnetic moment (3.0 μ_B).

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Structural, Electronic and Magnetic Properties of Three Filled Skutterudites Nd_xSm_{1-x}Fe₄Sb₁₂ (x =1, 0.5 and 0)

Tanmay Chaki and Pradip Kumar Mandal

Department of Physics, University of North Bengal, Siliguri -734013, WB

*Corresponding author: mandalpk.phys@nbu.ac.in

Abstract

Structural, electronic and magnetic properties of three filled skutterudites NdFe₄Sb₁₂, Nd_{0.5}Sm_{0.5}Fe₄Sb₁₂ and SmFe₄Sb₁₂ have been studied using density functional theory. Optimized lattice constants are found to be 8.9673 Å, 9.1564 Å and 9.1461 Å respectively. The electronic band structure and DOS show the half metallic behaviour of the doped material with effective magnetic moment of 6.00 μ_B whereas the two pure systems exhibit metallic and weakly ferromagnetic nature.

Introduction

Filled skutterudites are a class of compounds which exhibit properties ranging from ferromagnetic to thermoelectric [1] due to the diverse combinations of the filler atoms situated in the cage formed by different transition metals and pnictogens viz., AB_4C_{12} (A=Alkali metals/Lanthanides etc, B= Transition metals, C= pnictogens). To see the change in structural, electronic and magnetic behavior due to half and full substitution of ${}^{60}Nd$ (4f⁴) by ${}^{62}Sm$ (4f⁶), a heavier atom with more number of magnetic electrons, in NdFe₄Sb₁₂, we have investigated three compounds $Nd_xSm_{1-x}Fe_4Sb_{12}$ (for x= 1, 0.5 and 0) using density functional theory. Further, Sm doping is expected to increase the thermoelectric performance since heavy filler atoms will reduce the lattice thermal conductivity.

Computational Details

The calculations were done by full potential augmented plane wave (FP-LAPW) method based on density functional theory (DFT) implemented in Wien2k code [2], generalized gradient approximation of the Perdew–Burke–Ernzerhof scheme (PBE-GGA) was used as exchange correlation potential. For doping, we replaced only the center or all the Nd atoms by Sm in a $2 \times 2 \times 2$ supercell of NdFe₄Sb₁₂. 2.5, 2.5, 2.2 and 2.0 a.u. for Nd, Sm, Fe and Sb respectively as R_{MT} values, k mesh of 5000 k points and the energy convergence criteria of 10⁻⁴ Ry were chosen.

Results and Discussion

 $\begin{array}{cccc} The & pure & skutterudites & NdFe_4Sb_{12} & and \\ SmRu_4Sb_{12} & crystallize & in & bcc & structure & with & {\it Im-3} \\ space & group & while & for & Nd_{0.5}Sm_{0.5}Fe_4Sb_{12} & the & space \\ \end{array}$



Fig 1. Unit cell structure of (a) RFe_4Sb_{12} (R = Nd, Sm), where R, Fe, and Sb are denoted by blue, red, and yellow spheres, respectively, and (b) doped filled skutterudites (Nd_{0.5}Sm_{0.5}Fe₄Sb₁₂).

group reduced to Pm-3, their structures are shown in figure 1. Volume optimization resulted in $a_0 = 9.1564$ Å in the half doped system which is larger than the optimized lattice constants of NdFe₄Sb₁₂ (8.9673 Å) and SmFe₄Sb₁₂ (9.1461 Å), larger dimension of Sm may be the reason for this increment. To show the distribution of electrons and holes in the Fermi energy level (E_F) we have analyzed the energy band diagram along the high symmetry points of the Brillouin zone. The band structures of NdFe₄Sb₁₂ and SmRu₄Sb₁₂ are similar in nature. E_F is well inside the top of the valance band in the up spin channel whereas in the down spin channel very few bands cross the Fermi level indicating their metallic behavior as reported earlier [3]. From the DOS plots we could identify the contributions of electronic states of different atoms. The peaks in the spin up and down channels are mainly due to the f states of the filler atom highly hybridized with the *d* state of Fe. In the up spin channel the Fermi level is mainly populated by the strongly hybridized f state of the filler atom with Fe-d and Sb-s electronic states. In the down spin channel mainly Fe-d and Sb-s states are weakly hybridized with f states of the filler atom. From the splitting of DOS of the *f* states of the filler atoms in the both spin channels we conclude the ferromagnetic nature of these two materials.



Fig 2. Band structure of $Nd_{0.5}Sm_{0.5}Fe_4Sb_{12}$ (a) spin up (b) spin down.

When the center atom of NdFe₄Sb₁₂ is replaced by Sm resulting in Nd_{0.5}Sm_{0.5}Fe₄Sb₁₂ we got a distinct change in the band structure as shown in figure 2. In the spin up channel the Femi level is more populated than the pure materials due to the contribution of both the filler atoms and the valance bands move toward the conduction band. However, in the spin down channel, the valance bands move away from the conduction band resulting in a distinct band gap of 0.778 eV. In other words, for spin up channel the doped compound behaves as a metal while in spin down channel it behaves as a semiconductor, showing a half metallic behavior. The DOS plots (figure 3) clearly show its half metallic nature, with occupancy of 19.71 states/eV in the spin up channel and no occupancy in the spin down channel. At the Fermi level Sm atoms, having more *f*-electrons than Nd, contribute more in spin up channel, and are strongly hybridized with Fe-d electrons. Obviously, for spin down channel there is no contribution at the Fermi level. Presence of highly concentrated flat valence bands in spin up channel also suggests that the doped system may exhibit a high value of Seebeck coefficient, calculation is in progress.



Fig. 3 Total and Partial DOS.

The total magnetic moment of the pure compounds are $1.81 \ \mu_B$ (NdFe₄Sb₁₂) and $3.91 \ \mu_B$ (SmFe₄Sb₁₂) whereas in the doped compound it substantially increases to $6.00 \ \mu_B$ due to the higher

concentration of the 4*f* electrons of the center-doped filler atom Sm. The Fe atoms are ferromagnetically coupled with both the filler atoms Nd and Sm instead of the single filler atoms of the pure compounds. Thus the doped system is exhibiting stronger ferromagnetic nature. The integer value of magnetic moment confirms the half metallic nature. Ferromagnetic behavior of the pure compounds NdFe₄Sb₁₂ and SmFe₄Sb₁₂ was experimentally observed below 16.5K and 43 K respectively [4,5].

Conclusion

PBE-GGA based DFT calculations clearly suggest that complete replacement of the filler Nd atom by another heavier filler atom Sm does not produce any qualitative change in the band structure and magnetic behavior of NdFe₄Sb₁₂. Both the materials exhibit similar metallic behavior and weak ferromagnetic property. However, when only the center Nd atom is replaced by Sm the resulting the doped system Nd_{0.5}Sm_{0.5}Fe₄Sb₁₂ exhibits а completely different band structure in the spin up and down channels suggesting its half metallic character with band gap of 0.778 eV in spin down channel. It also shows strong ferromagnetic nature having the total magnetic moment of 6.00 μ_B , which is roughly three times and one-and-half times of the magnetic moments of the two pure compounds NdFe₄Sb₁₂ and SmFe₄Sb₁₂ respectively.

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Electron and phonon properties of α-Uranium from first principles simulations

Aditya Prasad Roy¹, Naini Bajaj¹, Ranjan Mittal², and Dipanshu Bansal¹

¹Department of Mechanical Engineering, Indian Institute of Technology Bombay, Mumbai, MH 400076, India ²Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai, MH 400085, India **Corresponding author: roy.aditya.aditya@iitb.ac.in*

Abstract

 α -Uranium displays Kohn anomaly in multiple phonon branches at charge density wave (CDW) wavevector \mathbf{q}_{CDW} above the CDW transition. The Kohn anomalies are reflected in calculated phonon dispersions as sudden dips and unstable phonon branch(es) at \mathbf{q}_{CDW} . As shown in literature for 2H-NbSe₂¹, increasing electron smearing (indirectly electron temperature) in density functional theory calculations can stabilize unstable phonons arising due to the Kohn anomalies. We perform first-principles simulations on α -Uranium with a similar approach to obtain stable phonon dispersion. However, we find that phonon branch(es) remain(s) unstable at \mathbf{q}_{CDW} . Moreover, we calculate electrical conductivity and Seebeck Coefficient due to electron-electron scattering within constant relaxation time approximation and compare with available experimental data.

Introduction

CDW is a periodic fluctuation of conduction electron density, resulting in a symmetry-breaking static distortion in low-dimensional electronic systems². CDW can be driven by Fermi surface nesting (FSN)³, hidden nesting⁴, wavevectordependent electron-phonon coupling¹, or strong correlations⁵. An archetypal CDW material, α -Uranium undergoes CDW transition on cooling below T_{CDW} ~43 K owing to Fermi surface topology that facilitates FSN and hidden nesting⁴. Hereafter we refer α -Uranium as α -U.

a-U stabilizes in an orthorhombic phase between 43-935 K⁶. On cooling below T_{CDW} , CDW transition is accompanied by displacement of U atoms along the *a*-axis occurs^{4, 6}. However, $\mathbf{q}_{CDW} = (q_x, q_y, q_z)$ remains incommensurate⁶. At 37 K, q_x locks in at 0.5 r.l.u. and unit cell is doubled along the *a*-axis. q_y and q_z lock below 22 K to a value of 1/6 and 5/27 r.l.u., respectively⁶.

Our previous study investigated electronic states near the Fermi level (E_F) and found that combined FSN and hidden nesting leads to multiple Kohnanomalies in phonon spectra at $\mathbf{q}_{\text{CDW}}^4$. However, we did not explore the role of electron smearing parameter and whether increasing smearing parameter will remove Kohn anomalies, as reported in literature for 2H-NbSe₂¹. Moreover, we did not study how nested electronic states may affect the transport properties. A detailed understanding of transport properties is necessary for Uranium fuel's safer use in reactors and storage thereafter⁶. In this work, we calculate phonon dispersions for various values of smearing parameter, and investigate electrical conductivity (σ) and Seebeck coefficient (S) as a function of temperature. Our calculated values of σ and S are consistent with experimental data⁶ and previous *ab-initio* study⁷.

Methods

First principles Calculations: Electronic structure simulations were performed in framework of density functional theory (DFT) as implemented in Quantum Espresso version 6.4 (QE)8. The projectoraugmented-wave potentials explicitly included 10 valence electrons for U $(6s^26p^67s^25f^36d^1)$ within generalized gradient approximation (GGA) in the Perdew-Burke-Ernzerhof (PBE) parametrization. We used a converged 12x12x10 Monkhorst-Pack electronic k-point mesh with a plane-wave cutoff energy $E_{Gcut} = 1768$ eV. The total energy converged to less than 1 meV/atom for both E_{Gcut} and smearing parameter. The convergence criteria for selfconsistent electronic loop was set to 10⁻⁸ eV. We relaxed experimental structure (Cmcm, space group no. 63)⁹ with a 2-atom primitive cell for different smearing (Methfessel-Paxton) until atomic forces were less than 1 meV/Å. Relaxed lattice parameters agrees well with experimental parameters (difference <1% for all axes). A Q-grid of 6x6x2 was used to calculate phonons in density functional perturbation theory (DFPT) framework as implemented in QE. Square of convergence threshold for phonons was 10⁻ 12

Maximally-Localized Wannier Functions (MLWFs): We used WANNIER90 $(v3.1.0)^{10}$ to calculate MLWFs on a 32 orbital basis (2, 6, 10, and 14 *s*, *p*, *d*, and *f* orbitals, respectively of two U atoms). Electron band structure using MLWFs is consistent with the direct DFT calculations. Using MLWFs, we solve

Boltzmann transport equation with BoltzWann¹¹ code within constant relaxation time approximation (RTA) on a converged *k*-mesh of 80x80x80. Electron-electron scattering time (τ) was kept constant at 10 fs.

Results and Discussions

Fig. 1(a) shows phonon dispersion of α -U along Γ - Σ_0 for a smearing of 0.2 eV. Here Γ and Σ_0 are (0, 0, 0) and (0.3075, 0.3075, 0), respectively, in primitive cell notation. As we showed in our earlier study⁴, Σ_4 (LO) branch is unstable at X (0.25, 0.25, 0) point (shown as negative phonon energies $E_{\Sigma 4}$), suggesting CDW instability in room temperature structure of α -U. A recent DFPT calculation¹ on another CDW material 2H-NbSe₂ showed that the Kohn anomaly disappears along [100] on increasing electronic smearing to 0.18 eV. We follow a similar procedure, as stable phonons will allow us to accurately calculate lattice thermal conductivity due to electron-phonon coupling and electron transport properties. Fig. 1(b) shows $E_{\Sigma 4}$ at X point on varying smearing from 0.2-1.3 eV, $E_{\Sigma4}$ increases from -5 to -3 meV at X point on increasing smearing from 0.2-1 eV; however, $E_{\Sigma4}$ decreases again above 1 eV.



Fig. 1. Phonon Dispersion of α -Uranium for (a) 0.2 eV (red) smearing, showing all phonon branches (branch nomenclature is same as Ref.[1]) (b) Change in phonon energy of Σ_4 (LO) branch on increasing electron smearing parameter from 0.2 to 1.3 eV.

As phonons are not stable, electron lifetime due to electron-phonon coupling cannot be accurately calculated; consequently, we calculate σ/τ and S considering electron-electron scattering only. We use electronic bands obtained with smearing of 0.2 eV to calculate MLWFs and subsequently compute transport properties. Within constant RTA, σ/τ and S are independent of τ and depend only on electronic band structure. Fig. 2(a) shows σ/τ as a function of temperature for three crystallographic directions. Our results agree well with literature⁷, which were calculated with BoltzTrap code on 2×2×2 supercell (16 atoms) with a 23×23×12 *k*-mesh. From our simulations, electrical resistivity along x, y, and zdirections (ρ_{100} , ρ_{010} , ρ_{001}) are 16.34, 15.48, 17.28 $\mu\Omega$ -cm, respectively at 280 K, whereas measurements⁶ at 273 K report $\rho_{100} \sim 34.7$ -39.4 $\mu\Omega$ -cm, $\rho_{010} \sim 20.6$ -25.5 $\mu\Omega$ -cm and $\rho_{001} \sim 26$ -30.3 $\mu\Omega$ -cm. Our simulated values of σ are in reasonable agreement but lower than measurements as they do not include scattering from electron-phonon coupling, defects, vacancies, and grain boundaries.. Fig. 2(b) shows S as a function of temperature. S increases with temperature along the *x* and *y* axes, but shows a dip near 500 K along the *z*-axis. To our knowledge, S values are not reported in literature for comparison.



Fig. 2. (a) (σ/τ) and (b) S as a function of temperature.

In conclusion, we presented first-principles calculations on α -U to stabilize phonons at \mathbf{q}_{CDW} by increasing electronic smearing from 0.2-1.3 eV. We observed a minimal dip at X point in the Σ_4 branch for smearing of 1 eV. However, the Kohn anomaly persists. Moreover, to capture the effect of nested electronic states in transport properties, we calculated σ/τ and S from 40-900 K, considering electron-electron scattering. Our predicted σ agrees reasonably well with literature values and provide data for a wide range of reactor fuel operating temperatures, notably at higher temperatures where the electronic component contributes significantly.

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Mn K-edge EXAFS studies of Co₂MnAl

Swati Pathak^{*1}, R. Rawat², S. Khalid³, and R. Bindu¹

¹School of Basics Sciences, Indian Institute of Technology Mandi, Kamand, Himachal Pradesh-175005, India ²UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452 017, India ³National Synchrotron Light Source-II, Brookhaven National Laboratory, Upton, New York 11973, USA

*Corresponding author: d18042@students.iitmandi.ac.in

Abstract

We have investigated the local structure around the Mn site in Co₂MnAl Heusler alloy using Mn K-edge Extended X-ray Absorption Spectroscopic (EXAFS) technique. The polycrystalline sample of Co₂MnAl was prepared by arc melting method and characterized by X-ray diffraction (XRD) and field dependent magnetic measurements. The XRD result shows that the compound stabilizes in B2 cubic structure with lattice parameter 5.76 Å. The field dependent magnetic measurement gives a saturation magnetic moment of 4.20 μ B/f.u. which is nearer to the expected value for the B2 phase. EXAFS analysis suggests the local environment around the Mn site is different from the global structure as revealed by XRD.

Introduction

Heusler alloys are interesting from the perspective of unusual band structure and properties like half metallicity, giant anomalous Hall effect, thermoelectric behaviour. superconductivity, effect. magnetic memory inverse shape magnetocaloric effect. etc. [1]. Intermetallic compounds with general formula X₂YZ are known as full Heusler alloys where X and Y are transition metals, Z is a p-block element [1]. The basic interest in studying Co based full Heusler alloys is due to its high T_c values (ranging from 95 to 1100 K), half metallic nature, giant anomalous Hall conductivity etc. thereby finding its application in the field of spintronics and opening new venues from the fundamental physics point of view [2]. Co₂MnAl is one such compound that exhibits above properties. Depending on the preparation conditions, this compound stabilize either in $L2_1$ (T_c = 726 K) or B2 $(T_c=677 \text{ K})$ phase [3] and is ferromagnetic in nature with a saturation magnetic moment around 4 μ_B/f . u. [4]. Band structure studies reveal that Co₂MnAl has 15% of spin polarization in $L2_1$ phase and 76% spin polarization in B2 phase which is usually not found in other Co based Heusler alloys [5].

In this work we have investigated the local structure of Co_2MnAl compound by EXAFS technique. In these kind of compounds, the break in the inversion symmetry and the time reversal symmetry plays significant role in the realisation of its unique band structure and physical properties. Considering this fact, the local structure information plays significant role. Keeping this in mind, we have performed the EXAFS experiment on Co_2MnAl sample at Mn K-edge.

Experimental Details

Polycrystalline sample of Co₂MnAl was prepared by arc melting technique in argon atmosphere by taking stoichiometric proportions of Co, Mn, Al metals. The XRD measurement was carried out by using 9 kW Rigaku smartlab X-ray diffractometer with Cu Ka radiation in the Bragg Brentano focusing geometry. The field dependent dc magnetization was carried out at 5 K using magnetic properties measurement system (MPMS). EXAFS measurements were performed at Mn K-edge in Fluorescence mode at beamline QAS, National Synchrotron Light Source (NSLS-II), Brookhaven National Laboratory.

Results and Discussion

Fig.1(a) shows the room temperature (RT) XRD pattern of the Heusler alloy Co_2MnAl . In the $L2_1$ phase, the ordered reflections (111) and (311) are expected to be positioned at 2 θ values 26.8° and 52.7°, respectively. The absence of these reflections in the figure suggests the compound to be stabilised in the B2 phase. Hence, the XRD peaks have been indexed based on the B2 phase structure, Fig.1(a). The obtained lattice parameter is 5.7569(9) Å which is line with the



Fig.1. (a) RT XRD pattern and (b) Magnetization vs. applied magnetic field collected at 5 K of Co₂MnAl.

earlier report [4]. The dc magnetisation as a function of applied magnetic field collected at 5 K is shown in Fig.1(b). The value of the saturation magnetic moment obtained is ~4.2 μ_B /f.u., agrees with the literature value [3]. These results suggest that the sample is in single phase. The RT Mn K-edge x-ray absorption spectrum (XAS) of the compound is shown in Fig.2(a). The absorption edge as obtained from the first inflection point in the region of the absorption edge is ~6539 eV. The EXAFS fitting was carried out using DEMETER software [6]. The weighted oscillatory part of the



Fig.2. (a) RT x-ray absorption spectrum (XAS) of Mn Kedge. The weighted oscillatory part $(k^2 \chi(k))$ is shown in the inset. (b) Fourier transform of $k^2 \chi(k)$. (c) First co-ordination shell fit in q space for the Mn k-edge of Co₂MnAl.

EXAFS spectrum after background subtraction is shown in the inset of Fig.2(a). To obtain the structural parameters surrounding the Mn atom, Fourier transform to the r-space was taken in the k-range 3 to 12.7 Å⁻¹, Fig.2(b) with a Hanning window. The figure shows the first and the higher coordination shells. To fit the first coordination shell, theoretical EXAFS function was obtained using FEFF6 [7]. The overall many body reduction factor was fixed to 0.84. The back scattering amplitude and phase shifts were calculated using FEFF6 for L2₁ phase. In this phase, in the first coordination shell Mn is surrounded by 8 Co atoms (8 model) at bond distance 2.49 Å. The R-factor obtained is 0.06. Our results show that the 8 model does not represent the experimental data, top panel of Fig.2(c). Hence, the local structure was modelled using two shells (6+2), where Mn is surrounded by six and two Co atoms at different bond distances. The Rfactor thus obtained is ~0.002. The fit obtained using (6+2) model gives a better representation of the observed spectrum. Such distribution in the first

coordination shell suggest that the local structure is different from the global structure as revealed by the XRD. To understand the significance of the local environment on the magnetic moment and hence the physical properties, detailed XAS analysis at the Co K-edge is also in progress.

Conclusion

We study here the Mn K-edge x-ray absorption spectrum of Co_2MnAl polycrystalline alloy. Our EXAFS results show distortion in the environment around the Mn site. To have a better understanding of the physical properties, local structure studies around the Co site is in progress.

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Enhancement of Adsorption Performance of NH₃ Gas Molecule towards Cyclo[18]Carbon: An Effect of Substitutional Doping

Shardul Vadalkar¹, Darshil Chodvadiya¹, Narayan N. Som², Keyur N. Vyas¹, Prafulla K. Jha^{1,*} and Brahmananda Chakraborty^{3,4}

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat, India-390002,

²Materials Design Division, Faculty of Materials Science and Engineering, Warsaw University of Technology, 141 Wołoska Str., 02-507 Warsaw, Poland

³High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, India-400008,

⁴Homi Bhabha National Institute, Mumbai, India-400094

*Corresponding author: shardulvadalkar@gmail.in

Abstract

In this work, we have studied the potential of the pristine; B and N doped C_{18} nanocluster for toxic NH₃ molecule adsorption. We have evaluated the structural change, adsorption energy, electrical conductivity and recovery time to understand the effective sensing mechanism. B and N doping modulated the electronic properties of C_{18} nanocluster. After B and N doping E_G is reduces to 6.15 eV and 4.72 eV from 6.74 eV. The large adsorption energy and drastic change in electrical conductivity after NH₃ gas molecule adsorption over B doped C_{18} nanocluster indicates very strong interaction between them. Recovery time calculations suggest that B doped C_{18} nanocluster can be used as NH₃ gas molecule remover from specific environments.

Pressure Induced Topological Phase Transition in c-YN

Ramesh Kumar^{1*}, Ramesh Kumar², and Mukhtiyar Singh¹

¹Department of Applied Physics, Delhi Technological University, New Delhi-110042 ²Department of Physics, Guru Jambheshwar University of Science & Technology, Hisar-125001

*Corresponding author: ramesh_2k19phdap506@dtu.ac.in

Abstract

We present a first-principles based analysis of quantum phase transition in cubic (*c*)-Yttrium Nitride. We propose that the *NaCl-type* YN can host a topological phase transition under applied hydrostatic pressure, in the presence of Spin-orbit Coupling (SOC). Under ambient conditions, YN is an insulator but it shows topological phase transition at Gamma point under the external pressure of 20 GPa without breaking any symmetry. The topological phase transition pressure (20 GPa) is much lower than the structural phase transition pressure (170 GPa) for YN.

Introduction

Topological Insulators (TIs)¹⁻² is a class of quantum materials which shows the inversion of valance and conduction band at high symmetry points near the Fermi level. These inversion points are time-reversal invariant momenta (TRIM) points in the Brillion zone (BZ). The three-dimensional TIs are having insulating bulk with massless and inverted surface energy bands, known as surface Dirac cones. This appearance of band inversion can be characterized by $Z_2 = 1$; the topological invariants¹. Topological phase depends upon structure & composition of particular compound and show different physical properties like Quantum Spin Hall Effect (OSHE) as in CdTe/HgTe quantum well³. Such different physical properties make these materials appropriate for Thermoelectric, Spintronics, and Quantum Computing^{2,4,5}. TIs are currently at center of research from both theoretical and experimental studies fronts^{2,7}.

YX (X=N, P, As, Sb) family exhibits different properties like hardness, high melting point, moderate transition temperature for superconductivity and most importantly they are strongly correlated systems⁸. Strong correlation in these compounds may leads to a topological phase transition in these systems. It was reported that YSb shows a phase transition at a hydrostatic pressure of ~12 GPa without breaking any symmetry⁹.

In this paper, we have been studied the electronic properties of Yttrium Nitride (YN) under external hydrostatic pressure using the first-principles calculation and we proposed that YN shows a nontrivial topological phase under a hydrostatic pressure of \sim 20GPa at gamma symmetry point without breaking any symmetry.

Computational Details:

The Density Functional Theory (DFT) based Vienna Ab Initio Simulation Package (VASP)¹⁰ has been used to perform all electronic structure calculations with projected augmented wave (PAW) formulism. The exchange-correlation energy was incorporated by Perdew-Burke-Ernzerhof (PBE) formalism through Generalized Gradient Approximation (GGA)¹¹. First of all, a k-point optimization was performed and found that a 11x11x11 Monkhorst-Pack mesh of k-points sampled for Brillion zone and plane-wave cutoff energy of 520 eV was sufficient enough to get reasonable energy convergence. Further, the force relaxation of less than 0.02 eV/Å for each atom in the unit cell was achieved. The band structure calculation was performed under hydrostatic pressure ranges 0 to 20 GPa. After relaxing the crystal structure at different applied pressure, band structure calculation was performed with inclusion of spin-orbit coupling (SOC).

Result & Discussion:

Under ambient pressure, YN has *NaCl-type* structure with space group Fm3m (#225), with Y atom at origin (0,0,0) and N atom at (0.5,0.5,0.5) (Fig. 1(a)). Yassine et al, have shown that with application of external pressure first-order phase transition takes place and a sixfold *NaCl-type* structure is converted into a more stable eightfold *CsCl-type* structure. This phase transition take place at ~170GPa¹². This finding suggests that the stability YN in *NaCl-type* structure holds for 0-170 GPa.



Fig. 1: (a) Primitive Unit Cell (b) Band Structure at ambient condition (c) Band structure at 20 GPa hydrostatic pressure with SOC.

We have performed the band structure of YN at ambient pressure with and without SOC. We have plotted the band structure along high symmetry point L to Γ , Γ to X, and X to W since we are interested in Time-Reversal Invariant (TRIM) Points. It is found that YN behaves as topologically trivial at ambient pressure as shown in Fig. 1(b). It is topologically trivial because there is no band inversion found in its band structure. It is observed from fig. 1(b) that near the fermi level valance band is mainly contributed by the *p*-orbital of N and the conduction band is mainly composed of *d*-orbital of Y. To explore the topological phase transition in YN under applied external pressure, we again calculated its band structures at different applied pressure values between 0 to 20GPa with the inclusion of the SOC effect. When we checked all TRIM points from 0 to 19 GPa, we found that topological band inversion is absent on all of them. But when we increase our pressure from 19 GPa to 20 GPa, a band inversion is found at Γ TRIM point (Fig. 1(c)). It should be noted that 20 GPa pressure for the quantum phase transition is much below the structural phase transition¹². It is observed that after band inversion have taken place, it is clear from the inset of Fig. 1(c) that the inverted bands in conduction band and valence band are respectively consist of p-N and d-Y orbitals. This verifies the non-trivial nature of YN in cubic structure at ~20 GPa.

Conclusion:

Based on the first-principles calculation, we have analyzed the electronic structure of c-YN. It has been found that YN undergoes a trivial to non-trivial topological phase transition under an applied hydrostatic pressure of ~20 GPa. This study is in very early stage and these results are preliminary. We are exploring other aspects of this study in order to have more insight in the quantum phase transition of this material.

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Prediction of Two Dimensional Wide Bandgap Semiconductor PbBr₂ Monolayer Using First Principle Calculations

Atanu Betal, Jayanta Bera, Chayan Das, and Satyajit Sahu*

Department of Physics, Indian Institute of Technology Jodhpur, Jodhpur 342037, India

*Corresponding author: satyajit@iitj.ac.in

Abstract

The wide bandgap semiconductors can be used as high temperature electronic devices, RF signal processing, visible range lightemitting diode application, and many more. Two-dimensional wide bandgap semiconductor material PbBr₂ has been predicted using density functional theory. A positive phonon dispersion curve suggested the dynamical stability of the material. The band structure indicates that it's an indirect bandgap semiconductor with bandgap of 2.74 eV.

Introduction

The emergence of two-dimensional (2D) materials during the beginning of the 20th century was a big debatable issue in the physics community because of its thermodynamic instability in any finite temperature in the classical physics approach. Science got a scientific breakthrough when the first single layer of graphene was exfoliated by Novoselov and Geim with a scotch tape¹. After the discovery of graphene, many 2D materials were predicted and experimentally synthesized. The outstanding optoelectronic, thermoelectric, piezoelectric properties with excellent tunability due to applied strain or other perturbation made 2D material center of interest in current research. Very popular 2D material MoS₂, WS₂, HfS₂, ZrS₂ monolayers have been studied, and their property enhancement with applied strain is also predicted^{2,3}.

Recently, many 2D metal halide has been synthesized. Using physical vapor deposition, 2D PbI₂ has been synthesized by a research group⁴. After that, thermoelectric properties of PbI₂ have been shown with a high figure of merit (ZT) and ultralow lattice thermal conductivity⁵. The stability of other metal halide monolayers such as SnI₂ and SiI₂ has been predicted, and their optoelectronic and thermoelectric properties are also studied by first principle calculations⁶.

Here, we have predicted 2D metal halide monolayer PbBr₂ using density functional approach. PbBr₂ monolayer has hexagonal structure with a wide bandgap of 2.74 eV. The positive phonon dispersion curve shows that the material has dynamical stability as a monolayer. The strain-dependent electronic properties also have been studied for biaxial compressive and tensile strain. The bandgap is decreasing for applied tensile strain and increasing for compressive strain.

Computational Details:

Quantum espresso package⁷ has been used to carry on the calculations with PBE Vanderbilt ultrasoft pseudopotential⁸. A sufficient vacuum of 20 Å has been kept along the C direction to isolate the layer. $20 \times 20 \times 1$ k-mesh sampling was taken into account. A force convergence threshold of 10⁻⁴ ev/Å has been achieved to relax the atoms. For phonon calculation, $10 \times 10 \times 1$ q-mesh grid has been taken and calculated using the QE package.

Results and Discussions:

The predicted PbBr₂ monolayer has hexagonal structure with space group 164 (P-3 m1). The unit cell consists of two Br atoms and on Pb atom and lattice constant of its relaxed structure is a=b=4.49Å. The side and top view of the PbBr₂ supercell is shown in figure 1. The figure shows that one Pb atom is surrounded by six Br atoms to make hexagonal honeycomb structure with Pb atom at the center. The height (h) of the monolayer was found to be 4.22 Å and bond length of Pb-Br is 3.08 Å. The atoms made an angle of 93.85° for \angle Pb-Br-Pb and 86.46° for \angle Br-Pb-Br.

Thermodynamic stability has been checked by studying phonon dispersion relation along high symmetric path Γ -K-M- Γ as shown in figure 2 (a). No imaginary frequency can be found, which

confirms that the monolayer $PbBr_2$ is dynamically stable. Three acoustic and six optical modes are found for the unit cell having three atoms.



Fig. 1. The Top view and side view of the PbBr₂ monolayer.

The highest phonon frequency has been found to be 132.14 cm⁻¹ at Γ point. The ZA, TA, LA modes are found zero value at Γ point and increase linearly along the K point. The LA mode has overlapped with an optical mode at High symmetric K and M points which increases the collision between phonons and may decrease the lattice thermal conductivity.



Fig. 2. (a) Phonon dispersion curve (b) electronic band structure and PDOS of relaxed PbBr₂ monolayer unit cell.

The electronic band structure has been studied along a high symmetric path K- Γ -M-K to have an idea about the electronic property. Figure 2 (b) shows that the material is an indirect wide bandgap semiconductor with VBM at K point and CBM at Γ point. The bandgap of monolayer PbBr₂ is found to be 2.74 eV. The PDOS shows the mapping of orbital contribution at the band edges. The VBM mainly contributed by p orbital of Br atom although there is the significant contribution of p orbital of Pb atom. The CBM is primarily contributed by the p orbital of Pb atom.



Fig. 3. (a) The change of VBM and CBM with applied strain (b) The bandgap variation with applied biaxial strain.

Strain engineering is a well-known process to tune bandgap of materials. Here we have applied biaxial tensile and compressive strain to study the corresponding change in bandgap of the material. The change of CBM and VBM position and bandgap with applied strain are shown in figure 3 (a) and (b), respectively. The CBM and VBM energy decreases with applied tensile strain and increases with compressive strain. Similarly, the bandgap decreases with applied positive strain and increases with applied negative strain. The bandgap varies from 3.08 eV to 2.54 eV within the -10% to 10% applied strain range.

In conclusion, we have successfully predicted the stability of monolayer $PbBr_2$ and studied its electronic properties with and without strain. The positive phonon dispersion curve shows the material is dynamically stable. The band structure shows monolayer $PbBr_2$ is a wide bandgap indirect semiconductor having bandgap 2.74 eV.

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Defects Optimization For Efficient All Inorganic CsPbI₂Br Perovskite Solar Cell

Deepak Yadav*, Monojit Bag, and K. L. Yadav

Department of Physics, Indian Institute of Technology Roorkee, Roorkee, 247667

*Corresponding author: deepak@ph.iitr.ac.in

Abstract

All-inorganic perovskite solar cells recently attracted the scientific community for their excellent stability over hybrid organicinorganic based perovskite solar cells. Their performance is, however, not high as of organic or hybrid counterparts. Here we simulated fully inorganic CsPbI₂Br based perovskite solar cells using SCAPS-1D software. Since defects at perovskite bulk material and the interface of perovskite play a vital role in the performance of perovskite solar cells, we suggested the fair value of defect density at perovskite bulk to be 10^{15} (cm⁻³) and for perovskite interfaces to be 5×10^{17} (cm⁻³) to be efficient perovskite solar cells. This work paves the way to develop highly efficient all-inorganic CsPbI₂Br perovskite solar cells.

Introduction

Photovoltaic devices can be helpful to prevent the energy crisis without causing a negative impact on climate. Halide perovskite (ABX₃) based solar cells can be the solution to the above problems, and they have attracted great attention due to low production cost, easy fabrication, and device efficiency, which has risen from 3.8% (2009) to 25.5% (2021).[1]

The perovskite materials have excellent optoelectronic properties like absorption coefficient, ambipolar charge transport, tunable bandgap, long charge carrier lifetime, large charge carrier diffusion lengths (~micro-meter), defect tolerance,[2] and solution processability.

As the organic-based perovskite solar cell is more prone to degradation[3], here in this work, we have simulated the fully inorganic planer and inverted CsPbI₂Br based perovskite solar cell because of its enhanced stability against heat and light, using SCAPS 1-D. The gap between Shockley–Queisser limit (~26% for CsPbI₂Br) and practical efficiency (16.37%) is enormous. This gap can be filled with the help of optimization of different layers using modelling. Also, the quality of the absorber layer plays an essential role in device performance. More defects in the absorber layer lead to several recombinations, resulting in lesser charge transport and ultimately leading to a less efficient device.[4]

Here, we studied the effect of defects in bulk and interface of the perovskite absorber layer on the device performance. We have suggested the optimum value of defects density of perovskite absorber layer be 10^{15} (cm⁻³). For perovskite interface, the optimum defect density is 5×10^{17} (cm⁻³) to develop a highly efficient all-inorganic perovskite solar cell. We have also simulated the electronic band structure to

eliminate the spike at the perovskite-HTL interface to fascinate the charge transfer (not shown here).

Theory and Computational Details

In this work, we have used SCAPS 3.3.09 software to simulate planer and inverted perovskite solar cells. The device parameters like short circuit current density (J_{sc}) , open-circuit voltage (V_{oc}) , Fill Factor (FF), Quantum efficiency (QE), Power conversion efficiency (PCE) are obtained by solving the Poisson equation with electron and hole continuity equations.

Planer inverted perovskite solar cell used for simulation have the structure: FTO/NiO/IDL1/ CsPbI₂Br/IDL2/ZnO/Ag. Here FTO acts as a front electrode, NiO acts as hole transport layer (HTL), IDLs are interface defects layers, CsPbI2Br is used as absorbing materials where generation of charge carriers takes place, ZnO is used as electron transport layer (ETL), and silver acts as a back electrode. The device and material parameters used in SCAPS software are shown in table 1 where Eea, Nt, Nd, Na, stands for electron affinity, defect density, donor density, acceptor density and rest the symbols have their usual meaning. The type of defects in perovskite material is considered as neutral with a cross-section of electrons and holes of 2×10^{-14} cm² and the thermal velocity for electrons and holes is regarded as 10⁷ cm s⁻¹. The value of defect density in interface layers and bulk perovskite layers is varied from 10¹¹ to 10^{20} cm⁻³. The simulation was performed under 1000 W/m² illumination, at 300 K and an air mass of AM 1.5G.

Results and Discussion

In this work, we have varied the defect density of the $CsPbI_2Br$ perovskite absorber layer in all-

inorganic perovskite solar cells to see how the defect density is affecting the performance of perovskite solar cells. Fig. 1., efficiency Vs defect density (N_t) of perovskite absorber layer, shows the decrement in efficiency with the increasing density of defects in

Table 1. Parameters For Inorganic Solar Cell Simulation.					
Parameter	NiO	IDL1/2	CsPbI2Br	ZnO	
t (nm)	10	10	500	80	
Eg (eV)	3.5	1.86	1.86	3.3	
Eea (eV)	2.1	3.8	3.8	3.9	
ε _r	11.75	8.6	8.6	9	
DOS _{CB} (cm ⁻³)	2.5E20	2.2E18	2.2E18	1E19	
DOS _{VB} (cm ⁻³)	2.5E20	1.8E19	1.8E19	1E19	
$\mu_e (cm^2/Vs)$	1E-3	11	11	200	
$\mu_h (cm^2/Vs)$	1E-3	11	11	50	
N _d (cm ⁻³)	0	1E15	1E15	5E17	
N _a (cm ⁻³)	1E19	0	0	0	
N_t (cm ⁻³)	-	Range	Range	-	



Fig. 1. The Effect of Defect Density of Perovskite Absorber on the Efficiency of Perovskite Solar Cell.



Fig. 2. The Effect of Defect Density of Perovskite Interface on Efficiency of Perovskite Solar Cell.

the perovskite absorber layer. Here, Green zone (I) shows the range of defect density for highly efficient devices, which is $<10^{14}$ cm⁻³. Yellow zone (II) is a transition region (10^{14} to 10^{16} cm⁻³) that separates highly efficient devices from poor devices on a defect density scale. Red zone (III) gives the range of defect density for very inefficient devices (> 10^{16} cm⁻³). Fig.2., shows how the density of defects (N_t) of perovskite interfaces affects the efficiency of inorganic perovskite solar cells. Here, the green zone (I) for highly efficient devices is extended to $< 10^{17}$ cm⁻³. It offers almost no impact on efficiency up to defect density of 10¹⁷ cm⁻³, and after that, it shows significant decrement. The transition region is narrower $(10^{17} \text{ to } 10^{18} \text{ cm}^{-3})$ in case of interface defects and beyond 10¹⁸ cm⁻³ there is red zone. The optimum value of defect density is 5×1017 cm-3 without sacrificing the performance of the cell.

Conclusion

In this work, we have varied the defect density of the CsPbI₂Br perovskite bulk as well as interface and the optimum value of defect density of bulk perovskite as well as interface is suggested to be 10^{15} cm⁻³ for bulk perovskite and 5×10^{17} cm⁻³ for interfacial defects to develop highly efficient perovskite solar cells. Above this, there will be a decrement in the overall performance of devices since defects are responsible for several types of recombination[5] and eventually hinders the charge transport. In conclusion the optimum values of interface and bulk perovskite defects are provided in this work for highly efficient All-inorganic perovskite solar cells.

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Molecular Dynamics Simulation of Primary Radiation Damage in Tungsten using Two-Temperature Model

Aaditya V. Majalee¹, H. Hemani¹, U. Bhardwaj¹, P.V. Lakshminarayana³ and M. Warrier^{1,2}

¹Computational Analysis Division, Bhabha Atomic Research Centre Facility, Visakhapatnam, 531011 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094 ³Department of Nuclear Physics, Andhra University, Visakhapatnam, 530003

**Corresponding author: aadityam@barc.gov.in*

Abstract

Molecular Dynamics simulations have been performed to assess the primary radiation damage that occurs in Tungsten using an electronic stopping model called Two-Temperature Model (TTM). There are other electronic stopping models available like Lindhard-Scharff (LS). In this study, we perform high energy MD simulations in Tungsten and compare the results of TTM model with MD results of LS model and also compare the results without considering electronic stopping.

Introduction

Primary radiation damage in materials is created by a displacement cascade which forms in a very short time-scale (few picoseconds) when high energy particles like neutrons/ions interact with atoms. Secondary damage is the long-time scale phenomenon ranging from ns to few years. When a high energy particle interacts, it transfers part of its energy to an atom in the material, called the primary knock-on atom (PKA). If the transferred energy exceeds the threshold displacement energy, atom is displaced from its position. The displaced atom inturn can displace other atoms if it has sufficient energy, thereby forming a displacement cascade. Within a few ps, the collision cascade causes local damage comprising of many interstitials, vacancies and defect clusters.

The collision cascades can be simulated using Molecular Dynamics (MD). Earliest known computer simulation of radiation damage was performed by Vineyard *et.al.* [2] in 1960. Maximum PKA energy was only 400eV with a maximum of around 1000 atoms. But with the advent of high-end super computers, we are able to perform radiation damage simulations for very high energy of 200 keV in over 50 random directions of launch of PKA.

Computer Simulation Model

We have used the Large-scale Atomic Molecular Massively Parallel Simulator (LAMMPS) [3] to simulate of the primary radiation damage. MD codes use interatomic potentials to simulate the interaction between atoms. These inter-atomic potentials do not have in-built electronic stopping of energetic atoms. The energy lost in electronic stopping increases with increasing PKA energies and becomes an important channel for energy loss above a few tens of keV. Hemani *et.al.* [4] included electronic stopping in LAMMPS using Lindhard-Scharff (LS) model. This takes into account the electronic stopping as a friction term for atoms above a certain cut-off velocity.

Another method of electronic stopping included with the LAMMPS suite is the Two-Temperature Model [5,6]. In the Two-Temperature Model (TTM), electronic stopping (ES) is included as a friction term and electron-ion interactions are included as a coupling term by creating a separate electron heat bath. Heat diffusion equation as given below describes the energy of the electronic system.

$$C_{e} \frac{\partial T_{e}}{\partial t} = \nabla \left(\kappa_{e} \nabla T_{e} \right) - g_{p} \left(T_{e} - T_{a} \right) + g_{s} T_{a}^{'}$$

 T_e is the temperature of the electronic system and T_a is the temperature of the atomic system. g_p is the coupling constant, g_s is the coupling parameter determined by the rate of energy loss due to electronic stopping. All the above parameters are related to parameters of MD simulation using energy balance equations. In order to couple the electronic energy with the MD simulations, the simulation box of the system of atoms is sub-divided into a number of numerical cells, each containing a few hundred atoms where the electronic temperature is assumed to be constant. These cells represent the computational grid for integration of the heat diffusion equation and the cell size is not expected to affect the results of the simulation.

Computational Results

We have performed MD simulations of primary radiation damage in Tungsten (W) using LAMMPS and utilized Two-Temperature Model (TTM) for electronic stopping, stiffened Interatomic potential of Björkas [7].

We have performed simulations for high PKA energies of 50, 150 and 200 keV. For 200 keV PKA simulation, 222 × 222 × 222 box comprising of 21.88 million atoms was used with periodic boundary conditions and Temperature control at the edge with varying time step. PKA was launched in 50 random directions for all energies to have a good statistical average. Equilibration was performed for 16ps and PKA simulation was launched for 30ps.



Fig. 1. Comparison of number of defects for various energies for LS, TTM and without ES model.

Figure 1 & 2 show the comparison of number of defects & number of clusters in 50, 150 and 200 keV PKA energies for LS, TTM model and without ES. Results show that the number of defects and clusters is overestimated when no ES model is used. Hence inclusion of ES model in high energy PKA simulations is a requirement and cannot be neglected. Change in number of defects or number of clusters is very negligible when the ES model is changed.



Fig. 2. Comparison of number of clusters for 50, 150 and 200 keV for LS, TTM and without ES model.

Figure 3 & 4 show that the max clusters size of interstitials is smaller in comparison with vacancies. Spread in cluster size of vacancies is more compared to that of interstitials.



Fig. 3. Comparison of interstitial max clusters size for 50, 150 and 200 keV for LS, TTM and without ES model.



Fig. 4. Comparison of vacancy max cluster size for 50, 150 and 200 keV for LS, TTM and without ES model.

Conclusions

Primary radiation damage simulations for high PKA energy using LAMMPS and utilizing TTM model has been successfully compared with results from LS model. Number of defects are overestimated when electronic stopping is not used. Changing the ES model has negligible affect on the number of defects and number of clusters.

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Effect Of Strain On Electronic And Optical Properties Of The Lead Free Photovoltaic Material Cs₂AgInBr₆: DFT Study

Brij Kumar Bareth, and Madhvendra Nath Tripathi^{*}

Department of Pure and Applied Physics, Guru GhasidasVishwavidyalaya (Central University), Koni, Bilaspur, CG, India 495009

*Corresponding author: ommadhav27@gmail.com

Abstract

Recently the double perovskite (DP) $Cs_2AgInBr_6$ is reported to be the prominent solar absorber material due to its direct nature of band gap value of 1.33 eV lying in the visible region. It emerged as potential alternative to lead-based hybrid halide perovskites and is expected that the physical properties may be further enhanced by band gap tuning. We employ the Density functional theory to investigate the effect of the compressive and tensile strains on the electronic and optical properties of the $Cs_2AgInBr_6$. It is observed that the band gap changes about 7.55 (9.43) % under the 10% tensile (compressive) strain without changing the direct nature of band gap at Γ point in addition to higher hole mobilities under compressive strain due to high dispersive nature of Valence band maximum (VBM). The absorption peaks exhibit red shift by varying compressive to tensile strain however, reflectivity is almost flat in low energy region. Henceforth, the band gap tuning without affecting the direct nature of band gap with higher mobilities of both charge carriers along with optical properties enhancement under the strain indicates potential photovoltaic material $Cs_2AgInBr_6$ with improved photo-conversion efficiency.

INTRODUCTION

Inorganic halide double perovskites have recently emerged as the potential lead-free ecofriendly photovoltaic materials. A good photovoltaic material should have suitable direct band gap, high optical absorption, high carrier mobility and long carrier lifetime. Among the front-runner double perovskite materials, the Cs₂AgInX₆ (X=Cl, Br) are expected to be building blocks of lead-free nanophotonics. The Cs2AgInCl6 has wide direct band gap value of almost 3.23 eV [1] and shown huge optoelectronic prospective for applications. Moreover, this wide band gap situation may be improved by Br replacement at Cl but such Br replacement is less explored [2]. Very recently; the synthesis of Cs₂AgInBr₆ has been realized by overcoming the inherent complexity in synthesis process [3]. Further, it is predicted that the lead-free Cs₂AgInBr₆ based solar cells may reach an ideal solar efficiency of 28% and is considered as potential alternative of the lead based perovskite solar cell CH₃NH₃PbI₃ with ideal efficiency of 30%. To further increase the photo-conversion efficiency of the Cs₂AgInBr₆ over wide spectrum of the visible light, the tunability of the band gap may be achieved by applying strain engineering.

In present paper, the effect of the compressive and tensile strains ranging from -10% to 10% on the structural, electronic and optical properties of the $Cs_2AgInBr_6$ is investigated using first-principles calculations to explore the suitability of the composition as solar absorber for wide range of solar spectrum.

COMPUTATIONAL DETAILS

The DP Cs₂AgInBr₆ crystallizes in facecentered-cubic (fcc) phase with a space group of Fm-3m. The structure is basic double perovskites in which B-site is alternatively occupied by In and Ag atoms with corner sharing alternating octahedral formed around Ag⁺ and In³⁺as backbone and the Cs⁺ ions occupies the cubo-octahedral voids (12-fold) coordinated positions (Fig. 01). The structural optimization, strained structures and electronic structure calculations were performed using DFT as implemented on CASTEP [4]. The generalized gradient approximation (GGA) formulated by Perdew, Burke, and Ernzerhof (PBE) was used to express exchange-correlation functional. Lattice parameters were taken for different values of the applied strain ranging from 10% compressive strain to 10% tensile strain. The plane wave expansion of the wave function with the cut off energy value of 350 eV is used within the GGA-PBE approximation along with ultrasoft pseudo potential to describe electron ion interaction [5]. The Monkhorst-Pack grid of 4x4x4 k-mesh was used for integration over the Brillouin zone for energies and electronic structure calculations respectively [6]



Fig.01. Crystal structure of Cs₂AgInBr₆



Fig.03. Variation of band gap under compressive strain (a) and (b), and under tensile strain (d) and (e).

RESULTS AND DISCUSSION

The calculated lattice parameter value of 11.18 Å of the geometrically optimized Cs₂AgInBr₆ crystal structure within GGA-PBE is in good agreement with the experimental value of 11.00 Å [7]. The octahedral formed by the halide around Ag is slightly larger than the octahedral around In for all with or without strain crystal structures due to larger radius of Ag^+ ion. The calculated bang gap shows direct nature with band gap value of 0.15 eV which is well known underestimated within GGA-PBE henceforth a scissor operator 1.17 eV is applied to estimate the change in band gap value reported earlier 1.33 eV by using HSE functional [8]. The effect of the applied compressive and tensile strain on the band gap and lattice constant are shown in Fig. 02. It is observed that the variation rate of the band edges under compressive strain is higher than tensile and band gap changes about 7.55 (9.43) % for the 10% tensile (compressive) strain without changing the direct nature of band gap at Γ point.



Fig.02. Variation in energy band gap and lattice constant under applied compressive and tensile strains.

The conduction band minimum (CBM) contributed primarily In 5s states becomes more dispersive if we increase the compression and it decreases by increasing tensile strain. The significant effect of strain is evident on the upper valence band. Under the applied compressive strain the valence

band becomes dispersive and broad (Fig. 03). Moving from Fig. 03 (a) to 03 (e), the lattice parameter increases under tensile strain and the valence band maximum (VBM) contributed mainly by Ag 4d states and Br 4p states becomes almost flat which shows the large effective mass and hence very small mobility of charge carriers under tensile strain. This clearly indicates under compressive strain Cs₂AgInBr₆ shows better carrier mobilities and it may be realized by squeezing or a high-pressure atmosphere experiment in consistent with recent report [8]. The tunability of the band gap may be achieved in the composition under strain for absorbing solar radiation in wide spectrum. The variation in absorption and reflectivity under strain are shown in Fig. 04 and 05 respectively. It is evident that under tensile strain, more number of states in valence band with smaller band gap resulting in almost two times increase in absorption in the visible region as compared to without strain situation. However, for higher energy region, absorption under compressive strain is better than tensile strain. The flat regions of reflectivity in visible region under tensile strain are better than compressive strain.



Fig.04. Variation of absorption under strain.



Fig.05. Variation of reflectivity under strain.

CONCLUSIONS

The effects of the tensile and compressive strains are investigated on the electronic and optical properties of the $Cs_2AgInBr_6$ using DFT. It is observed that band gap tuning may be achieved under strain conditions with improved optical properties to enhance the absorption of solar radiation. Red shift in absorption peaks are observed moving from compressive strain to tensile strain. High dispersive nature of VBM is observed under compressive strain resulting in higher hole mobility. The significant tuning of the band gap and improvement in absorption properties under strain conditions indicate the potential application of the $Cs_2AgInBr_6$ as flexible and efficient solar photovoltaic material.

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Strain Driven Electronic Topological Transition in Half Heusler LiCdAs: A Cubic Symmetry Breaking Approach

Bhautik R. Dhori^{1,*}, Raghottam M. Sattigeri¹ and Prafulla K. Jha¹

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat – India 390002

*Corresponding author: bhautikdhori6421@gmail.com

Abstract

The present work investigates the uniaxial strain induced Electronic Topological Transition (ETT) in Half-Heusler (HH) compound LiCdAs employing density functional theory. LiCdAs exhibits semi-metallic (SM) nature under normal condition, whereas, on breaking cubic symmetry at 2% uniaxial strain a spin-locked surface state is observed. The calculated Z_2 invariant predicts the non-trivial signature of LiCdAs. (i.e., $Z_2 = (1, 0 \ 0)$). Such sensitive electronic properties under strain of LiCdAs makes it a suitable applicant for spintronics and nano-electronics applications.

Introduction

In the past few decades, topological insulators (TI) gained a lot of attraction due to their insulating bulk and conducting surface behaviour. Several 3D TI was found in Bi-based alloy such as $Bi_{1-x}Sb_x$, Bi_2Te_3 , Bi_2Sb_3 etc. due to their strong Spin Orbit Coupling (SOC) effect [1]. There are different mechanisms to alter the electronic properties of atoms and to get a non-trivial TI state. The application of strain in the specific crystallographic plane is an efficient method to alter the electronic properties because it enhances the strength of SOC and systems transit from trivial to non-trivial topological phase [2]. Strain driven band inversion near the Fermi level is an important feature to investigate the quantum phase transition.

Several Half-Heusler (HH) compounds such as LaPtBi, AgSrBi etc were reported as non-trivial TI employing strain engineering [3]. Most of the proposed TI in the HH family contain Bi due to its heavier atomic mass, larger radius and strong relativistic effect [4]. Apart from Bi, other compounds from the same pnictogen family such as As, Sb etc. are less studied. Motivated with this fact, we planned to study the non-trivial nature in HH LiCdX (X=As, Sb, Bi) using density functional theory based first principles calculations [5]. For this we first performed the study on LiCdAs and found that the LiCdAs shows intrinsically semi metallic nature with and without spin orbit coupling. The electronic topological transition (ETT) in HH compound LiCdAs is observed by breaking cubic symmetry using uniaxial strain. The Z_2 invariant calculations are also performed to check the type of the topological transition.

Methodology

Electronic properties of LiCdAs (F $\overline{4}$ 3m) were calculated using state-of-art density functional theory (DFT) based first principles method implemented in the Quantum Espresso code [6]. The pseudopotential method is based on Martins-Troullier with exchangecorrelation of Perdew-Burke-Ernzerohf (PBE) functional type. To consider the SOC effect in our calculation we used, projector augmented wave (PAW) sets with PBE exchange correlation. The system was optimized under proper convergence in terms of global minima to obtain the true ground state of the system. Plane wave with a kinetic energy cutoff of 80 Ry was adopted as a basis set. The optimized kmesh of $8 \times 8 \times 8$ was used in the self-consistent calculation with a convergence threshold of $< 10^{-6}$ Ry. Using real space maximally localized Wannier functions (MLWFs), we generated tight binding model for LiCdAs using Wannier90 code [7] and appraised our results by calculating Z₂ invariant employing Wannier Tools [8].

Results and discussion

The HH compound LiCdAs has a face centred cubic (FCC) structure with F $\overline{4}3m$ space group. The primitive cell vectors are defined as, $v_1 = (a/2)(-1,0,1)$, $v_2 = (a/2)(0,1,1)$ and $v_3 = (a/2)(-1,1,0)$ for Li, Cd and As respectively (Fig. 1(a)). The lattice constant is obtained under generalized gradient approximation (GGA) as a = 6.37Å which assent with previous theoretical work [5]. LiCdAs exhibits zero bandgap degenerate conduction and valence bands except at high symmetric point Γ as shown in Fig. 1(b). This shows that the LiCdAs in normal condition is semi metallic (SM) (Fig. 2(a)).



Fig. 1. (a) face centred cubic (fcc) structure of LiCdAs (b) electronic band structure without spin orbit coupling indicating SM nature of LiCdAs.

Fig. 2(b) clearly depicts that the semi metallic nature of LiCdAs is retained even in the presence of SOC. To get topologically non-trivial nature in semi-metallic HH compounds, the breaking of cubic symmetry and reducing crystal symmetry are some efficient methods. We examined the band gap variation of LiCdAs by employing uniaxial strain along the [010] crystallographic plane. The strain breaks the cubic symmetry.



Fig. 2. electronic band structure of LiCdAs (a) without SOC (b) with SOC (c) with broken cubic symmetry at 2% (d) computational surface states at 2% uniaxial strain

The calculated electronic band structure of LiCdAs at 2% uniaxial strain along [010] plane introduces 49 meV bandgap at high symmetric point Γ (Fig. 2(c)). Since low energy electronic properties are analysed near the Fermi level, we restrict our analysis in this region. To understand the individual orbital contribution of all atoms in LiCdAs, we calculated the local density of states (LDOS). Under the normal condition, in the valence bands, major contribution is due to the Cd-s, As-s, As-p orbitals and As-p orbital is dominating in the conduction band. However, near the Fermi level As-p orbital contribution is large. The

degeneracy of Γ point lifts at around 2% indicating the orbitals exchange which is governed by s and p orbitals near the Fermi level. The As-p orbital contribution arises in the conduction band with s orbital of Li, Cd and As.

We qualitatively analysed the non-trivial topological state of non-centrosymmetric HH LiCdAs by calculating surface states and computing Z_2 invariants. The Z₂ invariants using $v_0 = [(Z_2)_{(ki=0)} + (Z_2)]$ (ki = 0.5) (mod 2) and $v_i = (Z_2)$ (ki = 0.5) are calculated along six time reversal invariant planes (TRIP) i.e., $\mathbf{k}_{x=0,\pi}$, $\mathbf{k}_{y=0,\pi}$ and $\mathbf{k}_{z=0,\pi}$ in the BZ. Due to the lack of inversion symmetry in LiCdAs, Z₂ invariants are computed in terms of Wannier charge centred in the vicinity of the Fermi level. The corresponding surface states are evaluated along [111] crystal direction using iterative Green's function method are presented in Fig. 2(d). The Z_2 at 2% uniaxial strain is (1, 0 0 0) which indicates that the LiCdAs is a strong topological insulator.

Conclusions

In conclusion, employing density functional theory based *first principles* calculation we predict uniaxial strain-induced ETT in HH compound LiCdAs. Our calculations show that the LiCdAs exhibits SM nature under normal conditions as well as with SOC effect. Under 2% uniaxial strain, in LiCdAs gap opens up with 49 meV near the Fermi level and system undergoes ETT and exhibits strong topological insulator (1, 0 0 0). We expect our work will provide guidance for experimental validation.

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Computational Modelling of Morphology Evolution in Multifunctional Tin-Oxide

Mahak Chhabra¹, Sakshi Kansal², Rahul Ravindran¹, Surbhi Priya², Debabrata Mandal³ and Amreesh Chandra^{1,2,3*}

¹Department of Physics, ²School of Energy Science and Engineering, ³Department of Nano Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur – 721302, India *Corresponding author: achandra@phy.iitkgp.ac.in

Abstract

With the growing need to detect toxic gases in closed environments, functional and semiconducting metal oxide materials are being employed as gas sensors. In this paper, we report the effect of particle morphology on the sensing capabilities of tin-oxide (SnO₂) using molecular dynamics (MD) simulations. The results of MD simulations are used to model SnO₂ layers with different porosities, morphologies, dopants, and corresponding diffusion coefficients are calculated at room temperature. It is observed that, amongst different structures simulated in this work, the CNT decorated hollow nanostructures of SnO₂ show the highest diffusion coefficient (3982 Å²/ps) for methane gas detection. Improved diffusion corresponds to a shorter response time, leading to faster signal generation and rapid methane gas detection.

Introduction

In these times of deteriorating environmental conditions, the need for toxic or greenhouse gas sensors has become essential. One significant greenhouse gas is methane, which shows 28 times greater global warming potential than carbon dioxide.^[1] Therefore, the prevention and faster detection of methane gas leakage from transmission pipelines and other oil or gas production activities is becoming an absolute necessity. Therefore, methane gas sensors, with low response times, are being sought by a large number of industries.

There are various gas sensing methods, but the metal oxide semiconducting (MOS) gas sensors have become a preferred choice due to their advantages like low cost, small size, and simple design. One of the significant components of the MOS gas sensor is its sensing material. In this paper, we study the capability of tin-oxide (SnO₂) as a gas sensing material. This MOS is one of the promising gas sensing material due to its higher stability and sensitivity towards various analyte gases. Depending upon the functional requirements, one can tune the properties of the gas sensing material, which can be done by changing the morphology, incorporating dopants, etc. Therefore, in this paper, by using Molecular Dynamics Simulations, the favourable morphologies for having faster diffusion of analyte gas is proposed. The MD simulations were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software. Using LAMMPS, we modelled various morphologies of SnO₂ sensing layer In this paper, we present and compare the diffusion coefficient of methane gas over the SnO_2 surface having morphologies mentioned

Methodology

Various studies show that the gas sensor's response time directly correlates with the diffusion coefficient of analyte gas over the sensor's surface.^[2] Therefore, to obtain a sensor with faster detection, one can improve the diffusion coefficient by tuning the sensing layer's morphology. The diffusion coefficient of various morphologies, with methane as the analyte gas, was calculated using the Einstein -Smoluchowski, that is:

$$D = \frac{1}{6} \frac{d}{dt} \langle r^2 \rangle \tag{a}$$

where D is the diffusion coefficient and $\langle r^2 \rangle$ is the Mean Square Displacement (MSD). Thus, the diffusion coefficient can be calculated from the slope of the MSD vs Time plot.

The SnO₂ has a rutile tetragonal lattice structure with lattice constants a = b = 4.82 Å, c = 3.12 Å. This paper mainly focuses on 7 different morphologies. The first morphology is a porous SnO₂ layer (with dimensions 10 nm x 10nm x 2nm), where the percentage of the porosity is varied. The effect of 0.1%, 0.5%, 1%, and 10% porous SnO₂ on the diffusion coefficient value was studied. The second morphology is a SnO₂ layer (with dimensions 10 nm x 10 nm x 2 nm) with a graphene layer over it. Also, hollow nanospheres of SnO₂ (with radius 6 nm) and CNT decorated hollow nanospheres of SnO₂ were also modelled. In the input script, for each of the morphologies mentioned above of SnO₂, we first relaxed the system and equilibrated it at 300K using the *fix* NVT for 10 ps with damping factor 1 ps. Subsequently, we used the *fix nve* command after the *compute msd* command as *compute msd* is calculated at every step of this *fix*. The simulation ran for about 20 ps to calculate the diffusion coefficient of methane gas for small time scale MD simulations. The choice of the force field for interaction between Sn, O, C and H was confined to the combination of Lennard-Jones and Coulombic Force Fields. The LJ parameters that are vital for calculations in LAMMPS are calculated by Snoeberger et al. ^[4] The system constituted of 75 molecules of methane.



Fig. 1. Different morphologies of SnO_2 (a) 0.1 % Porous SnO_2 (b) Graphene layer over SnO_2 layer (c) SnO_2 hollow nanoparticles (d) CNT decorated SnO_2 hollow nanoparticles

Results and Discussions

The value of diffusion coefficients was calculated from the slope of the MSD vs time plot. As seen from Table 1, one can compare the value of diffusion coefficients (D) of methane gas over SnO₂ surface for various morphologies. The D values were observed to be minimum for the thin film of SnO_2 with 0.1% porosity (25 Å²/ps). On increasing the porosity, the D value also increases. This is because of the increase in the mean free path of the analyte molecules over the SnO_2 surface. More the porosity, lesser will be the hindrance experienced by the analyte molecules for diffusion. Further, the layered structure of graphene/ SnO_2 has a higher D (2908 Å²/ps), which could be attributed to graphene's high surface area and electrical conductivity. The hollow nanospheres (radius = 6nm) of SnO₂ were also modelled, and the D was calculated. It is observed that the value of D (38601 Å²/ps) was more significant than the thin film and layered structure of SnO₂. This increase could be because of the higher surface to volume ratio of this morphology. This kind of morphology has advantages like size effects and higher empty spaces, favouring diffusion and faster response time. The study has

shown that the dopants tend to improve the gas sensor's performance. We also used the carbon nanotube as a dopant for the hollow nanospheres of SnO₂. The value of D (3997 Å²/ps) for the CNT decorated hollow SnO₂ nanospheres was higher than the rest of the three structures mentioned above. The exceptional performance on the addition of CNT has been observed owing to the channel like hollow structure. This structure favours the diffusion as there is a lesser hindrance for the analyte gas molecules.

Table 1	Diffusion	coefficients	for	various	SnO ₂
	n	norphologies			

Morphology	Slope (Ų/ps)	Diffusion Coefficient (Å ² /ps)
0.1% porous SnO ₂	149	25
0.5% porous SnO ₂	255	43
1% porous SnO ₂	405	68
10% porous SnO ₂	447	75
SnO ₂ /graphene layer	17455	2908
SnO ₂ spherical hollow nanoparticles	23164	3861
CNT decorated hollow nanoparticles of SnO ₂	23894	3982

Conclusion

It has been observed that as the porosity of the SnO_2 layer increases, the diffusion coefficient increases. Further, the CNT decorated SnO_2 hollow nanospheres had the maximum diffusion coefficient. It is owing to its channel like hollow structure, offering a high surface to volume ratio. Therefore, gas sensing layer with this morphology has a shorter response time, leading to faster gas detection.

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Layer Dependent Semiconductor to Metal Transition in PtSe₂: From First Principle Calculation

Vishal K. Pathak¹, N. Meenakshisundaram² and Pramoda K. Nayak^{1*}

¹Department of Physics, 2D Materials Research and Innovation Group and Micro Nano and Bio-Fluidics Group Indian Institute of Technology Madras, Chennai 600 036, India

²Department of Physics, Vivekananda College, Tiruvedakam West, Madurai 625234, India

*Corresponding author: pnayak@iitm.ac.in

Abstract

Platinum-based transition metal dichalcogenides (TMDs) have been gaining renewed interest due to their intriguing physical properties for both fundamental research and potential applications in electronics, optoelectronics and so on. Here, we investigate layer-dependent tuneable electronic properties of platinum di-selenide (PtSe₂) by using only first principle calculation, *i.e.*, density functional theory (DFT). First principle calculation predicts that the lattice constant increase with the increase in layer numbers along with the finding that the nature of mono- and bilayers are indirect semiconductors with band gaps of 1.42 eV and 0.43 eV, while few-layers and bulk counterparts shows metallic nature. From the energy band diagram, we observe the decrease in the indirect band gap values with increase in thickness due to quantum confinement and interlayer interaction. The aforementioned tuneable electronic properties make PtSe₂ a suitable candidate for the future nanoelectronics and optoelectronics applications.

Introduction

Since the discovery of graphene in 2004, other classes of two-dimensional (2D) materials are evolving rapidly and this research topic is one of the emerging areas in the field of nanoscience and nanotechnology. 2D materials are regarded as layered materials, which are stacked together by weak van der Waals (vdW) interaction along the out of plane direction and strong covalent bonding within the layer and they reveal themselves having unique layer-dependent features distinct from their bulk counterparts. In the family of 2D materials, TMDs are desirable both for fundamental research and technological advancement due to their interesting optical and electronic properties, and their mechanical stability^[1].

Among TMDs, apart from well-known Mo and W dichalcogenides, Pt dichalcogenides have also attracted interest due to their (semi)metallic electronic structures. Besides their bulk form, 2D Pt dichalcogenides are promising materials for nanoelectronics device applications due to their intriguing electronic properties such as the transition from metal to semiconductor. Among the possible structures of TMDs (1T, 2H and 3R), 1T structure is found to be more stable in the case of PtSe₂^[2]. It has been an attractive layered material in recent years due to its helical spin structure as reported by Yao et al [3], which is induced by local Rashba effect and also strong interlayer coupling. DFT calculations suggest

that interlayer interactions are particularly strong in the $PtSe_2$. When the material is thinned to single molecular sheets with the transition from (semi)metallic to semiconductor, there is a significant opening in the band gap in monolayer.

Although the band structure evolution of this layered PtSe₂ has been reported in few literatures so far, but the study is still in nascent stage. Here, we investigate the electronic properties of PtSe₂, specially focused on the thickness dependence of band structures by varying the number of layers from monolayer up to trilayer as well as bulk 1T PtSe₂.

Computational methods

The *ab initio* calculations are performed with the density functional theory by using BURAI – a GUI software based on quantum-espresso code ^[4]. Calculations were performed using the projectoraugmented wave functions with spin-polarized generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE) functional. Correction for the van der Waals (vdW) to the PBE functional was done using the DFT-D2 method of Grimme. The top-to-top (AA) arrangement of the layers are taken since it has the lowest ground state energy value and also most favourable stacking order. The kinetic energy cut-off for a plane-wave basis set was taken as 800 eV. The convergence criteria for selfconsistent calculations for electronic structures was set to 10⁻⁶ eV. All crystal structure relaxations were conducted until the residual force acting on each atom is less than 0.01 eV/Å and pressure values less than 1 kbar. We sampled the first Brillouin zone using Γ -centered *k*-point mesh of 15 x 15 x 15 and 15 x 15 x 1 for bulk and thin film structures, respectively. At least 14 Å vacuum space added in *z*-direction to minimize the interaction between the neighbouring atomic layers.



Fig. 1. (Left) Bulk PtSe₂ structure (Right) Top and Side view of 1T-PtSe₂ monolayer.



Fig. 2. Band structures of 1T PtSe₂ with varying thickness: (a)-(c) 1L - 3L and (d) bulk structure.

Table 1.	Calculated	parameters
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a = b	a = b	
(Å)		(eV)
1L PtSe ₂	3.70	1.43
2L PtSe ₂	3.73	0.42
3L PtSe ₂	3.74	0
Bulk PtSe ₂	3.78	0

Results and Discussion

Fig.1 shows the crystal structure of octahedral 1T PtSe₂. The optimized lattice parameters together with calculated parameters are shown in Table 1 and Fig.2, respectively.

Our electronic structure calculations using the PBE functional show that while moving from monolayer to bilayer, the indirect band gaps decrease from 1.43 to

0.42 eV. It is also found that $PtSe_2$ crystals having a thickness larger than two layers exhibit metallic behavior. Bulk 1T-PtSe₂ structure is found to be (semi)metallic with lattice constant a = 3.786 Å, c = 5.525 Å close to experimental values of a = 3.728 Å, c = 5.0313 Å.

Looking at the band structures, one can see that 1T-PtSe₂ monolayer has its valence band maximum (VBM) at Γ point and conduction band minimum (CBM) within Γ -M point. While going from monolayer to bilayer and higher layers, we observe that position of CBM at Γ -M point is fixed and VBM shifted from Γ point to within K- Γ high symmetry point. The decrease in band energy of CB states and increase in VB states leads to metallization starting from trilayer^[5].

In this study, we were able to observe an increase in band gap with decrease in layer numbers from bulk down to monolayer structures. Unlike other TMDs like MX_2 (M = Mo and W; X = S and Se) which are direct bandgap semiconductors at monolayer, there is no shift from indirect-to-direct band gap with decrease in number layers from bulk to monolayer limit. This may be due to the difference in crystal structure – MX_2 has 2H structure and PtSe₂ has 1T structure. Nevertheless, we were able to observe the inverse relationship between the band gap and number of layers, which is governed by factors such as quantum confinement effect and interlayer interaction.

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Crystal Dynamics of Cu₃Au using pseudopotential theory

Nupur Vora¹, Priyank Kumar², S. M. Vyas¹, N. K. Bhatt³, and V.B. Gohel¹

¹Department of Physics, School of Science, Gujarat University, Ahmedabad- 380009, Gujarat, India. ²Department of Science & Humanities, Government Polytechnic, Dahod - 389151, Gujarat, India. ³Department of Physics, M. K. Bhavnagar University, Bhavnagar - 364001, Gujarat, India.

*Corresponding author: nupurvora94@gmail.com

Abstract

In the present study, theory of pseudopotential has been used to calculate lattice dynamics of Cu_3Au alloy. For the evaluation of phonon frequencies (in symmetry & non-symmetry directions) and elastic constants, a recently proposed pseudopotential is employed which is determined using Generalized Pseudopotential Theory (GPT). Computed results are found to be in good agreement with available experimental results. The computed results justify the present pseudopotential's ability for transition metal's alloy.

Introduction

Phonon Dynamics is the study of vibration of atoms in the crystal. Various attempts have been made over the last few decades to understand the thermodynamic, optical, electronic and elastic properties of the crystalline solids. For a better understanding of electrical conductivity and superconductivity, the interaction between conduction electrons and lattice vibration is crucial. [1-3].

In the present study, we have calculated phonon dispersion of Cu_3Au alloy using pseudopotential. Cu_3Au is a face centered cubic alloy because ordering transition takes place to the L12 structure near 661 K, with copper atoms are on the face centers and gold atoms at cubic unit cell's corner [4]. Au-Cu alloy are widely used in many fields such as a catalysis, electronics, and biological materials and some new functions of the alloy have been discovered in nano-crystal and thin-film materials [5].

It is very rare to use local pseudopotential to investigate comprehensive physical properties of transition metal's alloys due to its complicated chemical and electronic structure. It has been found that non-local pseudopotentials are more preferable, but they are intricate mathematically and their computational cost is high. In the present study, we have used new form of pseudopotential proposed by Bhatia et al. [1] which comprises one non-local and another local term in q-space and it is directly extracted from Generalized pseudopotential theory (GPT). Cu₃Au has been analyzed by several experimental and theoretical researchers to explore order- disorder transformation [6]. In the recent past, we have calculated phonon dispersion and elastic constants of Cu₃Au using George pseudopotential

and our results are in good agreement with experimental results [7].

Theory

The pseudopotential employed in the present study has following form in q- space [1].

$$v_{ion}(q) = \frac{1}{\Omega} \left[\frac{-8\pi z}{q^2} \frac{\cos qr_c}{1 - \frac{4\pi r_c^2}{\Omega} \left(\frac{j_1(qr_c)}{q} \right)} + \beta \exp\left(-q^2 r_d^2 \right) \right]$$
a)

Here, Ω =atomic volume, β = hybridization parameter. r_c =core radius, r_d = radius of d- electron, $j_1(qr_c)$ is the first-order spherical function. To calculate the phonon frequency $\omega_{\vec{q},\lambda}$ for \vec{q},λ mode, one requires to diagonalize the dynamical matrix for different values of \vec{q} . To calculate dynamical matrix, we have taken expression from [8]. Further, the phonon density of states is also calculated including the phonon frequencies in non-symmetric directions as well. The dynamical elastic constants can be calculated and relevant expression are taken from [9].

Results and discussion

A simplified method for determining the pseudopotential parameters has been provided. The parameters β and the ratio r_d/r_c are adjusted to achieve an overall good agreement with experimental phonon frequencies and the zero-pressure condition, assuming that the radius of the *d*-electron is 20–30% greater than the core radius [1]. we have adjusted our parameters in such a way that overall good agreement is observed at zone boundary with experimental results for Cu and Au metals. Using Vegard's rule, we have calculated input parameters for Cu₃Au and tabulated in table 1. The calculated phonon dispersion curves in symmetry directions for Cu₃Au are shown in Fig.1 and compared with experimental results [4].

 Table 1. The input parameters of Cu₃Au. (All are in a.u. except mass. Mass is in a.m.u)

Z *	Ω	Μ	r_c	r_d	β
1.2194	88.36	96.905	0.4342	0.478	37.5

Although, overall good agreement is observed, the maximum deviation in T-branch in [0.5, 0.5, 0.5] plane is about 35%. The sensitivity of the potential is also reflected in shear elastic constant (C₄₄). This discrepancy can be attributed to non-angular pairpotential used to measure vibrational response.



Fig. 1. Phonon Dispersion Curves for Cu₃Au in symmetry directions. Experimental points are due to [4].



Fig. 2. Phonon Density of states for Cu₃Au.

The phonon density of states is plotted in Fig. 2. The elastic constants are determined from the knowledge of long-wavelength limit of the phonon frequencies along major symmetry directions. Results are displayed in Table.2 and compared with experimental results [10]. The calculated values of C_{11} , C_{12} , C_{44} and B are in good agreement with variation 4.1%,5.6%,29% and 5.42% respectively. Results advocates that the Born elastic stability criteria is fulfilled with relatively large Cauchy's pressure $(C_{11} - C_{44})$ but small shear constant $\frac{1}{2}$ ($C_{11} - C_{12}$).

Table 2. Dynamical elastic constants of (C_{11}, C_{12}, C_{44}) and Bulk modulus(B) for Cu_3Au . (All quantities are in 10^{12} dyne/cm²)

	Present	Expt. results [10]
C11	1.8121	1.89
C12	1.2361	1.31
C44	0.5157	0.73
В	1.4281	1.51

Conclusion

In the present communication, we have analyzed lattice dynamics, elastic constants and phonon density of states of Cu₃Au using the new form of pseudopotential which is directly extracted from GPT. In lieu of the Born-Mayer type term, we believe that our results are in reasonable agreement with experimental results. Further, it is adequate to prove the crystal stability in the cubic fcc phase. The present study also validates the Vegard's rule in examining the vibrational properties of the Cu₃Au crystal.

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First Principles Study on Structural and Electronic Properties of CsPbI_{3-x}Br_x (X = 1, 2) Under Strain

Dibyajyoti Saikia, Atanu Betal, Jayanta Bera and Satyajit Sahu*

Department of Physics, Indian Institute of Technology Jodhpur, Jodhpur 342037, India

*Corresponding author: satyajit@iitj.ac.in

Abstract

Mixed halide cesium-based perovskites (CsPbI_{3-x}Br_x) have gained extensive attention as promising photovoltaic materials for highly efficient solar cells. In this study, we have studied the structural and electronic properties of CsPbI_{3-x}Br_x) (x = 1,2) using first principles calculations. The band gap values of CsPbI_{3-x}Br_x) (x = 1,2) have been varied from 1.04 to 1.81 eV in the strain range of -3 to 3%.

Introduction

Organic-inorganic perovskite solar cells (PSCs) have advanced significantly in the last decade, achieving 25.5% certified PCE. However, the longterm stability and volatile nature of certain organic species hinder their large-scale commercialization. Recently, all inorganic CsPbX₃ perovskites (X = Cl,Br and I) are considered as an excellent candidate for stable and efficient PSCs due to their high thermal stability and improved optoelectronic properties. Among these inorganic perovskites, cubic α -phase CsPbI₃ exhibits a band gap of 1.73 eV; demonstrated PSCs over 20% PCE [1]. Unfortunately, α -CsPbI₃ transforms to yellow phase δ -CsPbI₃ at ambient condition, which is unsuitable for solar cell application. Surprisingly, mixing of halide components was found to stabilize the cubic inorganic perovskite phase [2]. For instance, CsPbI₂Br have demonstrated excellent thermal stability having direct band gap of 1.91 eV. Recently, Ozturk et al. recorded 17.1% PCE on CsPbI₂Br PSCs by incorporating FeCl₂ into the perovskite precursor [3]. On the other hand, CsPbIBr₂ exhibits a band gap of 2.05 eV and stable up to its melting point more than 460 °C [4]. However, the PCE of CsPbI₂Br and CsPbIBr₂ PSCs is lower than that of CsPbI₃ based PSCs. The low efficiency is due to their higher band gap values that attributes large energy loss in mixed halide inorganic PSCs.

Strain has been demonstrated as an effective and a practical tool for modulating electronic and optical characteristics of halide perovskites. The electrical and optical characteristics of perovskite materials under strain have been studied in a number of experimental and theoretical works. A mild stress can lower the band gap while simultaneously increasing carrier lifetime [5], both of these are beneficial to solar cell (SC) application. In strain ranges of -5% to 5%, CsPbI₃band gap have been tuned from 1.03 to 2.14 eV

[6]. Here we have studied the strain tunning electronic and optical characteristics of α -phase CsPbI_{3-X}Br_X (x = 1,2) perovskites using first-principles calculations.

Computational **Details: OUANTUM** ESPRESSO package has been employed to execute the calculations using ultrasoft pseudopotentials within PBE-GGA for exchange-correlation (XC), and an energy cut off of 520 eV. To optimize the structures a $(10 \times 10 \times 10)$ k-point mesh, and for electronic properties calculation, a denser $(15 \times 15 \times 15)$ k-point mesh has been applied. The structures were completely relaxed till force convergence on each atom site was less than 0.01 eV/Å. Hydrostatic strain is modelled by simultaneously varying the lattice parameter, defined by $a = a_o (1 + \varepsilon)$. Here, a_o is the lattice parameter with no strain, and the value of ε changes from -3% to 3% in unit of 1%.



Fig. 2. Optimized structures of (**a**) CsPbI₂Br and (**b**) CsPbIBr₂ using PBE functional.

Results and discussion: Staring from CsPbI₃, which possesses a cubic phase with *Pm-3m* space group at high temperature, geometric structures of CsPbI_{3-X}Br_X (x = 1,2) is modelled by replacing I with Br atoms as shown in figure 2. The lattice parameter of CsPbI₃ was calculated to be 6.40 Å from first principles calculation, while its experimental value is 6.29 Å. The optimized lattice parameter of CsPbI₂Br and CsPbIBr₂ has been calculated to be 6.28 Å and 6.15 Å, respectively, consistent with the previous

calculated results [7]. Furthermore, the tolerance factor of $CsPbI_2Br$ and $CsPbIBr_2$ have been calculated to be 0.855 and 0.858, respectively, slightly higher than that of $CsPbI_3$ (0.847). The increased tolerance factor corresponds to the improved phase stability observed in experiments.

To study the stability of these compounds, decomposition energy E_d has been calculated by using the following two equations:

 $E_{d} = E(CsPbI_{2}Br) - E(CsI) - E(PbI_{2}) - E(PbBr_{2})$ (1)

 $E_{d} = E(CsPbIBr_{2}) - E(CsBr) - E(PbI_{2}) - E(PbBr_{2})$ (2)

The calculated E_d values of CsPbI₂Br and CsPbIBr₂ were found to be -0.06 eV and -0.11 eV respectively, greater than that of CsPbI₃ (0.07 eV), indicating more stability of mixed halide cesium-based perovskites.

Electronic Structure: The band gap of a material is one of the significant properties for SC application. All the studied compounds exhibited a direct band gap at R point as shown in figure 2. The band gap values have been calculated to be 1.41 and 1.54 eV for CsPbI₂Br and CsPbIBr₂, respectively. However, the calculated bandgaps are much lower than the experimental values 1.91 and 2.05 eV due to the underestimation of PBE functional.



Fig. 2. Calculated band structures of (**a**) CsPbI₂Br and (**b**) CsPbIBr₂ using PBE functional.

To investigate the significance of strain on structural and electronic properties strain has been applied form -3% to 3% in both the compounds. Figure 3 (a) and (b) showed the variation of energy with applied strain for CsPbI₂Br and CsPbIBr₂, respectively. For both the materials, the minimum energy was found at 0% strain, indicating the most relaxed structure.

To examine the dependence of electronic properties with applied strain band gaps have been calculated. As shown in figure 3 (c), band gap increases linearly with increasing applied strain. In the range of applied strain -3% to 3%, the band gap values

change from 1.04 to 1.68 eV and 1.17 to 1.81 eV for CsPbI₂Br and CsPbIBr₂, respectively. The variation of band gap with applied strain is because of the change of Pb-X-Pb bond angle and Pb-X bond length.



Fig. 3. Energy vs. strain for (a) CsPbI₂Br and (b) CsPbIBr₂, and (c) dependence of band gap with strain

In conclusion, we have studied the structural and electronic properties of $CsPbI_2Br$ and $CsPbIBr_2$ perovskites. These findings would help one to fabricate highly efficient PSCs. As PBE underestimates the band gap, further calculation is needed with advanced XC functionals such as HSE for the detailed study of these compounds.

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Ab-initio Simulations of Generalized Stacking Fault Energies in Cu

Raviraj Mandalia¹, Arjun Varma R.², Rahul Chigurupati², M. P. Gururajan², and Vaishali Shah¹

¹Department of Scientific Computing, Modeling, and Simulation, Savitribai Phule Pune University,

Pune, 411007 INDIA

²Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Powai, Mumbai, 400076 INDIA

email: ravirajmandalia@gmail.com, vaishali@unipune.ac.in

Abstract

First principles simulations were performed to calculate the structural parameters and generalized stacking fault energy (GSFE) of Cu with two different PAW pseudopotentials. Our results show that the GSFEs are more sensitive to the type of the pseudopotential than to the number of layers used to simulate the system with stacking faults. The GSFE surface generated using the energy values was incorporated into a phase field dislocation dynamics (PFDD) model. The dissociation of screw dislocations into leading and trailing partials are shown using this multi-scale model, as a first step towards validation.

Introduction

The deformation behavior of metallic systems is primarily governed by the creation, movement and evolution of dislocations. Stacking fault energy is a vital parameter that determines the dissociation of dislocations into partial dislocations and the separation between the partials. It is possible to incorporate the generalized stacking fault energy (GSFE) surface obtained from the atomic scale density functional theory (DFT) calculations, by representing it as an energy term in a phase field dislocation dynamics model (PFDD). [1, 2] In this study, we have obtained the GSFE surface for Cu and incorporated it into the PFDD model by approximating the GSFE surface with a Fourier series. The aim is to determine the optimal system size for the atomistic simulations to predict the appropriate mesoscale behavior. This study is a first step towards better understanding dislocation evolution and deformation behaviour in the Cu rich Cu-Al system.

Methodology

The optimized bulk lattice parameter and the GSFE values are calculated using *ab-initio* total energy calculations based on density functional theory, implemented in the Vienna Ab-initio Simulation Package (VASP) [3]. Standard PAW potentials [4] with the valence electronic configuration Cu: $3d^{10}4s^1$ (Type-1) and Cu: $3p^63d^{10}4s^1$ (Type-2) are used for the electron-ion interactions and the GGA-PBE approximation for exchange-correlation energies of electrons. Γ -centered Brillouin zone (BZ) as in the Monkhorst-Pack scheme [5] is integrated based on

the Methfessel–Paxton smearing method [6] with a smearing width of 0.2 eV. The total energy is converged to 1.0 μeV and the forces on all atoms to 1 $meV {\rm \AA}^{-1}$. Plane wave energy cut-off of 600 eV is used.



Figure 1: The structures of the (a) perfect crystal, rigid displacements (b) G2, (c) G and (d) the special points in the $\{111\}$ plane used to generate the γ -surface corresponding to normalized displacements along the two slip planes.

Cu Bulk	Type-1	Type-2	Expt.
$a_0(Å)$	3.63	3.62	3.61 [7]
C ₁₁	169.9	185.2	169
C ₁₂	121	126.9	122
C ₄₄	75	83.9	75.7

Table 1. The lattice parameter and elastic constants of Type-1 and Type-2 pseudopotentials compared with experimental values [8].

The GSFEs are calculated by displacing the upper eight (and five) layers of the optimized perfect crystal slab structure of 16 (and 10) {111} layers in the <110> and <112> directions as shown in Fig. 1(b) and (c) and relaxing the structure only in the <111> direction. The structures are periodic in the x, y direction with a 15 Å vacuum spacing in the z direction to avoid interactions with periodic images. The rigid displacements with respect to the perfect crystal unit cell (Fig. 1(a)) used to generate the γ -surface are shown in Fig. 1(d)). The GSFE value for any rigid displacement is determined as the difference in the ground state energy of the displaced crystal and the perfect crystal per unit area.

Results

Type-1 pseudopotential shows good agreement of the lattice parameter and predicts elastic constants (Table 1) in better agreement with experiments. The GSFE values are sensitive to the type of the pseudopotential and do not vary significantly with the number of layers. Our GSFE values for 16 layers are in better agreement with the literature [2] and with the experimental value (41-45 mJ m⁻²) [9].

Displacement	Layers			Ref.
Points	Type-1		Type-2	[2]
	10	16	16	
A	0.0	0.0	0.0	0.0
G1	81.6	81.9	89.5	87.5
G2	153.7	155.1	163	163.7
G3	103.1	107.0	115.2	112.8
G	31.3	37.8	38.3	38.5
T1	287.9	285.6	293.1	288.5
Т	516.6	502.8	521.9	509.4

Table 2. Energies at the special points on γ -surface (units in mJm⁻²). Point G and G2 are the intrinsic and unstable stacking fault, respectively.

Fig. 2(a) shows the γ -surface based on the Type-1 Cu pseudopotential for 16 layers which agrees well with literature [2]. The energy values in Table 2 is incorporated into the phase field model using a complex Fourier series expression [2] to define the GSFE component. In all the three cases, (10 and 16 layers with Type-1 and 16 layers with Type-2 pseudopotential) simulations using a straight screw dislocation dipole in the simulation cell resulted in the dissociation of dislocations into partials as shown in Fig. 2(b). The separation between the partials were measured as the distance between these two peaks and was observed in our simulations to be between 5–6b (b is the Burgers vector) which is in the same range reported in earlier atomistic studies and anisotropic elasticity theory calculations [2].



Figure 2: (a) 16 layer GSFE based γ -surface obtained using Type-1 pseudopotential and (b) dissociation of a perfect screw dislocation in the (111) slip plane into two partial dislocations, indicated by the two peaks. d Δ /dx represents the slope of the cumulative order parameter η [1, 2].

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First Principles Insights of Dzyloshinkii-Moriya Interaction in TiI₃ Monolayer

Vidit B. Zala¹, Rishit S. Shukla¹, Sanjeev K. Gupta² and P. N. Gajjar¹

¹Department of Physics, University School of Sciences, Gujarat University, Ahmedabad-380 009 ²Computational Materials and Nanoscience Group, Department of Physics, St. Xavier's College, Ahmedabad-380 009

*Corresponding author: pngajjar@gujaratuniversity.ac.in, sanjeev.gupta@sxca.edu.in

Abstract

The first principles investigation of the structural and electronic properties of TiI₃ monolayer (ML) has been performed. TiI₃ ML has a triagonal structure with lattice parameter 7.25 Ű. The spin-polarized electronic properties propose TiI₃ ML as a ferromagnetic semiconductor. The hybridization of *p-d* orbital near the valence band maxima (VBM) and conduction band minima (CBM) can be observed, in both spin up and spin down cases. The feeble variations in the structural parameters, viz. bond length and bond angle, in presence of external electric field is evocative of weak Dzyloshinkii-Moriya interaction among nearest Ti spins, resulting in frail magnetoelectric effect within TiI₃ ML.

Ab-Initio Insights on the Electronic and Optical Properties of ZnS/CNT Core/Shell Nanowire

Rishit S. Shukla¹, Vidit B. Zala¹, Sanjeev K. Gupta^{2,*}, and P. N. Gajjar^{1,*}

¹Department of Physics, University School of Sciences, Gujarat University, Ahmedabad 380 009. ²Computational Materials and Nanoscience Group, Department of Physics and Electronics, St. Xavier's College, Ahmedabad 380 009.

*Corresponding author: sanjeev.gupta@sxca.edu.in, pngajjar@gujaratuniversity.ac.in

Abstract

Theoretical calculations of electronic and optical properties of ZnS/CNT(n,n) core/shell (c/s) nanowires (NWs) was carried out. It was observed that ZnS core with (9,9) chiral armchair carbon nanotube (CNT) is the most stable c/s configuration. Dirac metallic cones were observed in the band structures of CNT(9,9) and an indirect bandgap of 3 eV was observed in bare ZnS NW. The optical properties of ZnS/CNT(9,9) seemed to be a superposition of the bare counterparts, with high absorption in the ultraviolet (UV) and infrared (IR) regions.

Effect of Mn doping in Bi₂Se₃ topological insulator: probed by DFT and ARPES

R. Kumar^{1,*}, Soma Banik², Shashwati Sen³, A.K. Yadav¹and D. Bhattacharyya¹

¹Atomic & Molecular Physics Division, ³Technical Physics Division, Bhabha Atomic Research Centre, Mumbai-400085, India

²Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India

*Corresponding author: raoravi.kumar77@gmail.com

Abstract

Magnetic ion doping in topological insulators has emerged out to be important both from technological point of view and for experimental verification of exotic fundamental physical concepts. Magnetic ion doping not only opens up the energy gap in surface states of a TI but also changes its bulk band structure significantly. To observe the effect of magnetic ion doping on electronic band structure of TIs we have performed high-resolution angle-resolved photoemission spectroscopy measurements and first principal DFT calculations on pure and Mn doped Bi₂Se₃.

Influence of Fe Doping on the Electronic Structure of Kagome Semimetal CoSn

Kritika Vijay^{1, 2, a)}, Archna Sagdeo^{1, 2}, Pragya Tiwari¹, Mukul Gupta³ and Soma Banik^{1, 2}

¹Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India ³UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, India

a) Corresponding author: kritikavijay@rrcat.gov.in

Abstract

Electronic structure of Kagome semimetallic compounds $Co_{1-x}Fe_xSn (x=0, 0.2)$ studied using synchrotron photoemission and xray absorption spectroscopy. Compared to CoSn the Co 2p core-level peaks in $Co_{0.8}Fe_{0.2}Sn$ are found to be broader with reduced spin orbit splitting. The valence band of $Co_{0.8}Fe_{0.2}Sn$ also showed increased bandwidth of the d bands as compared to CoSn with prominent decrease in the intensity of the localized states near the Fermi level. The increased width of both the valence band and core level features in $Co_{0.8}Fe_{0.2}Sn$ indicates strong hybridization between Fe 3d and Co 3d states while decrease in the spin orbit splitting is related to the near neighbour electronic d-d interactions. We find that there is an interplay between the hybridization and electron-electron interaction in the Fe doped CoSn compound which influences the reported magnetic properties.

Introduction

Kagome metals attract considerable attention due to the presence of the both dispersive (Dirac fermions) as well as dispersion-less flat bands [1-2]. Due to special geometric arrangement of the Kagome network, the flat bands show novel quantum phenomena, fractional quantum hall effect, and unconventional superconductivity which have fundamental importance as well as potential technological applications [3]. CoSn is a Pauli paramagnet with B35 Hexagonal structure [1,3]. Co atoms in CoSn are stacked in Kagome network in ab plane separated by inequivalent Sn atomic layers along the c-axis [3]. Fe doping in CoSn will behave like hole doping. It is theoretically predicted that Fe doping in CoSn will bring flat bands closer to the Fermi level and leads to increase in magnetic ordering [3,4] which needs to be explored experimentally. In the present work, we dope Fe in CoSn and investigate the changes in the electronic structure using both the valence band (VB) and corelevel (XPS) photoemission spectroscopy (PES).

Experimental Methods

Polycrystalline ingots of $Co_{1-x}Fe_xSn$ (x=0, 0.2) were prepared using arc melting technique followed by annealing at 750°C for 168 hours in a vacuum sealed quartz ampoule. The crystal structure is determined by a commercial X-ray diffractometer (Bruker model D8 Advance). The chemical compositions of the ingots were determined by a commercial scanning electron microscope (Philips, XL30CP) equipped with an energy dispersive spectrometer (EDS) Bruker, XFlashr Silicon Drift Detector. The bulk compositions obtained from EDS for x=0 and 0.2 are Con 99Sn1 01 and Con 78Fen 22Sn. Soft X-ray absorption spectroscopy (XAS) measurements were performed at SXAS beamline BL-01, Indus-2 at the Co L_{2.3} edge. High resolution PES measurements were performed at ARPES beamline BL-10, Indus-2. The atomically cleaned surface was obtained by initial scrapping followed by Argon ion sputtering at 1.5 keV for 1 h. The VB studies performed using monochromatic He-1 source from SPECS (UVS 300) and synchrotron excitation energy at 480 eV. XPS studies performed using 1078 eV synchrotron photon energy. Both the VB and the XPS data were recorded using SPECS Phoibos 150 electron energy analyzer Base pressure during measurement was 7×10^{-11} mbar.

Results and Discussions

XRD patterns of CoSn and $Co_{0.8}Fe_{0.2}Sn$ are shown in Fig. 1. XRD patterns of both the samples are indexed with B35 type hexagonal crystal structure and P6/mmm space group [3-5]. The lattice parameters



Fig. 1. XRD patterns of CoSn and Co_{0.8}Fe_{0.2}Sn with the crystal structure of CoSn shown in the inset.

were determined by the Le Bail refinement. The lattice parameters of CoSn are: a = 5.2814(2) Å and c = 4.2630(4) Å and Co0.8Fe0.2Sn are: a = 5.2839(5) Å and c = 4.3073(8) Å. It is found that both a and c increase with the Fe doping in CoSn which is because Fe is less soluble in Sn than the Co in Co_{1-x}Fe_xSn [5].



Fig. 2. Co 2p Core level XAS spectra shown in (a) and XPS spectra shown in (b). Shaded peaks in (b) shows the correlation satellites.

The XAS spectra recorded at Co $L_{2,3}$ edge of both the samples are shown in Fig 2 (a). XAS peaks showed the difference in the $2p_{3/2}/2p_{1/2}$ intensity ratio in CoSn (3.39) and Co_{0.8}Fe_{0.2}Sn (2.77) with much broader 2p peaks for the Fe doped CoSn sample. Moreover, the spin-orbit splitting (SOS) is found to be higher in CoSn as compared to Co_{0.8}Fe_{0.2}Sn in both XAS and XPS spectra (see Fig. 2 (a) and (b)). In XPS spectra we find that the intensity of the correlation satellite (shaded peaks in Fig. 2(b)) decreases in $Co_{0.8}Fe_{0.2}Sn$. Both the decrease in SOS and correlation satellite with doping depends mainly on the near neighbor d-d interactions [6]. In CoSn, the d-d interaction is between the Co atoms at different sites in Kagome network while in the Fe doped CoSn, there are two different d-d interactions between the Co atoms at different sites and the Fe and Co atoms. Co-Co d-d interactions give rise to the localized states while the Fe-Co d-d interactions give rise to more delocalized states in Co_{0.8}Fe_{0.2}Sn which are responsible for the spin polarization and magnetic ordering [3,6].

The VB studies performed with two different energies at 480 eV (SR) and 21.2 eV (He-I) to understand the orbital character of the valence band features. At 480 eV the photoionization cross-section of Sn 5p is much lower (310 times) than at 21.2 eV excitation energy which is quite evident in Fig. 3 (a) and (b) (see the intensity of features C and D). The VB features in Co_{1-x}Fe_xSn are compared with the VB features of pure Co, Fe and Sn metals in Fig. 3(b). In Fig. 3(a) we find the intensity of feature A corresponding to Co 3d states decreases with the Fe doping while the intensity of the feature B corresponding to the hybridized Fe 3d and Co 3d



Fig 3: The valence band spectra of CoSn and Co_{0.8}Fe_{0.2}Sn with two different energies (**a**) at 480 eV and (**b**) at 21.2 eV compared to elemental Co, elemental Fe, and elemental Sn.

states increases. The broadening of the d band in compared to CoSn indicates strong hybridization between the Fe 3d and Co 3d states. The energy position of the feature A ($\approx 0.3 \text{ eV}$) in CoSn matches with the flat band position and feature B is close to the Dirac point position [1]. Instead of flat band being closer to E_F with Fe doping in CoSn as reported in Ref. [4] we find the increase in the density of the delocalized states. So, d-d electronic interactions give rise to dominating localized states in CoSn while Fe doping in CoSn give rise to both the localized and the delocalized states.

Conclusions

We find that Fe doping in CoSn not only increases the broadening of the valence d bands but also decreases the electron-electron d-d interactions. The similar effect of broader Co 2p core-levels peaks with the reduced SOS and less intensity of correlation satellite indicates that there is interplay between the hybridization and electron-electron interactions in this system which are responsible for the origin of magnetic ordering with the Fe doping.

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Spectroscopic and DFT based Computational Investigation of Nonlinear Optical Responses of Pyrrolidine derivative

Vivek Dhuliya^{1*}, Shradha Lakhera²

¹Department of Physics, Dr. P. D. B. H. Govt. P.G. College, Kotdwara, Pauri Garhwal, 246149, Uttarakhand India

²Department of Physics, School of Sciences, Uttarakhand Open University, Haldwani, 263139, Uttarakhand, India

**Corresponding author: vivekdhuliya@gmail.com*

Abstract

The organic nonlinear optical (NLO) compounds are considered more efficient than the inorganic ones. Therefore, we had considered organic derivative of pyrrolidine for the present work. A computational study was performed to examine the NLO activity of 1-(4-nitrophenyl)-2-pyrrolidinemethanol using density functional theory with B3LYP/6-311G basis set. The Mulliken charges and the molecular electrostatic potential are computed to predict the intramolecular charge transfer within the molecule. The molecular orbital calculations and macroscopic NLO properties were also discussed in detail in the present work. **Keywords:** Nonlinear optical compounds; Mulliken charges; Pyrrolidine; Polarizability

1. Introduction

Nonlinear optical (NLO) materials are attracting attention in the research area due to their wide applicability in optical frequency conversion, lasers, photonics, telecommunications, etc [1]. The delocalization of electron cloud between the donor and acceptor moieties is the major reason for the NLO behavior of such materials [2]. The research works reported so far validates the efficiency of organic NLO materials over inorganic ones [3]. Motivated by this fact, the present study is done with a derivative of the organic compound pyrrolidine that is a cyclic secondary amine. The present study deals with the computational analysis of NLO behavior of 1-(4nitrophenyl)-2-pyrrolidinemethanol (NPM). The Mulliken charge analysis and molecular electrostatic potential (MEP) analysis was done to predict the intramolecular charge transfer (ICT) [4]. Frontier molecular orbital (FMO) parameters like ionization potential (IP), electron affinity (EA), chemical potential (CP), electronegativity (χ), hardness (η), and softness (S) were also calculated to verify the chemical reactivity of the molecule [5]. The spectra analysis (UV-Vis and Raman) was reported to check the electronic and vibrational properties of the molecule. NLO parameters like total dipole moment (μ_{total}), mean isotropic polarizability (α), anisotropic polarizability $(\Delta \alpha)$, and hyperpolarizability (β) were also computed to verify the NLO behavior of the probe molecule [6]. 2. Computational tools and methods

The computational work was performed with the help of the software "Gaussian 09". The structure of NPM was obtained from the database "PubChem" and optimized to its ground state. The optimized geometry was used to calculate all the FMO parameters using Koopman's equations [7]. UV-Vis analysis was done using the TD-SCF method to report the electronic properties of the molecule. Frequency optimization was done to obtain vibrational spectra of the molecule. **3. Results and Discussion**

3.1 Optimized structure and charge analysis

The structure of NPM (inset of Fig.1(a)) is a fourmembered molecule (C, O, H, and N). There is one hydroxy (-OH) and one nitro (NO₂) group associated with the molecule. NPM has electrostatic potential energy equal to -20752.37eV and a dipole moment of 9.1Debye that shows the high intramolecular interactions of the molecule.



Fig.1. (a) Mulliken charges distribution graph of NPM. The inset of Fig. 1 represents the optimized structure of NPM. (b) HOMO-LUMO.

The positive charge contribution of H atoms and the negative charge contribution of N and O atoms was observed from the Mulliken charge distribution graph (Fig.1(a)). However, the charge contribution of C atoms varies from -0.415e (8C) to 0.387e (11C). The 4N has a maximum negative charge of -0.712e. This variation in charge suggested the presence of ICT within the NPM molecule.

3.2 Chemical reactivity

The computed values of highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) (Fig. 1(b)) energies for NPM molecule were -6.06eV and -2.45eV respectively. The difference between these energies (ΔE) was 3.61eV that predicts the high

polarizing ability of the molecule [8]. The values of IP and EA were 6.06eV and 2.45eV. The change in energy of the molecule by shifting of the electron cloud is given by the value of CP (-4.25eV). χ had a value of 4.25eV that represents the interactions of free electrons with the -OH and -NO2 group. The values of η (1.8eV) and S (0.55eV) show the stiffness of the molecule. All the FMO parameters show the chemical stability and reactivity of the molecule.

3.3 MEP analysis

MEP of the NPM (inset of Fig.2(a)) molecule shows the presence of electron donor with electron cloud (N atoms) and the acceptor part (O atoms). Due to the presence of nucleophilic (blue) and electrophilic (red) part, there is a great possibility of ICT that shows the stability of the NPM molecule.

3.4 UV-Vis analysis

Due to the presence of π - π * and n- π * transitions, UV-Vis spectra of NPM was denoted by a strong absorption band ranging between 300nm to 500nm wavelength (λ) (Fig.2(a)). The transition observed on the maximum λ (372.29 nm) is represented by S₀ \rightarrow S₁ with energy 3.33eV and oscillator strength (f) 0.0001. The transition $S_0 \rightarrow S_2$ was observed at λ 355.97nm with 0.4485 f and energy 3.48eV. The value of λ for transition $S_0 \rightarrow S_3$ is 318.41nm with maximum energy of 3.89eV and 0.0003 f. The raised values of λ and energy denote the high interactions between electron cloud (n-electron) and π electrons. The availability of such types of transitions ensures the high polarizability of the molecule.

3.5 Vibrational analysis

The obtained Raman spectra of NPM had four major peaks (Fig.2(b)). The 16C-5N bond of the -NO₂ group (49446.44cm⁻¹) shows linear stretching that disturbs the whole geometry. The -OH group shows stretching of the bond at intensity 385.30cm⁻¹. Mainly these two modes show the high vibrations with the functional groups. Other modes and their intensities are shown in Fig.2(b). The high values of the Raman intensities validate the vibrational stability of the molecule. Thus, the NPM molecule might possess high polarizability.



Fig.2. (a) UV-Vis absorption spectra of NPM molecule with transition levels and oscillator strength. The inset of Fig. 2(a) represents MEP surface of NPM. (b) Raman spectra of NPM. The inset of Fig. 2(b) represents comparison of NLO properties.

3.6 NLO analysis

The polarizability parameters for NPM and Urea (known NLO material) are compared (inset of Fig.2(b). The value of μ_{total} for NPM is found to be 3.57Debye which is more than twice that of Urea (1.52Debye). The value of α and $\Delta \alpha$ are computed as 23.52×10^{-24} esu and 67.04×10^{-24} esu respectively. The value of α is found to be four times that of Urea (5.66×10⁻²⁴esu) and the value of $\Delta \alpha$ is more than ten times that of Urea (6.30×10^{-24} esu). β for NPM is found to be 27.85×10^{-30} esu that is thirty-five times higher than that of Urea $(0.781 \times 10^{-30} \text{esu})$. The extremely high values of polarizability parameters of the NPM molecule have a high possibility to act as an NLO material.

4. Conclusion

In the present study, we had detected the NLO responses of the NPM molecule computationally. The high values of dipole moment and electrostatic potential energy shows the presence of intramolecular interactions. Mulliken charge and MEP represent the high variation in charge and charge transfer respectively. The FMO parameters have acceptable values that verify the chemical stability of the compound. The vibrations of both the functional groups show high Raman intensity. The absorption band of UV-Vis spectra shows transitions at high wavelengths that denote the ability of the molecule to undergo electronic transitions. Although, the values of μ_{total} , α , and β are comparable to that of Urea. By this comparison, we can conclude that the NPM molecule has shown the NLO responses by computational mode and it may have the probability to show NLO behavior in experimental work also. Thus, the NPM has strong candidature to be used as an NLO material in the future

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Multi-band slotted Microstrip Patch Antenna for S-band, C-band, X-band & Ku-band Applications

P. Arockia Michael Mercy¹, K. S. Joseph Wilson^{2*}

PG & Research Department of Physics Arul Anandar College, Karumathur – 625514, India. *Corresponding author: mercypackia@gmail.com*

Abstract

A great antenna magnificent gave on account microstrip patch slotted antennas owing to their conciseness and incorporation in the field of communication. So as to refine gain and bandwidth, large-scale research is executed in the patch antennas. Several investigators have been communicated the systematic forms like circular, rectangular, and square patches. A novel design of six rectangular cuttings with a T-Slot patch antenna is considered and analyzed in this research article. To tune the characteristics and to enhance the outcomes of rectangular patch antenna (RPA) slot cutting techniques are used. Quint-bands are realized by introducing slots in the rectangular patch. It achieves five-band resonant frequencies having the highest gain of 15 dB, the radiation efficiency of 1.5815 at 14.79 GHz having the dimensions of 26 x33 x 1.6 mm. It is evident from the outcomes that gain became greater, the radiation efficiency is enhanced, return loss is minimized and quint band frequencies are achieved in a wide band range having the slots on patch antenna. The proposed construction makes the antenna reliable in design and facile for fabrication by enrolling slots in the patch. It covers the application of weather radar, surface ship radar, WiMAX (3.52 GHz), long-distance communication (7.72 GHz), satellite and space communication, terrestrial broadcast radar, amateur radio (11.50 GHz, 11.85 GHz), Satellite communication (14.79 GHz).

Keywords: Patch antenna, slot cutting techniques, return loss, gain

Introduction

The leading wireless applications stand in need of multiuse and concise patch antennas. It could be accomplished by the Microstrip Patch Antennas (MPA) of progressive conformation exploits [1]. The size reduction of MPA can be actualized by the usage of heightened methodology thus configuration mutation, high permittivity materials usage as substrates, etc. Even so, the utilization of substrates with high permittivity materials makes less its characteristic impedance which causes to mismatching of impedance and bringing about low efficiency with decadence in antenna execution [9]. The objection of forming a profitable miniature-size microstrip patch slotted antenna which operates at the operating frequency of 2.4 GHz is not an obvious assignment. The antenna's size and gain are in proportion to one another at once. Crowds of endeavor have been carried out by researchers recently for the size reduction of the antenna [10]. In order to overcome the challenges of the above said, also to tune the antenna parameters with enhanced outcomes of gain, radiation efficiency, and to achieve multi-band operation in a broadband range at 2.4 GHz, T- slotted antenna with six rectangular slot cuttings is proposed and it can be economical.



Design and Configuration of Antenna

Fig.1. Configuration of Rectangular Pach antenna

Figure1 displays the conformation of the designed antenna such as antenna without slots, antenna with six rectangular slots, and antenna with Tslot. The antenna is fabricated on FR4 substrate which is low-priced possessing a height of 1.6 mm, dielectric constant of 4.4, and tangential loss of 0.019. High-Frequency Simulating Software (HFSS) is utilized to simulate the designed antenna. The crucial work of this antenna is to tune the antenna characteristics of return loss, VSWR, Gain, Directivity, and Radiation efficiency and to achieve the multi resonance frequencies at the operating frequency of 2.4 GHz. The proposed antenna consists of six rectangular slots and T-slot cutting on the patch of the antenna to enhance its parameters. The flow of surface current could be realized, excited to flow at the slot cut structure by the

slot cutting techniques. The measurements of the considered antenna are displayed in the table.1 **Table.1**

Antenna	mm
parameters	
L _P	15
WP	9
Ls	33
Ws	26
Н	1.6
L _G	33
W _G	26
Feedline width	3
Feedline	12.4
length	-

Result and Discussion



Fig.2 Effect of slots on return loss characteristics

Fig.2 exhibits that the antenna designed with slots produces lesser return loss than that of the antenna without the slots on the patch. The antenna having no slots resonates at four bands at 3.94 GHz, 11.08 GHz, 12.34 GHz, and 14.72 GHz with the return loss of -12.2939 dB, -24.3799 dB, -13.1643 dB, -10.5102 dB respectively. To realize the aim of this work of tuning the antenna characteristics, to broaden up the resonance frequency range for the various applications, slot cutting techniques are used. By the introduction of the six rectangular slots on the patch, the antenna yields quad-bands at 3.52 GHz, 7.72 GHz, 12.2 GHz, and 14.79 GHz with the return loss of -11.1958 dB, -19.3630 dB, -20.9553 dB, and -10.4334 dB respectively. Again T-Slot is introduced on the patch then the antenna resonates at five bands of 3.52 GHz, 7.72 GHz, 11.50 GHz, 11.85 GHz, and 14.79 GHz with the return loss of -10.2216 dB, -16.8821 dB, -10.2263 dB, -28.2553 dB, -32.8527 dB respectively. Overall, the performance of the antenna can be enhanced by incorporating features such as measurements, patches, slots., etc. Choosing proper measurements for cutting slots on the patch is a vital role in achieving multi-band features, tuning the antenna parameters, and realizing better outcomes.



Fig.3 Comparative Analysis of Gain & Radiation efficiency with and without the slots

The above figures reveal that the function of slots on the patch and how it yields better results with multi-band features for multipurpose. Fig 3 shows the gain and radiation efficiency versus resonant frequencies without and with the slots. As the resonant frequency increases gain also increases however at a particular frequency it yields the maximum gain of 10 dB holding maximum efficiency of 1.0134 without the slots added in the patch but after the insertion of six rectangular slots and T-slot, the antenna achieves the maximum gain of 15 dB while it arrives at 1.5815 of radiation efficiency successfully. The above analysis confirms that Slot-cutting techniques not only enhance the characteristics of the antenna but also it brings out multi resonant frequency in a broadband range.

Conclusion

A new type of six rectangular slots and T-slot microstrip patch slotted antenna was suggested and analysed employing HFSS Software. The antenna with a slotted patch has resonated at five different frequencies with enhanced outcomes in a broadband range. Hence the slot cutting techniques are more opted for tuning and enhancing the antenna characteristics in a broadband range, reducing the size of the antenna, achieving multi-band features with the best results for various applications in the communication field.

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Thermal Effects on Mc-Si Ingot Growth Through Directional Solidification Process with Conventional and Modified Retorts: A Numerical Investigation

T. Keerthivasan, G. Aravindan, M. Srinivasan*, and P. Ramasamy

Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Chennai - 603110.

*Corresponding author: srinisastri@gmail.com

Abstract

In this paper, the results of the ingots grown with the conventional retort and modified retorts which are insulation inserted in bottom, center, and top of the retort respectively are compared with each other. The heat dissipation was analyzed by placing two thermocouples TC1 and TC2 near the side graphite heater and heat exchanger block respectively. By controlling the heat dissipation, the melt crystal interface could be maintained as convex or flat interface shape which is one of the key factors to grow good quality mc-Si ingot. The results shows that the ingot grown by the directional solidification furnace by modified retorts have more heat dissipation due to the insulation inserted in the retort as compared to the conventional retort.
Enhanced Optoelectronic Properties of 2D Hetero-bilayer HfS₂/GaS

Abhishek Patel^{1*}, Deobrat Singh², Yogesh Sonvane³, P.B. Thakor¹ and Rajeev Ahuja^{2,4}

¹Department of Physics, Veer Narmad South Gujarat University, Surat 395007, India;

² Condensed Matter Theory Group, Materials Theory Division, Department of Physics and Astronomy, Uppsala University, Box 516, 75120 Uppsala, Sweden;

³Department of Physics, Sardar Vallabhbhai National Institute of Technology, Surat 395007, India; ⁴Department of Physics, Indian Institute of Technology Ropar, Rupnagar 140001, Punjab, India

*Corresponding author: arpatel14@hotmail.com

Abstract

In the present study, the stability, electronic structure, and optical properties of the 2D van der Waals (vdW) have been systematically discussed within the framework of the Density Functional Theory (DFT). For the different stacking arrangements, the HfS2/GaS has exhibited the semiconducting characteristics with reduced electronic direct and indirect bandgaps. It has shown strong optical absorption in comparison to single-layers HfS2 and GaS. The enhanced optical and electronic properties of the HfS2/GaS suggest it as potential materials for applications in optoelectronics and nanodevices.

Introduction

The 2D materials such as monolayers, bilayers, multilayers and hetero-structure of them got highly remarkable attention due to their efficient performance, novel and innovative properties and potential applications¹. The monolayers GaS and HfS₂ have been experimentally realized and they have desirable structural, electronic, optical and other properties for potential applications at nano-scale^{2,3}. By designing the heterostructure of 2D materials, the modification, one can achieved the improvement and enhanced in the various properties of the material can be achieved^{4,5}. Inspired by these interesting facts, the stability, electronic structure and optical absorption spectrum of the hetero-bilayer HfS₂/GaS have been systematically analyzed in this study.

Computational Method and Materials



Fig. 1. Optimized Structure of hetero-bilayer HfS_2/GaS in the stacking AA, AB_1 and AB_2 .

The simulations and computations based on the DFT calculations have been performed using the VASP code⁶. Applying the energy cut-off of 500 eV,

the projected augmented wave method has been utilized with the Generalized Gradient Approach of Perdew-Burke-Ernzerhof^{7,8}. The optimized structures have been obtained using the Monkhorst-Pack k-point mesh of the dimensions $11 \times 11 \times 1$ under the electronic energy converge criteria of 10^{-8} eV and the force minimizing criteria of 10^{-2} eV/Å. The interaction of periodic layers has been prevented by using vacuum of 25 Å.

The very small lattice mismatch (0.5%) between the structure of 2D single layers 1T-HfS₂ (3.629 Å) and GaS (3.609 Å) allows the formation between them. In the structure of hetero-bilayer HfS₂/GaS, the HfS₂ and GaS has been separated by interlayer spacing of 3.1 Å. The determined lattice constants of hetero-bilayer HfS₂/GaS are 3.619 Å, 3.618 Å and 3.617Å in the 2D hexagonal lattice with binding energies -0.211 eV, -0.201 eV, -0.202 eV for the stacking AA, AB₁ and AB₂, respectively. The negative biding energies confirms the stability of this hetero-bilayer for the stacking AA, AB₁ and AB₂.

Electronic and Optical Properties

The hybrid electronic band-structure of the 2D vdW hetero-bilayer HfS₂/GaS with elemental projected has computed over symmetry k-path Γ -M-K- Γ using the HSE06 functional which has been illustrated in Fig. 2. For the stacking arrangements AA, AB₁ and AB₂, the hetero-bilayer HfS₂/GaS exhibits electronic bands 1.72 eV, 1.69 eV and 1.72 eV of the indirect character, respectively. Similarly, it also shows the direct electronic gaps of 2.42 eV, 2.41 eV and 2.44 eV for the stacking arrangements AA, AB₁ and AB₂, respectively. The significant reduction in the direct

and indirect electronic bandgap of vdW heterobilayer HfS₂/GaS has been observed.



Fig. 2. Electronic band-structure of hetero-bilayer HfS₂/GaS with elemental projection via HSE06 functional.

 Table 1. Computed electronic bandgap using HSE06 functional.

Material (2D)	Indirect Bandgap (eV)	Direct Bandgap (eV)
Heterostructure	1.72 ^(a) , 1.69 ^(b) ,	2.42 ^(a) , 2.41 ^(b) ,
HfS ₂ /GaS	1.72 ^(c)	$2.44^{(c)}$
Monolayer HfS ₂	2.09	2.99
Monolayer GaS	3.28	3.64

*(a) Stacking AA, (b) Stacking AB₁, (c) Stacking AB₂



Fig. 3. Optical absorption $(\alpha(\omega))$ spectra of heterostructure HfS₂/GaS, monolayer HfS₂ and monolayer GaS

As illustrated in Fig. 2, the sulfur (S) has predominant contribution in the construction of valence band of this HfS_2/GaS . In the valence band near forbidden gap, there is also noted small contribution coming Ga atom. The Hf atom has main contribution in formation of the conduction band near the forbidden gap while Ga atom has dominantly contribution in conduction band far from the forbidden gap. The S atom has also significant contribution in the conduction band formation.

The optical absorption spectrum of the 2D heterobilayer is systematic combination of components single layers HfS_2 and GaS (see Fig. 3). Initially, the optical absorption of this hetero-bilayer has been very close with single-layer HfS_2 for the electro-magnetic radiation with low photon-energy. Then, the optical absorption of HfS_2/GaS has been changed toward that of single-layer GaS for higher ultraviolet frequencies (photon energy). For the photon energy more than 5.5 eV, the 2D HfS_2/GaS absorbs optical radiation more efficiently than its single layer components HfS_2 and GaS. Here, the vdW hetero-bilayer HfS_2/GaS has more efficient optical absorption in comparison with single layers HfS_2 and GaS.

Conclusion

In the concluding remark, the electronic structure and optical absorption spectra of 2D hetero-bilayer material HfS_2/GaS have been systematically analyzed. With exhibiting semiconducting nature, the 2D vdW hetero-bilayer HfS_2/GaS has reduced indirect and direct electronic band-gaps in comparison with single layers HfS_2 and GaS_2 . With like to be a systematic composition of optical absorption spectra of HfS_2 and GaS, the 2D heterobilayer HfS_2/GaS has more efficient optical absorption property. Due to desirable electronic and optical properties, the HfS2/GaS has potential applications in nanoelectronics and optoelectronics.

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Exploring Topological Features in Chalcopyrite ZnXBi₂ (X = C, Si, Ge, Sn, and Pb)

Vikrant Chaudhary¹, Tashi Nautiyal², and Hem C. Kandpal¹

¹Department of Chemistry, ²Department of Physics, Indian Institute of Technology Roorkee, Roorkee, 247667

*Corresponding author: hem.kandpal@cy.iitr.ac.in

Abstract

After the discovery of topology in materials, researchers are intensively searching for promising topological material candidates. We carried out a computational search for the topological features in the chalcopyrite family $ZnXBi_2$ (X = C, Si, Ge, Sn, Pb). We checked the stability of these materials at different hydrostatic pressure. These materials show thermodynamic stability at negative pressure. ZnSnBi2 is the least unstable material in the family and can be a good candidate for experimentalists to hunt for. We searched for the Weyl points and corresponding Chern numbers. The number of Weyl points and Chern number is found to be consistent with symmetry operations of the space group $I\bar{4}2d$.

Introduction

The phases of materials have always been a central theme in materials science research. The discovery of topological phases in materials drastically changed the subject. In the last decade, scientists around the world have been actively hunting for topologically non-trivial materials. Now, there are many experimentally confirmed 2D and 3D topological materials. Some of the known topological insulators are HgTe/CdTe quantum well [1], Bi₂Se₃, Bi₂Te₃, Sb₂Te₃ [2] etc. Topological phases are also known in gapless materials. Na₃Bi is one of the earliest experimentally realized 3D topological Dirac semimetal [3].

There is a well-known, but least understood relation between thermoelectric properties and topology in materials. Many topological insulators are known to be good thermoelectric materials and *vice-versa* [4]. While searching the literature, we found a good thermoelectric material, namely ZnSnSb₂ [5]. This material could show non-trivial surface states under the application of uniaxial strain and hydrostatic pressure. The role of pressure in tuning the phases of materials is well known among the scientific community. This motivated us to investigate the thermoelectric and topological properties of the chalcopyrite family ZnXBi2 (X = C, Si, Ge, Sn, and Pb).

These chalcopyrite family compounds are not experimentally known. Therefore, we checked the thermodynamic stability of these compounds. All of these are not stable at ambient pressure. The instability is least in ZnSnBi₂. This compound becomes stable by applying negative hydrostatic pressure, which can be induced by doping bigger atoms or can be synthesized epitaxially on a bigger substrate. This is something that experimentalist can explore from their experiences.

Results and Discussions

As discussed in the last section, we optimized the chalcopyrite family $ZnXBi_2$ (X = C, Si, Ge, Sn, and Pb) compounds by substituting X for Sn and Bi for Sb in ZnSnSb₂. We used a 15×15×15 Monkhorst pack scheme for structural optimization with a plane wave energy cutoff value of 500 eV. We took bismuth (Bi) because of its high spin-orbit coupling value, a critical factor in realizing topologically nontrivial states. We calculated the formation energy for the entire family. The Bi-based chalcopyrite family is found to be thermodynamically unstable based on density functional theory (DFT). Although, there are many known metastable (from DFT predictions) materials that were successfully synthesized either at ambient pressure or by applying pressure [6]. Thus, we checked the stability of these materials with the changing hydrostatic pressure as implemented in the Vienna ab-initio simulation package (VASP) [7].

These systems show stability by inducing negative pressure. $ZnCBi_2$ requires the highest amount of pressure on the negative side and $ZnSnBi_2$ least. We need to reduce the pressure by an amount larger than 5.5 GPa for $ZnCBi_2$. On the other hand, $ZnSnBi_2$ has a formation enthalpy of 0.065 eV/Atom at ambient pressure, and it becomes thermodynamically stable at -1.5 GPa. Thus, $ZnSnBi_2$ seems to be the most promising candidate in the family.

Table 1. Lattice parameters of ZnSnBi₂ in $I\bar{4}2d$ space group.

Pressure (GPa)	a (Å)	c (Å)
Ambient	6.5962	13.3035
-1.5	6.7110	13.5151

Therefore, we picked $ZnSnBi_2$ and investigated the topological properties. The energy above the convex hull (E_{Hull}) at ambient pressure is very small, and the chance of synthesis is not categorically ruled out. We already know from the literature that the synthesis of metastable $Fe_2V_{0.8}W_{0.2}Al$ was successfully done by thin film deposition [8]. Therefore, we cannot claim based on density functional theory only that ZnSnBi₂ will not exist experimentally.

After selecting a promising candidate, we calculated the electronic band structure with the fullpotential local-orbital (FPLO) code [9]. We observed many Weyl-like crossings near the Fermi level in the directions $\Gamma \rightarrow \Sigma$ and $X \rightarrow \Gamma$, as shown in figure 1.



Fig. 1. Band structure of ZnSnBi₂ with spin-orbit coupling. The insets show the magnified regions indicated by arrows.

The red bands in the top left inset show the dispersion near the Fermi level in the vicinity of X, and the blue bands in the bottom-right inset show the dispersion above Fermi level near the Γ point. The orbital contribution near the Fermi level is dominated by the Zn (4s), Sn (5p), and Bi (6p) states. We took these states and calculated a tight-binding Hamiltonian using Wannier [10] interpolation. This Hamiltonian was used for searching Weyl points and their Chern numbers by using the pyfplo module of FPLO.

ZnSnBi₂ is nonmagnetic, and the space group of the compound is non-centrosymmetric. Thus, the inversion symmetry is broken, and time reversal is present in the system. The time-reversal symmetry will ensure a partner Weyl point at the time-reversal invariant momenta (TRIM) with the same chirality. If these points have a +1 Chern number, there should be two more Weyl points with a -1 Chern number. The total Chern number should remain zero. Therefore, the Weyl points should occur in the multiple of four. We found eight Weyl points in k-space with +1 and -1 Chern numbers are at $(\pm 0.052, \pm 0.043, 0)$ and $(\pm 0.043, \pm 0.052, 0)$ respectively. These Weyl points are connected with the eight symmetry operations of the space group $I\bar{4}2d$.

There is always a partner Weyl point with the opposite Chern number. One Weyl point acts as a source and one as a sink of Berry flux. The presence of Weyl points tells us about the topological signatures in ZnSnBi₂. We have seen that non-trivial topology enhances the electronic and heat conductivity. Although we do not see topological materials being used in large-scale applications, these materials will help us develop energy-efficient electronics and, hopefully, quantum computers in the future.

Conclusion

The first experimental realization of non-trivial topological material was reported in 2007. We are still looking for materials that can be used for the large-scale purpose. Keeping this in mind, we started searching for new candidates. We found that Weyl points exist near the Fermi level in ZnSnBi₂. This finding suggests that we should look for the experimental existence of ZnSnBi₂ and confirm the presence of Weyl points.

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Numerical Investigation on mc-Si Growth process by Directional Solidification for enhancing solar cell efficiency

S. Sugunraj¹, P. Karuppasamy¹, G. Aravindan¹, M. Srinivasan^{1*} and P. Ramasamy¹

¹SSN Research Centre, SSN college of Engineering, Chennai-603110, India.

*Corresponding author: srinisastri@gmail.com

Abstract

2D numerical simulation was carried out for growing high quality mc-Si ingot by directional solidification (DS) for enhancing performance of solar cells. The finite volume method is used for the discretization of DS system. The melt-crystal interface has a crucial role in controlling the impurities and dislocation generation in grown crystals. In this present work, the melt-crystal interfaces were studied for the different growth stages. Also, we have investigated the carbon (C) and oxygen (O) impurities.

Sodium Decorated Gallenane Layer for CO₂ Adsorption

Mohammad Ubaid^{1*}, Anver Aziz¹, and Bhalchandra S. Pujari²

¹Department of Physics, Jamia Millia Islamia, New Delhi, 110025

²Department of Scientific Computing, Modeling & Simulation, Savitribai Phule Pune University, Pune, 411007, India

*Corresponding author: ubaidm020@gmail.com

Abstract

In this work, we investigate the results from the first-principles method based on the electronic structure calculations and study the adsorption properties of CO_2 molecule on gallenane (GaH) and sodium decorated gallenane (Na@GaH). The most stable configuration for adsorption on Na@GaH is determined, and the structural parameters, adsorption energies and electronic structure are calculated. The adsorption energies of CO_2 on Na@GaH are significantly improved as compared to GaH and CO_2 is chemisorbed on Na@GaH. Our findings indicate that Na@GaH could be a promising candidate for molecule adsorption.

Introduction

Very recently, gallenene, a monolayer of gallium has been added to the family of two-dimensional lavered materials (2DLMs). Gallenene (Ga100 & Ga010) was successfully obtained by exfoliation of the solid-melt interface of gallium droplets on multiple substrates.[1] The electronic structure of the gallenene monolayers is metallic and highly anisotropic with a combination of partially filled Dirac cones and nonlinear dispersive bands, which can lead to new fundamental phenomena and a wide range of applications for Ga-based 2DLMs.[1] Generally, 2DLMs are being extensively studied for gas sensors to the inherent large surface-to-volume ratio. Recently, calcium-decorated/doped and idiumdoped phosphorene has been studied for the adsorption of various gas molecules such as CH₄, CO₂, H₂, H₂O and NH₃, which reveals that the Calcium-decorated and doped phosphorene are suitable for molecule adsorption as compared to the pristine phosphorene. [2,3]

In this work, hydrogenated-Ga010 (GaH) is considered for the calculations, which is dynamically stable.[4] We have studied Na-decorated GaH (Na@GaH) layer for CO₂ sensing. Here, we report our findings on GaH and Na@GaH with CO₂ molecule. We examine their structural parameters, electronic structure and adsorption properties.

Computational details

Our work was performed based on density functional theory calculations using the Quantum ESPRESSO.[5] The pseudopotential is generated by the projector-augmented wave (PAW) method.[6] The kinetic energy cutoff of 700 eV was used for the planewave basis set. The first Brillouin zone was sampled with a 6 X 6 X 1 and 12 X 12 X 1 Monkhorst-Pack [7] grid for the optimization and static calculations, respectively. To avoid the interaction between periodic images, the thickness of the vacuum of 15 Å was considered. Upon relaxation, the adsorption energy of the CO_2 molecule is calculated by,

$$E_{ads} = E_{GL+CO_2} - E_{GL} - E_{CO_2}$$

where E_{CO_2} , E_{GL} and E_{GL+CO_2} are the total energies of the isolated CO₂ molecule, isolated GaH layer and CO₂ adsorbed GaH layer, respectively.

Results and discussion

In this section, the structural, adsorption and electronic properties of GaH are investigated. As a benchmark, the unconstrained structural optimization of the GaH layer is performed and structural parameters are obtained. The optimized lattice parameters of the GaH layer are found to be 3.96 Å which is in good agreement with the reported by Kochat. et al. [1]. The electronic density of states (DOS) of GaH (see Fig. 2 (a)) indicates the metallic nature of GaH with a DOS of 4.5 eV at the Fermi level. Adsorption on GaH: To understand the favorable position of the CO2 molecule on GaH, CO2 was allowed to fully relax over the GaH layer. The relaxed structure of CO₂ adsorbed GaH is depicted in Fig. 1(b), showing no covalent bonding between molecule and layer, which indicates the physisorption. The adsorption energy and corresponding binding distance are given in Table. 1. The small adsorption energy and large binding distance along with non-covalent bonding showing the weak interaction between molecule and layer. Further, the DOS of CO2 adsorbed GaH is calculated and is depicted in Fig. 2(a). Upon

adsorption of CO_2 on GaH, no significant changes have been observed in the DOS, which are consistent with small adsorption energy and large binding distance.



Fig. 1 Top and side views of (a) GaH, CO₂ adsorbed (b) GaH and (c & d) Na@GaH layers. The Ga, Na, C, O and H atoms are represented by violet, cyan, gray, red and white colors, respectively.

Adsorption on Na@GaH: Foremost, single sodium (Na) is placed at three high-symmetry sites on the relaxed GaH layer and find the most favorable adsorption site (top of the valley of the Ga atom). The Na atom makes the covalent bond with the Ga atom and its calculated adsorption energy on the GaH layer is found to be -1.95 eV. The DOS of Na@GaH is shown in Fig. 2(b), indicates the higher electronic states at the Fermi level. This indicates the enhancement in the electrical conductivity of the GaH layer, which is beneficial for gas adsorption. We now shift the focus to the CO₂ molecule adsorbed on the Na@GaH layer. Initially, CO2 is placed on the Na@GaH layer and then relaxed the system. The relaxed structures of CO2 adsorbed Na@GaH are shown in Fig. 1 (c & d). The two most favorable sites of CO2 on Na@GaH are obtained, namely, (i) CO2 oriented vertical to the layer (Na@GaH-V) and parallel to the layer (Na@GaH-P). In both cases, strong chemisorption is found via covalent bonding between the Na and O atoms. Their calculated adsorption energies and corresponding binding distances are listed in Table 1. The adsorption energies are increased significantly for both cases, suggesting strong interaction between Na@GaH and CO2 molecule. To gain more insight into the adsorption of CO2 on Na@GaH, its total DOS is calculated and depicted in Fig. 2(c). As shown in Fig. 2(c), upon adsorption of CO₂, strong hybridization is observed in the orbitals of Na@GaH and CO₂, which is consistent with the strong chemisorption. The peaks observed at 1.4 eV and 2 eV for both cases indicate the influence of the CO₂ molecule on the Na@GaH layer.



Fig. 2 Total electronic density of states of (a) CO₂ adsorbed GaH, (b) Na@GaH and (c) CO₂ adsorbed Na@GaH.

Table 1. Calculated adsorption energy (E), adsorption height (h_{GL-CO2}), Ga-Na distance (d_{Ga-Na}) and O-Na distance (d_{O-Na}) of CO₂ on different layers.

Parameters	GaH	Na@GaH-	Na@GaH-
		V	Р
E (eV)	-0.10	-0.31	-0.47
hgl-co2 (Å)	3.19	4.35	3.23
d _{Ga-Na} (Å)		2.99	2.95
d _{O-Na} (Å)		2.42	2.45

Conclusions

In summary, using the DFT calculations, we have systematically studied the CO_2 adsorption on GaH and Na@GaH. The adsorption energy of CO_2 significantly increases upon the decoration of the Na atom on GaH. Also, adsorption energies reveal that the CO_2 is physisorbed and chemisorbed on GaH and Na@GaH, respectively. In conclusion, our study suggests that Na@GaH could be used as a potential candidate for CO_2 adsorption.

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Electronic Structure Studies of Dihydrated 2,4,6triaminopyrimidinium-3,5-dinitrobenzoate Proton Transfer Complex: A Comparative Analysis

Ziya Afroz^{1,*}, Mohd. Faizan², Mohammad Jane Alam³, Shabbir Ahmad³.

¹Department of Chemistry, Aligarh Muslim University, Aligarh-202002, Uttar Pradesh, India. ²Department of Physics, Mirza Ghalib College, Gaya-823001, Bihar, India. ³Department of Physics, Aligarh Muslim University, Aligarh-202002, Uttar Pradesh, India.

*Corresponding author: zia19a@gmail.com

Abstract

Herein, the electronic structure of the dihydrated proton transfer complex 2,4,6-triaminopyrimidinium-3,5-dinitrobenzoate has been compared with its constituents. Henceforth, molecular electrostatic potential mapping of the titled molecular complex along with its reactant molecules have been investigated thoroughly. Further, the effect of natural atomic charge rearrangement after complex formation has been examined critically by theoretical calculation at DFT/B3LYP/6-311++G(d,p) level of theory.

Introduction

Electronic structural studies play significant role in the determination of physico-chemical properties of charge transfer (CT) or proton transfer (PT) complex where the selection of acceptor or donor molecule is a challenging task. After exploring the different dimensions of the electronic structure of the synthesized PT complex, one can able to predict the suitability from the point of view of its application in pharmaceutical. material and opto-electronic industries and modulate its selective physicochemical properties by either changing the functional group with the donor/acceptor molecule or donoracceptor combination [1,2].

Presently, the electronic structure in terms of molecular electrostatic potential (MEP) mapping of dihydrated PT complex of 2,4,6-triaminopyrimidine (TAP) and 3,5-dinitrobenzoic acid (DNBA) has been compared with its reactant and after that, the Natural atomic charge rearrangement has been critically examined from its constituents; TAP and DNBA.

Computational Details

The structure optimization was carried out at DFT/B3LYP/6-311++G(d,p) level of theory. The absence of negative vibration has been taken into account for the stabilization of optimized geometry [1]. The mapping of molecular electrostatic potential and Natural atomic charge calculation have been

performed at the same level of theory using Gaussian 09 [4].



Fig. 1. Structure optimization of dihydrated PT complex with atomic numbering at DFT/6-311G++(d,p) level of theory. Reprinted with permission © Elsevier 2021 [1].

Results and Discussions

Molecular Electrostatic Potential Mapping

The MEP mapping assists to predict the possible donor or acceptor site associated to the molecular system [3]. For the titled molecular system, the MEP surface has been depicted by Fig. 2 with colour scale; the red colour represents the most electronegative potential site, green for the neutral region and blue for the most electropositive potential site. The MEP surface of the DNBA suggests that the possibilities of involvement of –COOH group because of the presence of high positive and slightly negative potential available on the -COOH group of DNBA. Then after, three NH₂ group of the TAP have the high electropositive potential while two nitrogen on pyrimidine ring have high electronegative potential. The water molecules have both high electropositive and electronegative potential sites. Further, during the formation of PT complex, the -COO⁻ group of DNBA interacts with one - NH₂ and one nitrogen (N6) is accepted the proton from -COOH group of DNBA and forming $O^-...H^--N^+$ type ionic intermolecular interaction. Moreover, the water molecule is also interacting with -COO⁻ of DNBA (as suggested by the crystal structure [1]). After that, this very water molecule is connected to another water molecule. The MEP of PT complex enables us to say that there will be the availability of possible binding sites, 1) the electropositive potential on the two -NH₂ group on the surface above the TAP part and 2) the slightly electronegative potential sites present above the -NO₂ group of DNBA part.



Fig. 2. 2D illustration of MEP mapping of dihydrated proton transfer complex of TAP and DNBA.

Natural Atomic Charge Analysis

Analysis of Natural atomic charge within the molecular system is useful for the identification of preferable binding site due to the electronic charge rearrangement [5,6]. Fig. 3 represents the comparative analysis of Natural atomic charge of PT complex with its reactants.

From Fig. 3, after the PT complex formation, the positive atomic charge at C2 is increased by 0.05 e. In a similar manner, the positive charge at H5 atom is also enhanced by 0.05 e after the complex formation. The negative charge on O26 and O27 of DNBA has been increased by 0.13 and 0.14 e, respectively after the formation of PT complex from its constituents. The noticeable amount of negative charge on O39 and positive charge on H41 on water molecule has been increased by 0.07 and 0.05 e, respectively due to the formation of intermolecular hydrogen bonding

with the neighbouring molecules. The remaining atomic charges are changed accordingly due to the formation of inter and intramolecular hydrogen bonding for the stabilization of dihydrated PT complex.



Fig. 3. Comparative Natural atomic charge depiction of dihydrated PT complex of TAP and DNBA with its reactants; TAP, DNBA and H₂O.

Conclusion

The MEP analysis of dihydrated PT complex enables us to predict the possibility of electrophilic and nucleophilic attack positions. Moreover, one may easily observe a large amount of atomic charge rearrangement at O26 and O27 by Natural atomic charge analysis. This will suggest the strong possibility of ionic type intermolecular hydrogen bonding i.e., O⁻...H-N⁺ type which is already confirmed by its crystal structure studies and FTIR studies [1]. Further, from the replacement of suitable electron donating group (EDG) or electron withdrawing group (EWG) with available -NH₂ or -NO₂ group, one may control the extent of charge transfer from one molecule to another in order to achieve the desirable physico-chemical properties and modify the intermolecular hydrogen bonding along with associated electronic bandgap for the corresponding molecular complex.

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First Principles Study of Structural, Elastic & Electronic Properties of Hafnia Polymorphs

Diana Denice¹, Ashok Arya², Manoj Kumar¹, and Gopika Vinod³

¹Control Instrumentation Division, ²Glass & Advanced Materials Division, ³Reactor Safety Division, BARC, Trombay, 400085

*Corresponding author: dianad@barc.gov.in

Abstract

Hafnium dioxide (HfO₂) is a technologically important material in the semiconductor industry. However, there is a limited literature on the elastic and electronic properties of all five polymorphs of HfO₂. We report structural, elastic and electronic properties of monoclinic, tetragonal, cubic and two orthorhombic phases of HfO₂ using Density Functional Theory (DFT) simulations and compare our results on structural and elastic properties with available experimental and other DFT results.

Spectroscopic Characterization and DFT Study of (E)-2-(1-(3-oxo-1,3-diphenylprop-1-en-2-yl) pyridin-2 (1H)-ylidene) Malononitrile Sankaran Nampoothiri V¹, Dr. Lynnette Joseph¹, Merin George¹

¹Centre for Advanced Functional Materials, Department of Physics, Bishop Moore College, Mavelikara-690110, Kerala, India

*Corresponding author: lynnettejohn@gmail.com

Abstract

Nonlinear optical (NLO) crystals having good stability, high transparency in the visible region and superior nonlinear susceptibilities are noteworthy due to their influence on the development of laser technology and optoelectronic industry. Theoretical study of nonlinear optical behaviour was done using B3-LYP/6-311G (d) basis set in Gaussian 09 program. The first hyperpolarizability of the molecule was computed by density functional theory. The observed vibrational wavenumbers in the experimental spectra were compared with the calculated results. From UV-vis absorption spectrum, excitation energy, maximum absorption wavelength and optical energy band gap have been performed. The HOMO-LUMO energy gap of the compound is calculated. HOMO and LUMO energies reveal the chemical reactivity, kinetic stability and hardness of molecule.

Introduction

Organic nonlinear optical materials (NLO) have been examined broadly owing to their potentially high nonlinearities and fast reaction in electro-optic effect. Among common natural NLO materials, organic chalcone NLO subsidiaries are found to have marvelous attraction from scientists and analysts of all around the world due to their different applications in medical and NLO technological field [1]. (E)-2-(1-(3oxo-1,3-diphenylprop-1-en-2-yl) pyridin-2 (1H)ylidene) malononitrile is composed of three fragments:one (pyridin-2-ylidene) malononitrile moiety, one benzoyl group and one phenyl ring [2].

Computation Details

All the quantum chemical computations were carried out using the Gaussian 09 program package using B3LYP/6-31++G (d,p) level to derive the optimized geometry. The optimized geometry of (E)-2-(1-(3-oxo-1,3-diphenylprop-1-en-2-yl) pyridin-2 (1H)-ylidene) malononitrile is shown in Fig. 1. The NBO analysis has also been carried out at the B3LYP/cc-pvtz level using NBO 3.1 program [3].

Results and Discussion

The optimized molecular structure of (E)-2-(1-(3-0xo-1,3-diphenylprop-1-en-2-yl)pyridin-2 (1H)ylidene) malononitrile calculated using DFT theory at B3LYP/6-31++G(d,p) level. The (pyridin-2ylidene) malononitrile group is connected to chalcone unit.



Fig. 1. Fig. 1 Optimized geometry of (E)-2-(1-(3-oxo-1,3diphenylprop-1-en-2-yl) pyridin-2 (1H)-ylidene) malononitrile.

The electric dipole moment (μ) and the static first hyperpolarizability ($\beta(0;0,0)$) values of the investigated molecule have been computed using ab initio quantum mechanical calculations. The calculated first hyperpolarizability is 9.90×10^{-29} esu, predicted theoretically for the first time in this compound, which is 13 times that of urea. The electric dipole moment was found to be 9.747 which is three times higher than that of urea.

The NBO analysis performed utilizing NBO 3.1 program included in Gaussian'09 bundle is utilized for understanding electronic delocalization impact. The interaction energy $E^{(2)}$ approximated by second-order perturbation theory may be a degree of electron donor-acceptor interaction and conjugation of the full system [4].

In the Phenyl ring, π (C₂₈-C₄₀) conjugates with π^* (C₁₇-C₃₀) and π^* (C₆-C₂₄) leading to a stabilization energy of 75.19 and 89.96 kj/mol respectively. The bond π (C₁₇-C₃₀) which further conjugates with π^* (C₆-C₂₄) and π^* (C₂₈-C₄₀) contributes an additional energy of 85.73 and 90.96kJ/mol to the system.



Fig. 2. Simulated electronic absorption spectra of (E)-2-(1-(3-oxo-1,3-diphenylprop-1-en-2-yl) pyridin-2 (1H)-ylidene) malononitrile employing B3LYP/CC-PVTZ functional performed in gas phase.

The low energy electronic excited states of the title compound have been calculated at the B3LYP/CC-PVTZ level using the TD-DFT approach on the previously optimized ground-state geometry of the molecule. The absorption spectra in most of the organic molecules is observed due to transitions from π - π * and/or n - π * in the range of 200–700 nm [5]. One strong peak observed at 315nm. The simulated spectrum shows a strong peak at a wavelength of 315 nm due to $\pi \rightarrow \pi^*$ transition within the molecule. Similarly, the computed spectrum gives transitions at 541.64, 396.92, 364.52, 324.95 and 313.73 nm with energy 220.85, 301.39, 328.17, 368.13 and 381.30 kJ/mol-1 respectively. This shows the presence of bathochromic shift. This says that shift of a substance to lower energy state with a longer wavelength. So the computed transition energy is shifted because of the charge transfer interaction.

The HOMO–LUMO energy gap of the title compound was calculated at the B3LYP/6-31++G (d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO as an electron acceptor represents the ability to obtain an electron,

and HOMO represents the ability to donate an electron. The calculated energy value of HOMO is -0.2119 eV and LUMO is -0.1027 eV. The energy gap (0.1091 eV) of HOMO–LUMO explains the eventual charge transfer interaction within the molecule, which influences the biological activity of the molecule. Consequently, the lowering of the HOMO–LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-acceptor group [6].



Fig. 3. (a) HOMO plot of the title compound at B3LYP/6-31++G (d,p) and (b) LUMO plot of at B3LYP/6-31++G (d,p)

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Structural and Electronic Properties of α-Ca₃N₂ : A First Principles Study

P. Meena^{1,*} K. Kabra¹ and G. Sharma¹

¹Department of Pure & Applied Physics, University of Kota, Kota-324005, India

*Corresponding author: pinkeshmeena35@gmail.com

Abstract

In this paper, we investigated the structure and electronic properties of α - Ca3N2 compound using the first principles linear combination of atomic orbital (LCAO) method. Structural properties are determined by optimizing the experimental structural parameter under DFT-GGA framework. The electronic properties of optimized structure show semiconducting nature of α -Ca3N2. The energy band gap of α -Ca3N2 lies within the range of optimum energy of solar spectrum, hence making it suitable candidate for photovoltaic applications.

Introduction

Importance of *ab initio* calculation, in exploring various ground state properties is well recognized and appreciated as well. Calcium Nitride (II-V group semi-conducting compound) is reported to show wide band gap semiconducting properties which have potential applications in electronic and optoelectronic devices [1]. The band gap energy of these compounds is reported to lie between the energy range of the solar spectrum. The experimental investigation shows that there exist 4 different phases of Ca₃N₂ corresponding to high pressure values that is α , β , δ and ε . Among these four phases, α-Ca₃N₂ is reported to the most stable phase at ambient condition. Therefore, the present work shows first principles investigation of the ground state properties like structural and electronic properties.

Computational Details

The ground state properties like structural parameters and electronic properties of α-Ca₃N ₂ are investigated using first principles methods embedded in code [2]. CRYSTAL17 The self-consistency calculation are performed by launching the state-of-art function within the density functional theory under the scheme of generalized gradient approximation. For the exchange-correlation potential we have used Becke as exchange functional and for correlation VBH is used. Experimental geometry [3,4] has been taken as the starting point and equilibrium geometry is achieved by performing full optimization of the structure (lattice parameter and atomic positions). Gaussian basis sets of Ca and N atoms are taken from Ref.[5]. The Monkhorst-pack grid with 12 x 12 x 12 mesh of kpoints is used, resulting 98 k-points in first irreducible

Brillouin zone (IBZ). Convergence criterion on total energy is taken as 10^{-8} a.u.

RESULTS AND DISCUSSION

Structure of Ca₃N₂ is cubic with atomic positions embellished by space group Ia-3 (space group no. 206). Unit cell of α -Ca₃N₂ contains 80 atoms, corresponding to 16 formula unit [6]. The optimized structural parameter with a = 11.7233 Å is found to be in agreement with experimental data. The optimized data is used to determine other structural properties like bulk modulus (B₀) and its pressure derivative (B₀') by using equation of state (EOS) corresponding to Birch-Murnaghan. B₀ and B₀' obtained from calculation are 75.19 GPa and 3.93, respectively show in figure 1.



Fig. 1. Energy versus volume curve of α -Ca₃N₂.

The electronic properties are explored from energy band structure (BS) and electronic density of state (DOS). BS and DOS are plotted in figure 2 and 3, respectively. From figure 2 presence of valance band maxima (VBM) at N-point of BZ and conduction bond minima at Γ -point of BZ indicate presence of indirect gap with Eg=1.51 eV. The experimental band gap is reported to be 1.55eV [7]. Thus, our results are within the limit of experimental error, justifying the computational results.

From DOS it is observed that VBM is dominated by **p**-orbital of N atom where contribution of N1>N2. Though, the contribution **p**-orbital of Ca atom is significant across the E_F in valence region. The maximum unoccupied state of Ca-p orbital is observed in conduction region. Hence, the existence of semiconducting nature in α -Ca₃N₂ dominated by p-orbital of N atom in VB region and C atom in conduction band region.

The overlapping band in higher valence states are due to hybridization of energy states of Ca-p and N-p orbitals as evident from the density of states in figure 3.



Fig. 2. Electronic band structure of α -Ca₃N₂.



Fig. 3. Projected density of states for α -Ca₃N₂.

Conclusions

The ground state properties α -Ca₃N₂ have been studied by first principles LCAO method. The structural parameters obtained from EOS indicate that α -Ca₃N₂ is mechanically stiff owing to large value of bulk modulus, thus suitable from the applications point of view. Electronic properties show indirect band gap with E_g=1.5 eV. The energy band gape value for the α -Ca₃N₂ solid is found in the region of solar energy spectrum, thus it indicates that its photovoltaic applications.

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Electronic And Elastic Properties Of CeX (X=Cd&Hg) Intermetallics: An Ab-Initio Study

Hansa Devi¹, Anjna Devi¹, Arun Kumar¹ and Om Prakash²

¹Department of Physics, Swami Vivekanand Government College Ghumarwin, 174021, India ²Department of Chemistry, Abhilashi University Chail Chowk, Mandi (H.P.) 175028, India

*Corresponding author: <u>hansa.phy@gmail.com</u>

Abstract

An ab-initio calculations have been performed to investigate the electronic and elastic properties of CeCd and CeHg intermetallics using density functional theory. The electronic properties have been studied throughout the calculations of the band structure and charge density distributions. From band structure calculations, it is revealed that both the intermetallics exhibit metallic character. The ductility or brittleness of these compounds is predicted from Pugh's rule (B/G_H) ratio.

Introduction

Rare earth (RE) intermetallic compounds with B_2 structure have attracted significant attention due to their enormous fundamental physical and technological applications. The 4*f* electrons present in rare earth elements are highly localized and are responsible for the large magnetic moments as well as the distinctive optical, electronic and magnetic properties of the rare earth compounds [1].

The CeCd and CeHg crystallizes in cubic CsCltype structure (space group symmetry of Pm3m (No.221). Presence of $4f^{1}$ -electrons in cerium and its compounds attract considerable attention due to the intricate electronic and magnetic properties and exhibit a variety of phenomena like heavy-fermions, mixed-valency and Kondo behaviour. Numerous experimental studies have been made on these intermetallics due to their fascinating features. Lattice parameters of these CeCd and CeHg intermetallics have been reported by Indelli et. al. [2] using X-ray study and suggested that these compounds have CsCl type structure. Since there is no theoretical and experimental calculation on electronic and elastic properties of CeCd and CeHg compounds in the literature, only experimental data for the lattice parameters exist for these compounds. The lack of information has motivated us to explore the electronic and elastic properties of these compounds by using density functional theory (DFT).

Method of Calculations

The present calculations have been performed by using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code [3], based on the DFT. The generalized gradient approximation (GGA) [4] and local spin density approximation (LSDA) [5] are used in all calculations to describe the exchange and correlation energy. In order to predict the chemical bonding between RE element with Cd atom we have plotted charge density plots along (110) plane for these compounds. As a good compromise between computational efficiency and accuracy, we have considered a number of basis functions up to $R_{MT} \times K_{max} = 7.5$ for CeCd and CeHg compounds, where R_{MT} is the smallest atomic radius in the unit cell and K_{max} gives the magnitude of the largest *K* vector in the plane wave expansion.

Results and Discussion

To determine the ground state properties like lattice constant (a₀), bulk modulus (B) its pressure derivative (B') and magnetic moment (μ_B), we have calculated the total energy as a function of volume and fitted to Birch equation of state [6]. All the values are listed in Table 1. It is noticed that theoretically predicted lattice parameters for CeCd and CeHg compounds are in good agreement with existing experimental measurements. [2]. The second order elastic constant are calculated by using the method developed by Charpin in the WIEN2k package [3]. It can be noticed from Table 2 that our calculated elastic constants at ambient pressure satisfy the stability criterions: $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B < C_{11}$.

TABLE 1. Calculated ground state and electronic properties of CeX (X=Cd &Hg) intermetallics in B₂ -phase.

Solids	Approx	ao	В	B'	(µв)	N(E _F)
		(Å)	(GPa)			
CeCd	GGA	3.840	46.19	4.73	1.34	-
	LSDA	3.7007	57.44	4.23	1.24	7.75
	Expt.	3.865 ^a	-	-	-	-
CeHg	GGA	3.821	57.45	3.49	1.39	-
	LSDA	3.702	68.89	4.21	1.36	12.84
	Expt.	3.816 ^a	-	-	-	-
aD ([0		D	1			

^aRef. [2], Expt. – Experimental

The spin polarized electronic band structures along high symmetry direction of CeCd as well as CeHg are presented in Figure 1, where Fermi level (E_F) is considered at the origin. The lowest lying bands around 8.3 eV in CeCd and 7.5 eV in CeHg are mainly due to the '4*d*' states of Cd and '5*d*' states of Hg in CeX compounds whereas '4*f*' states of Ce lie sharply at E_F and are responsible for the strong metallic behaviour of these intermetallics. The calculated value of DOS at Fermi level N(E_F) in States/eV for CeX are presented in Table 1. Finite value of DOS, suggesting the metallic nature of CeCd and CeHg.



Fig. 1. Band Structure (BS) for CeX (X=Cd & Hg) intermetallics using LSDA approximation.



Fig. 2. Charge density plots for CeX (X = Cd & Hg) intermetallics.

Charge density distributions serve as achieving a complementary tool for proper understanding of the electronic structure of the system being studied. If the electronic charge contours are isolated from each other the bonding will be purely ionic and when there are overlapping in the electronic charge density between the cation and anion, the bonding may be covalent in nature. From the analysis of the charge density characteristics, it is found that there are predominant

covalent interactions between Ce and Hg as the charge density is shared between the cation and anion whereas a predominant ionic bonding characteristic is observed between the Ce and Cd atoms in CeCd.

 TABLE 2. Calculated elastic constants for CeCd and

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CeHg using GGA and LSDA approximations in B ₂ -phase.						
Solids	Approx	C11	C12	C44	$\mathbf{B}/\mathbf{G}_{H}$	
		(GPa)	(GPa)	(GPa)		
CeCd	GGA	85.49	30.09	23.01	1.95	
	LSDA	71.58	58.40	49.58		
	Expt.	-	-	-	-	
CeHg	GGA	122.81	28.54	42.86	1.34	
	LSDA	125.03	31.23	34.04		
	Expt.	-	-	-	-	

As suggested by Pugh [7], a material will be ductile if $B/G_H > 1.75$. From Table 2, it can be seen that the calculated values of B/G_H for CeCd and CeHg are found to be 1.95 and 1.34 respectively, which shows that CeCd is ductile while CeHg is covalent in nature.

Conclusion

The FP-LAPW method has been used to investigate the ground state, elastic and electronic properties of CeCd and CeHg compounds. From band structure, we found that the metallic nature of these intermetallics is mainly due to the 4f states of Ce which are located sharply at E_F . The bonding character of CeCd and CeHg is investigated through electronic charge density plots. From the values of Pugh's criteria (B/*G_H*) the ductile and brittle nature of this compounds is predicted.

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Thermodynamic Properties of Pure and Li Adsorbed Graphene From Vibrational Modes

Gagandeep Kaur^{1*}, Savita², Sarita Mann², Nibraa Mossa Umran³, Ranjan Kumar^{2,4} and Keya Dharamvir⁴

¹Department of School Education, SSA, Chandigarh, 160014, India ²Department of Physics & Centre of Advanced Studies in Physics, Panjab University, Chandigarh, 160014, India ³Department of Physics, University of Kerbala, Kerbala, Iraq ⁴Department of Physics, King Abdulaziz University, Jeddah, Saudi Arabia

*Corresponding author: gaganj1981@gmail.com

Abstract

Various thermodynamic properties of pure and lithium-adsorbed graphene ($\text{Li}@G_{32}$) are calculated using their phonon dispersion curves. The phonons are calculated using Ab initio density functional perturbation theory (DFPT). The phonon dispersion curves show significant change at low frequencies on Li adsorption. The density of states (DOS) reflects the presence of Li atom and the specific heat, entropy and free energy of these two systems have been plotted as a function of temperature.

Introduction

Phonons play a crucial role in determining the properties of graphene, such as thermal conductivity, specific heat and free energy. In addition, phonons are given paramount importance in quasi-particle dynamics [1], while heat transport properties are helpful in improving heat dissipation, safety and stability in lithium-ion batteries [2,3]. Our choice of Li-adsorbed graphene sheet as a test case for exploring thermal and vibrational properties is motivated by the technological applications of lithium-graphite intercalation compounds as rechargeable solid-state Li-ion batteries [4]. Moreover, concerns regarding temperature rise in Li-ion batteries are resolved to a larger extent by graphene incorporation. To the best of our knowledge, there exists no systematic study describing phonon dispersion and thermodynamical properties of metal adsorbed graphene.

Computational Details

We have used VASP (Vienna ab initio Simulation Package) code [5,6] based on density functional theory (DFT) in line with phonopy code [7] under the generalized gradient approximation (GGA) of Perdew, and Ernzerhof (PBE) [8] for calculating phonon dispersion and consequent thermodynamic properties of pure and Li-adsorbed graphene. To avoid coupling between layers, the vacuum separation between them was set to 9.8Å. The plane wave cut-off energy of 750 eV was found to be sufficient. For sampling the Brillouin zone, the Monkhorst–Pack scheme was used [9]. The structure was fully relaxed with Gamma centered $7 \times 7 \times 1$ k-mesh. Tetrahedron methodology with Bloch corrections was used to treat the partial occupancies [10]. The positions of all atoms are allowed to fully relax until the Hellmann– Feynman force on each atom is less than 0.005 eV/Å. We consider a 4x4 supercell consisting of 32 atoms with one Li atom placed at a distance of 1.69 Å over the hollow position of graphene [11]. The adsorbate atomic concentration is then 3.125%.

Results and Discussions

Phonon Dispersion Curves of Pure and Li Adsorbed Graphene

In a work carried out by us [12], for graphene lattice with a basis of two atoms in the primitive cell, reproduced the standard results [13]. Hence the same computational parameters were adopted. Phonon dispersion curve for pure G_{32} shows 3N = 3X32 = 96phonon branches. Upon Li adsorption, the highest LO frequency increases to 48.46 THz (fig. 1) from 47.79 THz (for comparing with phonons in pure graphene pl. refer to [12]), the degeneracy of ZO and ZA is removed at K-point and it tries to compress certain out of plane ZA and TA phonon modes causing them to flatten in the lower frequency region indicating a slight instability in the structure, manifested by a significant dip of one of the branches below zero frequency. A slight down-shift of out of plane optical phonon (ZO phonon mode) is also noticed (fig. 1). Under appropriate strain and charging, these imaginary frequencies disappear. Therefore, for calculating thermodynamic properties, we assume these modes to be at zero frequency.



Fig. 1. Phonon dispersion curves of Li adsorbed graphene where units of frequency are in THz.

Phonon Density of States (DOS)

At higher frequencies the DOS curve (Fig. 2) for $Li@G_{32}$ is nearly same as that of pure G_{32} except for the disappearing of one peak. Positions and heights of the peaks are barely shifted. Results These negligible changes can be explained on the basis of low concentration of adsorbent. However, $Li@G_{32}$ shows three additional peaks at low frequencies.



Fig. 2. Phonon density of states for pure graphene (G_{32}) and Au adsorbed graphene $(Li@G_{32})$.

Thermodynamic Properties of Pure and Li Adsorbed Graphene

The molar heat capacity Cv, entropy S and free energy have been plotted in figure 3. Cv and S follow the expected rise with temperature. The curves for Cv are seen to tend towards the Dulong - Petit value (25 JK⁻¹mol⁻¹) K [14]. Entropy shows almost straight line behavior after 400K in both systems. The increase in entropy may be attributed to increase in disorder as well as instability upon Li adsorption. The variation of free energy with temperature shows expected trend.



Fig. 3 Variation of specific heat, entropy and free energy with temperature for pure (G_{32}) and Li-adsorbed graphene with 3.125% concentration of adsorbent.

Conclusion

For 3.125% lithium adsorption on graphene, significant change is found in modes lying in lower (< 10THz) frequency range of graphene. Our analysis may serve as a basis for facilitating the improvement in thermal management in graphene intercalated Li-ion batteries.

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Photoemission Spectroscopy of $ACu_3Ru_4O_{12}$ (A = Ca/La)

B. H. Reddy^{1,2}, Asif Ali¹ and Ravi Shankar Singh^{1*}

¹Department of Physics, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal - 462066, M.P., India

² Department of Physics, Government College (A), Rajahmundry – 533105, A. P., India

*Corresponding author: rssingh@iiserb.ac.in

Abstract

We investigate the electronic structure of A-site ordered cubic perovskites $ACu_3Ru_4O_{12}$ (A = Ca/La) using x-ray photoemission spectroscopy and *ab-initio* band structure calculations. Valence band spectra exhibit large intensity at Fermi level, E_F , for CaCu_3Ru_4O_{12} and LaCu_3Ru_4O_{12} commensurate with highly metallic character of these systems. Band structure calculations within local density approximation (LDA) fail to capture the position of Cu 3*d* derived features, while all the features are well reproduced by inclusion of strong correlation for Cu 3*d* electrons within LDA+U (U_{Cu 3d} = 4 eV). While the delocalized Ru 4*d* states hybridize strongly with O 2*p* states, the Cu 3*d* states are essentially localized and appear above 2 eV binding energy. Observation of larger intensity of O 2*p* spectral features in the valence band spectrum of LaCu_3Ru_4O_{12} than that of CaCu_3Ru_4O_{12} may be related to larger La - O hybridization in LaCu_3Ru_4O_{12}.

Dynamical Studies for bcc Niobium A.V. Nag¹, P. Kumar², D.S. Tripathi³, N. K. Bhatt⁴ and V.B.Gohel³

¹Department of Physics, L.J.I.A.S., Gujarat University, S. G. Highway, Ahmedabad- 382210, Gujarat, India.
 ²Department of Science & Humanities, Government Polytechnic, Dahod -389151, Gujarat, India.
 ³Department of Physics, School of Science, Gujarat University, Ahmedabad- 380009, Gujarat, India.
 ⁴Department of Physics, M. K. Bhavnagar University, Bhavnagar - 364001, Gujarat, India.

*Corresponding author: aditin706@gmail.com

Abstract

In this study, we proposed a transition metal pseudopotential (TMPP) and demonstrated its credibility by carrying out lattice dynamical studies for bcc Niobium (Nb). The generalized pseudopotential theory (GPT) is used to derive our proposed pseudopotential. We have calculated the values of phonon dispersion curves, dynamical elastic constants in long-wavelength limit ($\vec{q} \rightarrow 0$) and bulk modulus using this potential. In comparison to experimental data and other theoretical approach our results are quite encouraging.

Introduction

For understanding interactions inside bcc transition metals, lattice dynamics and lattice mechanical properties are crucial. These properties can be explored using pseudopotential approach [1-3] which is rather an uncomplicated, less challenging and physically more transparent than the first principles method [4]. In the present communication, we have computed phonon dispersion curves in symmetric directions, dynamical elastic constants using long-wavelength limit and bulk modulus for bcc Niobium (Nb). The manuscript is organised as follows, section 2 comprises the mathematical explanation for calculating the lattice dynamics and its properties. In section 3, we presented our computed results in graphical and tabulated form. We also compared our results to experimental values in this section. Finally, in Section 4, the paper is summarised.

Theory

The values of phonon frequencies were calculated using the formulation given by [5]. The transition metal pseudopotential derived from generalized pseudopotential theory having three parameters r_c core radius; r_d - radius of d-electron and β hybridization parameter has following form in qspace [6],

$$V_{ion}(q) = \frac{1}{\Omega} \left[\frac{-8\pi Z^*}{q^2} \times cosqr_c + \frac{\beta}{[1+q^2r_d^2]^4} \right]$$
a)

Here, Z^* represents effective valency and Ω represents atomic volume.

The elastic constants in the long-wavelength limit ($\vec{q} \rightarrow 0$) are calculated using theoretical method described in [7,8].

Results and Discussion

To determine the pseudopotential parameters, a simplified approach has been provided. Here, three parameters r_c , r_d and β have been reduced to two. In the current method, r_d/r_c is kept within the limited range of 1.1 to 1.5 and the hybridization parameter β is set to match computed longitudinal phonon frequencies at the zone boundary [0 0 1] to the experimental results. The input parameters for Niobium used in the calculations are tabulated in table 1.

 Table 1. Pseudopotential parameters and input parameters

 for Niobium used in the calculations (all in a.u.)

Z*	Ω	r _d	rc	β
1.5	121.300	0.3025	0.2725	52

Fig. 1 shows phonon dispersion curves for Niobium. Here, the computed results were found to be in good agreement with the experimental data [9], which used inelastic neutron scattering to measure phonon dispersion relations in symmetric directions at room temperature. The maximum deviation of 34.8 % was observed at longitudinal [0 1 1] branch. Here, we have adjusted our parameter in such a manner that overall good agreement is seen at the zone boundary, which is the cause of this discrepancy.



Fig. 1. Phonon dispersion curves for Niobium. The experimental points are represented by symbols that are due to due to [9].

Table 2. shows the calculated values of elastic constants and bulk modulus along with experimental values given by [10]. In addition, we have tabulated theoretical results[11] obtained using first principle's calculations. Here, the calculations were based on the density functional theory to study the elastic properties and mechanical properties on Molybdenum and Niobium. The calculated values are in good agreement with the experimental findings. The computed values of C_{44} were unsatisfactory (with more than a 50% variation). The cause needs to be further investigated.

Table 2. Dynamical elastic constants (C_{11} and C_{12}) and Bulk modulus for Niobium. All quantities are measured in 10^{12} dyne/cm². Values in parenthesis "()" shows the percentage variation of our results with respect to the experimental values.

Refer	C 11	C ₁₂	В
Present study	2.527 (2.51)	1.701 (26.4)	1.976 (15.0)
Experimental values [10]	2.465	1.345	1.718
Theory [11]	2.478	1.331	1.713

Conclusion

The present investigation shows that Transition Metal Pseudopotential, which is developed directly from generalised pseudopotential theory (GPT), is extremely useful in understanding lattice dynamical and mechanical properties for bcc transition metals. The experimental evidence for Niobium accords well with the pseudopotential theory. The hybridization effect can be explained using the parameters determined by the current method. In this case, observed results are in good accord with our phonon dispersion curves. In addition, when compared to experimental data and other theoretical values, our computed elastic constants and bulk modulus are overall satisfactory.

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Electron Correlation in (Ca/Sr)Pd₃O₄

Asif Ali¹, B. H. Reddy^{1,2}, and Ravi Shankar Singh^{1*}

¹Department of Physics, Indian Institute of Science Education and Research Bhopal, Bhopal Bypass Road, Bhauri, Bhopal - 462066, M.P., India

² Department of Physics, Government College (A), Rajahmundry – 533105, A. P., India

*Corresponding author: rssingh@iiserb.ac.in

Abstract

We investigate the role of electron correlation in narrow bandgap semiconducting ternary palladates (Ca/Sr)Pd₃O₄ using valence band *x*-ray photoemission spectroscopy and *ab-initio* band structure calculations. Experimental valence band spectrum exhibits negligible intensity at Fermi level, E_F . Overall description of the experimental spectrum is well captured in band structure calculation within local density approximation (LDA) but leads to a metallic ground state in contrast to semiconducting behavior. Electron correlation is included within LDA+U framework, which leads to opening of a gap at E_F for U > 4 eV. LDA+U (U = 4.5 eV) calculations exhibit direct bandgap at Γ point with bandgaps of 0.062 eV and 0.049 eV for CaPd₃O₄ and SrPd₃O₄, respectively.

Introduction

4d transition metal oxides (TMOs) are of interest due to observation of numerous exotic properties. It is generally believed that the electrons in 4d TMOs feel weak on-site Coulomb repulsion than 3d TMOs due to extended nature of 4d orbitals than 3d orbitals. However, in some of the 4d TMOs the importance of electron correlation has been realized [1]. In this regard, the electronic structure of Ruthenates and Rhodates have been explored in past decades [2]. The other 4d TMOs are less explored and among these palladium-based oxides are gaining interest due to their high catalytic activity. Ternary palladates (Ca/Sr)Pd₃O₄ exhibit narrow bandgap semiconducting properties [3]. Both CaPd₃O₄ and SrPd₃O₄ are isoelectronic with $4d^8$ electronic configuration and isostructural having a cubic structure with Pm3n space group. The Pd is surrounded by four oxygens sitting in a plane, and a square planar PdO₄ configuration is obtained. Two parallel square planes along the z-axis increase the energy of the d_{z2} band, and the energy level follow d_{xz}/d_{yz} , d_{xy} , d_{z2} and d_{x2-y2} and a gap is obtained between d_{z2} band and d_{x2-y2} band in Pd⁴⁺ $(4d^8)$ configuration.

Here, we report the valence band of $(Ca/Sr)Pd_3O_4$ using *x*-ray photoemission spectroscopy and compare the results with *ab-initio* band structure calculations.

Experiment and calculation details

The polycrystalline samples of (Ca/Sr)Pd₃O₄ were prepared using high purity ingredients as reported in [4]. Room temperature photoemission experiments were performed on *in-situ* fractured samples using Scienta-R4000 analyzer with base pressure ~ 4×10^{-11} mbar. Monochromatic Al K_{α} x-rays ($h\nu = 1486.6 \text{ eV}$) were used and total energy resolution was set to 0.4 eV. Band structure calculations were performed using local density approximation (LDA) and LDA+U method using WIEN2k package [5]. Experimentally found lattice parameters were used for all the calculations. $8 \times 8 \times 8$ k-mesh was used and energy and charge convergence criteria were set to 0.1 meV and 10^{-4} electronic charge per formula unit, respectively.

Results

Fig. 1 shows the room temperature valence band photoemission spectra of (Ca/Sr)Pd₃O₄. The valence band is formed by the hybridization between Pd 4dstates and O 2p states, while Ca/Sr states do not contribute in this energy range. The spectrum consists of four distinguishable features at ~ 0.5 eV, ~ 2 eV, ~ 3 eV and a broad feature between $\sim 4 - 9$ eV binding energy for both systems as marked by A, B, C, and D, respectively. The first three features below E_F , predominantly have Pd 4d character and the broad feature between $\sim 4 - 9 \text{eV}$ binding energy has O 2p character [4]. Both spectra exhibit negligible intensity at E_F commensurate with the semiconducting nature of both systems. We observe a shift of about 0.2 eV in features B and C towards lower binding energy while going from CaPd₃O₄ to SrPd₃O₄. To understand these results, we compare experimental spectrum with band structure calculation performed within LDA and LDA+U. LDA calculated band structure and density of states (DOS) are shown in Fig. 2. A complex band structure is obtained, whereas only few bands (mainly d_{z2} and d_{x2-y2} bands) appear around E_F . These bands cross E_F around Γ and X points, leading to a metallic ground state in both the systems. The



Fig. 1. Room temperature valence band photoemission spectrum for $(Ca/Sr)Pd_3O_4$.

DOS have broad peak like structures at around 1.5 eV and 2.5 eV binding energies similar to experimental spectrum. The obtained metallic ground state does not agree with observed semiconducting transport behavior, suggesting electron correlation may be playing role and approximation beyond LDA must be considered. Thus, we show the results of LDA+U calculations in Fig. 3. It is to note here that U > 4 eVis required to open up a gap. Band structure and DOS are shown for U = 4.5 eV. It is clearly seen that the bands around E_F have moved away from the Fermi level in occupied and unoccupied part and direct gap is observed at Γ point. The obtained bandgap for CaPd₃O₄ and SrPd₃O₄ are 0.062 eV and 0.049 eV, respectively. The obtained bandgaps are smaller than



Fig. 2. Band structure (left) and DOS (right) using LDA method for CaPd₃O₄ (black) and SrPd₃O₄ (red).



Fig. 3. Band structure (left) and DOS (right) using LDA+U (U = 4.5 eV) method for CaPd₃O₄ (black) and SrPd₃O₄ (red).

gaps obtained from transport measurements [3] suggesting underestimation in the current calculation. However, an unrealistic large value of U (U > 4 eV) in these 4*d* systems is required for a gapped state which suggests the approximation beyond LDA+U such as DMFT or GW are required for a correct description of the electronic structure.

Conclusion

In summary, we have studied the valence band of ternary palladates using *x*-ray photoemission spectroscopy and band structure calculations. LDA provides an overall description of experimentally observed features but is incapable of producing a gapped ground state as observed in transport as well as valence band photoemission measurements. The gapped ground state is obtained using LDA+U method with direct bandgaps of 0.062 eV and 0.049 eV for CaPd₃O₄ and SrPd₃O₄, respectively, with U = 4.5 eV, suggesting importance of electron correlation effects in these 4*d* TMOs.

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Molecular Dynamics Simulations of Evolution of Radiation-Induced Defects in Nickel due to Low Energy Self-Ions

Uttiyoarnab Saha*, Argha Dutta, N. Gayathri, Santu Dey, P. Mukherjee

Radiation Damage Studies Section, Materials Science Studies Division, Variable Energy Cyclotron Centre, Kolkata - 700064, West Bengal

*Corresponding author: ua.saha@vecc.gov.in

Abstract

The ion-induced primary radiation damage phenomena in pure nickel are investigated by simulating the evolution of cascade of 2, 5 and 10 keV Ni PKAs using molecular dynamics technique. The damage formation stabilizes after about 10, 15 and 18 ps for the 2, 5 and 10 keV PKAs, respectively. Large size clusters of point defects form as the system progresses towards the heat spike phase and after the system has evolved sufficiently, the interstitial clusters tend to remain in larger sizes as compared to the vacancy clusters. The formation of defects, especially in the form of large number of small clusters induce an average volumetric strain in the material which initiate around the local heat spike region. The system evolves to a state where defect formation has saturated and there is a reduced remnant average volumetric strain accounted to the existing stable point defects and larger clusters.

Analytical Approximation for Neutron Thermal Scattering Law with a Novel Form for Phonon Density of States

R S Keshavamurthy^{1*}, Razmi Das¹, Ananth S Iyengar¹, Devesh Raj² and Mala N. Rao³

¹Ramaiah University of Applied Sciences, BENGALURU 560054, ²Reactor Physics Design Division, and ³Solid State Physics Division, BARC MUMBAI 400085

*Corresponding author: keshava54@gmail.com

Abstract

Evaluation of Neutron Thermal Scattering Law $S(\alpha,\beta)$ is quite involved as the integrand has Fourier transform in the exponent which has no closed form expression. Computation of $S(\alpha, \beta)$ requires many approximations and extensive numerical calculations. We propose a novel form for the Phonon Density of States which gives closed form expressions for Fourier transform and leads to analytical approximations for $S(\alpha,\beta)$ making its evaluation far easier. These new approximations obtained are compared with values for example cases for BeO available in the literature.

Proposing and modelling chalcogenide prism model with hyperbolic metamaterials for surface plasmon resonance based biosensing applications

R.D. Balaji S¹, Ancemma Joseph^{2*} and R.Vasantha Jayakantha Raja³

^{1&3}School of Electrical and Electronics Engineering, SASTRA Deemed to be University, Thanjavur, ²Department of Physics, Fatima College, Madurai

*Corresponding Author: ancyjoseph20@gmail.com

Abstract

A conventional biosensor detects higher molecular weight biomolecules quiet easily but detecting lower molecular weight biomolecules is a challenging task. We intend to over come this difficulty by proposing prism coupled Surface Plasmon Resonance (SPR) biosensor model that detects the lower molecular weighted biomolecules. In our proposed model, we have considered a chalcogenide prism with metal-dielectric (HMMs) multilayers and an analyte stacked over the prism in the krestchmann surface plasmon resonance (SPR) configuration and analysed the performance of the sensor metal-dielectric (HMMs) multilayers. Graphene and silicon carbide (SiC) is considered as one of the (HMMs) multilayer and the sensitivity of graphene-SiC (HMMs) multilayer structure based biosensor is determined by trans fer matrix approach.

INTRODUCTION

Hyperbolic metamaterials (HMMs) is the artificially designed metal-dielectric multilayer structure which works in plasmonic resonant frequency and terahertz regime. They are the subclass of left handed materials^[1] in which one of the principal component either permittivity or permeability is opposite to one another. HMMs is widely used in the applications like negative refraction, sub diffraction imaging, heat transport and thermal emission engineering. Apart from these applications, HMMs are receiving acclaim for its widespread usage sensing applications for the detection of biomolecules [2,3]. Detection of lower molecular weight biomolecules is still the challenging factor in sensing application. Particularly in detecting some noxious species of pathogenic bacteria, viruses, fungi etc. In our work we have proposed prism coupled krestchmann SPR configration optical biosensor along with the hyperbolic metamaterials. By this proposed model, we detect one among the noxious species of Bacillus family, B.cereus, the harmful species next to Eschericia coli which cause diaorrhea, vomitting and emetic disease in humans. The efficiency of the sensing aspect of the utilized HMM, namely the graphene-SiC based HMMs is analysed employing Transfer matrix method to calculate the transmittance power and the sensitivity. It is shown in this intended work that the SPR biosensor based on HMMs enhances the sensitivity and overcomes the difficulties in detecting lower molecular weight biomolecules.

EXPERIMENTAL TECHNIQUE

Various techniques like fourier transform infrared spectroscopy, nuclear magnetic resonance, fluorescence spectroscopy (FS), size exclusion chromatography and surface plasmon resonance (SPR) are used for characterizing and to study biophysical interactions. Surface plasmon resonance (SPR) is the phenomena of excitation of surface plasmons (SPs) when the incident light strikes the surface of metaldielectric interface.SPs are the collective pocket of plasma and excited by the evanescent wave. The excitation of SPs by evanescent wave is called as surface plasmon resonance (SPR). Kretschmann and otto are the two configurations of SPR technique. The krestchmann configuration is distingushed from otto configuration by the sandwich of metal-dielectric layer with prism. And that model is followed up here in this work employing hyperbolic metamaterials. This technique is widely emerging in the field of food safety, pharmaceuticals, homeland security and environmental monitoring [4,5].

MODELLING AND ANALYSIS

A model of proposed prism coupled SPR biosensor using graphene-SiC based hyperbolic metamaterial is proposed. In this case, graphene-SiC based hyperbolic metamaterial is examined alternatively in order to compare the sensitivity of biological element based on this structure. Krestchmann SPR configuration is followed throughout the procedure. Graphene-Sic based HMMs is constructed in which carbon nanostructured (Graphene) material has simple electron band structure. Monolayer graphene-SiC doesnot behave as the metamaterials. But at the same time periodic arrangement of multilayer graphene-SiC as proposed in the Figure behaves as the HMMs. Graphene has an excellent property of absorption over biological element which acts as a biomolecular recognizing element. This property avoids the use of another substrate in the structure. It also has the property of tuning the dispersion by varying the chemical potential



Fig.1 Prism coupled SPR biosensor using graphene-SiC based HMMs

. Therefore the effective permittivity of HMMs is calculated by EMT and the effective permittivity of graphene metal which is obtained from Drude model. The relations of permittivity and permeability are utilized in the transfer matrix method for the determinance of normalized transmitted power.

RESULTS AND DISCUSSION

By effective medium theory, frequency dependence of real part of permittivity for graphene-SiC based HMMs is graphically represented in Fig.2. By fixing the thickness of silicon carbide (SiC) layer as 10 nm and chemical potential as 0.3 ev. The transmittance power is calculated in order to observe how much of incident light is transmitted in the transmission medium. The transmitted power for graphene SiC based HMM ranges between 0.03 and 0.32 for different thickness of B.cereus. Fig. 4 ensures that the incident angle variation with respect to different thickness of B.cereus is placed on graphene-SiC based HMMs. The incident angle decreases exponentially as increase in thickness. 35.5 and 15.2 is the maximum and minimum incident angle gained at the thickness of 0.1nm and 1.0 nm



Fig.2 Effective permittivity for real component of grapheneSiC based HMMs in frequency domain.

From this, the sensitivity of the SPR biosensor is determined by the ratio of difference in incident angle

to that of difference in thickness of B.cereus. The maximum sensitivity enhanced by SPR biosensor using the Eqn. (4.1) is -22.5/ nm thickness of B.cereus



Fig. 3 Transmitted power for different thickness of B.cereus using graphene-SiC based HMMs.



Fig.4 Sensitivity for different thickness of B.cereus which is placed on graphene-SiC based HMMs.

CONCLUSION

A prism coupled krestchmann SPR configration optical biosensor along with the hyperbolic metamaterials is proposed. Transfer matrix method was employed to calculate the transmittance power and the sensitivity for graphene based HMMs. It is found that SPR biosensor based on HMMs enhances the sensitivity and overcomes the difficulties in detecting lower molecular weight biomolecules.

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Fermiology of Topological States in the Chiral Crystal RhSn

Birender Singh* and Bahadur Singh

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400005, India

*Corresponding author: birender.physics5390@gmail.com

Abstract

Chiral crystals with well-defined handedness feature chiral massless excitations at the time-reversal-invariant-momentum (TRIM) points in the Brillouin zone. Here based on first-principles theoretical modeling, we discuss the role of crystal chirality in driving the chiral fermions in the momentum space in RhSn. We show that RhSn hosts multifold chiral fermions with associated surface Fermi arcs states that span the whole surface Brillouin zone. We also discuss the multiple topological gap structure and associated surface states in RhSn. Our study unfolds RhSn as a new Kramers-Weyl fermions semimetal with exceptionally long Fermi arc states that would be ideal for fundamental science and device applications.

Structural, elastic and anisotropic properties of Fe₂Zr and FeZr₂ intermetallics

Kawsar Ali^{*1,2}, and A. Arya^{1,2}

¹Glass & Advanced Materials Division, Bhabha Atomic Research centre, Mumbai 400085 ²Homi Bhabha National Institute, Mumbai, 400094

*Corresponding author: ali.ksr71@gmail.com

Abstract

Fe-Zr based alloys, *viz.*, SS-15 wt% Zr and Zr-8 wt% SS are found to be promising materials for high level nuclear metallic wasteform. It has been observed that Fe₂Zr and FeZr₂ intermetallics appear dominantly in these alloys and act as a host for the radionuclides present in the waste. In this work, we have studied the thermodynamic, elastic and anisotropic properties of the Fe₂Zr and FeZr₂ intermetallics. It has been found that both the phases are thermodynamically as well as mechanically stable. The bulk (B), shear (G) and Young's moduli (Y) of Fe₂Zr phase are higher than that of the FeZr₂ phase. Both the phases are found to be ductile in nature. The anisotropic properties show that FeZr₂ phase is more anisotropic than the Fe₂Zr phase.

Electronic and optical response of twisted MoS₂/MoSe₂ heterostructure

Shivani Rani, Saurav Sachin, Puja Kumari and Soumya Jyoti Ray

Department of Physics, Indian institute of Technology Patna, Bihta, Bihar-801106, India

*Corresponding author: shivani.pph17@iitp.ac.in

Abstract

In recent time, twistronic is a center of attraction in the field of research for tuning and enhancing the physical properties of 2D bilayer and hetero-structures. In the present work, First-principles based Density Functional Theory (DFT) was used to investigate the opto-electronic properties of twisted $MoS_2/MoSe_2$ hetero-structure. Optical response shows that the twisted hetero-structures exhibit highest optical absorption in the visible regions. With varying the twist angle between the layers of hetero-structure, they make transitions between direct and indirect band gap semiconductors. These properties make the twisted hetero-structure as a promising candidate for application in next-generation Nano and optoelectronic devices.

A theoretical study of the electronic and magnetic structure of NiTe₂

Debarati Pal¹, Sambhab Dan¹, Swapnil Patil^{1*}

¹Department of Physics, Indian Institute of Technology (Banaras Hindu University), Varanasi-221005, India *Corresponding author: <u>spatil.phy@iitbhu.ac.in</u>

Abstract

Topological materials with protected electronic states hold promise for rich physics and various applications in spintronics. We investigate electronic topological property of type II Dirac semimetal NiTe₂ in which Lorentz invariance is broken. NiTe₂ exhibit type 2 Dirac fermions near the Fermi level. Our calculations show titled Dirac cones along along Γ -A high symmetry points. The metallic density of states (DOS) and the dominating contribution of Ni-3*d* and Te-5*p* orbital to the band structure is noticeable. This d-p hybridization allows the dirac point to exist close to Fermi energy.

Introduction

Topological semimetals instigate a new era in the recent research of condensed matter physics with exploration of massless relativistic quasiparticles in crystalline materials. When the Fermi level aligns with the Dirac/Weyl points, a point-like Fermi surface forms in the most of Topological semimetals (TSMs). However, in some of the TSMs the Dirac/Weyl cones are tilted strongly along a certain momentum direction due to broken Lorentz invariance. Specifically, Cd₃As₂¹ and Na₃Bi² are type-I Dirac semimetals (DSMs), while the transition metal dichalcogenides (TMDs) PtTe₂, PtSe₂, and PdTe₂ ³⁻⁵ are type-II DSM. Because of the diverse physical properties and possible uses in electronics $^{6-8}$ and optoelectronics⁹, layered TMDs have piqued interest in recent condensed matter physics. TMDs have the generic formula MX_2 (M = transition metal; X = S, Se, or Te), with van der Waals interactions holding neighbouring X-M-X layers together. NiTe₂ consist of CdI₂ crystal structure with spacegroup P-3m1. Importantly, The Dirac points of $NiTe_2^{10}$ are discovered to be just 0.02 eV above the Fermi level, which is much closer than its homologues PtTe₂ (0.8 eV) 4 , PdTe₂ (0.5 eV) 3 and $PtSe_2 (1.2 \text{ eV})^5$ making it more reliable for topological applications. Specifically, the study the magnetic properties of three selected TMD monolavers, viz., FeTe₂, VS₂, and NiTe₂ are widely investigated¹¹. The magnetic properties in NiTe₂ is rarely been explored. Monolayer calculation of NiTe2 reported no spin polarization. But HSE06 results signify that the monolayer NiTe₂ is a magnetic metal with a relatively small magnetic moment (less than 1μ B). However, controversies are still there with the magnetic character of NiTe₂. The experimental verification of NiTe₂ is widely studied but the theoretical discussions are not well nurtured. Here, we calculate the electronic and magnetic structure of NiTe2 with GGA-PBE approximations.

Methods

We calculated the electronic structure using Vienna *ab-initio* simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) functional used for the implementation of generalized gradient approximation (GGA) approximations. For DOS calculation, spinorbit coupling was taken into account and spin polarized calculations were carried out for the calculation of magnetic moment. We use an energy cut off of 400 eV for our plane-wave basis set and optimized lattice parameters, wyckoff positions were adopted from ¹² for NiTe₂ theoretical calculations.

Results and Discussions

Figure 1a shows the bulk band structure of NiTe2



Fig. 1. Electronic bandstructure of Dirac type II semimetal NiTe₂ (a) with SOC and (b) without SOC.



Fig. 2. Partial density pf states for NiTe₂; inset: total DOS.

along the Γ -M-K- Γ -D-A-L-H-A direction. Figure 1b is the band-structure without the spin orbit coupling. Along $(A-\Gamma-A)$ direction, the Dirac cone is titled. This suggests the characteristic feature of the type-II Dirac fermions as reported in other type II DSMs like PtTe₂ and PdTe₂. Two hole dominant bands and two electron bands touch each other at the Dirac point along Γ -A direction. The ground state of NiTe₂ is nonmagnetic with GGA-PBE prediction (not shown). The density of states is mainly contributed by Ni-3d $(3d^94s^1)$ and Te-5p $(5s^25p^4)$ states. Moreover, the Ni-3d states stimulates the *d-p* hybridization and tunes the bulk dirac point very close to Fermi level as clear from the DOS (Figure 2). The crossing of Te p_z and $p_{x,y}$ bands occur near the A point, and the p_z bands show a significant hybridization with Ni *d*-orbitals, unlike in other MX₂ compounds.

Conclusion

We have investigated the electronic structure with abinitio calculation and it predicts that the ground state of NiTe₂ is non- magnetic metal with GGA-PBE approximation. The tilted Dirac point is clear along Γ -A direction and is very close to Fermi level makes it a potential candidate for applications.

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Charge Transfer Mediated Hydrogen Evolution Reaction Over Co Loaded g-C₃N₄

B.R. Bhagat^{1*} and Alpa Dashora¹

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, 390002

*Corresponding author: bhagatbrajesh1996@gmail.com

Abstract

Highly photoactive transition metal decorated graphitic carbon nitride $(g-C_3N_4)$ possess greater visible spectra absorption and large photo-generated charge separation attributing to formation of intermediate in narrowed forbidden region. Site dependent study of hydrogen evolution reaction (HER) using adsorption of H-molecule along with water molecule and role of charge transfer mechanism are reported for Co decorated $g-C_3N_4$ (Co-C₃N₄) using density functional theory. Adsorption of water molecule with H-atom over bay-Carbon (C_b) atom in Co-C₃N₄ shows 5.6, 7.3 and 4.6 fold decrease in overpotential than pristine $g-C_3N_4$, H-atom adsorbed at C_b and H-atom adsorbed at corner-Carbon (C_c) atom, respectively. Significant change in potential barrier is attributed to π -delocalization and charge transfer among H-atom and the C atom of Co-C₃N₄ for enhanced photocatalytic activity.

Introduction

Current scenario directs us for the design and development of photocatalyst, materials utilizing solar spectrum in visible region for energy conversion and pollutant degradation by increasing the reaction kinetics. Polymorphic and ecofriendly g-C₃N₄ has recently established itself as emerging photocatalyst with high absorption efficiency, lamellar structure for large surface area and wide band gap to accommodate various cationic, anionic and co-ionic functionalization. Increment in reaction sites as modification over the π -conjugated system has been observed to increase lifetime of photo-generated charge carrier [1].

Transition metal is widely utilized for doping and decoration in the tri-s-triazine based $g-C_3N_4$ and have reported enhancement in the visible absorption region as narrowing of band gap result into the red shift, while formation of intermediate impurity states has reduced the recombination rate along with increasing charge separation as deep trap sites provide metastable state for longer lifetime for charge carriers.

Theoretical and experimental studies performed on Co-doping, Co-loading and Co-embedded heptazine based $g-C_3N_4$ system showed 3 times higher hydrogen evolution rate than pure, decrease in band gap value upto 0.72 eV with built in electric field for suppression of recombination rate and emphasis on Co (3d)- N (2p) interaction for red shift and improved photoelectric property of $g-C_3N_4$ [2-4].

Despite extensive research with cation doped $g-C_3N_4$, thorough study on the role of charge transfer and its impact on rate determining step still lacks.

Methodology

For the present work, Quantum Espresso code was used for structural optimization and study of electronic property using 5X5X1 MP **k** point grid with convergence threshold of 10^{-6} Ry and kinetic energy cutoff of 60 Ry. van der Waals (Grimme-D2) corrections are also included for accurate calculations. [5-7].

Results and Discussion



Fig. 1. (a) Optimized Structure and (b) Electron Localization function (ELF) for $Co-C_3N_4$. In ELF, red-green-blue denotes covalent-metallic-ionic bonding.

Relaxed structure of Co-C₃N₄, as presented in Fig. 1 (a) shows formation of chemical bond between Co-N₂/N₃ explains the decrement of charge on N₂/N₃ from Table 1. while change in C_b/C_c/N₁ signify charge redistribution over the plane, as seen from Fig. 1(b), weak binding for Co-N₂/N₃ activates edge N (N_{edge}) along with delocalization as N-C π -

hybridization is affected due to creation of charge transfer pathway [3].

Volmer-Heyrovsky mechanism for HER directs us for the conversion of electron-proton pair into H_2 molecule through H* formation which require feasible adsorption-desorption process. Water molecule in vicinity of H provides polar interaction making it electrophilic to maintain weak binding strength. Therefore, it's important to consider different sites for adsorption along with number of H₂O molecule to simulate and study experimental conditions for efficient computation and high quantum yield.

Calculated value of adsorption energy (Eads) for H atom adsorbed on C_b site (H-C_b), on C_c site (H-C_c), also for H atom with water molecule at C_b site (H₃O-C_b) and same at C_c site (H₃O-C_c) on Co-C₃N₄ are -1.23, -0.91, -0.35 and 0.09 eV, respectively. The charge is reduced on the C atom on which H adsorption takes place (Cb and Cc) respect to the corresponding C atom in Co-C₃N₄. For H₃O-C_b, after optimization, H atom gets attached to the Co atom while for H₃O-C_c, H atom is attached to the N_{edge} and H₂O molecule drift away. Co-H and Co-N_{edge} interaction result in 0.20e⁻ increment and 0.37e⁻ decrement over H atom affecting adsorption strength of the system. This charge compensation through formed channel is verified by the decrement and increment of 0.4e and 0.33e from C_b and N_3 for respective cases.

$$\Delta G_{H^*} = \Delta E_{H^*} + 0.35 \qquad \text{a}$$

Using Eq. a), free energy change (ΔG_{H^*}) is calculated and plotted in Fig. 2. The value of ΔG_{H^*} for H₃O-C_b was found to be 0.12 eV to be least while, positive E_{ads} for H₃O-C_c eliminate its occurring probability. Large value for H adsorption in H-C_b and H-C_c is attributed to C_b/C_c-H bonding with 0.16e⁻ charge decrement on H atom and strong binding that would make desorption process endothermic.



Fig. 2. Gibbs free energy plot for hydrogen evolution reaction with H^* and H_3O^* intermediate.

Table 1. Löwdin charge difference for H and H_3O adsorption .

	Со	Cb	Cc	N1	N_2	N 3
Co-C ₃ N ₄	46	.38	.31	03	29	27
H - C _b	42	.23	.38	08	33	31
H-Cc	46	.35	.23	05	35	30
H ₃ O-C _b	44	.40	.39	05	28	23
H ₃ O-C _c	47	.29	.32	07	22	33

Conclusion

Systematic study of charge migration over the surface for Co decorated g-C₃N₄ is performed along with consideration of electron accumulation centers as adsorption site for isolated hydrogen atom and hydronium molecule as intermediate in hydrogen evolution reaction. Interaction of metal-nitrogen through p_{π} -d_{\pi} coupling, formation of charge transfer channels and activation of multiple sites over the surface is observed.

Further investigation of reduction reaction over bay and corner carbon atom despite their low electronegative nature in the polymeric layer showed strong adsorption that results in reduction of barrier height of reaction. Large electron transfers between H-Co and hydrogen bonding between H_2O-N_{edge} plays crucial role in considering water molecule as necessary requisite for simulating experimental type situation.

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Impact of Spin-Orbit Coupling on the Electronic states of Ir ions in Rare Earth Double Perovskites Nd₂ZnIrO₆

Ramandeep Kaur, Arshdeep Kaur

Department of Physics, Akal University, Talwandi Sabo, Punjab-151302

*Corresponding author: ramandeep_phy@auts.ac.in

Abstract

First Principle Study on Rare earth double perovskite Nd_2ZnIrO_6 gives antiferromagnetic arrangement within Nd and Ir ions as the ground state for the system. With the application of spin-orbit interaction, the Ir d states split up into jeff = 3/2 and jeff = 1/2 states and open up a small gap at the Fermi level and make the system a candidate for $j_{eff} = 1/2$ mott insulator.

Effect Of ZnO Electron Affinity On Organic-Inorganic CH₃NH₃PbI₃ Perovskite Solar Cell

Sachin Kumar*

Department of Physics, JC Bose University of Science and Technology, Faridabad, 121006

*Corresponding author: sachinyadav100497@gmail.com

Abstract

In this work, a Lead-based perovskite solar cell $CH_3NH_3PbI_3$ was simulated using the solar cell capacitance simulator. Theoretical validation of experimental results in perovskite solar cells with efficiencies of 27.53% is presented. The simulation effort is focused on the adjustment of the electron affinity of the electron transport material (ZnO) on photovoltaic properties of solar cell devices. Here we found a spike which acts as a barrier potential in the transportation of electrons from perovskite active layer to ZnO electron transport material by optimization of value of electron affinity to 4.0 eV and reducing this spike we got the efficiency of perovskite solar cell above 27.53%.

Introduction

Today's peer group rely upon technology and computer, consequently during this time energy contributes a big part. The source of energy is focused on fuels but are short in supply and overpriced. That being the case, solar energy is a tremendous resource, as it is low-priced with quality efficiency.

Perovskite was the most acquainted hybrid material because of excellent optoelectronic properties like high mobility and absorption coefficient, lowexciton binding energy, suitable optical bandgap which is also tunable and high charge carrier mobility.

To seize the optoelectronic properties of lead perovskite, we work on $CH_3NH_3PbI_3$ as a photovoltaic material which has a direct bandgap (E_g) of 1.5 eV and has a suitable range for being absorbed.[1] The previous literature reported that the lead containing perovskite solar cell devices show excellent power conversion efficiency (PCE) up to 25.5% .[2] Here we study $CH_3NH_3PbI_3$ based perovskite solar cell because it has a good light harvester due to its optoelectronic properties like ideal bandgap, broad absorption spectrum, suitable career transport mechanism, ease of fabrication on the flexible substrate and long diffusion length. The Electron Transfer Material (ETM) plays a crucial role in PSC to achieve a high PCE. We use ZnO as an ETM.

Here, we studied the effect of the electron affinity of ZnO material. It has a relevant band gap to block the hole transport and favours the electron transport. It is also studied that ZnO is a promising candidate having high electron mobility, chemical stability, and ecofriendly nature. Device simulation of CH₃NH₃PbI₃ elicits a healthy way to enhance the PSC's efficiency after the streamline of the electron affinity of ZnO (ETM). Here, we have suggested that the optimum value of electron affinity of ZnO be 4.0 eV.

Methodology and Device Structure

This simulation work is perform using SCAPS 1D (version.3.3.09) simulation software under the illumination condition of AM1.5G, which is developed by the department of electronics and information system (ELIS) of the University of Ghent, Belgium. This simulation software is mainly solves the Poisson equation, hole continuity equation, electron continuity equation.[3] In this software we can employ some adjustments in properties like electron affinity, density of defects, and thickness of the active layer, electron transport material and hole transport material that may be useful to enhance the performance of perovskite solar cells.

The structure of the perovskite solar cell which is used for simulation is FTO/ZnO/CH₃NH₃PbI₃/Spiro-OMATED. Here, FTO acts as a front electrode, ZnO acts as ETM, CH₃NH₃PbI₃ acts as absorber layer, Spiro-OMATED acts as Hole Transport Material (HTM) and Au a back electrode. A combination of FTO as the front electrode and gold as the back electrode is best for the device performance.[4] CH₃NH₃PbI₃ layer is a sandwich in between ETM and HTM. The various parameters used for this simulation work are summarized in table 1. The symbols are presenting in have their usual meaning. This work is focused on the study the effect of the electron affinity of ZnO material on device performance.

Results and Discussion

With the help of parameters Table (1) electron efficiency, Fill Factor (FF) characteristics of the cell was plotted below. The simulation parameters such as Open circuit Voltage (V_{oc}), current density (J_{sc}), Fill
Factor(FF), and Power Conversion Efficiency(PCE) are obtained.

Parameter	FTO	ZnO	MAPbI ₃	Spir
Thickness	400	30	700	80
Bandgap (eV)	3.5	3.3	1.5	3
e affinity (eV)	4.0	4	3.9	2.2
ε _r	9	9	6.5	3
N _{CB} (cm ⁻³)	2.2E18	4.0E18	1.8E18	2E18
N _{VB} (cm ⁻³)	1.8E18	1.0E19	1.8E19	1E19
$\mu_e (cm^2/Vs)$	20	100	20	1E-4
$\mu_h (cm^2/Vs)$	10	25	20	1E-4
N _d (cm ⁻³)	1.1E19	1E18	1E9	0
N _a (cm ⁻³)	0	1E5	1E9	2E19
$N_{\rm c}$ (cm ⁻³)		2E17	1E13	1E15

Table 1. Parameters For CH₃NH₃PbI₃ Solar Cell Simulation.



Fig. 1. The Effect of Electron affinity of ZnO on the Efficiency of Perovskite Solar Cell.



Fig. 2. The Effect of Electron affinity of ZnO on the Fill Factor of perovskite solar cell.

Figure (1) displays SCAPS based simulation results of improvement in efficiency with improvement in electron affinity of ZnO. The PCE exceeds 27.53% by increasing affinity from 3.3 eV to 4.2 eV which is due to the ease in the transportation of electrons i.e., the barrier for electrons transportation between perovskite LUMO level and ZnO conduction band diminised abd below 3.7 eV there is a spike. This spike blocks the electron's transportation from perovskite to ZnO and acts as a potential barrier. Therefore, it is difficult for the perovskite region to contribute to the photocurrent. Figure(2) display the FF of the perovskite solar cell.

Conclusion

A theoretical study of an n-i-p solar cell with SCAPS simulations that the PCE of the device can be significantly enhanced by tuning the electron affinity of ZnO. The experimentally measured bandgap and absorption spectrum of ZnO was used in the simulation. The primary reasons for the improvement in the power conversion efficiency are reduced conduction band offset that results in an increase in the minority carrier current and reduction in the dark current. Simulated results reveal that the efficiency of this solar cell is 27.53%. The premier values calculated for open-circuit voltage, short circuit current density, and fill factor are 1.28 V, 25.75 mA/cm², and 83.44, respectively, for ZnO having a bandgap of 3.3 eV and electron affinity of 4.0 eV.

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Investigations into Heme detoxification protein of malaria parasite

Rahul Singh^{1,2}, Ashwani Kumar¹ and Ravindra D. Makde*¹

¹Beamline Development and Application Section, Bhabha Atomic Research Centre, Mumbai, India. ²Homi Bhabha National Institute, BARC- Mumbai.

*Corresponding author: ravimakde@rrcat.gov.in

Abstract

Abstract. Sequestration of cytotoxic free heme into inert hemozoin is a bottleneck in the physiology of malaria parasites. Heme detoxification protein (HDP) has emerged as the most prominent mediator for catalytic conversion of free heme to Hz. Despite the importance, we still do not fully understand the mechanistic insight behind HDP functionality. Partly, the culprit for this is the inability to recombinantly produce native HDP. In this study, we have purified a native fusion protein of HDP in complex with GroEL chaperonin. The crystals of this complex were diffracted on the PX-BL21 beamline at the Indus-2 synchrotron. The data was collected at 3.5Å resolution and processed in the P121 space group with unit cell dimensions of 283.48 Å, 135.53 Å, 283.62 Å, 90.00° 117.51° 90.00° [a, b, c (Å), $\alpha, \beta, \gamma, (°)$]. The asymmetric unit has 28 chains (1,605.2 kDa) of GroEL, but we could not trace any chain for HDP fusion protein. The final model is been refined to $R_{\rm free}$ of 26%.

Growth and Characterization of 2-Ethylimidazolium D(-) tartrate Crystal

T.P.Srinivasan^{1*}, R.Indirajith² ¹Department of Physics, H. H. The Rajah's College, Pudukkottai – 622 001, Tamilnadu ²Department of Physics, B. S. Abdur Rahman Crescent Institute of Science and Technology, Chennai-600 048.

*Corresponding author:sri1965102@gmail.com

Abstract

Single crystals of 2-ethylimidazolium d-tartrate (C₉N₂O₆H₁₄) were grown by slow evaporation solution growth technique at ambient temperature in deionised water as solvent. The grown crystals were characterized by single crystal XRD using MoK_{α} (λ =0.71073Å) radiation and the lattice parameters have been obtained. The Fourier Transform Infrared Spectroscopy of 2-ethylimidazolium d-tartrate reveals the presence of ethyl and carboxyl functional groups in the compound. The optical transparency window in the UV-Vis region is found to be good for nonlinear optical applications. The TGA and DTA reveal that the title compound incipient melting occurs at 148.34°C. The theoretical factor group analysis predicts 372 optical modes in the grown title compound. The SHG behavior of the title compound was demonstrated using Q-switched Nd: YAG laser.

Crystallization Of Insecticidal Toxin, Txp40 From Xenorhabdus nematophila

Omkar Kinkar^{1,2}, Arpit Parashar³, Ashwani Kumar², Ramesh Hire^{1,3,*} and Ravindra Makde^{1,2,*}

¹Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094, ²Beamline Development and Application Section, BARC, Mumbai, 400085, ³Nuclear Agricultural and Biotechnology Division, BARC, Mumbai, 400085

*Corresponding author: ravimakde@rrcat.gov.in; rshire@barc.gov.in

Abstract

Abstract. Txp40 is 42 kDa potential and ubiquitous toxin from *Xenorhabdus* and *Photorhabdus* bacteria, it is active against wide range of insect pests. Txp40 shares no significant structural match to proteins with known structures or functions, which suggests that it is a novel protein. Here, crystallization and preliminary x-ray analysis of Txp40 toxin from *Xenorhabdus nematophila* (ATCC 19061) is reported. Purified Txp40 was crystallized using under oil microbatch technique. Single crystal X-ray diffraction data was collected on the PX-BL21 beamline at the Indian synchrotron to 2.2 Å resolution with 100% completeness. Crystal belongs to $I2_12_12_1$ space group with unit-cell parameters a = 94.44, b = 97.62, c = 148.97 Å, Calculated Matthews coefficient was 2.06 Å³ Da⁻¹, with a corresponding solvent content of 41%. Structural analysis of Txp40 will provide new insights about mode of action of this toxin and because of its novel status it is highly possible that crystal structure of this protein will introduce a new domain and/or motif in the area of insect toxicity.

Crystal Growth, Structural and Optical Characterizations of 1,2,3- Benzotriazole 2-chloro-4-nitrobenzoic Acid (BCNB) Single Crystal for Nonlinear Optical Applications

B. Sahaya Infant Lasalle*, T. Kamalesh, P.Karuppasamy, Muthu Senthil Pandian and P. Ramasamy

SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai-603110, Tamil Nadu.

*Corresponding author: <u>sahayainfant@gmail.com</u>

Abstract

The third order nonlinear optical organic single crystal of 1,2,3- benzotriazole 2-chloro-4-nitrobenzoic acid (BCNB) was grown by slow evaporation solution technique (SEST) using methanol as the solvent. The lattice parameters of the grown crystal were confirmed by single crystal X-ray diffraction (SXRD) analysis. It shows that BCNB single crystal belongs to the monoclinic crystal system with the space group P2₁/n. UV-Vis-NIR analysis shows that the grown crystal has good optical transmittance in the entire visible region. The grown crystal was subjected to the photoluminescence (PL) and the emission peaks were obtained at 363 nm and 448 nm. The laser damage threshold (LDT) value of BCNB was found to be 13.8 GW/cm².

1. Introduction

The organic nonlinear optical (NLO) materials have more advantages than inorganic NLO materials in technical and scientific applications. Organic materials were used in optical data storage, photonics, ultra-compact laser, optical switching, optical logic and electro-optical amplitude modulations etc., (1).

The nature of benzotriazole is different from other triazole derivatives, because benzene ring is attached with triazole and formed a large conjugated system with π - π stacking interaction. The three nitrogen atoms make hydrogen bonds and these bonds are coordinate to react easily with other materials. Benzotriazole-based single crystals have high physiochemical, electrical, mechanical, wide transparency visible range and a high second and third harmonic efficiency than potassium dihydrogen phosphate (KDP) (2). 2-chloro-4-nitrobenzoic acid (CNBA) is a benzoicacid derivative containing one electrophilic group and labile group substituent in its aromatic ring. Habeeb et al., has done in-depth investigation on CNBA and amine hydrogen bonded complexes (3).

In the present work, the BCNB single crystals were grown by SEST and it is characterized by SXRD, UV-Visible-NIR, Photoluminescence and laser damage threshold analysis.

2. Synthesis and crystal growth

BCNB crystal was synthesized by using 1,2,3benzotriazole and 2-chloro-4-nitrobenzoic acid at molar ratio (1:1) using methanol as solvent. The saturated solution was prepared and filtered using Whatman filter paper and poured into the glass dish. Then it was fully covered using thick polythene sheet to avoid the dust particles falling from the atmosphere. The quality of the synthesized material was improved by successive recrystallization process. High quality single crystal with good transparency was obtained in a period of 20 days. The reaction scheme of BCNB is shown in fig.1 (a) and the grown BCNB crystal is shown in the fig.1 (b).



Fig. 1. (a) The reaction scheme (b) grown BCNB crystal

3. Results and discussion

3.1. Single crystal XRD Analysis

The lattice parameters of grown BCNB crystal were analysed by using a Bruker AXS Kappa diffractometer with monochromatic MoK_a radiation (λ =0.71073Å). The obtained lattice parameter values are a=7.059Å, b=11.77Å, c=16.09Å, α = γ =90°, β =93° and V=2367 Å³. The obtained parameters are in good agreement with the reported values by Ishida et.al (4).

3.2. UV-Visible analysis

The optical transmittance is most important for the crystal which is used for NLO applications (5). The optical transmittance spectrum was recorded using Perkin-Elmer Lambda-35 spectrophotometer in the range of 200-1100 nm and it is shown in Fig.2 (a). UV-Visible spectrum shows that the crystal has a maximum transmittance of 89% and the lower cutoff a)

wavelength is 350 nm. The strong absorption occurring at 350 nm is attributed to the $n-\pi^*$ electronic transitions. The wide transmittance window between 420 and 1000 nm makes the material a suitable candidate for various optical applications. The band gap energy of BCNB compound was determined by Tauc's formula.

$$\alpha h \nu = A(h \nu - E_{a})^{\overline{2}}$$

fig.2 (b). The optical band gap of the BCNB was found to be 3.2 eV.



Fig.2. (a) Optical transmittance spectrum (b) optical band gap energy diagram

3.3. Photoluminescence study

Photoluminescence study is an important tool for analyzing the luminescence behaviour of the materials. The BCNB sample was excited at 339 nm. It was carrying carbonyl ion with delocalized π electron. The emission spectrum is shown in Fig.3. The emission peaks of BCNB are observed at 363 nm and 448 nm. It shows that the BCNB has blue emission spectrum. This may be owing to the contribution of protons from phenol to nitro group. After 450 nm, it decreases gradually and this is due to the vibrations affected by thermal oscillations of atoms, the temperature deviations and vibrational relaxations.



Fig.3. Photoluminescence spectrum of BCNB.

3.4. Laser damage threshold studies

The nonlinear optical (NLO) devices not only depend on the linear and nonlinear optical (NLO) properties, but also need to withstand high laser power. Hence, high optical damage stability is one of the considerations in the choice of a material for NLO applications. In the present work laser damage threshold value of BCNB crystal was measured using a Q- switched High energy Nd: YAG Laser (QUANTA RAY Model: LAB – 170-10) wavelength (λ =1064 nm) laser operating in transverse mode (TM₀₀) and pulse width of 6 ns in the frequency rate of 10 Hz. Focal length of the biconvex lens (f) = 10cm. The LDT is shown in Fig.4. The LDT of the grown crystal was determined using the following formula.

powerdensity
$$(p_d) = \frac{E}{\pi \pi r^2} (GW / cm^2)$$
 b)

The determined LDT value of BCNB is 13.8 GW/cm^2 .



Fig.4. The laser damaged pattern of BCNB crystal

4. Conclusion

Good quality single crystal of BCNB was grown using SEST with methanol as solvent. The lattice parameters of the grown crystal were confirmed by SXRD analysis. It shows that BCNB single crystal belongs to the monoclinic system with the space group P2₁/n. The UV-Vis-NIR transmittance spectrum shows that the grown BCNB crystal has good optical transmittance with lower cutoff wavelength of 350 nm. The photoluminescence study shows that the BCNB crystal has a blue emission. The surface laser damage threshold was found to be 13.8 GW/cm². Therefore, the grown BCNB crystal may be useful for NLO applications.

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Single Crystal Growth, Electrical, and Magnetic Properties Studies on Hexagonal Co_{0.82}Se

Shubham Purwar*, Sayan Routh, and Setti Thirupathaiah

Department of Condensed Matter Physics & Material Science, S.N.Bose National Centre for Basic Sciences, Kolkata, West Bengal, 700106

*Corresponding author: shubhampurwar1996@gmail.com

Abstract

We successfully have grown high quality single crystals of $Co_{0.82}$ Se by flux-free melt growth process. Structural and elemental analysis have been performed using X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDXS), respectively. The XRD patterns confirm hexagonal crystal structure of the compound with a P6₃/mmc space group. We have measured electrical resistivity of $Co_{0.82}$ Se within the temperature range of 2-300 K. From the Bloch-Grüneisen (BG) fitting of the resistivity data suggest for a dominant electron-phonon scattering in this system with a Debye temperature of 254 K. Magnetization measurements suggest that these are paramagnetic systems in nature.

Antielectrostatic Hydrogen Bonding between oxyanions and their tendency to form proton wires within crystals: A Cambridge Structural Database Study

Rajul Ranjan Choudhury* and R. Chitra

Solid State Physic Division Physics Division, Bhabha Atomic research Center, Trombay, Mumbai, India, 400085

*Corresponding author: rajul@barc.gov.in

Abstract

Cambridge Structural database (CSD) was searched for salt crystals containing oxyanions HSO4¹⁻, HSeO4¹⁻, H₂PO4¹⁻, H₂PO4¹⁻,

Introduction

Molecular oxyanions are negatively charged polyatomic ions containing oxygen; these ions play a pivotal role in formation of inorganic as well as organic salts. Some of the commonly occurring molecular oxyanions extensively found in both organic as well as inorganic salts are HSO₄¹⁻, HSeO₄¹⁻ , $H_2PO_4^{1-}$ $H_2AsO_4^{1-}$, NO_3^{1-} , ClO_4^{1-} all these ions exhibit hydrogen bonding propensities but the most interesting aspect of these ions is their capacity to hydrogen bonds between themselves. form Traditionally hydrogen bonds are considered to be a manifestation of electrostatic attraction between a partially negatively charged acceptor atom (A) and a partially positively charged H atom covalently bonded to an electronegative donor (D), but the paradoxical existence of Antielectrostatic hydrogen bonds (AEHB) between like charged ions was first predicted theoretic by Weinhold and Klein [1] and have been subsequently confirmed experimentally. Stability of these AEHBs is a result of the covalent contribution to the hydrogen bond interactions; here the short-range donor-acceptor covalency forces overcome the powerful long-range electrostatic opposition between ions of like charge.

This manuscripts looks into the existence of oxyanionic clusters within the crystals of organic salts that are stabilized by the AEHBs, our search lead us to a whole class of salt crystals which had 0D, 1D, 2D as well as 3D networks of such AEHB between commonly occurring molecular ions listed above. One of the most striking properties of these AEHB networks is that they can act as channels for proton transport, some of the most studied proton

conductors like $CsHSO_4$ and CsH_2PO_4 contain such networks of AEHB that play a pivotal role in the conduction protons within the crystals.

Data Mining

Cambridge Structural database (CSD) [2] is both a repository and a validated and curated resource for the three-dimensional structural data of organic and organometallic molecules. Search of the CSD utilises the program ConQuest, we have searched the database using the DRAW option available in ConQuest, here a molecular segment is drawn and database is searched for all the structures that posses the specified molecular segment. For example in order to list the structures containing hydrogen bonded HSO41- ions and H2PO41- ions the molecular segments shown in figure-1a,b were used. CSD version 5.40 (November2018) was used for the search, searches were restricted to single crystal structures only since their atomic distance are generally more reliable. Table-1 lists the general summary of our search results for hydrogen bonds between like oxyanions.



Fig. 1. Molecular segments used in the DRAW option of ConQuest to list hydrogen bonded HSO_4^{1-} and $H_2PO_4^{1-}$ ionic structures.

Discussion

As a first step towards studying the strength of O-H---O bonds between the molecular oxyanions, properties of a general O-H---O bonds where there is no restriction on the chemical association of the donor and acceptor O atoms is obtained. 67350 structures having molecular fragment O-H----O where O---O distance is less than $2R(O_{vdW})+0.1$ Å and <O-H---O between 110° to 180° were listed (2R(O_{vdW}) is the Vander Waal radius of O). These structures had in all 168539 hydrogen bonds with structural characteristics within the above mentioned limits, the average O-O distance and <O-H-O angle are 2.7746 Å and 160.48° respectively. These can be taken as the structural characteristics of an average O-H-O bond in organic crystals. Looking at the statistics given in table-1 it is clear that all oxyanions listed in the introductions except for ClO₄¹⁻ have a tendency to make stronger than average O-H—O hydrogen bonds between themselves. Looking at the statistics in table-1 we observe that these AEHBs have O-O distance in the range 2.5Å< R(O - O) > 2.6 Å and < O - H - O angle within the range 162°-170°. According to the Gilli and Gilli classification of hydrogen bonds [3] these belong to the category of strong homonuclear Negative Charge-Assisted Hydrogen Bonds (-)CAHBs, all such strong homonuclear H-bonds are essentially three-centrefour-electron covalent bonds, most of these hydrogen bonds have dissociation enthalpies in the range of 0.5-1eV.

It was observed that in many crystal structures these oxyions made extended networks and chains of AEHBs which can in principle act as channels for proton transport. Our search results showed that almost 50% of crystal structures containing H₂PO₄¹⁻ oxyions had such extended networks of AEHBs, whereas no extended networks were found in crystal structures containing NO31ions. Some of the crystal structures containing HSO₄-¹ ions like Pyrazinium hydrogen sulphate (CCDC Refcode:DUVYEZ01) had chains of HSO4-1 ions held together by AEHBs similar to those found in proton conductor CsHSO₄ in which these chains acted like "Proton Wires" allowing fast conduction of H⁺ ions by Grotthuss mechanism which is also called the hop-turn mechanism [4]. Figure-2 gives a comparison between the possible proton transport mechanics in DUVYEZ01 to that observed in CsHSO₄. A comparison between the potential energy contours (figure-2) for O-H---O bonds in DUVYEZ01 as well as CsHSO₄ calculated using Diabatic state model for hydrogen bonds [5] shows that the hydrogen bonds in both the crystals are of similar strength hence energy required for the proton transport can also be expected to be similar for the two crystals.

Conclusions

An attempt to search for materials possessing oxyanion clusters led us to class of salt crystals containing chains or layers of oxyanions held together by strong anti electrostatic hydrogen bonds, cooperative hydrogen bonding overcomes like-charge repulsion in these clusters. The AEHBs found in such cluster have large covalent character with high shared charge densities, hence these are highly polarisable. It is proposed that the chains and layers of oxyanions held together by AEHBs can act as channels for proton transport making these salt crystals a potential candidate for the technologically important class of materials namely Proton conductors.



Fig. 2. Potential energy contours for the O-H—O bonds in CsHSO4 and DUVYEZ01 (D=120Kcal/mol) and comparison between the proposed proton transport mechanism for the two structures.

Table-1 Data Statistics for AEHBs

	Number of Structures	Average OO (Å)	Average <o-ho (°)</o-ho
O ₃ PO-HOPO ₃	372	2.5824	165.06
O ₃ SO-HOSO ₃	33	2.5727	161.88
O ₃ SeO-HOSeO ₃	8	2.6127	168.95
O ₃ AsO-HOAsO ₃	37	2.6039	162.40
O2NO-HONO2	6	2.5375	163.13
O ₃ ClO-HO	194	2.8912	153.83
О-НО	67350	2.7746	160.48

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The croconic acid glycine crystallization and decomposition

R.Chitra¹, R.R.Choudhury¹, Frederic Capet² and Pascal Roussel²

¹Solid State Physics Division, Bhabha Atomic Research Center, Trombay, Mumbai-400085, India, ²UCCS, CNRS UMR 8181, ENSC Lille UST Lille, BP 90108, 59652 Villeneuve d'Ascq Cedex France, rchitra@barc.gov.in

Abstract. In an attempt to form new class of complexes of organic ferroelectric, it was decided to complex the organic ferroelectric croconic acid with glycine. The crystallization resulted in complex, ammonia oxonium di oxalic acid oxalate hydrate. It is seen that both croconic acid and glycine have undergone oxidation to oxalate and ammonia. The oxidation of croconic acid may be due to exposure to light, even though extreme care was taken to avoid light exposure. The oxidation of glycine though seen in animals and humans in the presence of enzyme, here it occurs due to croconic acid.

Structural and Spectroscopic Study on Ytterbium Tri Chloride(YbCl₃)

S.Ariponnammal, S.Anusha and N.G.Basil Ralph

Department of Physics, Gandhigram Rural Institute, Deemed To Be University, Gandhigram-624302, Dindigul District, Tamilnadu, India

*Corresponding author: <u>ariponnammal@gmail.com</u>

Abstract

The crystals of YbCl₃ were grown by the slow evaporation technique and characterised by scanning electron microscopy, x-ray diffraction, uv-vis, fourier transform infrared spectroscopy and photoluminescence. The crystal is crystallized in monoclinic structure. The energy gap is deduced as 4.41 eV which confirms the insulating nature and Urbach energy is 0.6567 eV. Photoluminescence study showed the presence of Ytterbium vacancy-related defects.

Growth of Cd_{0.90}Mn_{0.10}Te Single Crystal by Vertical Bridgman-Stockbarger Method

Manivel Rajan¹, Rajesh Paulraj^{*}, P. Vijayakumar², Edward Prabu Amaladass^{2,3} S. Ganesamoorthy^{2,3}, Ramasamy Perumalsamy¹

^{1*} Department of Physics, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Chennai-603110 ²Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102 ³Homi Bhabha National Institute, Mumbai-400 094

*Corresponding author: rajeshp@ssn.edu.in

Abstract

CdMnTe (CMT) is a cadmium telluride-based compound semiconductor crystal for application in room temperature radiation detection. This material attracts interest to replace CdZnTe (CZT) because of its uniform segregation co-efficient of Mn, high resistance and tunable bandgap of the crystal. This manuscript reports the growth and structural characteristics of the grown crystal. In this work the $Cd_{0.90}Mn_{0.10}Te$ single crystal was grown by vertical Bridgman-Stockbarger method. The grown single crystal was characterized by powder X- ray diffraction, Laue diffraction, NIR and Fourier Transform Infra-Red spectroscopy.

1.Introduction

CdMnTe (CMT) has its own potential feature over CdZnTe (CZT). This material has unique tunable band gap property based on Mn concentration [1]. The phase diagram of the compound CMT shows that the increase in Mn concentration decreases the melting point of the material [2]. The homogeneity of the elements present in the compound is a mandatory feature to fabricate a high-quality radiation detector. The Cd_{0.90}Mn_{0.10}Te single crystal was grown by vertical Bridgman-Stockbarger (VBS) method. The as grown crystal was characterized by various characterizations such as powder X-ray diffraction analysis (PXRD), X-ray Laue pattern, UV-Vis-NIR and Fourier Transform Infra-Red (FTIR) spectroscopy.

2. Experimental methods

CMT crystal growth comprises two processes namely synthesis and crystal growth [1,2]. The ampoules were made with sharp tip and cleaned as per the standard procedure., Quartz ampoule was carbon coated to avoid reaction and sticking of the grown CMT crystal. [3]. The starting elements Cd, Mn & Te with 99.999% purity have been taken in stoichiometric ratio. The weighed elements were loaded in the carbon coated synthesis ampoule. The ampoule was evacuated up to $2X10^{-5}$ Torr and sealed. A horizontal synthesis furnace with 7°C/cm temperature gradient was used to synthesize the CMT polycrystalline material. Step wise synthesis was carried out by temperature oscillation method. During the synthesis the ampoule was rotated at 3-15 rpm. The furnace temperature was raised above the melting point of the material. Then the CMT polycrystalline material was synthesized ~ 1100°C and the furnace temperature was cooled at the rate of 30°C/hr to room temperature. The synthesized polycrystalline CMT was characterized by PXRD to confirm the phase formation. Further the synthesized sample was loaded in another ampoule to carry out the crystal growth. The growth was carried out using Bridgman-Stockbarger method. The growth ampoule was transferred to furnace and the temperature was raised at the rate of 20°C/hr above the melting point. After sufficient homogenization the ampoule was translated at a rate of 0.5 - 1 cm/day. After the solidification, the furnace temperature was cooled at a rate of 30°C/hr. The cut and polished wafer from as grown CMT single crystal is shown in Fig.1.

8 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9 9

Fig.1. Cut and polished wafer from as grown crystal

3. Results and Discussion

3.1. Powder X-ray diffraction analysis

Synthesized CMT polycrystalline sample was characterized by PXRD measurements and the recorded pattern is shown in Fig.2. It confirms the single phase of CMT. The obtained peaks are in good agreement with the reported results (PDF#65-8867). This pattern belongs to zinc-blende structure [5]. The synthesized compound was highly oriented in the (220) plane.



3.2. Crystalline quality

The Laue pattern of the as grown CMT single crystal is shown in Fig.3. The Laue pattern indicates the sample to be of perfect single crystalline nature.



Fig.3. X-ray Laue pattern of the CMT single crystal

3.3. Transmission spectrum analysis

The cut and polished wafer of CMT single crystal was characterized by both NIR and mid-IR analysis. The transmission property of the CMT single crystal is an important parameter to find the band gap and the crystalline perfection [4]. The obtained NIR spectrum is shown in Fig.4. Based on the lower cut off at 800 nm the band gap was calculated to be $E_g \sim 1.55$ eV. The NIR transmittance of the CMT crystal was nearly 40 percent.

FTIR spectrum of the CMT single crystal is shown in Fig.5. The FTIR spectrum was recorded from 400 cm⁻¹ to 4000 cm⁻¹ and 50% transmission

was observed. No absorption band was observed in this region [4,5].



Fig.5. FTIR spectrum of CMT single crystal

4. Conclusion

The Cd_{0.90}Mn_{0.10}Te single crystal was grown by vertical Bridgman-Stockbarger method. The CMT phase formation and zinc-blende crystal structure of the CMT single crystal was confirmed by PXRD. Xray Laue diffraction pattern confirms that crystalline perfection of the as grown CMT single crystal. The calculated band gap is $E_g \sim 1.55$ eV and transparency in NIR region is found to be nearly 40 percent from NIR studies. The IR transparency percentage of the CMT was found to be nearly 50 percent from FTIR spectrum. These results confirm that the grown crystals are suitable for radiation detector fabrication and testing.

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Single Crystal Growth Of LiCoO₂ Using Optical Floating Zone Technique

Tanya Verma¹, A. Jain^{1,2,*}, Ashwin Mohan³, S.M Yusuf^{1,2,*}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India, ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, ³ Department of Physics, Institute of Chemical Technology, Mumbai 400019, India

*Corresponding author: E-mail address: smyususf@barc.gov.in (S.M. Yusuf), ajain@barc.gov.in (A. Jain)

Abstract

High purity, phase pure single crystals of LiCoO₂, with various excess Li concentration (8% and 12%), and no excess Li, were grown using the optical floating zone furnace. The single crystals of LiCoO2 have been known for their potential applications as an active cathode material in rechargeable Li-ion batteries The rigorous experiments and observations conclude that the phase pure single crystals of LiCoO₂ can only be grown by optimizing the parameters governing the stability of the molten zone i.e. the crystals are grown in the Argon atmosphere with a pressure of 8.5 bar, with growth speeds of 1.0-2.5 mm/h, using no excess Li concentration. The Laue diffraction studies confirms the crystal structure to be Rhombohedral with space group $R\overline{3}m$. The dc magnetization studies of the grown crystal show a metal-insulator transition at around 270K and a short-range magnetic ordering at 110K. The LiCoO₂ single crystal shows no hysteresis even at higher temperatures.

1. Introduction

The single crystals of LiCoO₂ have gathered immense attention over the past years for their application as advanced high capacity energy storage systems for optimized utilization of energy. They are known for their potential applications as an active cathode material in rechargeable Li-ion batteries because Lithium is a good electronic conductor and allows easy addition or removal of electrons during the electrochemical reaction, also it contains a readily reducible/oxidizable ion (i.e. Cobalt)[2].In the work presented here, we report a series of experiments that led to the growth of high purity, single phase crystals of Lithium Cobaltate using optical floating zone technique.

1.1 Experimental details

The polycrystalline samples of LiCoO₂ with different concentrations of excess Li, including 8%, 12%, and no excess Li concentrations, were prepared by the standard solid- state reactions. Compounds required as starting material are Li₂CO₃ (LTS research lab Inc.) and Co₃O₄ (Alfa Aesar Inc.), both of 99.9% purity. The balanced reaction for the formation of LiCoO₂:

 $0.5 Li_2CO_3 + 0.33 Co_3O_4 + 0.08 O_2 \implies LiCoO_2 + 0.5 CO_2$

The grinded powder, consisting of initial reactants, is heated at 700°C for 24 hours in tube furnace in the presence of oxygen gas.

2. Results and discussions

2.1 Crystal growth

The single crystal growth process is a comprehensive process. The feed and seed rods of the polycrystalline LiCoO₂ were made, and sintered at 900°C for 25 hours in presence of air. Then, the feed and seed rods were placed inside the optical floating zone furnace, (Crystal Systems Co., Japan, FZ-T-10000-H-VII-VPO-PC) equipped with four 300 W halogen lamps, and the growth parameters were optimized. The single crystals were grown in Argon gas atmosphere at a pressure of 8.5 bar with 1.0-2.5 mm/h growth speed.



Fig 3. LiCoO₂ single crystal with no excess Li

Excess Li	Feed rod	Rotation	Growth	Grown crystal	Remarks
conc.	specifications	speed(rpm)	speed	length (cm)	
		Seed-Feed	(mm/h)		
			Feed-Seed		
12%	Length = 5.8 cm	20-24	1.0-2.3	7.3	Visible sign of melt is
	Diameter = 6 mm				observed at a power of 52.9%
					_
8%	Length = 5.8 cm	30.0-30.0	1.0-2.5	9.8	1. Frozen zone of previous
	Diameter = 6 mm				used.
					2. Visible melt at 37%
					power.
No excess	Length = 4.5 cm	16.0-19.0	1.0-2.5	6.0	Visible signs of melt at 56%
Li	Diameter = 6 mm				power.

Table1. Observations of the growth process

3. Conclusions

X-Ray and Laue diffraction studies shows that the LiCoO₂ compound crystallizes in **rhombohedral** crystal structure with space group $R\bar{3}m$ having lattice constants: a=b=2.814 Å and c=14.048 Å, $\alpha=\beta=90^{0}$ and $\gamma=120^{0}$. The grown crystals were found to be crack - free and appeared shiny, and also had uniform stoichiometry throughout the length. Dc magnetization studies of LiCoO₂ is shown below: $\chi(T)$ plot depicts that the magnetization peaks around 270K, indicating a metal-insulator transition at this temperature. Also, a small peak around 110K depicts a short-range magnetic ordering in LiCoO₂ single crystal. The M-H plot confirms that there is no hysteresis in the sample at both low and high temperature values.



Fig 4. (a) Temperature dependence of dc magnetic susceptibility of $LiCoO_2$ single crystal at different values of applied magnetic field i.e. B=0.02T, 0.05T, 0.1T, and 1T. (b) M-H hysteresis plot at T= 5K and 275K.



Fig 5. A photograph of single crystal growth with a stable molten floating zone



Fig 6. X-Ray Laue diffraction pattern confirming Rhombohedral crystal structure

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Thermal Investigation Of CuFeS₂ Single Crystals

Bhoomi S. Shah^{1,a}, Sunil H. Chaki^{1,b}, Ranjan Kr. Giri¹, Jolly B. Raval¹, and Milind P. Deshpande¹

¹P. G. Department of Physics, Sardar Patel University, Vallabh Vidyanagar – 388120, Gujarat, India.

Corresponding authors ^a: sbhoomis810@gmail.com (Bhoomi S. Shah); ^b: sunilchaki@yahoo.co.in (Sunil H. Chaki)

Abstract

The thermal behaviour of $CuFeS_2$ single crystals grown by chemical vapour transport technique are discussed in this paper. The thermogravimetric, differential thermogravimetric and differential thermal analysis curves of the grown crystals are measured between ambient and 1203 K temperatures. The thermocurves are measured in argon atmosphere for three heating rates of 10, 15 and 20 K·min⁻¹. The kinetic parameters are evaluated employing three different relations and obtained kinetic parameters are discussed.

Keywords: CuFeS₂, single crystals, growth, thermal analysis

INTRODUCTION

The transition metal chalcogenide semiconductors showing high chemical stability and absorption coefficient are promising materials for various optoelectronic applications. Amongst them the ternary semiconductors possessing chalcopyrite structure belonging to I-III-IV₂ family has promising properties [1]. In the ternary, the copper iron sulphide CuFeS2 (CFS) possesses tetragonal unit cell structure having space group I-42d with sp³ hybridization. The low optical band gap of ~0.53 eV [2] make it favourable for photovoltaic [3] applications. The CFS has shown potential as thermoelectric materials due to its large electrical and small thermal conductivity. This property of CFS makes it imperative to know its stability at high temperature. The detailed deliberation of the recorded thermocurves and kinetic parameters determined by three methods are described.

EXPERIMENT

The growth of CFS single crystals is done by chemical vapour transport (CVT) technique. The halogen iodine is employed as transporting agent. The source and growth zones temperatures are kept as 1253 K and 1203 K respectively. The growth duration is of 168 hrs. The grown crystals structure and phase is determined by powder X-ray diffraction (XRD), Figure 1. The sharp peaks of the XRD stated good crystalline nature. The grown CFS possess tetragonal unit cell structure with lattice parameters of; a = b = 5.29 Å and c = 10.32 Å.

The stoichiometric composition of the CFS crystals is determined by energy dispersive X-ray analysis(EDAX) technique. The observed weight percentages along with standard weight percentage in bracket of the elements are; Cu: 34.32 % (34.62%); Fe 30.22 % (30.43%) and S: 35.46 % (34.95%). The data shows the grown crystals are stoichiometric without any contaminant. The thermogravimetric and differential thermogravimetric curves are recorded for three heating rates of 10, 15 and 20 K·min⁻¹. The samples weight ranged between 8 to 10 mg in each thermal analysis. The range of temperature is ambient (303 K) to 1203 K which is lower than melting point of CFS, 1223 K.

KINETIC ANALYSIS

The TG curves, Figure 2(a), analysis showed the weight loss for 10 K·min⁻¹ in temperature range of ambient to $581\cdot32$ K is 0.31 %, for 15 K·min⁻¹ in



Fig 1. The XRD of grown CFS crystals.

temperature range of ambient to 592.38 K is 0.39 %; and for 20 K·min⁻¹ in temperature range of ambient to 605.14 K is 0.17 %. At higher temperatures the weight losses are; for 10 K·min⁻¹ is 8.59 %, for 15 K·min⁻¹ is 10.04 % and for 20 K·min⁻¹ is 10.93 %. The above TG observations states the grown CFS single crystals are stable between ambient and nearly 600 K. These minor weight losses are observed due to loss of adsorbed atmospheric water molecules and loss of loosely bound constituents. It is observed that as the heating rate increases the weight loss increases. The increased weight loss with increased heating rate arises due to uneven heating of the analysis samples [4][5]. This observation is supported by movement of DTG peak positions, Figure 2(b), to higher temperature values with increase of heating rates. The DTG peak positions for 10 K·min⁻¹ is 666.02 K, for 15 K·min⁻¹ is 669.06 K and for 20 K·min⁻¹ is 675.87 K.

The kinetic parameters like thermal activation energy, change in enthalpy, entropy and Gibbs free energy is determined using relation of Kissinger-Akahira-Sunose (KAS) [6][7], Friedman (FR) [8] and Li-Tang [9] methods. The determined values of the kinetic parameters for the grown CFS crystals are tabulated in Table 1.



Fig 2. The (a) TG and (b) DTG curves of CFS crystals.

Table 1. Kinetic parameters of CFS single crystals

Methods Parameters	KAS	FR	LT
E (kJ·mol ⁻¹)	240.02	242.22	259.12
$\Delta \mathbf{H} (\mathbf{kJ} \cdot \mathbf{mol}^{-1})$	215.61	235.82	252.71
$\Delta \mathbf{S} (\mathbf{J} \cdot \mathbf{K}^{-1} \cdot \mathbf{mol}^{-1})$	13.86	14.29	14.12
$\Delta \mathbf{G} (\mathbf{kJ} \cdot \mathbf{mol}^{-1})$	222.64	224.81	234.13

The determined thermal activation energy values are nearly same in all the three methods stating the reliability of the analysis. The enthalpy change values are positive in all the three methods, stating absorption of heat. The heat absorption by CFS leads to decomposition. The decomposition is corroborated by the weight loss observed in the corresponding TG curves, Figure 2(a). The entropy change values are positive stating enhanced disorder. The Gibbs free energy change is positive stating the sample decomposition due to heat absorption is spontaneous.

CONCLUSION

The CFS single crystals are grown by chemical vapour transport technique using iodine as transporting agent. The XRD and EDAX analysis showed the crystal possess tetragonal unit cell structure and are stoichiometric respectively. The thermal analysis by TG and DTG showed the grown crystal to be stable between ambient and nearly 600 K. The kinetic parameters determined by three methods; KAS, FR and LT, showed the CFS crystals

decompose spontaneously due to heat absorption during heating.

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Seebeck Coefficient of Ni doped Bi₂Te₃

Labanya Ghosh¹, Neha Patel¹ and Sandip Chatterjee¹

¹Department of Physics, Indian Institute of Technology (BHU), Varanasi

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

In order to study the thermoelectric properties of Ni doped Bi₂Te₃ compounds, the desired materials were synthesized by melt growth process. X-Ray diffraction pattern confirmed that the obtained crystals were easily cleaved along (00L) plane direction. Thermoelectric properties were investigated evaluating the absolute values of Seebeck coefficient. Temperature dependency of Seebeck coefficient indicated the changeover in carrier type as a result of Ni doping in Bi₂Te₃. Which results in the suppression of carrier mobility and electrical resistivity reducing the Seebeck coefficient with increasing doping concentration.

Optical and Laser Characteristics of Nd doped LuVO₄ Single Crystal Grown by OFZ Method

M. Soharab^{*1,3}, Indranil Bhaumik^{#1,3}, R. Bhatt^{1,3} and A. Singh²

¹Crystal Growth and Instrumentation Section, Laser and Functional Materials Division, Raja Ramanna Centre for Advanced Technology, Indore-452 013, India

²Laser Technology Division, Raja Ramanna Centre for Advanced Technology, Indore-452 013, India ³Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400 094, India

*Corresponding authors: *sohrab@rrcat.gov.in; #neel@rrcat.gov.in*

Abstract

Single crystals of Nd (0.5 at.%) doped LuVO₄ were grown by optical floating zone technique. The strong absorption band of Nd:LuVO₄ crystal centered at 810 nm can be used for efficient pumping of the Nd:LuVO₄ laser gain medium by using a diode laser operating \sim 810 nm wavelength. The PL intensity at 1065 nm is the highest for both the excitation wavelengths at 810 and 880 nm. CW Laser emission at 1066 nm was demonstrated and the output power for Nd:LuVO₄ element 360 mW.

1.

Influence of Thermal Field on the Reduction of Stress and Dislocation Density in the Growth of mc-Si in DS Process

S. Sanmugavel*, and P. Ramasamy

Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Chennai – 603 110

*Corresponding author: sanmugavels@hotmail.com

Abstract

Global modelling and transient simulation have been carried out on bulk multi-crystalline silicon (mc-Si) growth in an industrial directional solidification furnace. Modification on the heaters has been made to understand its influence over the thermal stress and dislocation densities. The uniform temperature distribution was achieved. The simulation confirms that the stress and dislocation density is decreased by controlling the thermal field of the furnace. The results show that, the influence of the temperature distribution can enhance the quality of the ingot which can be used to produce high efficiency photovoltaic cells.

In-house Development and Demonstration of Low Energy Gamma-ray Spectrometer Based on CdZnTe Single Crystals

P.Vijayakumar¹, E.P.Amaladass^{1,2}, K.Ganesan^{1,2}, O.K.Sheela¹, R.M.Sarguna^{1,2}, S.Chinnathambi¹, S.Ganesamoorthy^{1,2,*}, Awadhesh Mani^{1,2} and N.V. Chandra Shekar^{1,2} ¹Materials Science Group, Indira Gandhi Centre for Atomic Research, Kalpakkam-603102, Tamil Nadu.

²Homi Bhabha National Institute, Mumbai 400 094.

*Corresponding author: sgm@igcar.gov.in

Abstract

 $Cd_{0.9}Zn_{0.1}$ Te (CdZnTe), single crystals were grown by the traveling heater method (THM). The crystal growth parameters, including growth rate, ampoule rotation, temperature profile, Te solvent and growth temperature were optimized to yield large-grained CdZnTe. The CdZnTe wafers were characterized for its structural and electrical properties. Fabricated CdZnTe detector with planar gold electrode was tested using a ²⁴¹Am source. The spectrum was acquired for 511 s at a bias voltage of 350 V with a shaping time of 0.5 μ s. Photo peak of ²⁴¹Am at 59.6 keV is well resolved. The energy resolution of this detector was found to be 8.46 % at 59.6 keV.

Investigation of Pyroelectric Energy Harvesting Potential of LiTaO₃ Single Crystal

B.K. Sajith¹, M. Soharab^{1,2}, A. Sexana¹, R. Bhatt^{1,2} and Indranil Bhaumik^{1,2}

¹Crystal Growth and Instrumentation Section, Laser and Functional Materials Division, Raja Ramanna Centre for Advanced Technology, Indore-452 013, India ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400 094, India

*Corresponding author: bksajith@rrcat.gov.in

Abstract

Pyroelectric energy harvesting is gaining attention for harnessing waste thermal energy into useful energy. We are reporting pyroelectric energy harvesting studies performed on LiTaO₃ (LT) crystal wafer using an in-house developed experimental set up. Setup consists of a thermoelectric Peltier heating module and LABVIEW based electronic control circuit & data login interface. [001] oriented wafers of 15mm dia. and 0.7mm thickness were fabricated from the grown crystal. Experiments were performed for different heating/cooling rates. The heating/cooling cycle of LT wafer from 30 to 45°C generated a peak voltage ~ 25 μ V for Δ T~15 °C, which depicts the energy harvesting potential of LT crystals.

Growth of High Quality Single Crystals of Bi₂Se₃ Topological Insulator via Vertical Bridgman Technique

D S Sisodiya¹, G D Patra², S G Singh², M Ghosh², Shashwati Sen^{*1,2}

¹Homi Bhabha National Institute, Mumbai 400094 India.

²Technical Physics Division , Bhabha Atomic Research Centre, Mumbai 400085, India.

*Corresponding author: Shash@barc.gov.in

Abstract

Topological insulators (TI) are the new state of quantum matter with unique surface properties which has several applications in the field of spintronics and other modern technologies. Device applications require a very good quality sample. Till now people have tried several methods for designing TIs. Here, we used vertical Bridgman technique for growing good quality single crystals of pure and Mn doped Bi₂Se₃. X-Ray diffraction has been performed to confirm single phase and Hall measurement done for studying the electronic properties of Bi₂Se₃ and Mn doped Bi₂Se₃ single crystals. It is observed that Mn in Bi₂Se₃ decreases the mobility of charge carrier which explained in terms of crystal defects which produces due to charge compensation. And also Hall coefficient is found increasing due to Mn doping.

Synthesis and Structural Characterization of Methylammonium Lead Bromide Single Crystal, Grown by ITC Method

Shankar Dutt^{1,2,*}, Preeti Pokhriyal^{1,2}, Archna Sagdeo^{1,2}

Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India
 ² Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India

*Corresponding author: shankard@rrcat.gov.in

Abstract

Bulk single crystals of a Lead halide perovskites perform better than the corresponding polycrystalline samples in many applications and hence, the preparation of large-sized as well as high-quality single crystals is necessary to enhance the device performances. In the present study, Methylammonium lead bromide single crystals are synthesized with a slight modification in the well-known inverse temperature crystallization method reported in literature. The structural characterization of the synthesized single crystals was performed using synchrotron x-ray diffraction technique. Peaks corresponding to only a particular set of planes were observed confirming the formation of single crystal. Powder diffraction was also performed on the same sample to check for the phase purity of the prepared sample.

Introduction

The organic inorganic metal halide perovskites like Methylammonium lead bromide (MAPbBr₃) having structure similar to CaTiO₃ show very interesting properties like tunable band gap, high light absorption, low recombination, high open circuit voltage etc., which make them very interesting in the photovoltaic research field [3]. They have emerged as a promising solar cell material because of the drastic increase in their efficiency since their discovery. Structure of MAPbBr3 crystal is cubic at room temperature having band gap ~ 2.15 eV. The single crystals of these materials are reported to show better stability, higher carrier mobility and lower defect concentration, due to homogenous crystal orientation. Several methods have been reported in the literature demonstrating the growth of single crystals. In the present study single crystals of MAPbBr₃ have been prepared with slight modification in the well-known inverse temperature crystallization (ITC) method reported in literature [1]. The size of the prepared single crystal can be increased by using well known seed method [2].

Experimental Details

The single crystal samples have been prepared using modified inverse temperature crystallization (ITC) method. The prepared single crystals and their quality were tested using Synchrotron XRD (SXRD) at ADXRD beamline BL-12, Indus-2. The measurements were performed using 15 keV photon beam energy. The prepared single crystals were crushed to powders for testing the structure and phase purity of the prepared samples using lab source based x-ray diffraction, with Bruker D8 Advance diffractometer equipped with LYNXEYE detector.

Sample Preparation

Methylamine (CH₃NH₂) (40 wt.% in water), Hydrobromic acid (HBr)(48 wt.% in water) and Lead Bromide (PbBr₂) were used as starting materials. To synthesize CH₃NH₃Br, stoichiometric proportion of CH₃NH₂ and HBr were mixed in a conical flask. The solution was stirred with 400 rpm at 0°C in an ice bath. After two hours of stirring, when the two were completely mixed, the resulting solution was heated at 55°C for first 11/2 hour, then at 60°C for next 3 hours and finally at 70°C for another one hour to form a precipitate. In the present work, a three step heating process has been adopted, which is different as compared to that reported in literature. In the available reports the heating is done at single fixed temperature between 50-60°C for a fixed duration. However, with this method we were not able to get the precipitate and hence the method was modified. With this modification, the obtained precipitate was then washed with diethyl ether in ultrasonic bath, three times for 15 minutes each time and filtered using Whatman filter papers (42) having diameter 125 mm. The filtered precipitate which is CH₃NH₃Br was heated at 70°C for 5 minutes and then kept in a vacuum desiccator for about 45 hours to avoid moisture absorption. After 45 hours a mixture of CH₃NH₃Br and PbBr₂ powders were taken in the ratio of 1:1 and was mixed in DMF (dimethylformamide) which is used here as a solvent to make total volume of the solution 25 ml having 1M concentration. This

solution was stirred at 300 rpm for 21/2 hours until the salts were completely dissolved in DMF and a transparent solution is formed. The resulting solution was kept overnight at room temperature.. This solution which is formed is CH₃NH₃PbBr₃ or also denoted as MAPbBr₃ precursor solution. To make single crystals of MAPbBr₃, well known ITC method was used. A small quantity of MAPbBr₃ precursor solution was taken in a beaker and heated at 80°C for around 3 hours until very small sized crystals were formed. To increase the size of the as-grown crystals, we have placed one of these crystals in a fresh precursor solution and heated it at 80°C and after around 30 minutes, the increase in the size of the seed crystal is observed. This increased sized crystal was then used as seed in a fresh precursor solution and heated for 1 hour at 80°C. With this process \sim 3 mm x 3 mm sized crystals were successfully prepared.

Structural Characterization

Fig. 1 shows the as-grown single crystal of MAPbBr₃ perovskite prepared by ITC method with a slight modification in the process.



Fig. 1. MAPbBr₃ single crystal synthesized by ITC method followed by seeding method



Fig. 2. SXRD pattern of MAPbBr₃ single crystal. Peaks corresponding to only a particular set of plane (100) confirm the single crystal formation.

Fig. 2 shows the SXRD pattern of MAPbBr₃ single crystal. Sharp diffractions peaks at 2θ values 7.9^{0} , 15.9^{0} , 24.1^{0} , 32.3^{0} , 40.8^{0} , and 49.4^{0} corresponding to (100), (200), (300), (400), (500) and (600) planes respectively, can be observed.

Peaks corresponding only to a single set of planes are observed confirming the single crystal formation with (100) orientation. The quality of the single crystal was checked by performing the rocking scan of (100) peak. FWHM of the rocking curve, as shown in inset of fig. 2, is found to be 0.12° which matches well with the reported results, confirms that the quality of our single crystal is comparable to that reported in literature. Figure 3, shows powder x-ray diffraction pattern of MAPbBr3 sample. Presence of no extra peaks, confirms the phase purity of the prepared sample. Rietveld refinement of data has also been performed assuming cubic structure having space group Pm-3m at room temperature, as shown in fig 3. Inset shows the quality of fitting at higher angles. The refined lattice parameter is found to be 5.947Å.



Fig. 3. Rietveld refined Powder xrd pattern of MAPbBr₃ confirming phase purity of the prepared sample.

Conclusions

In this study, we have observed the synthesized MAPbBr₃ single crystal by using ITC method with some modifications. X-ray diffraction pattern confirms the formation of single crystal.

Acknowledgement

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Synthesis and Optical Characterization of Bi_{1-x}Z_xO (x=0.15) Thin Film

A. K. Sahoo¹ and M. R. Panigrahi²

^{1,2}Department of Physics, Veer Surendra Sai University of Technology (VSSUT), Burla, India-768018

*Corresponding author: <u>mrpanigrahi@vssut.ac.in</u>

Abstract

Bismuth Zinc Oxide (BZO) is a potential material for different application due to its small bandgap(~2.92eV) and shows highefficiency photocatalytic activity. The adopted method (modified Sol Gel) is a cost-effective method in comparison to the available methods like solid-state reaction, traditional sol-gel method, wet chemical method etc. The optical parameters like band gap, dielectric constant, transition strength, energy loss function are estimated for the film and observed to be a suitable candidate for industrial applications in photovoltaics.

Introduction

This Bismuth Oxide emerges to be an important potential material for different types of application as a semiconductor material, photocatalysis due to its excellent properties including high bandgap, high refractive index and remarkable photoluminescence. Bismuth oxide is also involved in various fields like solid oxide fuel cell, different types of gas sensors, superconductor materials of high-temperature, catalysis and ceramic materials [1]. The search for optical characteristics of a material is growing day by day because of its various applications in the optics related and many other different fields. It is very important to correctly establish optical constants as the quantitative optical behaviour of the material, primarily optical absorption, is very important and helpful for a good understanding of the electronic structure of the material. A very important aspect is the complex dielectric function, since many of the optical properties like interband transition strength, SELF and VELF can be extracted from this function.

In this work, the optical properties of thin films of BZO (synthesized by eccentric sol-gel method) were studied in the wavelength range (300-900) nm. Sol-gel is emerged to be a successful technique for the generation of samples with a strong homogeneity but due to some advantages over conventional sol-gel techniques, such as: low cost, energy-saving, simpler manufacturing route and small rooms for the completion of the sample preparation process[2] the modified sol-gel method was chosen. This method is therefore adopted as a prospective, affordable and reliable route for material synthesis.

Materials and Methods

A modified sol-gel method was used to prepare the

Zinc doped Bismuth oxide (BZO) thin film. Here, at first, Bi₂O₃ (Loba Chem, 99% pure), ZnO (Loba Chem, 99% pure), acetic acid were taken in a 250 ml beaker and a lump-free paste was obtained by stirring continuously for 30 min using a glass rod. Then hydrolysis was done to obtained lump-free paste by dropwise addition of DI water, followed by a continuous stirring with the glass rod. Later on, the stirring process was continued with a magnetic stirrer machine (IKA C-MAG HS 4) at temperature 120 °C and 230-250 rpm until a clear solution was obtained. Then, 1Molar nitric acid was added with DI water added to the solution dropwise, also the temperature was raised to 150°C and the rpm to 300. At last, after 5 hours, the BZO gel was obtained and deposited on glass slides by doctor's blade technique. The fabricated thin films of BZO was subjected to UV-Vis spectrophotometer (Electronic India 2377) for optical characterization.

Results and Discussions

The absorption spectra as shown in Fig.1 was recorded as a function of wavelength with UV vis spectrometer in a scan range 300-900nm. This curve decreases in both UV and visible region with some minor traces. This behaviour may be due to the ratio of the amount of reacting materials, Bi_2O_3 and ZnO respectively. The band gap is estimated as 2.92 eV for the BZO thin film using Tauc Method[3]. The complex dielectric constant(ε) can be defined as

 $\begin{array}{ll} \epsilon = \epsilon_1 + i\epsilon_2 & (a) \\ \text{where } \epsilon_1 = \eta^2 - \kappa^2 \quad \text{and } \epsilon_2 = 2\eta\kappa & (b) \\ \eta = \text{refractive index and } \kappa = \text{extinction coefficient. The } \\ \text{real dielectric constants}(\epsilon_1) \text{ is connected with the } \\ \text{refraction property (reduction of the velocity of light } \\ \text{the material). Imaginary dielectric constant } (\epsilon_2) \\ \text{measures the amount energy absorbed due to the } \end{array}$

the dipole electric field Fig.3 shows an increase in $\epsilon_{\rm l}.$



Fig.1. Absorbance spectra of BZO thin film



Fig. 2. Bandgap of BZO thin film



Fig. 3. real and imaginary part of dielectric constant

This means there occur an electronic excitation and hence electron transfer takes place to conduction band from valance band in the material. using ε_1 and ε_2 , the interband transition strength (Jcv) can be derived as

$$J_{cv} = J_{cv1} + J_{cv2} = \frac{m_0^2 4\pi^2}{e^2 h^2} \frac{E^2}{2} (\epsilon_2 + i\epsilon_1)$$
(c)

Fig. 4 shows J_{cv1} increases and from 3.75eV, it increases sharply while the J_{cv2} decreases sharply from the same energy level [3]. This means most of the electrons get absorbed and results in the enhancement of the excitation of the electrons from the valance band to conduction band. Surface and volume energy loss function (SELF) and (VELF) is defined as

surface
$$-\operatorname{Im}\left(\frac{1}{1+\varepsilon}\right) = \frac{\varepsilon_2}{((\varepsilon_1+1)^2+\varepsilon_2^2)}$$
 (d)
Volume $-\operatorname{Im}\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_2}{(\varepsilon_1+\varepsilon_2)^2}$ (e)

As shown in fig. 5, the highest value of Surface and Volume energy loss function refer to the energy of



Fig.4. real and imaginary interband transition strength

absorption due to the interband transition which takes place at \sim 4eV for SELF and VELF. The peaks at the



Fig. 5. SELF and VELF of BZO thin film

energies correspond to be the extinctions that takes place at this energy and the energy losses owe to the crossover of the first valance electron to the conduction band in the material of the films.

Conclusion

The BZO thin film was synthesized by modified Sol-Gel method and its optical properties like band gap, transition strength etc. were studied. The band gap was calculated to be 2.92eV which is significantly low due to doping. The optical parameters discussed above gives an idea about the application of the synthesized material for different application like energy harvesting for solar cell and infrared sensing devices

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Growth and Characterization 2AP4N Single Crystal by Immersing Ampoule Sankaranarayanan–Ramasamy (ISR) Method Muthu Senthil Pandian^{1*}, P. Karuppasamy¹, T. Kamalesh¹, P. Ramasamy¹ and Sunil Verma^{2,3}

¹SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai-603110, Tamil Nadu, India ²Laser Materials Development and Devices Division, Raja Ramanna Centre for Advanced Technology (RRCAT), Indore-452013, Madhya Pradesh, India

³Homi Bhabha National Institute (HBNI), Anushakti Nagar, Mumbai-400094, Maharashtra, India

*Corresponding author: senthilpandianm@ssn.edu.in; karuppasamyp@ssn.edu.in

Abstract

The optically good quality organic 2-aminopyridinium 4-nitrophenolate 4-nitrophenol (2AP4N) single crystal of length 120 mm and diameter 15 mm was grown by a novel Immersing ampoule Sankaranarayanan-Ramasamy (ISR) method. The water covered completely the glass ampoule containing growth solution in the unidirectional method for the first time in the literature. The ampoule was specially designed for the growth of good quality and bulk size unidirectional single crystals by slow cooling condition. The unwanted temperature gradient developed on the solution surface was completely avoided and hence the secondary nucleation developed on top of the glass ampoule is avoided. The growth apparatus and optimization parameters have been made simpler compared to the conventional SR method. The optical behavior of the grown 2AP4N crystal was analyzed by UV-Vis NIR spectrophotometer. The optical homogeneities of the grown 2AP4N crystal were analyzed by birefringence measurement. The growth of <001> direction was confirmed by the PXRD analysis. The crystalline perfection of different growth portions (bottom, middle and top) was confirmed and analyzed by HRXRD measurement. The various studies reveal that the ISR method grown single crystals are favorable for high performance optical device applications.

Introduction

Nonlinear optical (NLO) materials are of current research interest in material science for their various applications such as frequency tuning, optical bistability, optical data storage, image processing, biophotonics and etc. (1). Crystal engineering is a powerful technique that allows one to elucidate relationships between molecular structure and specific solid-state properties in a predictable manner. The SR method is unique for directional solution growth and also having many advantages such as defect-free, high transparency, good healthy bulk crystals in different orientations (2). Solute to crystal conversion efficiency 100% was achieved in SR method. The external morphology facets may induce strain through the lattices, it could be avoided in the single interface growth. Therefore, higher quality, large size, free from strain/stress and directionalcontrolled single crystals are more important for developing current research and technologies.

In the present novel ISR method, we have introduced the special types of glass ampoule and it is immersed entirely into the water bath under slow cooling condition. This modification is reported for the first time in the literature. It gives a better quality single crystal with reduced optimizing parameters compared to the conventional SR method. Investigation has been carried out on the ISR method grown bulk 2AP4N single crystal.

Synthesis and Crystal Growth

The 2-aminopyridinium 4-nitrophenolate 4nitrophenol (2AP4N) compound was synthesized by taking the raw materials of 2-aminopyridine and 4nitrophenol in 1:2 molar ratio in methanol solvent. The 2AP4N seed crystals and its morphology are shown in Fig. 1 (a) and (b) respectively. The seed crystal with <001> direction was selected for bulk growth in the ISR method.



Fig. 1. (a) As grown 2AP4N crystals & (b) its morphology

Growth by ISR Method

The ISR crystal growth method is a better way to grow a unidirectional bulk size single crystal and it is also requiring reduced optimizing parameters compared to SR method. The schematic diagram of ISR method is shown in Fig. 2. The major and important parameter for all the crystal growth methods is the temperature gradient (ΔT), hence the suitable temperature gradient provides to the growth system to achieve a better growth rate and can get high-quality single crystal. Probably most of the defects/dislocations formed in the growing crystal are due to the instability of the temperature in the growth system (3). In the SR method, the top thermal gradient will be developed between air and the top portion of the growth solution. If not optimized carefully this temperature gradient, initiates nucleation at top portion of the solution and it falls on the growing crystal. In the ISR method, this problem was completely avoided. This method is more convenient for controlling the formation of multinucleation around the seed crystal. Also the seed tilting problems of SR method can be easily avoided.



Fig. 2. Schematic diagram of ISR method



Fig.3. ISR method grown 2AP4N single crystal

Optical transmittance

The optical quality plays a major role for materials used in laser based device applications. The sliced 2AP4N single crystal wafers (bottom, middle and top) with the thickness of 2 mm have been subjected to the UV-Vis NIR spectrophotometer for finding its optical quality and their cut-off region. The percentage of optical transmittance gives the information about the crystal quality. The optical transmittance spectra of grown 2AP4N single crystals along <001> direction with the different growth regions (bottom, middle and top) are shown in Fig. 4. From the optical spectra, the characteristic cut-off wavelength of 2AP4N single crystal occurs at 470 nm and good photo transmittance (75-80%) in the visible and NIR regions.

Birefringence and HRXRD

Birefringence plays a major role in nonlinear optical (NLO) phenomena and it is widely utilized in many optical devices. The moderate birefringence required for materials used in frequency conversion applications. The double refraction or birefringence indicates the ability of an anisotropic crystal to separate incident light into O-ray and E-ray. This separation and their interference may be affected by many factors such as stress, strain, impurities, defects present in the grown crystal. From the figure.5, it indicates that the ISR method grown 2AP4N single crystals are of optically good quality and higher crystalline perfection. The FWHM of top, middle and bottom portions of the 2AP4N crystal are (9.780": 11.652"), (9.652": 9.512") and (9.009": 9.434") for the diffracted planes (002): (004) respectively.



Fig.4. Optical transmittance spectra 2AP4N single crystals



Fig.5. Birefringence patterns of 2AP4N single crystal at the different growth portions

Conclusion

The optically high quality with large size unidirectional organic 2AP4N single crystal was grown by a novel ISR method. The optical quality, crystalline perfection and optical homogeneity of the 2AP4N single crystal was confirmed by UV-Vis NIR, HRXRD and birefringence analysis respectively. From the results, it has been concluded that the ISR method grown 2AP4N crystal are more suitable for NLO and high-performance laser frequency conversion applications.

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Evidence of Cubic Structure and Topological Crystalline Behavior of SnTe at Low Temperatures

Ayanesh Maiti^{1,2}, Ram Prakash Pandeya², Ankita Singh², Kartik K. Iyer², Bahadur Singh², A. Thamizhavel², and Kalobaran Maiti²

¹Undergraduate Department, Indian Institute of Science, Bengaluru - 560012, India.

²Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai - 400005, India

Abstract

We investigate the growth of high quality single crystalline SnTe, a rare topological crystalline insulator and its topological property employing angle resolved photoemission spectroscopy (ARPES). The outstanding problem in SnTe is the transition from highly symmetric cubic phase to a relatively lower symmetric rhombohedral structure at low temperature which is less favorable for topological behavior. We have grown high quality single crystals of SnTe using modified Bridgman method. The structure analysis reveals cubic structure down to 2 K studied. ARPES results are found to be consistent with the band structure results. The data collected at low temperatures show Dirac cone, a characteristic of the topological behavior. These results suggest that the cubic structure is the ground property of SnTe and that the structural distortion observed in earlier studies maybe linked to the Sn-vacancy.

Directional growth, Structural and Optical Properties of 2-Amino-5-Nitropyridinium p-Toluenesulfonate (2A5NPT) Single Crystal for Nonlinear Optical (NLO) Applications

Sivasubramani Vediyappan*, Muthu Senthil Pandian, Ramasamy Perumalsamy

Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam-603110, Tamil Nadu

*Corresponding author: sivasubramaniv1989@gmail.com

Abstract

An efficient organic NLO single crystal of 2A5NPT was successfully grown by the modified SR method with a span of 60 days. The formation of the title crystal and its crystalline perfection were evaluated by SXRD and HRXRD analyses, respectively. The modified SR method grown crystal possesses 82% of optical transmittance in the visible and NIR region. The third-order NLO response of the grown crystal was determined by the single beam Z-scan technique using He-Ne laser of wavelength 632.8 nm. The obtained results evidence that the title crystal has the behavior of negative nonlinear refraction and reverse saturable absorption.

Single Crystal Growth Of Calcium Based Transition Metal Pnictides CaTX (T = Au, Ag, Cu and X = Bi, Sb, As) and Their Transport Properties

Souvik Sasmal^{1,*}, Gourav Dwari¹, Bishal Baran Maity¹, Arumugam Thamizhavel^{1,*}

¹Department of Condensed Matter Physics & Materials Science, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

*Corresponding author: <u>sasmalsouvik6@gmail.com</u>, thamiz@tifr.res.in

Abstract

Calcium base transition metal pnictides materials are interesting to their inherent electronic band structure. Here, we report detail single crystal growth techniques of CaAuAs, CaAgAs, CaAgBi and CaCuSb. All the mentioned materials are grown by flux method. All specified flux compositions and temperature profiles are mentioned for grow single crystals. Temperature dependent resistivity of these materials show a metallic nature. For CaAgBi and CaCuSb, the magnetoresistances (MRs) show a cusp like behavior, whereas this behavior is absent for CaAgAs and CaAuAs. This cusp like feature is reminiscent of weak antilocalization where the quantum interference plays a crucial role. MR in CaAgAs and CaAuAs are almost linear.

Introduction

The most key challenges in the condensed matter and material science are to search for a new topological materials. Topological materials host new type of Fermions and are expected to show exotic properties. Among them calcium-based transition metal pnictides are not much explored. Recently, they are found to be host of topological state by their own electronic structure [1-3]. These ternary compounds are difficult to grow. So that it is important to find proper flux, flux quantity, temperature profile and other optimized parameters. In this report, we have a detail discussion of growth techniques of CaAuAs, CaAgAs, CaAgBi and CaCuSb. We have presented their primary electrical transport properties up to applied magnetic field 14 T.

Crystal Growth

We have grown all the Ca-based transition metal pnictides compound using flux method. It is important to follow the flux quantity and temperature profile. In the Table. 1, we have specified composition of flux, molar ratio, heating rate, cooling rate and centrifuge temperatures for growth process of each compound. Initially, the high purity starting elements are taken in specified molar ratio in an alumina crucible (as given in the Table. 1). The alumina is sealed in a quartz ampoule under a partial argon (Ar) gas. The schematic diagram in Fig. 1(a) clearly indicates how the heating and cooling process has been run to grow a single crystal. Using a box type furnace, the sealed ampoule is heated to 1050 °C at the mentioned heating rate and held at this temperature for 24 h. Staying at high temperature for long time (~ 24



Fig. 1 (a) Schematic diagram of the temperature profile. As grown crystal image of (b) CaAuAs, (c) CaAgAs, (d) CaAgBi and (e) CaCuSb

h) is important for homogenization. Lastly, the ampoule is slowly cool to centrifuge temperature where the execs flux is removed by centrifugal force.

Here, Cu-Sb eutectic has been used to growth CaCuSb single crystal. Cu-Sb (35:65) eutectic has melting point of 530 °C, so that the sealed ampoule has been centrifuge at 630 °C (~ 100 °C above the melting point of Cu-Sb eutectic). Though Au-As or Ag-As eutectic flux are available, here, to grow CaAuAs and CaAgAs single crystal Bi flux has been used. As has high vapor pressure and there is a possibility of formation of other phases as well. Again, Bi has high solubility, lower vapor pressure and low meting point which makes Bi as much

Material	Flux	Molar	Heating rate	Cooling rate	Centrifuge	
		ratio	(°C/h)	(°C /h)	Temperature (°C /h)	
CaAuAs	Bi	Ca : Au : As : Bi 1 : 1 : 1 : 8	15	1	500	
CaAgAs	Bi	Ca : Ag : As : Bi 1 : 1 : 1 : 8	15	1	500	
CaAgBi	Ag : Bi	Ca : Ag : Bi 1 : 2 : 20	50	2	420	
CaCuSb	Cu : Sb	Ca : Cu : Sb 1 · 4 5 · 7 5	30	2	630	

T.I.I. 1 D / 1



Fig. 2 (a) Temperature dependent resistivity for all materials. (b) Magnetoresistance for I //ab- plane and B // c at T = 2 K.

preferred flux. It is important to mention that excess Ag has been used to grow CaAgBi, so that the used molar ratio of Ca, AG and Bi are 1:2:20. Otherwise, there is a large tendency all Ag comes out with the flux. To avoid any adverse consequences, we follow the growth process given in Tab. 1. Simultaneously, we centrifuge the ampoule the at desired temperature. In Fig. 1(b)-(e), all the as grown crystal images are given.

The temperature dependent resistivity data are shown in Fig. 2(a). Here, the resistivities have been measured for current (I) // crystallographic *ab*- plane and magnetic field along c- direction. All the compounds show metallic behavior. Among them CaAuAs has smaller residual resistivity and residual resistivity ratio (RRR), whereas high RRR value in CaAgBi and CaCuSb indicate good quality single crystal. Magnetoresistances (MRs) are shown in Fig. 2(b). Interestingly, MRs is CaAgBi and CaCuSb show a cusp like behavior at low magnetic field and become linear at higher field. This suggests the weak antilocalization (WAL) in the systems. Generally, it is observed in layered or 2D system where charge carriers are confined in 2D motion. When the phase coherence length large than the mean free path, the quantum interference happens between two charge

carrier paths. π - Berry phase or large spin orbit coupling can cause such WAL. Here, in bulk transport we observed WAL in both CaAgBi and CaCuSb. These are the layered in structure so that there is a possibility of charge transport in large parallel conduction channels. MRs are almost linear for CaAuAs and CaAgAs, suggest no WAL in these systems.

Above materials are topological semimetal on their own inherent band structure. Here, CaAgBi contains multiple Dirac points along $\Gamma - A$ line [1]. Whereas, a metallic topological surface state coexists (circular bulk band) at Fermi level in nodal-line semimetal CaAgAs [2]. Furthermore, recent experiment shows topological Dirac state in CaAuAs [3].

Summary

We have optimized the growth process of different Calcium based transition metal pnictides compounds. They are hexagonal in structure. Large spin orbit coupling causes interesting magnetotransport in those systems. Temperature dependent resistivities show metallic nature with high RRR values. Cusp like MR behavior in CaAgBi and CaCuSb is indicating WAL.

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Growth of Halide Scintillator Single Crystals Using Multi-Ampoule Bridgman Technique

G.D.Patra¹, D.S. Sisodiya², S.G. Singh¹, D.G. Desai¹ and Shashwati Sen^{1,2}

¹Technical Physics Division, BARC, Mumbai ²Homi Bhabha National Institute, Trombay, Mumbai, 400094

*Corresponding author: shash@barc.gov.in

Abstract

A multi ampoule Bridgman technique for growth of halide single crystal is developed, which enables growth of 4 single crystals simultaneously in single experiments and it helps for precise comparison in crystals without compromising in crystal quality. The scintillation performance of grown crystals are compared with standard data which is available in literature and found that there is no significant change in energy resolution. Multi ampoule Bridgman technique found to be very economical for research purpose.

Role of Nitrogen Incorporation in Growth of Large Area Homoepitaxial Single Crystal Diamond

Vivek Kumar Shukla¹, Lekshmi J.¹, Brajesh Singh Yadav², Padmnabh Rai^{1*}

¹School of Physical Sciences, UM-DAE Centre for Excellence in Basic Sciences, University of Mumbai, Kalina, Santacruz (E), Mumbai-400098, India ²Solid State Physics Laboratory, Timarpur, Delhi-110054, India

*Corresponding Author: padmnabh.rai@cbs.ac.in

Abstract

Due to the wide range of exceptional properties, diamonds have become a most promising candidate in the field of electronic and optical applications. High-density microwave plasma chemical vapor deposition technique was employed to grow a high-quality single-crystal homoepitaxial diamond films. It has been shown that the phase purity, surface morphology, and growth rate of deposited diamond increase by feeding a small concentration of nitrogen to the gases phase. Freestanding homoepitaxially synthesized specimens have been characterized using Raman Spectroscopy, XRD, and Atomic forced microscopy (AFM). An intense Raman peak at about 1332.8 cm⁻¹ confirms the Single phonon Brillouin zone centre corresponds to the Single crystal diamond. The surface morphology of grown samples using AFM measurement reveals that the sample with a high concentration of nitrogen (~ 9 ppm) gives a better result.

Introduction

Diamond is a wide bandgap semiconducting material having excellent electrical and optical properties which makes it well suited in the field of science and technology such as particle detectors in high energy physics, high-temperature electronic devices and quantum computing applications [1, 2]. Among the various techniques, microwave plasma chemical vapor deposition (MPCVD) method is found to be the most promising avenue available for the lab grown diamond which provides low-cost, high-quality single crystal diamond (SCD) materials.

Current research on the growth of MPCVD diamonds is mainly based on nitrogen incorporation and its influence on the growth rate and phase purity of single-crystal diamonds. The synthesized samples were characterized by Raman Spectroscopy which is a fast and non-destructive approach. XRD analysis was carried out to evaluate the quality of the grown samples. The root mean square values for roughness measurement using AFM reveals the surface morphology of the samples.

MPCVD System

The microwave plasma CVD system consists of a rectangular waveguide that allows microwave (2.45 GHz) generated from an MW generator to propagate with its dominant mode. The microwave from the rectangular waveguide is coupled to the resonant cavity through a quartz window and highly dense large-size plasma is created above the substrate. The gas flow rate was controlled by a mass flow controller (in sccm) and temperature above the substrate was monitored by a digital pyrometer.

Experimental Methods

The SCD films were synthesized by 2.45 GHz, 6.0 kW MPCVD system. The optimal growth conditions for synthesizing single-crystal diamond films were: CVD (100) Substrate, CH4/H2 flow rate 10%, chamber pressure 100-120 torr, Substrate temperature 900°C. The free standing grown samples ($8X8mm^2$) named as, DRM (Without any intentionally doped N₂), DRM-N (With N₂ incorporation up to 2-3ppm), and DRM-N1 (nitrogen concentrations 8.9 ppm) are synthesized.

Characterization of films

Raman Characteristic peaks at about 1333 cm⁻¹ confirm tetrahedral sp³ bonding of carbon and single phonon in brillouin zone center corresponds to the diamond material **[3]**. As shown in Fig.1. DRM-N with impurity concentration 2-3 ppm shows a sharp and more intense peak at 1332.8 cm⁻¹ defines better crystallinity. A slight shift in the peak position of the Raman band results in anisotropic stress present in the crystal lattice can be estimated using,

 $\sigma = k X (v_m - 1331.8) \text{ GPa}....(1)$

From equation (1), the value of k = 0.34 GPa-cm is calculated empirically for diamond.



Fig. 1. Raman spectra of free standing SCD Samples with varying N_2 concentration. (a) DRM sample without N_2 (b) DRM-N with N_2 concentration between 2-3 ppm and (c) DRM-N1 with N_2 concentration 8.9 ppm.

Also $(v_m - 1331.8)$ is the shift in wavenumber of the sp³ peak [4]. As listed in Table 1. below, positive stress is a consequence that the stress being tensile.

 Table: 1 Raman Shift and corresponding residual stress present in the samples.

Sample	FWHM (cm ⁻¹)	Raman Shift (v _m) (cm ⁻¹)	Amount of Stress (GPa)
DRM	4.244	1332.967	0.396
DRM-N	2.469	1332.804	0.341
DRM-N1	2.68	1333.220	0.483

From Fig. 2 shows the XRD of as grown SCD samples. XRD (002) w-scans reveal that the DRM sample has FWHM of 0.1628^{0} as compared with FWHM of 0.0306 for the DRM-N1. The slight broadening of FWHM for the DRM diamond sample indicates a small twinning [5]. Further, the surface roughness measurement of the samples was carried out at room temperature using Atomic force microscope (AFM). Fig.3 shows AFM images and the root mean square roughness (RMS roughness [Sq.]) values for $1x1\mu m^{2}$ scanned area. The roughness value improves as we increase nitrogen incorporation. So, it is confirmed that the N_{2} incorporated sample shows better crystallinity.

Conclusions

In summary, we have grown homo-epitaxial SCD samples with varying nitrogen concentration. By varying nitrogen concentration, we can achieve a growth rate of up to 15 μ m/hr. Here, DRM-N with N₂ impurity (2-3 ppm) gives a very small stress value

compared to DRM and DMR-N1. Moreover, the FWMH value from the XDR rocking curve shows high crystallinity for N_2 doped samples. Also, surface morphology is improved by adding nitrogen impurities.



Fig. 2. XRD (200) w-scan of grown SCD samples (a) DMR (b) DRM-N and (c) DRM-N1



Fig. 3. AFM images and corresponding RMS roughness values of the SCD surfaces.

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Third order nonlinearity of Ethyl p-amino benzoate (EPAB) single crystal grown by Solution and Bridgman technique – A Comparative Analysis

A. Muthuraja^{*}, V. Kowsalya^{*}, N. Malarvizhi^{*}, S. Saheera Banu^{*}, and B. Mithra^{*}

^{*}Department of Physics, Theivanai Ammal College for Women (Autonomous), Villupuram, Tamilandu. India

*Corresponding author: amuthuraja90@gmail.com

Abstract

Single crystals of Ehtyl p-amino benzoate has been grown by solution growth and Bridgman technique. A comparative analysis about the growth and optical properties of the grown crystals were carried out. It was found that the EPAB crystal grown from Bridgman technique is having a high value of third order nonlinear susceptibility when compared with the crystals grown by solution growth technique.

3-(Thiophen-2-yl)-5-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1Hpyrazole-1-carboxamide

Sahana D¹, Dileep C. S², and R. Gopalakrishne Urs¹

¹ Department of Physics, the National Institute of Engineering, Mysore 570008, ² Department of Physics, Vidyavardhaka College of Engineering, Mysore, 570002

*Corresponding author: dileepcs@vvce.ac.in

Abstract

Title compound was synthesized, and its crystal structure was investigated by X-ray crystallography. Title compound was synthesized, and its crystal structure was investigated by X-ray crystallography. The molecule belongs to the monoclinic system. The space group is C2/c. The lattice parameters are a = 32.999(2) Å, b = 9.7141(5) Å, c = 20.8477(12) Å and $\beta = 106.160(6)^{\circ}$. The final residual value is R1 = 0.1178. The molecule exhibits both intermolecular and intramolecular N–H...S, C–H...S and N–H...N, C–H...N hydrogen bonds.

Development of SEM Detectors using Indigenous YAP:Ce Scintillators

S. S. Pany¹, S. G. Singh², and Y. V. Chaudhari¹

¹SEM Development Section, Security Electronics & Software Systems Division, ²Crystal Technology Section, Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085

*Corresponding author: sspany@barc.gov.in

Abstract

Scanning Electron Microscope (SEM) is a significant micro-imaging and characterization tool that has gained popularity among all disciplines of science. Bhabha Atomic Research Centre, Mumbai has been involved in indigenous development of SEM to make the technology affordable for Indian academia and to cater to special requirements of the department. Here we discuss about design and development of indigenous SEM detectors using in-house developed YAP:Ce scintillators.

Introduction

Scanning Electron Microscope (SEM) is a specialized instrument used for imaging micro and nanoscopic features in specimen, by using the signals produced through interactions of focused electron beam probe with the specimen that yield microscopicscale information on size, shape, composition, crystallography, and various other physical and chemical properties of the specimen. Electron beamspecimen interactions in SEM produce signals in the form of Secondary Electron (SE), Back-Scattered Electrons (BSE), characteristic X-rays signals etc. are used for obtaining information about specimen topography, elemental contrast image and elemental characterization map. The advantage of SEM over similar variants is its accommodability to variety of sample without the need for specific samplepreparations. Due to this, SEMs are gradually becoming an All-One-Needs micro-characterization instrument for all disciplines of science. SESSD, BARC has been involved in indigenous development of SEM to make the instrument affordable for Indian academic institutions and research labs, in addition to gaining technological acumen to be able to customize the instrument to cater to special requirements of the department.

The SE and BSE detectors developed for indigenous BARC-SEMs use scintillators as primary detecting element. Commercially available inorganic scintillators typically used for SEM detectors are expensive and are available in some pre-defined configurations only. Collaboration with the Crystal Technology Section of Technical Physics Division, BARC has been instrumental in availability of inhouse developed scintillators for SEM detectors, in the forms and configurations warranted by the respective design specifications. In the subsequent sections, we discuss about development of SE and BSE detectors for BARC-SEM using in-house scintillators.

Development of SE Detector

SE detector is a primary and the most fundamental attachment to a general-purpose SEM, as it facilitates imaging of the specimen topographic features. Secondary electrons are low energy electrons (with max. energy below 50eV and mean energy about 5eV) generated through inelastic scattering of primary electron beam within specimen interaction volume. The popular detection scheme for secondary electrons involves acceleration of the SEs to a voltage of about 10-12 keV and using scintillators as detecting element for these accelerated electrons.

The SE detector for BARC-SEM has been designed from first principles. Fig. 1 shows the schematic of the SE detector assembly. The detector comprises of 10mm dia, 1mm thick scintillator maintained at a voltage of +10kV to accelerate the secondary electrons towards it. The scintillator is interfaced with quartz light-guide which is connected to a PMT on the other end. All optical coupling has been done using EJ-500 optical cement. The attractor electrode is maintained at a voltage ranging between +1kV to -1kV. While the purpose of the attractor electrode for most SE detectors is to attract the low energy SEs towards the detector, the purpose of this electrode in the current design is to focus the stray secondaries towards the scintillator. In this detector configuration, the electric field generated by scintillator potential directly exerts attracting force on SEs.



Fig. 1. SE detector schematic

Computational electromagnetic simulations have been used for design optimization of the SE detector assembly. The objective function for design optimization is the SE collection efficiency and collection time. The detector has a peak collection efficiency greater than 95% at working distance beyond 20mm and about 50% at lowest working distance of 8mm. Fig. 2 shows the collection of secondary electrons in SE detector.



Fig. 2. SE signal collection in detector

The SE detector is a formal attachment to all indigenously developed BARC-SEMs.

Development of BSE Detector

BSE signal yield elemental contrast image in SEM. BSE detector designed for BARC-SEM consists of an annular scintillator of OD 25mm, ID 6mm and thickness 1mm. The scintillator is mounted onto a specially designed quartz light-guide, which interfaces with a PMT on the other end. Optical cement EJ-500 was used at all optical interfaces. The BSE detector has been designed to double-up as SE detector also, as a positive potential of +10kV is applied to the scintillator. Fig. 3. shows the scintillator and lightguide of BSE detector. The detector is under assembly stage following which it will be integrated with SEM for thorough performance evaluation.



YAP:Ce Scintillator Quartz light-guide Fig. 3. Scintillator-lightguide assembly of BSE detector

Scintillator for SEM Detectors

The choice of YAP:Ce as scintillator for SEM detectors is based on its resilience to electron-beam impact, low photon decay constant of 25ns, low afterglow and relatively high photon yield. The choice of YAP:Ce for SEM detectors is also based on its low quantum efficiency in the red-orange region. Thermionic tungsten filament based electron source of the SEM emits photon in the red-orange spectral range, so low quantum efficiency of YAP:Ce in this range makes signal discrimination by the PMT easier.

Single-crystal YAP:Ce scintillators for the detectors have been Czochralski crystal growth technique in the form of an ingot of dia. 25mm and length 50mm, which has been further processed into scintillators of suitable diameter and 1mm thickness. The scintillators have been polished to optical finish. To prevent electron impact induced charge accumulation on scintillators, 50nm thick Aluminum layer have been deposited on scintillator outer surfaces using thermal evaporation system. The Aluminum layer also functions as specular reflector for back-propagating scintillation light-rays, and thus prevents light-loss.

Work Ahead

Further refinement in scintillator design for SEM detectors shall involve reduction in the thickness with the objective to minimize light-losses, and to incorporate novel conductive coating material that functions as diffuse reflectors, which have been shown to yield better collection efficiency than specular reflectors.

Multriticality in Quasi-kagome Ferromagnet URhSn

Arvind Maurya^{*1,3}, Dilip Bhoi², Fuminori Honda¹, Yusei Shimizu¹, Ai Nakamura¹, Yoshiki J. Sato¹, Dexin Li¹, Yoshiya Homma¹, M. Sathiskumar², Jun Gouchi², Yoshiya Uwatoko², and Dai Aoki¹

¹Institute for Materials Research, Tohoku University, Oarai, Ibaraki 311-1313, Japan ²Institute for Solid State Physics, The University of Tokyo, Kashiwa, Chiba, 277-8581, Japan ³Max Planck Institute for Solid State Research, Heisenbergstrasse 1, 70569, Stuttgart, Germany

*Corresponding author: arvindmaurya.physics@gmail.com

Abstract

We report high quality single crystal growth of ferromagnet URhSn, crystallizing in ZrNiAl-type hexagonal structure in which the magnetic U-atoms form potentially frustrated quasi-kagome two-dimensional net. Our measurements of electrical transport under hydrostatic pressures up to 11 GPa reveals two bicritical points concurrent at $P_C = 6.25$ GPa corresponding to its successive double phase transitions ($T_O = 54$ K, $T_C = 18$ K at ambient). Rermakably, the intermediate phase remains hidden as local probes like neutron scattering and Mossbauer spectra do not capture any new feature between the T_C and T_O . Our low temperature resistivity data under pressure points out a Fermi surface reconstruction across the P_C , corresponding to an unconventional class of quantum phase transition involving multicritical points. This picture is further ascertained by gradual development of $-\ln T$ behavior in 5*f*-derived electrical resistivity and appearance of $T^{5/3}$ behaviour in the pressure induced phase.

Reflux deposited ZnO Nanoparticles For Supercapacitor Application

Umesh Babar¹, Rohini Patil¹, Ashok Chougale², Rahul Patil³, and Pradeep Kamble^{1*}

¹Department of Physics, The New College Kolhapur-416012, ² Department of Chemistry, The New College Kolhapur-416012, ³Department of Physics, Shri Yashvantrao Patil Science College, Solankur.

*Corresponding author: pdkamble27@gmail.com

Abstract

In the present work, zinc oxide (ZnO) nanocrystals have been prepared by the reflux method. Their structural, morphological, optical and capacitive properties have been investigated. Structural characterization by X-ray diffraction reveals that polycrystalline nature. Integration of ZnO was confirmed from elemental analysis using EDX. SEM technique proved that the successfully coated the surfaces of the nanostructures. The as-optimized binder-free ZnO nanoparticle electrode exhibited a reversible electrochemical feature, providing a high specific capacitance of 335 F g⁻¹ at 5 mV s⁻¹. These performances of ZnO nanoparticle were attributed to its open mesoporous and large accessible area of hierarchical nanocrystals.

Introduction

Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors. In doing so, supercapacitors are able to attain greater energy densities while still maintaining the characteristic high-power density of conventional capacitors. Supercapacitors employ thin dielectric layers and high surface area electrodes. Consequently, they exhibit capacitances that are several orders of magnitude higher than traditional capacitors [1, 2]. In this work, we demonstrated the controlled Reflux method by synthetic parameters in a reaction bath to create the hierarchical nanostructures of ZnO nanoparticles [3]. During the preparation, all other parameters such as concentrations, pH and quantities of solution are optimized and kept constant [4]. Thus, controlled growth of ZnO leads to construct well-organized nanoflakes morphology composed of fine nanoparticles, providing good specific surface area with mesoporous structure and leading to enhanced electrochemical performance [5].

Experimental Details

ZnO nanoparticles were prepared by economically green reflux method. A 0.2M of zinc acetate $(ZnC_4H_6O_4)$ was dissolved in 20ml of absolute ethanol and stirred at room temperature for 30 min. Then 36mg of NaOH was dissolved in 20ml of ethanol. The NaOH solution was added to the zinc acetate solution in drop wise in constant stirring. The pH value of the solution was maintained to be 12 by adding aqueous ammonia under constant vigorous stirring in above mixture. The solution was continuously stirred for 2h at room temperature. The solution became turbid form which indicated the ZnO nanoparticles were formed. The solution then was refluxed about at 90° C for 3h.

Material Characterizations

The structural characterization of the pure and the Cd doped ZnO nanoparticles is carried out using X-ray diffraction (XRD) by BRUKER AXS D8 Advanced model X-ray diffractometer equipped with Cu radiation (K_{α} of λ = 1.54 Å) operated at 40kV. The morphological features of the pure and the Cd doped ZnO nanoparticles are analysed by scanning electron microscopy (SEM) JEOL JSM-6390. SEM technique is used to observe the grain size, rough morphology, and distribution of the particles on the surface of the system.

Results and Discussion

X-ray Diffraction

Fig. 1 (a) shows the observed XRD patterns can be indexed to hexagonal wurtzite crystals of assynthesized ZnO. All the obtained peaks well match with the hexagonal wurtzite crystal structure of ZnO (JCPDS card no. 79-2205) having lattice constants a=0.315nm and c=0.529nm. The observed diffraction reflections of ZnO are appeared at 31.71° , 34.41° , 36.24° , 47.52° , 56.6° , 62.8° , 66.3° , 67.9° , 69.1° , 72.4° and 76.9° correspond to the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) planes, respectively of ZnO.

Energy Dispersive spectroscopy (EDS)

To examine the elemental composition of ZnO nanocrystals were characterized by energy dispersive spectroscopy (EDS). Fig. 1 (b) exhibits the typical

EDS spectrum of pure ZnO nanocrystals. As can see from **Fig. 1** (b) EDS spectrum, the synthesized nanoparticles are made by Zn and O which confirms that the synthesized material is pure ZnO.

Scanning Electron Microscopy (SEM)

To investigate the general morphologies, the assynthesized ZnO nanoparticles were characterized by scanning electron microscopy (SEM) **Fig. 1 (c)** exhibit the pure ZnO is synthesized in high density and nanocrystal shaped structures. The SEM image reveals the polycrystalline, nanocrystal shaped morphology with the interconnected particle presents on the pure ZnO nanoparticles.



Fig. 1 (a) XRD, (b) EDS, (c) SEM, (d) Wettability, (e) Cyclic Voltagram., (f) Charge/Discharge curve of ZnO nanoparticles

Contact Angle

The static contact angle for the ZnO nanoparticle, the surface was found to be hydrophilic with a contact angle less than 90° . Which is useful for capacitive application.

Electrochemical Studies

To demonstrate the electrochemical performance of ZnO nanostructures, the electrochemical properties of nanocrystal samples were first characterized in three-electrode ECs with cyclic voltammetry and galvanostatic charge discharge measurements in 0.5M Na_2SO_4 aqueous solution [4]. The CV curves of untreated ZnO electrode collected at different scan rate of 5 to 100 mV s⁻¹ are shown in Fig. 1 (f). Fig. 1 (e) shows the galvanostatic charge discharge curves of ZnO electrodes collected at a different current density of 10 to 15 mA.cm⁻². Prepared ZnO electrode obtained maximum specific capacitance at 5 mV s⁻¹ is 335Fg⁻¹

Conclusion

In this study, ZnO nanoparticles synthesized via the reflux method was investigated. A single-phase zinc hexagonal wurtzite type of structure was detected in ZnO samples. The particle shapes of the ZnO nanoparticles were almost similar with a mixture of semi-spherical, sweet corn-like shape structures. The crystallite size of ZnO nanoparticles is approximately 57.94nm. EDS shows the proper elemental composition of ZnO. Wettability studies show Hydrophilic nature of ZnO material. The Capacitive properties of ZnO nanoparticle illustrates the high specific capacitance is 335 F g-¹ at 5 mV.s⁻¹. Hence it is concluded from above result nano crystal shaped ZnO material is highly suitable for Energy Storage application.

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Dissipative Quantum Transport In Single Molecular Transistor At Finite Temperature And Magnetic Field: A Tunable Spin-filter

Kuntal Bhattacharyya^{*}, Manasa Kalla and Ashok Chatterjee

School of Physics, University of Hyderabad, Hyderabad-500046, India

*Corresponding author: kuntalbhat22@gmail.com

Abstract

The effect of magnetic field and temperature on the quantum transport is investigated in a single molecular transistor where a quantum dot containing a single-quantized energy level is inserted in the center and coupled to the source and drain. This three-terminal device is mounted on an insulating substrate which plays the role of a phonon reservoir. The dot consists of an onsite electron-electron correlation, polaronic (electron-phonon) interaction and the coupling between quantum dot local phonon and the substrate phonon produces a quantum dissipative effect on the dynamics of conducting electrons. At first, the dot-substrate phonon interaction is eliminated by a canonical transformation. Then, the electron-phonon coupling is removed by a coherent-state phonon averaging via Lang-Firsov transformation under the framework of Anderson-Holstein-Caldeira-Leggett model followed by a mean-field Hartree-Fock technique to treat the onsite Coulomb correlation. Finally, we calculate transport properties such as spectral density function, tunneling current, differential conductance and spin polarization employing finite-temperature Keldysh non-equilibrium Green function method to see the out-turn of temperature and an external magnetic field in the presence of damping, electron-phonon interaction and Coulomb correlation. It is shown that temperature has an intervening effect on the spin-resolved transport properties which can be used as a tunable spin-filter.

Dynamics of Liquid Gallium-A Microscopic Approach

Jyoti Sood¹ and S.P.Tewari²

¹University Institute of Engineering and Technology, Panjab University Chandigarh-160014 ²#B-009,ICON Apartments, Plot No. GH-04 Sector CHI3, Greater Noida-201310. (Formerly : Department of Physics and Astrophysics, University of Delhi, Delhi-110007)

*Corresponding author: jyotisood@pu.ac.in

Abstract

The modified microscopic theory has been used to study the collective dynamics of liquid Gallium for the wave vectors close to its melting point. The obtained energy dependent spectra for the dynamical structure factor of the liquid Ga sample are very much in accordance with the experimental values of coherent inelastic X-ray scattering

Introduction

Coherent dynamical structure factor of a condensed system, a liquid for example, not only contains the complete information about its thermal equilibrium collective processes spanning long and short time scales, but can also be used to explore its microscopic behavior by analyzing its experimental energy dependent spectra obtained either by inelastic thermal neutron scattering (INS) or inelastic X-ray scattering (IXS)[1,2]. For simple liquid alkali metals, many such experiments have been performed and observed the collective dynamical spectra clearly show, for example, their characteristic feature: the presence of the Rayleigh-Brillouin triplet; which change considerably for larger values of, k and ω . Micro-dynamics of a liquid is quite complex and involved but the availability of high resolution accurate coherent inelastic X-ray scattering experimental results on liquids makes it worthwhile to understand their micro - dynamics better. In the present communication we study the micro-dynamics of liquid Gallium comparing with recently reported experimental measurements of IXS [3].

Element Gallium is a solid at room temperature but turns into a liquid when heated mildly to 303 K which is close to the melting point of Rubidium i.e., 312K. However chemically it is similar to multi - valency Aluminium which is above it in Group IIIa in the Periodic Table. Gallium, unlike Rb & Al, has a strong tendency to super - cool below its melting point. Bosio & Widsor [4] reported thermal neutron inelastic scattering measurements on the quasi elastic width in the temperature range 303K to 150K, the meta - stability limit, in highly super cooled Gallium droplets. This experiment yielded temperature dependent coherent dynamics. Ga being a predominantly coherent scatterer of thermal neutrons (it's incoherent scattering is hardly 8% of the coherent) which was explained by the microscopic dynamical theory [5], the modified form of which is being used here to analyze the accurate experimental results of Scopigno et al.[3] in liquid Ga at 315K obtained using high resolution IXS.

To explain the response of interacting fluid to an external incident radiation (whether a neutron or X-ray), a classical equation of motion with suitable history averages of the trajectories[7] is used where the Fluctuation - Dissipation theorem relates the imaginary part of the space time Fourier transform of the response function to the Dynamical Structure factor $S(k,\omega)$. The collective dynamics of a correlated fluid can be explained by introducing a characteristic relaxation time which although is not a free parameter but is related to the different physical parameters of the system and as a result the correlations between the distinct particles are incorporated [7]. If we generalize the diffusion coefficient, D, which is a real physical quantity in the fluid phase to D(k), it assumes a specific value for a given k. To give a quantitative description of $S(k,\omega)$ of varying correlated fluids, more realistic description of the intermediate self scattering function $F_s(k,t)$, acceptable in the entire time domain has to be considered. This is achieved not through the model of $F_s(k,t)$, which would introduce several free parameters but by making the diffusion coefficient frequency dependent [7]. The modified micro-dynamical theory which has earlier successfully explained $S(k,\omega)$ of liquid metals and expanded gaseous fluids has been used to prove the presence of collective modes for liquid metal Gallium.

Mathematical Formalism

A liquid is acted upon by a weak space – time dependent potential field when a thermal neutron or an X-ray photon interacts with a liquid which results in space-time dependent fluctuation of the equilibrium density of the liquid and is linearly dependent on the potential. This change in the density is related to the density-density response function, the Fourier transform of which is obtained using the microscopic dynamics of the liquid. Time-dependent displacement of an atom is obtained by solving the classical equation of motion [6] and as in a liquid, atoms are not fixed at their sites but are moving, one has to take suitable history averages of the trajectories. In order to incorporate the neglected timedependent correlation between the distinct particles, a relaxation time for the distinct part of the correlation function is introduced and is determined by satisfying the zeroth sum rule. The theory now yields much better realistic overall results of $S(k,\omega)$ and satisfies its first three sum rules. A recent modification [7] of the theory yields the detailed $S(k,\omega)$ which is in reasonable quantitative agreement with the corresponding experimental results. Making the diffusion coefficient frequency dependent, one finally obtains the following expression for $S(k,\omega)$ for a liquid which is an isotropic system:

$$\begin{split} S(\bar{k},\omega) &= \frac{k^2}{\pi n \beta} \begin{cases} \left[1 + \omega_k^2 \frac{(\beta^* + \gamma)^2 - \omega^2}{\left[(\beta^* + \gamma)^2 + \omega^2 \right]^2} \right] \frac{2\beta^*}{\left[(\beta^* + \omega^2)^2 - \right]} \\ & \omega_k^2 \frac{(\beta^{*2} - \omega^2)}{\left[(\beta^{*2} + \omega^2)^2 \frac{2(\beta^* + \gamma)}{\left[(\beta^{*2} + \gamma)^2 + \omega^2 \right]^2} \right]} \\ & \left\{ \left[1 + \omega_k^2 \frac{(\beta^* + \gamma)^2 - \omega^2}{\left[(\beta^* + \gamma)^2 + \omega^2 \right]^2} \right]^2 + \left[\omega_k^2 \frac{2\omega(\beta^* + \gamma)}{\left[(\beta^* + \gamma)^2 + \omega^2 \right]^2} \right]^2 \right\}^{-1} \end{split}$$
(1)

 $\beta'' = D_{eff}k^2 = D(\omega)k^2 \quad D(\omega)$ is the ω -dependent self diffusion coefficient and other symbols have been defined in earlier papers.

Results and Discussion

To explain the microscopic dynamics of a liquid, its interatomic potential, V(r) has to be known as it can be used to relate $S(k,\omega)$ to the microdynamics of the system. Although V(r) is not an observable quantity but its algebraic formcan be suggested by knowing the physics of the system and the computed potential can be compared with an observable measurable physical quantity which is dependent upon it. An effective two body potential for liquid metals can be suggested by taking into account the direct interaction between the ionized atoms of the metal and the screening effect of the conduction electrons. Such an analytical expression for the potential for liquid metals has been given by Bellissent -Funel et al [8] where effective potential is determined by approximating the Fourier inversion of experimental structure factor [9]. In the present communication an analytical form of potential V(r) has been suggested by comparing the given form of potential with that given by LRO potential [10]. Making use of the interatomic potential, V(r), and the corresponding static pair correlation function, g(r), of liquid Ga, r_0 and the maximum elastic frequency ω_E , have been evaluated and turn out to be 2.72Å and 1.4436 $\times 10^{13}$ s⁻¹ respectively.

 $S(k,\omega)$) for liquid Gallium in the wave vector range $3.25nm^{-1} \le k \le 125nm^{-1}$ has been calculated and compared with the observed IXS results[3] and have been plotted in Fig. 1 for the low values of k. The experimental results have been shown with the solid circles(•••) whereas, the solid curve(----) represents $S(k,\omega)$ computed with the modified microscopic theory where D_{eff} $= D(\omega)$ and the (---) denotes the $S(k,\omega)$ values when D_{eff} is taken to be independent of ω . It is evident that the modified microscopic theory yields $S(k,\omega)$ in reasonable agreement with the corresponding experimental results and the collective modes are well defined.



Fig. 1: Variation of $S(k,\omega)$ with ω for different values of k for liquid Gallium at 315K

The figure very clearly shows the presence of collective modes in the computed results for liquid Gallium near its melting point.

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Enhanced Electrical Transport Properties of Ex-situ Ball-milled Silver Doped Hydroxyapatite for Rectifying Applications

Tuli Chatterjee¹, Swapan Kumar Pradhan², and Ajit Kumar Meikap^{1,*}

¹Department of Physics, National Institute of Technology, Durgapur, Durgapur 713209, West Bengal, India ²Materials Science Division, Department of Physics, University of Burdwan, Burdwan 713104, West Bengal, India

*Corresponding author: meikapnitd@yahoo.com

Abstract

Silver-doped hydroxyapatite (Ag-H) synthesized by the hydrothermal method has been wet-milled for 30min (Ag-HM) and the structural, compositional and morphological characteristics have been compared before and after milling. Ag-HM shows improved ionic conductivity, significantly high dielectric permittivity, and less energy consumption at high temperatures than that of Ag-H without any adverse change in its compositions and stoichiometry. Nonlinear back-to-back Schottky diode-type rectifying behavior for high temperature regime (373-613 K) has been reported for the first time for milled silver-doped Hydroxyapatite.

Introduction

Laboratory synthesized monovalent silver ion (Ag^{1+}) substituted hydroxyapatite is suitable for several biomedical purposes due to its high biocompatibility with natural bone and tissues and antibacterial activities. But the applicability of such materials in high-frequency rectifying diode-based electronic industries with proper electrical and dielectric behavior, less energy consumption, and high efficiency have not been studied in detail so far.¹

In this present work, we have synthesized stoichiometric Ag-doped hydroxyapatite by simple hydrothermal method followed by ex-situ wetmechanical alloying process. X-ray diffraction (XRD) with Rietveld (MAUD 2.26) refinement, Field Emission Scanning Electron Microscopy (FESEM), and Energy Dispersive X-ray Analysis (EDAX) have been employed for the structural and microstructural investigations. The dielectric constant, ionic conductivity and current-voltage characteristics have been studied in detail to reveal the suitability of the materials for temperature-dependent electronic applications at various frequencies. The comparative XRD plots, morphological characterizations, relative permittivity (ϵ'), and ionic conductivity (σ_i) plots of the Ag-doped samples before and after (designated as Ag-H and Ag-HM, respectively) milling have been represented to elucidate the effect of wet-milling on the dielectric and electrical transport properties of the chemically synthesized Ag-substituted HAp nanostructures.

Material synthesis, Characterizations, Results and Discussions

The Ag-substituted HAp has been synthesized using the conventional hydrothermal method using precursors CaHPO₄.2H₂O, Ca(OH)₂ and AgNO₃ in the

molar ratio 6:3.9:0.1 for 10 mol% Ag doping at pH=10 and 140°C for 24 h. A planetary P6 ball-mill has been employed for 30min with consecutive 15 min wet-milling followed by 10 min pause at 300 rpm in acetone medium using chrome steel milling media. The Rietveld refined XRD patterns of Ag-H and Ag-HM materials in Fig. 1 have been indexed with pure HAp [JCPDS#09-0432] (~77.8%) and β -TCP [JCPDS#55-0898] (~22.2%) phases are coexisting due to replacement of Ca²⁺ ions by Ag¹⁺ ions within HAp lattice.



Fig. 1. (a) Rietveld refined comparative XRD patterns of Ag-H and Ag-HM samples, (b) EDAX spectra of Ag-HM sample, FESEM images of (c) Ag-H and (d) Ag-HM.

There is no β -TCP reflection in the Ag-H sample, whereas, Ag-HM sample contains significant β -TCP reflections. Incorporation of secondary β -TCP phase improves the goodness of fitting (σ =1.26 and 1.16, respectively for Ag-H and Ag-HM samples). Reduction in intensities of the overlapped significant peaks of the Ag-HM sample indicates a less crystalline nature due to milling. The average sizes of the nanocrystallites along the growth axis <002> are ~93.1 nm and ~50.4 nm and the average micro-strains are 3.5×10^{-3} and 6.4×10^{-4} respectively, for Ag-H and Ag-HM samples. Here the ex-situ ball-milling process creates mechanical shearing to break the monotonic growth of Ag-H long nanorods without affecting the chemical composition and crystallite size reduces accordingly. As evidenced from the EDAX spectra (1µm×1µm area), the atomic ratio of (Ca+Ag)/P is 1.73 for both the samples keeping the phase-purity and stoichiometry intact. As observed from FESEM images, the morphological nature of Ag-H is composed of long and thin uniform nanorods scattered randomly. They gradually turn into homogeneously distributed nanostructures for Ag-HM upon milling.

The current density (J)-voltage (V) characteristics of Ag-HM sample shows nonlinear back-to-back Schottky diode-type rectifying behavior within the voltage range ± 3.5 V for high-temperature (T) regime (373-613 K) in Fig. 2(a). The metal-semiconductor-metal hetero-junction created due to the applied silver electrode on both sides of the pelleted sample together with internal space charge within ionic grains and grain-boundary of HAp,² may be the reason for the asymmetric Schottky I-V behavior as shown in the inset of Fig. 2(a).



Fig. 2. (a) J-V characteristics fitted by Schottky diode equation (inset: Butterfly-like I-V nature for 373-613 K) and (b) Power-law dependent thermal variation of ϵ' (inset: Temperature versus σ_i) of Ag-H and Ag-HM.

The dissimilar potential barrier resulting from two oppositely polarized voltage drops between two back-to-back connected rectifying diodes explains such type of asymmetry¹ obeying the thermionic emission theory. The J-V characteristics curves for various temperatures are least square fitted ($R^2 \sim 0.9929$ -0.9967) with the following eqn. (a),

$$J = \frac{J_1 J_2 \sinh(\frac{qV}{2k_B T})}{J_1 \exp(\frac{qV}{2\eta_1 k_B T}) + J_2 \exp(-\frac{qV}{2\eta_2 k_B T})}.$$
a)
$$J_i = A^{**} T^2 \exp(-\frac{q\varphi_i}{k_B T}); i = 1, 2.$$

where, A^{**} is effective Richardson constant, J_i is the current density, φ_1 and φ_2 are two potential barriers, η_1 and n₂ are two ideality factors of the two diodes.³ The extracted barrier heights (φ_1 and φ_2) are 0.44-21.4 meV and 0.38-61 meV and ideality factors $(n_1 \text{ and } n_2)$ are 1.07-1.11 and 1.09-1.14. respectively for temperatures 373-613K. The relative dielectric permittivity and ionic conductivity of Ag-H and Ag-HM samples as a function of temperature has been plotted at 50 Hz frequency in Fig. 2(b) and Fig. 2(b) (inset). It is evident from both of the curves that the dielectric constant and ionic conductivity of Ag-doped HAp samples becomes significantly high due to ball-milling. Since crystallite size of Ag-H reduces for Ag-HM and the suppressed β -TCP phase exposes, both dipolar and space charge polarization effects arise in huge amount⁴ giving rise to excellent dielectric permittivity ($\sim 4 \times 10^3$) and ionic conductivity with considerably low dielectric loss (tan\delta~1.2 for 303 K; 50 Hz) of the milled sample. In Fig 2(b) the dielectric constant obevs a power-law type dependence ($\epsilon' \alpha T^m$; m=exponent). After milling the exponentially rising permittivity curve becomes steeper ("m" = $5.7 \rightarrow 8.1$ from Ag-H to Ag-HM).

CONCLUSION

Ag-substituted HAp with (10 mol%) synthesized by chemical route possesses significant structural and morphological changes upon mechanical alloying. Depending on the milling, physical properties also get modified, showing high dielectric permittivity and ionic conductivity with low dielectric loss. The I-V characteristics exhibit good back-to-back Schottky behavior that can be useful in high-temperature electronic applications.

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Temperature Dependent Dielectric Response of Ni Coated MWCNT/PVDF Nanocomposite Film

Chandan Kumar Raul^{1*}, Monalisa Halder¹, and Ajit Kumar Meikap¹

¹Department of Physics, National Institute of Technology, Durgapur, Durgapur 713209, India

*Corresponding author: ckr24071995@gmail.com

Abstract

Flexible and light weight nickel coated multiwalled Carbon Nanotube (Ni-MWCNT)/Polyvinylidene Fluoride (PVDF) Nanocomposite film is prepared by solution casting method to study its electrical transport mechanism. The inclusion of Nicoated MWCNT nanofillers in the polymer leads to an improvement in dielectric features of the film. Temperature dependent AC conductivity follows Jhonscher's universal dielectric response. The analysis of the dielectric property of the parallel plate capacitive configuration of the nanocomposite is elucidated using modified Cole-Cole model.

Introduction

In the era of high performance power electronics, energy storage systems with ultrafast dielectric response are very much essential. A series of nanocapacitors can be formed if conducting nanofillers can be added to polymeric matrix. Polyvinylidene Fluoride (PVDF) is a semi-crystalline piezoelectric thermoplastic with good chemical and mechanical stability. Carbon nanotube (CNT) has high electrical conductivity with good thermal and mechanical properties. Nickel (Ni) decorated multiwalled CNT (MWCNT) is reported to have enhanced mechanical strength and high dielectric permittivity [1].

In this work, flexible and light weight Ni coated MWCNT/PVDF nanocomposite has been synthesized to the electrical transport properties and the dielectric response of the sample.

Experimental Details

To synthesize the film, polyvinylidene fluoride (PVDF) powder was dissolved in Dimethylformamide (DMF) at 343K by continuous magnetic stirring. Using high frequency ultrasonic bath, Ni-MWCNT (0.35 wt%) was dissolved into 10 ml DMF and then mixed with 10 ml PVDF (8 wt%) solution under continuous magnetic stirring for 2 h. The homogeneous solution poured onto a glass Petri dish and was put within oven for evaporation of DMF for 5h. Finally the film was peeled off from Petri dish for further experiments.

The sample is characterized using X'pert Pro multipurpose diffractometer and scanning electron microscope (ZEISS EVO-MA 10). The electrical transport properties of the film is studied using Agilent E 4980A precision LCR meter.

Results and Discussions

The XRD pattern of Ni-MWCNT/PVDF nanocomposite is shown in Fig. 1. The XRD pattern presents peaks attributed to the crystalline phases (β , γ) of PVDF. The XRD pattern also shows the characteristic peaks of nickel. The average crystallite size is found to be 8 nm using Debye – Scherrer formula.



Fig. 1. Room temperature XRD pattern of Ni-MWCNT/PVDF nanocomposite (inset shows the W-H plot of the sample).

Crystallite size (D) and lattice strain (ϵ) of the film sample is determined using Williamson-Hall (W-H) equation as follows [1],

$$\beta\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta \qquad a)$$

where K is a constant = 0.94, β is the FWHM, λ is the wavelength. Fig. 1 (inset) shows the W-H plot and D and ϵ are found to be 6 nm and 0.9% respectively.

Fig. 2 shows the FESEM image of the film where prominent grains and grain boundaries are observed.



Fig. 2. FESEM image of the sample.

At different temperatures, AC conductivity of the film (parallel plate capacitive system: metal-film-metal) [shown in Fig. 3] obeys Jonscher's power law as follows,



Fig. 3. Frequency variation of temperature dependent AC conductivity of the sample (inset shows the temperature variation of *S*).

$$\sigma'(f) = \sigma_{dc} + \sigma_{ac}(f) = \sigma_{dc} + \alpha f^{s}$$
 b)

where σ_{dc} is the DC conductivity, *S* is a constant and the frequency exponent $S \le 1$. A gradual decrease of '*S*' with temperature is observed [Fig. 3 (inset)] irrespective of frequency implies the predominance of the Correlated Barrier Hopping (CBH) in charge transport mechanism.

The dielectric response of Ni-MWCNT/PVDF film is studied further. Fig. 4 shows the frequency dependence of real part $[\varepsilon'(f)]$ and imaginary part $[\varepsilon''(f)]$ of complex permittivity of the film sample respectively. The data are fitted using modified Cole-Cole model as follow,

$$\varepsilon'(f) = \varepsilon_{\infty} + \left[\frac{\left(\varepsilon_{s} - \varepsilon_{\infty}\right) \left\{ 1 + \left(\omega \tau\right)^{\beta} \cos\left(\frac{\beta \pi}{2}\right) \right\}}{1 + 2\left(\omega \tau\right)^{\beta} \cos\left(\frac{\beta \pi}{2}\right) + \left(\omega \tau\right)^{2\beta}} \right] + \frac{\sigma_{sp}}{\varepsilon_{0} \omega^{p}}$$

$$\varepsilon''(f) = \left[\frac{\left(\varepsilon_s - \varepsilon_{\infty}\right) \left\{ 1 + \left(\omega \tau\right)^{\beta} \sin\left(\frac{\beta \pi}{2}\right) \right\}}{1 + 2\left(\omega \tau\right)^{\beta} \cos\left(\frac{\beta \pi}{2}\right) + \left(\omega \tau\right)^{2\beta}} \right] + \frac{\sigma_{fc}}{\varepsilon_0 \omega^p}$$
d)

where β is a parameter, p is an exponent, τ is the most probable relaxation time, σ_{fc} and σ_{sc} are the free charge and space charge carrier conductivity

respectively.



Fig. 4. Temperature dependent real part of complex permittivity of the sample (inset shows the imaginary part of complex permittivity)

At low frequencies, free dipoles inside the sample align along the field, but they cannot orient when the frequency is high. The nanocomposite film exhibits enhanced dielectric constant value of ~ 100 as compared to the reported value of pristine PVDF (~8-13) [2]. As temperature increases, free charge conductivity and space charge polarization increase.

TABLE 1. Derived electrical parameters of Ni-MWCNT-PVDF nanocomposite film

Electrical	Temperature			
Parameters	303 K	333 K	363 K	383 K
au (sec)	0.005	0.004	0.0026	0.0018
	9	0		
β	0.56	0.67	0.85	0.91
σ_{sp} (S m ⁻¹)	5×10 ⁻⁹	8×10 ⁻⁹	4×10 ⁻⁸	7×10 ⁻⁸
р	0.78	0.81	0.88	0.90
$\sigma_{fc}~({\rm S~m}^{-1})$	1×10 ⁻⁸	3×10 ⁻⁸	8×10 ⁻⁸	2×10 ⁻⁷

Conclusion

Here, Ni coated MWCNT/PVDF nanocomposite is successfully prepared. The enhancement in dielectric response is clearly seen due to the inclusion of Ni-MWCNT nanofillers in PVDF matrix and it follows Cole-Cole model. The significant and tunable dielectric feature makes the film sample appropriate for potential applications.

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Hot Electron Cooling in Disordered Graphene in BG Regime through Coupling with Flexural Phonons

M. Obaidurrahman^{*} and S.S.Z. Ashraf

Department of Physics, Faculty of Science, Aligarh Muslim University Aligarh-202002, Uttar Pradesh, India *E-mail; khanobaid12@gmail.com

Abstract

We have studied the hot electron cooling rate F(T) in disordered graphene in the Bloch-Gruneisen regime due to coupling with flexural phonons using Keyldysh Green's function method. The cooling rate is calculated as a function of temperature (*T*) and mean free path (*l*). We obtain analytical results for F(T) in both the impurity and clean limits. Also, from the complete numerical evaluation of the integrals, we find that the temperature dependence of the F(T) is sensitive to the presence of disorder as disorder suppresses temperature dependence of F(T), changing the power law from T^2 to $T^{5/2}$. Also, at very low temperatures, F(T) with flexural phonon coupling is found to be smaller than F(T) due to acoustic phonon coupling with electrons in disordered graphene. These calculations not only indicate the influencing effect of flexural phonon coupling on the transport properties of Dirac Fermions at very low temperatures with impurities but also provide a comparative behaviour with that of acoustical phonons due to deformation potential coupling.

Keywords: Keyldysh method, graphene, deformation potential, disorder.

Introduction

The exploration of graphene forms one of the most vibrant areas of research in this era in condensed matter physics, both for its exciting physics and realistic scenarios of numerous device applications, with a huge interest of researchers (both experimentalists and theorists) devoted to the transport properties of graphene [1]. The properties such as thermopower, energy loss rate, relaxation rate, mobility, etc. are in general accounted by the electron deformation potential (DP) scattering. Graphene is the only system in which disorder aided cooling influences from very low to room temperature [2]. The electron-phonon (el-ph) interaction gives a width of energy that can be shared from higher energy electrons to phonons and in thermal metrology, it allows the measurement of phonon temperature if the inequilibrium continues for a sufficient duration of time. A large modification of the el-ph coupling due to the effects of disorder and scattering of the electrons has been shown in a recent theory [2]. The graphene lattice is characterized by the vibrations of two types of phonons, those vibrating in the plane of the layer with longitudinal and transverse acoustic branches, and others that vibrate out of the plane of the layer, named flexural phonons. The flexural phonon contribution was ignored for many years and it had been widely accepted that only acoustic phonons carry heat in graphene. But off late it has transpired that the flexural phonon modes in suspended graphene transport most of the heat at low temperatures as reported in a recent work, which contradicts the wellestablished result [3]. The interaction between the graphene layer and the substrate beneath changes significantly the characteristics of the out of plane vibrations of the whole system. The heat transfer between the two systems is due to coupling to a substrate [4]. In our work, we obtained analytical results of the cooling or energy loss rate due to flexural phonons in disordered graphene that reduces to the analytical result result result result [5].

FORMALISM AND ANALYTICAL RESULT

The heat flux between electrons and lattice through the energy control function F(T) as [6];

 $P(T_{ph}, T_e) = v \int \varepsilon d\varepsilon I_{e-ph}(\epsilon(\mathbf{k})) = F(T_e) - F(T_{ph})$ (1) has been calculated from the collision integral, the collision integral tells the rate of change of electronic phase-space of distribution function $[n(p, \epsilon(\mathbf{k}); t)]$ due to the absorption and emission of phonons. The electron-phonon collision integral is expressed as [7]

$$[I_{e-ph}(\epsilon)]_{DP} = \tau \int \frac{dq}{(2\pi)^2} \eta(\omega_{\alpha}, \epsilon) \mu^2 \left(\frac{\sqrt{q^2 l^2 + 1}}{q^2 l^2}\right)$$
(2)

Where $\eta(\omega_{\alpha}, \epsilon)$ is the combination of electronic and phononic distribution functions appropriate for phonon absorption and emission processes [7], $\mu = D_{dp}(\hat{\mathbf{e}}, \mathbf{q})/(2\rho\omega_{\alpha}\hbar^{-1})^{1/2}$ is the vertex of the el-ph interaction in which *q* is the phonon momentum, $\hat{\mathbf{e}}$ is the phonon polarization vector, D_{dp} is the Deformation potential constant, ρ is the graphene sheet mass density, and $\omega_{\alpha} = \alpha q^2$ is the quadratic energy dispersion relation of flexural phonons in the absence of strain with the flexural phonon diffusion constant α . The F(T) is given by the equation [6-7],

$$F(T) = \frac{D_{dp}^2 m}{\pi^2 \rho v_f \hbar} \int \frac{q^3 l dq}{(2\pi)^3} \left(\frac{\sqrt{q^2 l^2 + 1}}{q^2 l^2} \right) \left[N(\omega_q, T) \right]$$
(3)

After evaluation and subsequent integration of eq. (3) we obtain the analytical result for cooling rate F(T) in the disorder limit, ql <<11 for unscreened DP as

$$F(T) = \frac{D_{dp}^2 k_f k_B^2 T^2}{6\rho \alpha v_f^2 h^2 l}$$

$$\tag{4}$$

And in the clean limit ql >> from the Eq. (3) we have

$$F(T) = \frac{3 D_{dp}^2 k_f k_B^{5/2} T^{5/2} \zeta(5/2)}{4 \pi^{3/2} \rho v_f^2 \hbar^{5/2} \alpha^{3/2}}$$
(5)

Which is the same as the earlier reported result [5].

Results and discussion

The cooling rate F(T) of graphene has been computed as a function of the mean free path and temperature for disordered graphene with the material parameters from ref.5&7. The comparison with the approximate analytical results is most appropriate in the sub-Kelvin temperatures since the approximated formulae for collision integral, the equation (2) has been derived in the strong impurity limit, where ql <<1 or T < u



FIGURE 1: (1a) Cooling rate as a function of temperature, and (1b) Cooling rate as a function of mean free path.

In figures 1(a&b), we have plotted analytically and numerically calculated F(T) from equation (3) as functions of temperature and mean free path. In figures (a) and (b) the curve A corresponds to the analytical result (with l=20 nm and T=1.0K). Figure (1a) depicts the magnitude of F(T) by flexural phonons from equation (3) as a function of temperature for different values of *l* and curves B&C correspond to the full numerical computational with different values of mean free path (l=20 nm and0.2nm). From graph (1a) it is clear that the magnitude of F(T) increases with a decrement in value of l (that is the enhancement of the low-temperature F(T) with the increasing disorder are clearly evident). In figure (1b), the same behaviour is also confirmed when F(T)is plotted as a function of the mean free path for different values of temperature (T=0.5K and T=1.0K). From both the figures we observed that the F(T) increases (decreases) with an increase in temperature (mean free path). Also, from fig(1b), we observe that for a large value of l the curves B&C become flat which indicates the clean limit behaviour (al >>1) (since F(T) is independent of the mean free path in the clean limit).

Therefore, we conclude from the study that the electronic disorder modifies the magnitude of F(T) between electrons and flexural phonons. We find that the modification changes the power law from $T^{5/2}$ to T^2 . We also observe that the scattering by flexural phonons significantly changes the temperature dependencies from that of reported [6] due to acoustic phonons (i.e., from T^3 to T^2) but the mean free path dependencies remain the same as that of the acoustic phonons (i.e., 1/l).

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High Temperature DC Electrical Transport Property of Polyvinylidene Fluoride Flexible Film

Amit Kumar Das, Riju Karmakar, and Ajit Kumar Meikap*

Department of Physics, National Institute of Technology Durgapur, Durgapur-713209, West Bengal, India

*Corresponding author: meikapnitd@yahoo.com

Abstract

Pure Polyvinylidene fluoride (PVDF) has been prepared by solution casting method. The film is characterized by FTIR and PL technique and the surface morphology is studied by AFM analysis. The temperature variation of the DC conductivity of the film reflects the semiconducting behavior with theoretical VFT model fitting. The resistance-voltage characteristic of the flexible film shows hysteresis loop, leads to charge storage as well as memory device application of the film.

Introduction

In the last few years, due to rapid growth flexible electronic, researchers are started to focus on the polymer materials. It is very important to understand the basic properties of the polymeric materials to apply it in the industrial application. Out of all semicrystalline polymer Polyvinylidene fluoride (PVDF) as well as its β -phase is mostly used in the electronic world. This β -phase PVDF has net dipole moment due to proper orientation of electropositive H-atom and electronegative F-atom on the backbone of carbon chain.¹ Here, we have prepared β -phase PVDF flexible film and studied morphology and electrical transport properties in the experimental temperature window $303 \le T \le 413$ K.

Experimental details

Initially, PVDF (Mw=534,000, purchase from Sigma-Aldrich) powder was dissolved in dimethyl sulfoxide solvent at 363K under continuous magnetic stirring and obtained transparent solution of PVDF. After that solution was poured glass slide and dry in a control environment.²

Results and Discussion

The Fourier transform infrared (FTIR) spectra of pure PVDF film is shown in Fig. 1 (a). The FTIR spectra analysis is mainly helpful to identify the proper phase exist within the material. The PVDF film shows the transmission bands at 487, 532, 614, 761, 796, 880, 976, 1061, 1143, 1172, 1199, 1241, 1282, 1387 and 1417 cm⁻¹. The two strong transmission bands at 487 and 761 cm⁻¹ with a weak band at 532 cm⁻¹ arises due to deformation of CF₂. Also the strong band at 1417 cm⁻¹ arises due to deformation of CH₂. The strong band at 614 cm⁻¹ is assigned to the CF₂ wagging mode. The weak band at 796 cm⁻¹ and medium band at 1387 cm⁻¹ are expected to appear due to rocking and wagging mode of CH₂. The very strong band at 880 cm⁻¹ and strong band at 1061 are due to CC asymmetric stretching vibration mode. The medium band at 976 cm⁻¹ appear for twisting mode of the CH₂ group. The weak band at 1143 cm⁻¹ and medium band at 1172 cm⁻¹ represents CF₂ symmetric stretching mode of vibration. The medium band at 1241 cm⁻¹ with a shoulder at 1282 cm⁻¹ appear due to CF₂ symmetric stretching mode.³



Fig. 1. The FTIR (a) and PL (b) spectra of pure PVDF film.

The room temperature photoluminescence (PL) spectra of PVDF film is shown in Fig. 1 (b). The PL spectra is significantly different from previous report about PVDF. The PL spectra displayed three sharp and stable luminescence peaks at 352 nm, 405 nm and 526 nm. It indicates the semiconducting behaviour of the PVDF film. In case of pristine PVDF film a broad emission peak was observed. It is expected that due to orientation of CH₂ and CF₂ group along the main carbon backbone chain, we observed these emission peaks. These type of emission peaks were also observed for polyvinyl alcohol (PVA) film and that appeared due to orientation of CH₂ and OH group along the main carbon chain of PVA.4,5 Also by deconvolution of the whole PL spectrum, number of emission peaks appeared. These are probably attributed to the trap states within the forbidden gap of PVDF film. The deformation of the CH₂ and CF₂ group could produce surface as well as deep trap states in the forbidden gap. The high electronegativity of the CF_2 group in PVDF can produce orbital coupling which is the origin of trap states. It needs further details study to know the proper origin of these emission peaks in the PL spectrum of pristine PVDF film.³

The three dimensional (3D) AFM image of the PVDF film is displayed in Fig. 2 (a), in 10 μ m × 10 μ m scan area. The image shows completely different type surface topography of the film. The AFM image shows the 'Helictotrichon Sapphire' grasses like structure of film. During evaporation of DMSO solvent small PVDF crystallites fuse into fibers shape and as a result overall 'Helictotrichon Sapphire' grasses like structure is obtained.



Fig. 2. The AFM (a) and temperature variation of the DC conductivity of pure PVDF film.

The temperature variation of the DC conductivity of the film is shown in Fig. 2 (b). The DC conductivity of the film exhibits non-Arrhenius type behaviour with temperature. This type of behaviour can be described by Vogel-Fulcher-Tammann (VFT) law, $\sigma_{dc} = \sigma_0 \exp\left[-D/(T-T_0)\right]$,

where σ_0 is a pre exponential factor, *D* is a material constant and T_0 is called the Vogel temperature. This VFT equation is well fitted with the experimental data points and the obtained value of Vogel temperature (T_0) is 136 and the material constant (*D*) is 4563. Similar type of DC conductivity variation observed by different polymeric materials.

The temperature dependent resistancevoltage (R-V) characteristic for PVDF film have been depicted in Fig. 3 within the potential window \pm 50 V. The R-V characteristic demonstrates hysteresis behaviour i.e. typically resistive switching behaviour. The charge carriers within the semiconducting PVDF film initially (from 0 V to + 50 V) follows low resistance path. Since the well oriented PVDF fibers are helpful to develop a localization path for the charge carriers to flow through the film in between two electrodes. The presence of R-V loop characteristic indicates the memory storage ability of the film.



Fig. 3. The Resistance-Voltage characteristic of pure PVDF film at different experimental temperature.

Conclusion

The FTIR and PL spectra analysis reveal the formation of β -phase PVDF film. The luminescence peaks in the PL spectra indicates the semiconducting behaviour of the PVDF film, which strongly ensure from electrical transport properties analysis of this film. The temperature variation of the DC conductivity follows the VFT law and the temperature dependent resistance-voltage (R-V) characteristic demonstrates hysteresis behaviour. The PVDF film can be used as a part of flexible memory storage device.

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Extremely High Magnetoresistance in Perfect Electron-Hole Compensated WTe₂ Weyl Semimetal

Abhishek Singh, Souvik Sasmal, Kartik K. Iyer, A. Thamizhavel and Kalobaran Maiti

Tata Institute of Fundamental Research, Department of Condensed Matter Physics & -Materials Science, Homi Bhabha Road, Colaba, Mumbai 400005, India.

*Corresponding author: kbmaiti@tifr.res.in

Abstract

We have grown high quality single crystals of WTe₂ and studied its bulk properties. The Magnetoresistance of this sample is found to be as high as 5.1×10^5 % at a temperature of 2 K and applied field of 12 T. Kohler's plot indicates the presence of two types of charge carriers and a perfect e-h compensation is proposed based on H² fitting. Shubnikov-de-Haas (SdH) oscillations have been observed for temperature up to 10 K. Single peak feature in the Fast Fourier transform (FFT) of these data establishes perfect e-h compensation in the sample.

Electronic and thermoelectric properties of *p* type CeFe₄Sb₁₂

Nihal Limbu^{1,2}, Amit Shankar², and Atul Saxena¹

¹North-Eastern Hill University, Shillong, Meghalaya-793022.

²Condensed Matter Theory Research Lab, Kurseong college, Kurseong, 734203.

*Nihal Limbu: limbunihal08@gmail.com

Abstract

The study of electronic and thermoelectric properties of $CeFe_4Sb_{12}$ was studied considering generalized gradient approximation (GGA) as exchange correlation functional using density functional theory. The sample material revealed the degenerate *p*-type semiconducting nature with an energy gap of 0.21 eV. The positive magnitude of Seebeck coefficient predicted holes to be the majority of charge carriers. The computed value of Seebeck coefficient at room temperature was found to be 79.1 μ V/K, which is close to that experimental result. The nature of electrical conductivity suggested the degenerate behaviour of the sample alloy. The sample compound revealed lowest lattice thermal conductivity of 0.68 W/m-K with maximum *ZT* value of 0.53 at 800 K.

Introduction

Thermoelectric materials are the class of materials which convert industrial waste heat into usable electricity. The efficiency to convert heat into electricity is measured by the dimensionless figure of merit (ZT) of the material which is given by ZT = $S^2 \sigma T / (K_e + K_I)$, where, S is Seebeck coefficient, σ is electrical conductivity, T is absolute temperature, K_{e} and K_L are electronic and lattice thermal conductivities respectively. Filled skutterudites [1] have emerged as potential thermoelectric material because of their excellent electrical conductivity and low lattice thermal conductivity. CeFe₄Sb₁₂ belongs to the class of thermoelectric material. Nouneh et al. revealed the semiconducting behaviour of CeFe₄Sb₁₂ with energy band gap of 0.66 eV [2] whereas Hachemou et al. displayed the energy band gap of 0.125 [3]. Experimental investigation reflected that the compound exhibited Seebeck coefficient of 79.4 μ V/K at 300 K with maximum ZT value at 750 K [4].

In this manuscript, in order to tally the theoretical results with that experimental data, we have made an effort to analyse the electronic and thermoelectric properties of $CeFe_4Sb_{12}$ within generalised gradient approximation (GGA).

Computational details

The electronic properties of $CeFe_4Sb_{12}$ were explored using full potential linearized augmented plane wave (FP-LAPW) [5]. The exchange correlation interactions of the electrons were treated with GGA, For smooth band structure and transport properties calculations a grid of $10 \times 10 \times 10$ k points were considered. The energy convergence criterion was set to 10^{-6} Ry. The lattice thermal conductivity was calculated considering the Slack formalism [6]. And the thermoelectric properties were calculated using Boltztrap code [7].

Results and discussions

The energy band structures and the electronic density of states (DOS) are depicted in Fig. 1. The sample alloy reveals the semiconducting nature with top of valence band and minimum of conduction band occurring at Γ and Γ -H symmetry point respectively giving an indirect energy band gap of 0.21 eV. The valence band maximum at Γ point at the Fermi energy level (E_F) were found to be parabolic in nature (Fig. 1a) with an effective mass of 2.41 m_e whereas the dense and flat bands just above E_F is observed which is contributed from the Ce-*f* electronic state as revealed by electronic density of states (Fig. 1b).



Fig. 1. Energy band structure (a) and density of states (b) of $CeFe_4Sb_{12}$.

The projected density of states predicted that the conduction region close to E_F was mainly dominated by Ce-*f* states whereas the valence region was populated by Fe-*d* states. Hybridization between Fe-*d*, Ce-*f*, and Sb-*p* states are observed at 0.30 eV that gives enhanced DOS of 46.44 States/eV.

Figure 2a depicts the variation of Seebeck coefficient (*S*) with respect to temperature. The positive magnitude of *S* suggests hole to be a dominant charge carrier in CeFe₄Sb₁₂. *S* increases linearly with temperature with maximum value of 186 μ V/K at 800 K and the nature of the curve is consistent with the experimental data [4].



Fig.2. Variation of (a) Seebeck coefficient (*S*), (b) electrical conductivity (σ), (c) lattice thermal conductivity (K_L) and (d) *ZT* with respect to temperature T (K).

The estimated value of *S* at 300 K has been summarized in the table 1 which is in well agreement with experimental data. Electrical conductivity (σ) decreases (Fig. 2b) with enhanced temperature which suggests the degenerate semiconducting behaviour of the sample alloy. The heat carried by lattice phonons is measured with lattice thermal conductivity (K_L) and we found that it decreases linearly with temperature with lowest value of 0.68 W/m-K at 800 K (Fig. 2c). The dimensionless figure of merit which measures the efficiency for the sample material increases with increasing temperature (Fig. 2d). The computed value of *ZT* at roomtemperature is found to be 0.066.

Table 1. Room temperature Seebeck coefficient (*S*) in μ V/K, lattice thermal conductivity (*K*_L) in W/m-K and Maximum *ZT* of CeFe₄Sb₁₂.

Compound	S	K _L	$ZT_{\rm max}$
CeFe ₄ Sb ₁₂	79.1	2.17	0.53
	79.4 [4]	1.28[4]	0.80[4]

Conclusion

The electronic energy band structure suggests CeFe₄Sb₁₂ to be a semiconducting behavior with an energy gap of 0.21 eV. The valance and conduction region is dominated by Fe-d and Ce-f states respectively. The estimated Seebeck coefficient at room temperature is in good agreement with experimental results with holes as majority charge carriers. The nature of σ indicates the degenerate behaviour of the sample alloy. The highest value of ZT equal to 0.53 and lowest $K_{\rm L}$ of 0.68 W/m-k are observed at 800 K. Even though the computed value of ZT for the sample material is quite low for thermoelectric applications, the efficiency of the compound can be enhanced further to higher value by incorporating the suitable dopant atom at Ce. Fe and Sb sites which we are currently working on.

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Effect of Mo Doping on the Electrical and Magnetic Properties of Antiferromagnetic CrSe

Sayan Routh^{*}, P.K. Maheshwari, P. Singha Deo, and Setti Thirupathaiah

Department of Condensed Matter Physics & Material Science, S.N. Bose National Centre for Basic Sciences, Kolkata, West Bengal, 700106

*Corresponding author: sayanrouth95@gmail.com

Abstract

We report on the synthesis of Mo doped $Cr_{1-x}Mo_xSe$ (x=0.0, 0.01, and 0.03) polycrystalline samples using the solid-state reaction method. Room temperature powder X-ray diffraction (XRD) results suggest that all the samples are formed into the hexagonal crystal structure with a space group of P6₃/mmc. Electrical resistivity measurements suggest that all the samples are metallic in nature. Magnetization measurements suggest for a mixed magnetic phase at low temperatures, means, weak ferromagnetism is found in addition to the antiferromagnetic ordering for the parent system. Mo doping leads to a couple of additional antiferromagnetic transitions. We further observed decreasing magnetic moment with Mo doping.

Structural and Optical Characterizations of Multiferroic Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO₃ Manganites

Jyoti Shukla^{1*}, Prabhav Joshi¹, Shivendra Tiwari¹, and Ashutosh Mishra¹

¹School of Physics, Devi Ahilya University, Khandwa Road Campus, Indore, 452001

*jyotishukla12@yahoo.com

Abstract

In this work, polycrystalline samples of $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ (with x = 0.0 and 0.05) were synthesized by solid-state reaction method and their structural and optical properties have been investigated. The powder XRD patterns of the prepared samples confirm the formation of the hexagonal phase of the samples having $P6_3cm$ space group symmetry. The diffused reflectance spectroscopy analysis has been employed to evaluate the optical bandgap of the prepared samples. The bandgap is found to decrease for higher Ti^{4+} concentration (x = 0.05) sample.

Introduction

Multiferroic materials have become one of the most prime interests in functional ceramics due to the simultaneous existence of ferroelectricity and magnetic ordering in the same phase. These materials are technologically most important materials and they find their potential applications in storage devices, multiple state memories, spintronics, etc [1], [2].

YMnO₃ is a hexagonal rare-earth manganite and is an extensively studied multiferroic material, having high ferroelectric transition temperature ($T_c \sim 900$ K) and low antiferromagnetic transition temperature ($T_N \sim 70$ K). The crystal structure of YMnO₃ consists of the layers of Y³⁺ ions that separate the corner linked MnO₅ trigonal bipyramids in which each Mn³⁺ ion is surrounded by three in-plane and two apical oxygen ions [3]. The origin ferroelectricity has been attributed to the buckling of MnO₅ bipyramids, accompanied by the displacement of Y^{3+} ions and the magnetic order is derived from the Mn³⁺spins that align antiferromagnetically in ab plane of YMnO₃. YMnO₃ is recognized as a narrow band semiconductor. Several studies have been done on the effect of doping both in the A-site and B-site of h-YMnO₃. The dopants amend the microscopic structure of the material and thereby alter its physical properties [4], [5]. In this work, we report the synthesis of $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ with x = 0.0 and 0.05 concentrations and study the impact of Ti⁴⁺ on structural and optical properties of the Y_{0.95}Ba_{0.05}Mn₁₋ $_{x}Ti_{x}O_{3}$ manganites

Materials and Methods

Polycrystalline samples of $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ (with x = 0.0 and 0.05) were prepared using the solidstate reaction method. AR grade yttrium dioxide (Y₂O₃), manganese oxide (MnO₂), barium carbonate (BaCO₃), and titanium oxide (TiO₂) were taken in their stoichiometric ratios and were mixed thoroughly in an agate mortar pestle for 10 hours. The mixture was calcined at 1100 °C for 12 hours for the diffusion process to take place. The calcined powders were again reground and sintered at 1200 °C for 12 h to achieve better crystallinity.

The X-ray diffraction of the prepared samples was performed using Bruker D8 advance diffractometer by Cu-K α (1.5406 Å) radiation source in the angular 2 θ range $10^{\circ} \le 2\theta \le 70^{\circ}$ with a step size of 0.019°. The optical energy band gap of the samples was obtained using the UV-DRS technique with Perkin Elmer Lambda 950 spectrophotometer, taking BaSO₄ as a base sample. The wavelength range has been taken from 200 nm – 850 nm.

Results and Discussion

The room temperature powder X-ray diffraction patterns for $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ (x = 0.00 and 0.05) are shown in Fig. 1.



Fig. 1. X-ray diffraction patterns of $Y_{0.95}Ba_{0.05}MnO_3$ and $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$

The samples have been crystallized in the hexagonal phase having $P6_3cm$ space group symmetry, which is confirmed using JCPDS card no. 25-1079 and the peaks are indexed accordingly [6]. To take out further details concerning the phase of the samples, Rietveld's refinement was done. It is shown in Fig. 2.



Fig. 2. Rietveld's refinement of $Y_{0.95}Ba_{0.05}MnO_3$ and $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$

The acquired parameters from Rietveld's refinement are tabularized in Table 1. It has been observed that there is an increment in cell parameters of the $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$ sample, thereby there is an increase in the unit cell volume, which is ascribed to the difference in ionic radii of Ti⁴⁺ and Mn³⁺ ions. The average crystallite size of the samples has been computed by using Debye – Scherrer's formula,

$$D = \frac{0.9\lambda}{\beta cos\theta}$$

a)

Here, λ is the wavelength of CuK α_1 radiation, β is the FWHM of peaks, and θ is half of the diffraction angle. The average crystallite size of $Y_{0.95}Ba_{0.05}MnO_3$ and $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$ was found ~ 81.53 nm and ~ 66.84 nm respectively. The crystallite size is found to be decreased with the incorporation of Ti⁴⁺ at Mn-site.

The optical properties of $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ (x = 0.0 and 0.05) were investigated using diffused reflectance spectroscopy. In the case of polycrystalline material, *Kubelka-Munk's* approach is used to evaluate the absorption coefficient as the polycrystalline samples contain internal inhomogeneities [7]. K-M function is defined as

$$F(R_{\infty}) = \frac{k}{s} = \frac{(1-R_{\infty})^2}{2R_{\infty}} \qquad b)$$

Here, k denotes the absorption coefficient, S denotes the scattering coefficient and R_{∞} is the ratio of reflectance of sample to the reflectance of the base sample (BaSO₄).

$$[F(R)h\nu]^{\frac{1}{n}} = K(h\nu - E_g) \qquad \text{c})$$

K is the constant factor and the exponent n is associated with different types of transition [8]. The optical bandgap of the samples was obtained by plotting $[F(R)hv]^{1/n}$ (taking $n = \frac{1}{2}$ for direct bandgap) as a function of photon energy $(h\nu)$ and by extrapolating the linear portion of the curve. It is shown in Fig. 3. The obtained bandgap for $Y_{0.95}Ba_{0.05}MnO_3$ and $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$ are 1.556 eV and 1.525 eV respectively. The bandgap for Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O₃ is decreasing with the incorporation of Ti^{4+} ions on Mn^{3} site. The electronic features in most of the perovskite oxides can be varied via metal-oxygen chemical bond, where the B cation has a more significant impact on the altering of the optical energy bandgap of material [9]. The decrease in the bandgap of Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O₃ may be due to the creation of impurity levels inside the bandgap, which is attributed to the different valence of Ti⁴⁺. Also, the incorporation of Ti⁴⁺ (0.65Å) having a larger ionic radius compared to Mn^{3+} (0.58Å) creates the oxygen vacancies, thereby lowering the bandgap [10].



Fig. 3. Tauc Plot of $Y_{0.95}Ba_{0.05}MnO_3$ and $Y_{0.95}Ba_{0.05}MnO_3$

Table 1. Structural Parameters of Y_{0.95}Ba_{0.05}Mn_{1-x} Ti_xO₃

Samples	Y _{0.95} Ba _{0.05} MnO ₃	Y _{0.95} Ba _{0.05} Mn _{0.95} Ti _{0.05} O ₃
Lattice Parameters	<i>a</i> = 6.139	a = 6.151
(Å)	c = 11.393	c = 11.381
Volume (Å ³)	371.838	372.921

Density (gm/cm ³)	5.380	5.318
Chi-Square (χ^2)	2.06	2.6

Conclusions

In conclusions, $Y_{0.95}Ba_{0.05}Mn_{1-x}Ti_xO_3$ (with x = 0.0 and 0.05) samples have been prepared using solid-state reaction method. The X-ray diffraction reveals the hexagonal crystal structure of the samples. The optical bandgap of the prepared samples has been estimated using diffused reflectance spectroscopy. The bandgap is found to decrease with an increase of Ti⁴⁺ concentration (x = 0.05). Thus, $Y_{0.95}Ba_{0.05}Mn_{0.95}Ti_{0.05}O_3$ is suitable for optoelectronic devices.

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Investigation of structural and dielectric properties of fluorosubstituted zinc phthalocyanine films for electronic application

Anshul Kumar Sharma^{1,2} and Aman Mahajan^{1*},

¹Materials Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143005, India ²Centre for Sustainable Habitat, Guru Nanak Dev University, Amritsar 143005, India

*Corresponding author: aman.phy@gndu.ac.in

Abstract

In the present work, organic semiconductor films of hexadeca-fluorinated zinc phthalocyanine ($F_{16}ZnPc$) have been deposited using thermal evaporation technique on indium tin oxide (ITO) substrate and subsequently characterized for structural and morphological studies using Raman and field emission scanning electron microscopy (FE-SEM) techniques. Furthermore, dielectric and a.c. electrical characteristics have been analysed in the frequency range from 1 KHz to 1000 KHz at room temperature. The results on ac-conductivity reveal that conduction mechanism in film is found to be hopping transport model of charge carriers.

Optical and electrical transport properties of flexible PVA-chitosanhematite composite film

Riju Karmakar^{*}, Amit Kumar Das, and Ajit Kumar Meikap

Department of Physics, National Institute of Technology Durgapur, Durgapur-713209, West Bengal, India

*Corresponding author: rijukarmakar59@gmail.com

Abstract

Hematite (α -Fe₂O₃) nanoparticles have been synthesis by hydrothermal method and photoluminance (PL) study shows a strong UV region's peaks make this hematite nanoparticle as a promising candidate for UV detector. The crystallite size of the hematite nanoparticles is 48 nm and the polymer composite with hematite nanoparticles reflects the semicrystalline behavior of the film. The ac conduction study reveals the charge carriers within the composite film follow the CBH model and the maximum barrier height is 0.12 eV. This film can be useful as a charge storage device as the room temperature dielectric constant and dielectric loss at 1 kHz frequency are 104 and 0.59 respectively. The temperature-dependent J-E characteristic shows a prominent hysteresis loop, and it increases up to four orders with the rise of temperature from 303K to 383K.

Introduction

In the past decades, scientists have given attention to polymer-metal oxide composites due to the rapid development of flexible electronics. Hematite is the most thermodynamically stable, low bandgap n-type semiconductor ($E_g=2.1 \text{ eV}$).¹ On the other hand, PVA is water solvable, easily processable, low-cost polymer with low density, reasonable strength, and good electrical properties. Here, we have synthesis hematite nanoparticles by hydrothermal method and have done a detailed PL study of these nanoparticles. We also prepared PVA-chitosan-hematite (PCH-2) films using the solution casting method and the electrical transport properties of this film has been measure in the temperature window $303 \le T \le 383$ K. The detail synthesis has been discussed in our previous articles.¹

Results and Discussion

The X-ray diffraction (XRD) pattern of the hematite nanoparticle is shown in Fig. 1(a) and compared with the standard rhombohedral hematite structure with the space group R-3C (JCPDS file no. 01-087-1165). The XRD peaks of hematite nanoparticles contain finite width i.e. polycrystalline and the average crystalline size calculated from the Debye-Scherer formula is 48 nm. This polycrystalline structure and surfactant (PVP) on the hematite surface introduce a lattice strain 1.15×10^{-3} . It is evaluated from the linear plot of $\beta \cos\theta$ vs. $4\sin\theta$, using the Williamson-Hall (W-H) analysis technique (see inset of Fig. 1(a)). The XRD peak of PCH-2 films at $2\theta =$ 20.1° corresponds to overlapped of diffraction peaks from (110) and (TT0) planes of PVA and (102), (002) and (120) planes of chitosan.¹ The other humps at 40.7° are related to (220) crystalline planes of the hexagonal structure of PVA.

The field effect scanning electron microscope (FESEM) image of hematite nanoparticles looks like a grape branch consisting of 6-8 spherical nanoparticles (Fig. 1(b)). The average spherical particles size is 39 nm (see inset of Fig. 1(b)).



Fig. 1. (a) XRD pattern of hematite nanoparticles and PCH-2 nanocomposites film (b) FESEM image of hematite nanoparticles (inset image display particles size distribution).

Excitation-dependent PL spectra of hematite nanoparticles at room temperature are shown in Fig. 2 (a). In general, bulk hematite does not show any PL spectra due to local forbidden d-d transition but when the particle size is in between 20-70nm, then quantum confinement effect results in delocalization and quantization of the electronic state in the nanostructures: this relaxes the forbidden rule for d-d transition and the optical transition is partially allowed.¹ The PL spectra displayed two luminescence peaks at 368 nm and 452 nm above bandgap energy (=550 nm). The peak at 368 nm arises due to Fe^{3+} defect state of O²⁻ vacancy.² On the other hand, Fe-O bonding separation increases for the smaller nanoparticle, enhancing the magnetic coupling of the neighbouring Fe³⁺, responsible for the blue PL peak at 452nm. It has been observed that the UV peak shifted towards the higher wavelength and the intensity ratio of 452 nm and 368nm peak increases significantly with the higher excitation. For the details investigation of luminance spectra of hematite nanoparticles, we need further study to know the proper origin of these PL emission peaks.

The temperature-dependent frequency variation of real part dielectric constant (ε) (frequency windows 50Hz-1MHz) is fitted with the modified Cole-Cole equation is shown in Fig. 2(b). Fitted data shows that the static dielectric constant (ε_s) enhanced from 796 to 9703 with increase in temperature, it signifies increment of space charge accumulation between polymer-polymer interface and polymer-hematite interface stimulate. Also, rise in temperature relaxes the segmental motion of the polymer chain as a relaxation time from 2×10^{-3} s to 3×10^{-4} s at 303K and 383K, respectively. Room temperature dielectric constant and dielectric loss at 1 kHz frequency is 104 and 0.59 respectively, which can use as a batter charge storage device compare to PVA-hematite as reported earlier.



Fig. 2. (a) PL spectra of hematite nanoparticles. (b) Temperature-dependent frequency variation of ε' .

The temperature-dependent ac conductivity (σ') with frequency for PCH-2 nanocomposite film is shown in Fig. 3(b). In general, frequency variation of σ' in polycrystalline system is given by,³

$$\sigma = \sigma_{dc} + Af^{s} \tag{1}$$

Where symbols have their usual meaning. The free charge contribution i.e. frequency-independent DC part (σ_{dc}) increases nearly 2 order (i.e. 4.5×10^{-8} to 2.1×10^{-6} S/m) in the temperature range 303K to 383K. The charge transfers between defect states follow the Correlated barrier hopping (CBH) model as the frequency exponent *S* <1 and decrease with the higher temperature. The maximum barrier height calculated from the slope of inset of Fig. 3(a) is 0.12 eV.

The temperature dependent current density-electric fields (J-E) characteristic for PCH-2 film has been depicted in Fig. 3 (b) within the potential window \pm 5 V. A prominent hysteresis loop has been observed and

it indicates charge storage property of the composite film. The -OH bond in PVA, carbonyl group (-C=O) in chitosan and Fe³⁺ defect in the oxygen vacancy of hematite nanoparticles are mainly responsible for electron accumulation within the PCH-2 film. As the temperature increases, the dangling hydrogen bond is decomposed and more charge can be accumulated. As a results, the storage property increases up to three order (as loop area at 303K and 383K are 1.6×10^3 and 2.1×10^3 J/m³ respectively) in the temperature range 303K-383K.



Fig. 3. Variation of (a) ac conductivity with frequency (b) current density with electric fields at different experimental temperature.

Conclusion

Branch of grape-like spherical hematite nanoparticles with crystalline size 48nm and particle size 39 nm have been successfully synthesized by the hydrothermal method. A strong luminescence peaks at UV regions gives hematite nanoparticles as a promising candidate for UV detector. From ac conduction study of polymer-hematite composite film, charge carriers follow the CBH transport phenomena and obtains maximum barrier height of 0.12 eV. High dielectric constant, low loss, and significant hysteresis loop in the J-E curve make these PVA-chitosan-Fe₂O₃ film as a useful candidate for charge storage device and moisture sensor.

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Observation of charge density wave transition in V-doped Bi₂Se₃

Satyabrata Bera¹, Arnab Bera¹, Sk Kalimuddin¹, Raktim Datta¹, Biswajit Das¹, Mohan Kundu³, Subodh Kumar De² and Mintu Mondal^{1*}

¹School of physical sciences, ² School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

³Department of Physics, Acharya Prafulla Chandra College, New Barrackpore, Kolkata 700131, India

*E-mail: Mintu.Mondal@iacs.res.in

Abstract

Here we report the charge density transition in the Vanadium (V) -doped Bi2Se3 single crystals. The V-doped Bi2Se3 crystals were grown using a chemical vapor transport (CVT) method. Structural and compositional properties were confirmed by performing X-ray diffraction (XRD) and X-ray photo-electron spectroscopy (XPS). The four-probe resistivity measurement has been carried out in a low temperature cryostat down 5 K temperature. The variation of resistivity with temperature shows the pure metallic behavior with an anomaly around 250 K, the characteristic signature of charge density wave (CDW) transition.

An Ab-Initio Study Of Electrical And Thermal Transport Properties Of FeXBi (X = Nb and Ta) For Thermoelectric Applications

Rakshanda Dhawan¹, Sapna Singh², Mohd Zeeshan³, Tashi Nautiyal¹, and Hem C. Kandpal²

¹Department of Physics, ²Department of Chemistry, Indian Institute of Technology Roorkee, 247667, ³Department of Physics, Indian Institute of Technology Delhi, 110016 **Corresponding author: rakshanda@ph.iitr.ac.in*

Abstract

We investigated thermoelectric properties of 18-VEC half-Heusler (hH) alloys FeNbBi and FeTaBi under the framework of Density Functional Theory (DFT). Both hH alloys have a positive Seebeck coefficient, indicative of the p-type behaviour. The electronic feature suggests that the p-type doping at Bi-site will be more beneficial for achieving low lattice thermal conductivity. At 700 K, FeTaBi shows almost similar values on either p-type or n-type doping. Interestingly, at 1100 K, both the systems are found to have good power factor values. Overall, our results suggest potential new candidates of bismuth-based ternary compounds for high thermoelectric performance.

Introduction

Half-Heusler (hH) alloys having 18 valence electron count (VEC) have been extensively studied over the past few decades in search of better thermoelectric (TE) prospects for harvesting the waste heat into electricity. The best performing hH alloys experimentally investigated are stannides and antimonides of cobalt, nickel, and iron, stuffed with a third element from group-IV or group-V of the periodic table, e.g., MNiSn, MCoSb (M = Ti, Zr, Hf) and MFeSb (M = V, Nb). The n-type MNiSn, p-type MCoSb, and MFeSb based alloys are reported to have impressive power factor values, however, the performance is restricted by a high intrinsic thermal conductivity [1-3].

Notwithstanding that, a significant progress has been made in suppressing the lattice thermal conductivity. The discovery of CoZrBi based hH alloys is fascinating [4] and could be a benchmark for the synthesis of other Bi-based hH alloys. Most importantly, the pristine CoZrBi was reported to have a much lower thermal conductivity in comparison to the conventional hH alloys [4]. It could thus be interesting to investigate the bismuth-based analogues of previously reported hH alloys; from the viewpoint of a lower thermal conductivity contribution from heavy elements.

In this paper, utilizing an ab-initio approach and solving the linearized Boltzmann transport equation with the single-mode relaxation time method, we theoretically investigate the electrical and thermal transport properties of Bi-based hH alloy FeNbBi, and FeTaBi in cubic symmetry.

Result and Discussion

The optimized lattice parameters and band gap values are listed in Table 1. The existence of band gap in the materials is quite important as both semiconductors are the best choices for thermoelectric materials. The optimized ground state structures were used for studying the dynamic stability by carrying out phonon calculations using harmonic force constants. We observed that both the systems have real phonon frequencies throughout the Brillouin zone, validating their dynamic stability. The survival of band gap along with the dynamical stability of the proposed systems prompted us to investigate their electronic structure and transport properties.

Table 1. The optimized lattice constant 'a' and indirect (ID) band gap ' E_g ' values.

a (Å)	E _g (eV)
6.0130	0.64
6.0077	0.97
	a (Å) 6.0130 6.0077

Owing to the similar size and chemical properties of Nb and Ta, the compounds FeXBi (X=Nb, Ta) have similar features in their electronic band structure and density of states (DOS), which are displayed for FeNbBi in Fig. 1. In both, the VBM and CBM are located at L point and X point, respectively. The combination of heavy and light bands at VBM p-type electrical transport properties. facilitates Whereas the heavy bands improve the Seebeck coefficient on account of large effective mass, the light bands facilitate the mobility of charge carriers. As is clear from the DOS, the VBM is occupied by mainly the d-states of Fe and some states from X (Nb, Ta) while the CBM is almost equally occupied by d-states of Fe and X atoms. Notably, no significant contribution was observed from Bi (not shown for cl-



Fig. 1. Electronic bands and DOS (right panel) of FeNbBi. The zero of energy scale is set at the VBM.

-arity) either in VBM or CBM in both the systems. This suggests that doping at Bi-site for suppressing the lattice thermal conductivity (κ_L) will be highly effective as it would not affect the underlying band structure much, preserving the electrical transport properties.

Next, we calculated the transport properties of FeNbBi and FeTaBi by BoltzTraP code within the rigid band approximation (RBA). The Power Factor (PF) for FeXBi (X= Nb and Ta) as a function of doping at 300, 700, and 1100 K, assuming $\tau = 2 \times 10^{-15}$ s, is shown in **Fig. 2**. Initially, the PF increases with either n-type or p-type doping and then decreases gradually at high doping levels. However, p-type doping dominates in both the materials.

The PF values, though small at 300 K, improve with temperature, becoming fairly strong at 1100 K. Interestingly, comparable values of PF with both p-type and n-type doping suggest the potential of FeTaBi as both p-type and n-type thermoelectric material at 700 K. This is very encouraging, since for a good thermoelectric performance, both p-type and n-type legs of a thermoelectric module should be of same or similar materials, which usually is hard to achieve.

PF values wise, these materials offer a good competition to CoZrBi; now it remains to be seen if these have low thermal conductivity too. Temperature dependence of κ_L was evaluated using the PHONO3PY package employing anharmonic force constants. The room temperature κ_L of undoped FeNbBi and FeTaBi (**Fig. 2**) is 11.6 and 13.3 W m⁻¹K⁻¹, respectively, which is closer to the reported value of 10 W m⁻¹K⁻¹ for CoZrBi. A higher value of κ_L for FeTaBi compared to FeNbBi is due to smaller degree of anharmonicity in FeTaBi which we confirmed by estimating Grüneisen parameter (not presented here).

Finally, focusing on the figure of merit, the obtained zT value at 1100 K is 0.98 and 0.77 for p-type

FeNbBi and FeTaBi, respectively, Though lower than the value of 1.53 for CoZrBi, the value are likely to reach unity when the κ_L for the doped systems would be taken into account.



To sum up, Bismuth-based hH alloys FeNbBi and FeTaBi are promising TE materials. FeTaBi showing similar power factor values for both p-type and n-type dopings at 700 K can be a standalone TE material for applications. The maximum figure of merit obtained is 0.98 and 0.77 for p-type FeNbBi, FeTaBi, respectively. We emphasize that the proposed values are slightly underestimated on account of having considered lattice thermal conductivity of undoped systems. We hope that our findings on bismuth-based half-Heusler alloys, suggesting a good thermoelectric potential, would serve as a base for experimental study.

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Structural, Electrical And Mössbauer Study In $Co_{1-x}Fe_xS_2$ ($0 \le x \le 1$)

Suman Karmakar*, R. Rawat, V. R. Reddy, and Anil Gome

UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore-452001, MP, India

*Corresponding author: 89suman@gmail.com

Abstract

The results of X-ray diffraction, Mössbauer spectroscopy and resistivity measurements of $Co_{1,x}Fe_xS_2$ ($0 \le x \le 1$) are presented. The unit cell parameter follows Vegard's law across the series. The change in sign of temperature coefficient of resistivity around magnetic transition has been observed for intermediate compositions. Our Mössbauer studies show that both isomer shift and quadrupole splitting are correlated with electrical and structural measurements. Both the parameters vary linearly without any sign of discontinuity over entire composition range.

Introduction

The ground state of end members of Co_{1-x}Fe_xS₂ are reported to be ferromagnetic (FM) metal (x = 0)and diamagnetic insulator (x = 1) [1]. For intermediate compositions the temperature coefficient of resistivity is found to be negative in the FM state and positive in the paramagnetic (PM) state. This crossover has been attributed to change in density of states at the Fermi level on magnetic ordering [2]. In spite of itinerant nature of magnetism, Mossbauer studies show absence of magnetic moment at the Fe across the series [3]. The isomer and quadrupole shifts in these studies are shown to vary linearly with x but with a discontinuity around x = 0.5 [4]. It is anomalous, considering the linear change in lattice parameter and average number of d-electrons with x. Therefore, we investigated this series by preparing these samples using our modified solid state reaction method.

Experimental Details

Bulk polycrystalline samples of $Co_{1-x}Fe_xS_2$ ($0 \le x$ \leq 1) are prepared through modified solid state reaction method. First Fe and Co are mixed via splat quenching of arc melted Fe-Co. The alloys thus prepared are then sealed with sulphur in quartz ampoules under high vacuum. For solid state reaction these ampoules are subjected to thermal treatment up to 700° C. The structural characterization of the prepared samples is carried out using powder X-ray diffraction (XRD) with Cu K_{α} radiation. The temperature dependent resistivity measurements are carried out by standard four probe technique using a homemade resistivity setup along with 8T superconducting magnet system from Oxford Instruments, UK. Mössbauer measurements are carried out using a standard PC-based spectrometer calibrated with natural iron foil at room temperature. The Mössbauer spectra are fitted with the NORMOS program.

Results and Discussions

Fig. 1 (a) shows the measured XRD (black circle) pattern of x = 0.3 sample. The data can be fitted with cubic pyrite structure with space group Pa $\overline{3}$ using Rietveld refinement [5]. The analysis of all the prepared compositions shows that sample crystallizes in above mentioned crystal structure and is single phase. The lattice parameter obtained from the analysis follows Vegard's law showing a linear decrease with increase in x. It confirms the substitution of Co by Fe.



Fig. 1. (a) XRD data of x = 0.30 fitted with Rietveld refinement (b) Room temperature lattice parameter (open circle) and conductivity (closed circle) change with Fe concentration (the red line through the data points is guide to eye).

Fig. 2 (a)-(c) represents trend of electrical resistivity across the series. For small Fe substitution e.g. x =0.10, the resistivity is metal like with a small jump around PM to FM transition (T_C = 110-140 K). For higher $x \ge 0.9$), it is typical of low bandgap semiconductor. For intermediate e.g. x = 0.5, it shows positive temperature coefficient of resistivity (TCR) in the PM state and negative TCR in the FM state. The observed trend of resistivity is consistent with earlier work [2].

Mössbauer spectrum at room temperature is measured for all the samples. Some typical results are shown in Fig. 2 (d)-(f). It shows a quadrupole split doublet. The splitting increases with *x*. The fit to the measured data is shown by red line in the respective figure. The obtained hyperfine parameters fitted from Mössbauer data are presented in Fig. 3. The values of isomer shift are found to be in the range 0.27 to 0.34 mm/sec, which shows that iron is in low spin Fe⁺² state [4]. With increase in *x*, the isomer shift ($\Delta E_{LS.}$) is found to decrease whereas the quadrupole shift ($\Delta E_{O.S.}$) is found to increase linearly with *x*.



Fig. 2. (a)-(c) Temperature dependence of resistivity and (d)-(e) room temperature Mössbauer spectra for representative compositions of $\text{Co}_{1-x}\text{Fe}_x\text{S}_2$.

Our analysis of linear change in $\Delta E_{L.S.}$ and $\Delta E_{O.S.}$ is in contrast to two different slopes observed for Co rich and Fe rich composition by Nishihara et. al [1]. There it was correlated with the concentration dependent resistivity changes. The electrical and magnetic properties of CoS₂ are shown to arise from one electron/Co in eg band. On the other hand, the semiconducting nonmagnetic behaviour of isostructural FeS₂ arises due to absence of electron in e_g band. The value of quadrupole splitting shows that iron remains in low spin state across the series. Therefore in $Co_{1-x}Fe_xS_2$ solid solution, the average concentration of eg electron is expected to decrease linearly with x. This is shown in Fig 1 (b) in the form of conductivity vs. x. The variation of lattice constant as Vegard's law also supports this assertion. Therefore, due to the linear decrease in average number of eg electron, the isomer-shift decreases linearly with x. The decrease in unit cell parameter leads to enhancement of electric field gradient at the Mössbauer atom which is reflected in increased quadrupole splitting with *x*.

The difference in present and earlier work may be arising due to sample inhomogeneity. The difficulty in the preparation of Fe doped CoS_2 is well documented. The ambiguity due to sample quality

with change in x can be addressed by performing temperature dependent Mössbauer measurements. Here, the change in electronic density of state across magnetic transition and thermal expansion in a same sample will help in distinguishing the role of electronic and lattice changes.



Fig. 3. Concentration dependent isomer shift (black circle) and quadrupole shift (blue circle) along with linear fit for $Co_{1-x}Fe_xS_2$ samples at room temperature.

Conclusions

In conclusion, our room temperature Mössbauer study shows that isomer shift and quadrupole shift change linearly across the series. This variation is found to be consistent with the linear decrease in the average number of e_g electrons and lattice parameter change with *x*. The role of these two parameters and sample homogeneity will be further tested through low temperature Mössbauer studies.

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Optical, Electrical and Transport Properties of α-In₂Se₃ Crystal

Divya Rawat, Niraj Kumar Singh, Kewal Singh Rana and Ajay Soni*

School of Basic Sciences, Indian Institute of Technology Mandi, Mandi, 175075, HP India,

*Corresponding author: ajay@iitmandi.ac.in

Abstract

In₂Se₃ is an emerging 2D layered semiconductor which exists in different phases such as hexagonal and rhombohedral. We have synthesized single crystalline α -In₂Se₃ adopting a solid-state route with an optimized temperature profile. The phase purity of α -In₂Se₃ were investigated by XRD and Raman measurements. To understand crystal anharmonicity and thermoelectric application of α -In₂Se₃, we have examined electrical and thermal transport properties. The estimated Seebeck coefficient, power factor, thermal conductivity, and Grüneisen parameter are ~-173.74 μ VK⁻¹, ~2.47 × 10⁻⁵ Wm⁻¹K⁻², ~1.35 Wm⁻¹K⁻¹ and ~1.29 respectively at 300 K. Combined high Seebeck coefficient and reduced thermal conductivity suggest α -In₂Se₃ to be potential thermoelectric material.

Introduction

Layered 2D semiconductor materials such as In_xSe_y exists in different stoichiometric structures. The compounds like InSe, In₂Se₃, In₄Se₃, and In₆Se₇ have been widely studied for their optoelectronic and thermoelectric (TE) properties.[1] Specially, In₂Se₃ can exist in various crystalline phases such as the rhombohedral β -phase and α -phase, wurtzite γ -phase, and the hexagonal δ -phase.[2] Here, the quintuple structure of α-In₂Se₃ has tetrahedral covalent bonding between the Se and In of Se-In-Se-In-Se. The compound has been synthesized by various methods such as Bridgman, sputtering, chemical vapor transport techniques.[3] Here, we have studied the structural, optical and transport aspect of α -In₂Se₃ single crystal prepared by solid state melt grown method. Further, the applicability for TE has been studied by thermal conductivity ($\kappa(T)$) and crystal anharmonicity present in the material.[4]

Experimental Section

Single crystal of α -In₂Se₃ was synthesized by solidstate reaction method taking the stoichiometric amount of indium and selenium in sealed quartz ampoule. Obtained bulk single crystal was cleaved and mechanically exfoliated to obtain thin flakes of α -In₂Se₃. The α phase of In₂Se₃ was confirmed using a rotating anode Rigaku Smartlab X-ray diffractometer using *CuK*_{α} radiation and LabRam Horriba Raman spectrometer with 633 nm excitation laser in backscattering geometry. The layered nature was observed using field-emission scanning electron microscopy (Nova Nano SEM 450, FESEM). The TE properties were studied using the physical properties measurement system (PPMS, DynaCool, Quantum Design).

Results and Discussions

The X-ray diffraction (XRD) pattern of single crystalline α -In₂Se₃ along with Bragg reflections (blue lines) is shown in Fig.1(a). Observed XRD pattern is in good agreement with the α -In₂Se₃ as discuss in the



Fig. 1. (a) The powder XRD pattern and the crystal image (inset), (b) Schematic of crystal structure with R3m space group, (c) FESEM image showing layered nature of single-crystal α -In₂Se₃.

literature (space group R3m, 160).[3] Photograph of the prepared single crystal having dimension $\sim 1.2 \times$ 0.8 cm^2 is shown in the inset of Fig.1(a). The crystal structure of α -In₂Se₃ consists of alternate repeating atomic layers of Se-In-Se-In-Se separated from each other by weak van der Waal's gaps as shown in Fig.1(b). belonging to rhombohedral phase with crystallographic dimensions as a = b = 4.05 Å, c =29.64 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$.[3] FESEM image represents the layered nature of single-crystal α-In₂Se₃ as shown in Fig. 1(c). Existence of the α phase among different phases of single crystal In₂Se₃ is also studied by Raman modes. Irreducible representation for the Raman active phonons of α -In₂Se₃ at Γ point is represented as $\Gamma = 4A_1 + 4E$. Fig. 2 represents multiple Raman phonons are positioned at 20 cm⁻¹ (E^{1}), 25 cm⁻¹

¹ (Shear mode), 88 cm⁻¹ (E^2), 104 cm⁻¹ ($A^1(LO+TO)$), 157 cm⁻¹ (E^3), 180 cm⁻¹ (E^4), 186 cm⁻¹ ($A^2(TO)$), 192 cm⁻¹ ($A^3(LO)$) that corresponds the characteristic optical phonon of single crystalline α-In₂Se₃.[5]



Fig. 2. Room temperature Raman spectra and optical image (inset) of single crystal α -In₂Se₃.

The temperature dependence of resistivity $(\rho(T))$ of α -In₂Se₃ (shown in Fig.3(a)), decreases with raise in temperature indicating a typical semiconducting behaviour. The negative magnitude of the Seebeck coefficient (α (T)) indicates electron-dominated charge transport as shown in Fig.3(b). As $\rho(T)$ decreases while $\alpha(T)$ increases, the power factor (PF) increases with temperature (inset of Fig. 3(b)). Then PF is ~4.79 $\times~10^{-5}~Wm^{-1}K^{-2}$ at 350 K. To understand the TE applicability, temperature dependence of $\kappa(T)$ is also measured and shown in Fig.3(c). The κ has quite lowvalue ~1.3 Wm⁻¹K⁻¹ at 300 K. To further understand the origin of the low value of $\kappa(T)$, it is important to analyse the crystal anharmonicity present in the sample. The low-temperature heat capacity (C_n) measurement is shown in Fig.3(d), which can be fitted with $C_p = AT + BT^3$. The linear fit to the C_p/T vs T² data evaluates $A \sim 1.31 \times 10^{-2}$ J mol⁻¹ K⁻² and $B \sim 4.5 \times 10^{-1}$ ³ J mol⁻¹ K⁻⁴. The Debye temperature $(\theta_d) \sim 129$ K extracted using the relation: $\theta_d = (\frac{12\pi^4 pR}{5B})^{1/3}$. The Grüneisen parameter ($\gamma \sim 1.29$) at 300 K was calculated using the relation: $\gamma^2 = \frac{P\bar{M}\delta(\theta_d)^3}{\kappa_l N^{2/3}T}$ which signify the degree of crystal anharmonicity present in the α -In₂Se₃ [4]. The results suggest that α -In₂Se₃ can be a good TE material.



Fig. 3. The temperature dependence of (a) resistivity ($\rho(T)$), (b) Seebeck coefficient ($\alpha(T)$) and power factor ($\alpha^2 \sigma$) (inset), (c) thermal conductivity ($\kappa(T)$) in the temperature range of 2 K - 380 K, and (d) heat capacity (C_p) in the temperature range of 2 K – 200 K and low-temperature C_p analysis (inset) of single crystal α -In₂Se₃.

Conclusion

In summary, the phase purity α -In₂Se₃ has been investigated by XRD and Raman measurement and found to be consist of alternate repeating quintuplet layers. The electronic transport properties of α -In₂Se₃ are electron-dominated and have very low κ (T) due to a high degree of crystal anharmonicity which suggest it to be a good TE material.

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Magnetodielectric Coupling and High Frequency Relaxation Behaviour of Neodymium Doped Nickel Ferrite Nanoparticles

Shubhadip Atta^{1*}, Monalisa Halder¹, and Ajit Kumar Meikap¹

¹Department of Physics, National Institute of Technology, Durgapur, Durgapur 713209, India

*Corresponding author: shubhagnit@gmail.com

Abstract

The Rare earth material, neodymium doped nickel ferrite nanoparticles are synthesized by sol-gel technique. The effect of doping of rare earth material in electrical transport properties is studied. The dielectric permittivity enhances with the doping of Nd atoms. Complex electric modulus spectroscopic analysis shows the non-Debye type relaxation behavior of the material, and the relaxation peaks are widened with temperature. The room temperature magneto-dielectric coupling nature of the material exhibits a particular applied magnetic field value where the dielectric response is maximum. The doping of neodymium ions in nickel ferrite improves the magneto-dielectric response of the sample due to the crystalline strain-induced.

Introduction

Magnetic spinel ferrites with improved dielectric response are an important class of materials used vastly in nonvolatile high density magnetic recording, memory devices, energy storage devices, microwave devices, and antenna miniaturization. Spinel structured nickel ferrite (NFO) is widely used in electronic devices due to its large permeability at high frequency, low cost, chemically stability, higher electric resistivity, and higher mechanical hardness [1]. Researchers reported that the magnetic and dielectric properties of spinel ferrite NFO could be tuned with the cation distribution or doping of magnetic/non-magnetic ions.

In this work, rare earth material neodymiumdoped nickel ferrite nanoparticles (NPs) are synthesized and the electrical transport properties and magnetodielectric response are discussed.

Experimental Details

5 wt% neodymium (Nd) doped nickel ferrite (Nd-NFO) NPs are synthesized using a simple sol-gel technique. The precursor materials are nickel nitrate $[Ni(NO_3)_2, 6H_2O]$, iron nitrate $[Fe(NO_3)_3, 9H_2O]$, neodymium nitrate $[Nd(NO_3)_3]$ 6H₂O]. polyvinylpyrrolidone (PVP), citric acid. Initially, solutions of iron nitrate (0.25 M) and nickel nitrate (0.2 M) are mixed under magnetic stirring. 0.5 M solution of neodymium nitrate is mixed slowly in iron-nickel salt solution under stirring. Few drops of citric acid are added to maintain the convenient pH level (citric acid: nickel nitrate = 1:1). Stabilizing agent PVP is put into the solution. Then, the solution is kept in oven at 115° C for 20 hours to obtain a powder mixture of NiNd_{0.5}Fe_{1.5}O₄(Nd-NFO). Prepared Nd-NFO is calcined at 900°C to achieve crystallinity.

Agilent E 4980A precision LCR meter and an electromagnet (EM-250) under an external transverse magnetic field are used for the observation of electrical transport properties and magneto-dielectric properties of the parallel plate capacitive system (metal-sample pellet-metal) of Nd-NFO sample

Results and Discussions

To evaluate the space charge relaxation nature of Nd-NFO nanoparticles, complex electric modulus spectroscopic analysis is done.



Fig.1. Frequency dependent real part of complex electric modulus of Nd-NFO above room temperature (inset shows the FESEM image of the NPs)

A complex electric modulus is a powerful tool for analyzing the dielectric behavior of a dielectric material, which can be defined as the inverse of complex relative permittivity,

$$M^{*}(\omega) = M' + iM'' = \frac{1}{\varepsilon^{*}} = \frac{\varepsilon'}{(\varepsilon')^{2} + (\varepsilon'')^{2}} + \frac{\varepsilon''}{(\varepsilon')^{2} + (\varepsilon'')^{2}} a$$

At low frequency, due to the absence of electrode polarization, M' is zero (Fig. 1) but M' increase like a step function with increasing frequency. In M'' spectra, well-defined loss peaks appear (Fig. 2). The peaks shift to higher frequencies as temperature
increases. It indicates the thermally activated nature of relaxation time (inset of Fig. 2).



Fig. 2. Frequency-dependent imaginary part of complex electric modulus of Nd-NFO above room temperature (inset shows the temperature dependency of relaxation time)

Dielectric spectra express the electrical energy storage ability and the energy loss (in the form of attenuation) of material. The dielectric permittivity (real & imaginary) of Nd-NFO decreases with frequency (Fig.3). Maxwell-Wagner type polarization arises in heterogeneous Nd-NFO dielectric systems (Koop's phenomenological theory). The electrical dipoles couldn't orient in the high-frequency domain. The sample exhibits an enhanced dielectric constant value of ~ 280(1 kHz) at 473 K as compared to the reported value of pure NFO (~80) [1]. Space charge polarization accumulates more at the grain and grain boundary interface. So the dielectric permittivity increases.



Fig. 3. Frequency dependent real part and imaginary part (inset) of complex dielectric permittivity of Nd-NFO above room temperature

The room temperature magneto-dielectric response of the Nd-NFO sample is plotted (Fig. 4) using the following equation,

$$MD\% = \frac{\varepsilon'(H) - \varepsilon'(0)}{\varepsilon'(0)} \times 100^{\text{ b}})$$

Where $\varepsilon'(H)$ and $\varepsilon'(0)$ are the dielectric constant at a particular magnetic field H and zero fields, respectively.



Fig. 4. Room temperature magneto-dielectric coupling of Nd-NFO NPs.

TABLE 1. Derived electrical	parameters of Nd-NFO
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Peak frequency (M ^{//} vs. f plot)	1.2×10 ⁵ at 323 K	5.2×10 ⁵ at 363 K	9.2×10 ⁵ at 433 K	1.7×10 ⁶ at 473 K
MD %	At f = 15 MHz	0.009 (0 Gauss)	0.60 (7264 Gauss	0.53 (9460 Gauss)
Activation energy (E _a)	Calculated from Relaxation peaks (M ^{//} vs. f plot)		0.23	3 eV

MD% initially increases up to a particular specific field H, then decreases with a further rise in the magnetic field. The magneto-dielectric response is enhanced due to the magneto-crystalline strain developed Nd doping in NFO crystal.

Conclusion

Here, the successful synthesis of rare-earth neodymium (Nd)doped nickel ferrite (Nd-NFO) NPs and the magnetodielectric coupling and dielectric relaxation characteristics are discussed. Dielectric properties are significantly improved after Nd doping in NFO. It can be potentially used as a nonvolatile energy storage device. The magneto-dielectric response makes the material suitable for antenna miniaturization.

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High pressure structural and resistance study on quasi 1D compound Sr₂CuO₃

Subodha Sahoo^{1, 2*}, S. Karmkar^{1, 2}

¹HP & SRPD, Bhabha Atomic Research Centre, Mumbai, 400085, India, ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India.

*subodhas@barc.gov.in

Abstract

This report presents the pressure dependence of structural and electrical transport properties of Sr_2CuO_3 investigated via synchrotron-based powder x-ray diffraction (XRD) and resistance measurement using diamond anvil cell (DAC) at low temperature. Sr_2CuO_3 shows structural stability up to the highest pressure of our study (~18GPa), but highly anisotropy in axial compressibility, c-axis being the soft axis. The temperature dependence of resistance shows an insulating nature up to the highest pressure of our study with systematic decrease in activation energy. The application of further high pressure may turn this compound in to a metallic state.

IV Characteristics of Si PIN Diodes under Controlled Humid Conditions and Integrity of Surface Passivation Layer

Venkateswara Reddy Karrevula, S. Tripurasundari*, and Sekar Abhaya

Materials Science Group, Indira Gandhi Centre for Atomic Research, HBNI, Kalpakkam, Tamil-Nadu-603102,

India.

*Corresponding author: sundari@igcar.gov.in

Abstract

This work presents an investigation on reverse current voltage (IV) characteristics of commercial planar Si p-i-n (PIN) diodes from 0 to 100 V in ambient and controlled humidity conditions (Relative Humidity (RH) range from ~ 16 % to ~ 92 %). The reverse IV characteristics of the diodes showed differences in reproducibility for different diodes of the same batch. Similarly, experiments performed for both the adsorption and desorption cycles showed differences in the reversibility of the IV characteristics for different diodes. These behaviors are attributed to the differences in the integrity of the surface passivation layer in terms of the pores and are further corroborated using Depth-resolved Doppler broadening studies using positron beam.

Introduction

Silicon PIN diodes are known to find potential applications for a wide range of fields including radiation detection, charged particle spectroscopy, etc. These semiconductor devices are employed for field applications and are subjected to irradiation, temperature, and humidity. It is of both academic and technological interest to understand the effect of humidity on the performance of these diodes. Little reports are available on this aspects¹.

Experimental methods

Commercial Si PIN diodes of $5\text{mm} \times 5\text{mm}$ size were procured from M/s BEL, Bangalore (India). The diodes were placed in a customized light-tight chamber where the relative humidity (RH) was controlled using the flow of wet and dry nitrogen gas through bubbler and mass flow controllers. The humidity was monitored using a commercial RH sensor (Sensirion SHT21). Reverse current voltage (IV) measurements were carried out using a source measurement unit (Keysight B2912A) by varying the reverse bias voltage (V_{*RB*}) from 0 to -100 V with a step size of -20 mV at different values of RH during adsorption and desorption cycle in the RH range from ~ 16 % to ~ 92 %.

Depth-resolved Doppler broadening measurements were carried out using low energy positron beam setup at IGCAR². The positron beam energy was varied from 235 eV to 22 keV in steps of 0.5 keV and a Doppler broadened spectrum was obtained at each energy using HPGe detector, having 1.4 keV energy resolution at 662 keV. Defect sensitive S-parameter defined as the ratio of counts in the peak region from 510 to 512 keV to the total counts under the peak (P) from 501 to 521 keV was deduced from the Doppler spectrum. The positronium fraction (f_{PS}) which is a measure of porosity in the sample defined by $3\gamma/2\gamma$ was deduced using the relation (T-P)/P, where T is the counts from 50 keV to 521 keV³.

Results and Discussion

Reverse IV characteristics measured under ambient conditions for two typical diodes (diodes henceforth referred to as #67 and #77) are shown in fig.1. It is to be noted that the experiments were repeated three times to check the reproducibility of the IV characteristics. From fig.1, it is observed that



Fig.1. Variation of I_R as a function of V_{RB} on Si PIN diodes. Closed symbols and open symbols indicate measurements for diode 67 and diode 77 respectively. #1, #2, #3 represent reverse IV measurements repeated 3 times.

IV characteristics are reproducible for diode #77 unlike that of diode #67. From the literature, it is known that such differences in irreproducible behavior could be due to the non-integrity of the surface passivation layer¹ of the diode. However, as the detailed architecture of the Si PIN diode is proprietary information of the manufacturer, it is not disclosed to the client. Therefore, for further investigations about the differences in the non-reproducibility of the IV characteristics, measurements were performed under controlled humidity conditions. The variation of reverse leakage current (I_R) measured for both the diodes at V_{RB} of 90 V for RH values varying from ~ 16 % to ~ 92 % is shown in fig.2 for both adsorption and desorption cycles.



Fig.2. Variation of I_R as a function of RH during one RH increase and decrease cycle from ~ 16 % to ~ 92 % at V_{RB} of 90 V on diode 67 and diode 77.

For both the diodes, I_R varies from ~10⁻⁹ to 10⁻⁷ A for both adsorption and desorption cycles, with a magnitude of I_R being marginally larger for #67 than #77. It is very clear from the figure that diode #77 shows a nearly reversible behavior for the adsorption and desorption cycle unlike the stark contrast from diode #67. As little information is available regarding the architecture of the PIN diodes, low-energy positron beam measurements were carried out on the diodes to investigate the integrity of the passivation layer. The variation of the S-parameter and the corresponding positronium fractions (f_{PS}) with positron beam energy (Ep) is plotted in fig.3. The S vs. Ep curves for both the diodes follow metal-like behavior showing a decrease in S-parameter and then a saturation around 10-13 keV. Beyond 14 keV, the S-parameter starts to increase corresponding to positron annihilation in the interface/p+ Si. This behavior corresponds to the Al overlayer used as a contact and is coated above the Si p+ layer. Further from Fig.3b, it is observed that f_{PS} is high at the surface which then decreases and thereafter saturates at values beyond 4 keV. The saturation value of f_{PS} is higher for diode #67 indicating the presence of more pores/defects. This together with nonreproducibility in RH-driven leakage current

measurement (fig .1) on diode #67 suggests that more remnant water is present during the desorption cycle.



Fig.3. a) S- parameter and b) Positronium fraction as a function of positron beam energy for diodes #67 and #77.

Conclusions

IV characteristics carried out on commercial Si PIN diodes indicate that they are sensitive to RH variation. The irreversible nature of the adsorption and desorption cycles and their differences in terms of hysteresis indicates differences in the integrity of the passivation layer. This is corroborated by the variation of defect-sensitive S-parameter and positronium fraction with RH.

Acknowledgment

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Study of structural and transport properties of Al substituted Fe₂TiSn

P.A. Bhobe, Kulbhushan Mishra*, S. Chaudhuri[†],

Department of Physics, Indian Institute of Technology Indore, Khandwa Road, Simrol, Indore 453552 India

*Corresponding author: phd1901251009@iiti.ac.in

Abstract

The structural, transport and magnetic properties of an otherwise nonmagnetic full Heusler alloy, Fe₂TiSn, is studied using Al doping at Sn site. The pristine Fe₂TiSn is prone to Fe-Ti antisite disorder that gets reflected in the upturn in $\rho(T)$ data for T < 25 K. With Al doping, the upturn in the resistivity decreases, which could be because of magnetic order present in the samples.

Introduction

Heusler alloys display rich physical properties with simple lattice structure, like shape memory effect, magneto-crystallinity, half-metallicity etc. The stoichiometric full-Heusler alloys have chemical formula X₂YZ, where X and Y are transition metals and Z is main group element. It forms a cubic $L2_1$ structure (space group Fm-3m) consisting of 4 interpenetrating FCC sublattices in its ideal form. Fe₂TiSn is one such full Heusler composition that is non-magnetic semimetal with small pseudogap of 0.07eV at Fermi level [1]. But the composition is very prone to anti-site disorder between Fe and Ti, which drastically influences its transport and magnetic ground state properties. With proper substitution at Sn and Ti sites, it has been demonstrated that the anti-site disorder is controllable and system can be driven to half-metallicity [2,3,4]. In this paper, we examine the effect of Al substitution for Sn with an aim to explore such similar electronic ground state.

Experimental Method

The Fe₂TiSn_{1-x}Al_x (x = 0, 0.5, 1) compositions were prepared using an arc melting furnace. The constituent elements of purity \geq 99.99% were placed on water cooled copper hearth and melted several times in high purity Argon atmosphere. The beads so obtained, were sealed in an evacuated quartz ampoule (\geq 10⁻⁵ mbar) and annealed at 800°C for 72 hours to be subsequently quenched in ice water. The crystal structure and phase purity was confirmed by recording the powder X-ray diffraction (XRD, with λ = 0.622 Å) patterns at BL-11 Indus-2 synchrotron source, RRCAT, Indore. The standard four probe electrical resistivity and magnetic measurements were carried out using Quantum Design's PPMS and MPMS systems.

Results and Discussion

XRD profiles of all prepared samples are shown in Fig.1. All the peaks can be indexed to cubic L_{2_1} phase of Heusler alloy with space group Fm-3m. Upon refinement of the profiles using Rietveld method, it is found that the lattice parameters decrease linearly with increasing Al content, following the Vegard's law. The decrease in intensity ratio of (111) superlattice peak with respect to general (220) reflection, is indicative of B2-type disorder, while that of (200) with (220) represents A2-type disorder. In the present patterns both, the I111/I220 and I200/I220 decreases for 50% Al substitution and for 100% Al composition the I₂₀₀/I₂₂₀ shows an increase. However, the change in the intensity of the (111) and (200) peaks seen here is not due to disorder, but due to the difference in the atomic scattering factor of Al to Sn. The calculated profiles for L2₁ order perfectly match with the experimental data, thus indicating restoration of high symmetry with Al substitution.



Fig. 1. Synchrotron XRD profile for Fe₂TiSn_{1-x}Al_x.

Resistivity measured as function of temperature for all the three compositions is shown in Fig. 2. The residual resistivity decreases with the Al substitution, in accordance with perfectly ordered XRD patterns. Chaudhuri *et. al.* [4] has shown the p-type nature of Fe₂TiSn. Thus doping Al at Sn site adds hole to the system which fully justify the fall in the overall resistivity of the system. Also the upturn in the low temperature resistivity of the Fe₂TiSn, which is the signature of weak localization that occurs due to the coherent back scattering of the disordered system [5], seems to disappear with Al substitution.



Fig. 2. Temperature dependent resistivity.

Decrease in the anti-site disorder and the weak localization should reflect in the magnetic ground state of these compositions. To examine the magnetic properties, magnetization was recorded as function of applied magnetic field at 5 K and the data is plotted at Fig. 3. Both the Al-substituted compositions show ferromagnetic like increase in the magnetization, but the curves do not saturate even for field value as high as 7 T. The temperature dependence of ac magnetic susceptibility plotted as an inset to Fig. 3 is indicative of the high transition temperatures (~180 K) achieved in the Al-substituted Fe₂TiSn compositions.



Fig. 3. M-H curve for $Fe_2TiSn_{1-x}Al_x$, (in inset $\chi_{ac}(T)$ graph).

Conclusion

The work presented here is a preliminary inference of the changes taking place in the structural and transport properties of Fe_2TiSn upon Al substitution at Sn site. A perfect $L2_1$ order is established with increasing Al content, as established from Rietveld refinement of the synchrotron XRD patterns and low temperature resistivity. A long range magnetic order seems to evolve with replacement of Sn with Al, and indicative of the fact that much remains to be explored for this interesting class of materials. EXAFS study of these compositions is underway, and would help to get clear insight of the local structure and magnetic order.

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[†]Currently at National Taiwan University, Taipei City, 10617 Taiwan

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Estimation of Band Offsets and Quantum Transport Properties Study of GeSn Nanowire

Prabal Dev Bhuyan^{1, 2}, P. N. Gajjar² and Sanjeev K. Gupta¹

¹Computational Materials and Nanoscience Group, Department of Physics and Electronics, St. Xavier's College, Ahmedabad 380009, India ²Department of Physics, Gujarat University, Ahmedabad 380009, India

*Corresponding author: prabal.bhuyan@sxca.edu.in

Abstract

One dimensional semiconducting core-shell nanowires (NWs) have attracted a large attention due to its potential application in high mobility FETs, semiconductor-superconductor hybrid devices and spintronics devices. In the present work, we have reported electronic and quantum transport properties GeSn core-shell NW. The GeSn-NW shows direct band gap semiconducting behaviour. Further, we have estimated the band offset of NW and studied their transport properties. We have observed linear characteristics behavior in I-V graph for the GeSn nanowire. Our study could motivate experimental researchers to fabricate this new composition core/shell nanowire.

Topological Hall effect in a centrosymmetric Gd₂PdSi₃ single crystal

Gourav Dwari¹, Souvik Sasmal¹, Bishal Maity¹, Ruta Kulkarni¹, Arumugam Thamizhavel¹

¹Department of Condensed Matter Physics and Materials Science,

Tata Institute of Fundamental Research, Mumbai 400005

*Corresponding author: gourav.dwari@tifr.res.in

Abstract

Topologically non-trivial magnetic structure, skyrmion, can be observed in crystal with broken inversion symmetry due to presence of Dzyaloshinskii-Morya interaction. Here we report the existence of strong topological contribution in the Hall effect measurement in a centrosymmetric crystal Gd₂PdSi₃ grown using Czochralski pulling technique. Gd₂PdSi₃ crystallizes in *AlB*₂-type structure. The topological contribution persists only within a short window of temperature and magnetic field, that was initially identified as the skyrmion phase, stabilized by mainly geometrical magnetic frustration. Specific heat measurement shows evidence of magnetic transition corresponding to antiferromagnetic ordering and huge change in magnetic entropy.

Introduction

A large number of ternary rare-earth silicide and germanide with transition metals are known to exist and form a particular interesting class of compounds [1]. Among these, Gd compounds are of particular interest because of quenched nature of orbital moment and thus magnetism in Gd compounds come from purely spin only moment. Magnetic frustration in this kind of system can lead to a completely disordered state or it may give rise to more complex magnetically ordered state. One such emerging complex spin states is skyrmion which is a twisted, vortex-like spin structure with particle like nature. Skyrmions are initially thought to exist in non-centrosymmetric crystal structure, where absence of inversion symmetry causes Dzyaloshinskii-Morya (DM) interaction [2] that stabilizes such twisted spin textures. But studies reveals that it can also be stabilized in centrosymmetric structures with magnetic frustration.

In this article we discuss the crystal growth and anisotropic magnetotransport properties of Gd₂PdSi₃ crystallizes in a hexagonal centrosymmetric crystal structure and hosts skyrmion lattice.

Crystal growth and characterization

Single crystal of Gd_2PdSi_3 was prepared by Czochralski pulling method using tetra-arc furnace (Model: Techno Search, Japan) from the stoichiometric melt of high purity elemental Gd, Pd and Si. The elements are melted repeatedly by flipping the resulting ingot multiple times for better homogeneity. A seed crystal was cut from the ingot and used it as a seed to pull the crystal from melt at a very slow rate. We have grown nearly 100 mm long and 3-4 mm diameter single crystalline rod of Gd₂PdSi₃ as shown in Fig. 1(b). It is reported that Gd_2PdSi_3 crystallizes in AlB₂ type hexagonal structure with space group *P6/mmm* [3, 4]. Single crystalline nature of the pulled ingot is verified with x-ray Laue diffraction technique (Fig.1(a) left inset). The Laue pattern matches with the hexagonal symmetry of the crystal in (0001) plane. Also, to check the phase purity of the crystal, a small portion of the pulled ingot was ground for powder x-ray diffraction (XRD) in a PANalytical x-ray diffractometer equipped with a monochromatic x-ray source. The XRD pattern was refined with FullProf software and is shown in Fig.1(a). The peaks are matching well with the calculated pattern and shows no extra phase in the crystal.



Fig. 1. (a) Powder x-ray diffraction of grown Gd₂PdSi₃ single crystal. Solid line refers to the calculated pattern using FullProf software. (Left inset) Back-reflection Laue pattern of (0001) plane. (Right inset) Crystal structure of Gd₂PdSi₃. (b) As grown pulled crystal.

Hall measurement

We measured the Hall resistivity of Gd₂PdSi₃ in five probe geometry in a Physical Property measurement system (Quantum Design). The antisymmetrized Hall data is shown Fig.2(a), for current in the basal plane and magnetic field along [0001] direction. The Hall resistivity increases at low fields and remains flat before it drops down rapidly. For fields greater than 2 T the Hall resistivity is negative. The sudden rise and drop in the Hall resistivity is due to the two metamagnetic transitions which appears due to the spin reorientation as the magnetic field is increased [4]. In a recent work Kurumaji et al reported that in between the two metamagnetic transition there appears a magnetic phase, which they termed as A phase, where the spin texture goes into a topological phase transition as the magnetic field is increased [5]. In the A phase, the spin texture has non zero scalar spin chirality $(S_i, (S_i \times S_k))$ that acts as an imaginary magnetic field and deflects the electrons giving rise to an additional Hall signal. This additional Hall signal is termed as the topological Hall effect (THE).



Fig. 2. (a) Field dependence of Hall resistivity measured at different temperature. (b) Extracted topological contribution to the total Hall resistivity vs field. (c) Phase diagram according to topological Hall signal.

From the magnetization data, linear resistivity data and the Hall resistivity data, we extracted the topological Hall contribution. Total Hall resistivity ρ_H can be written as:

$$\rho_H = R_0 B + S_0 \rho_{xx}^2 M + \rho_H^T$$

where first term is the normal Hall resistivity proportional to applied field *B* and the second term is anomalous term proportional to magnetization *M*, the last term is the topological Hall component. Now from Fig.2(a) itself we see that the topological component vanishes when the field is above 1.5 T. Thus, in the high field region a linear fit of (ρ_H /B) vs $(\rho_{xx}^2 M/B)$ yielded the values of R_0 and S_0 and thus the topological component was extracted and is shown in Fig.2(b). A phase diagram (Fig.2(c)), plotted with the topological Hall component at different temperature, shows large response from the term is obtained in a closed region in *B*-*T* space implying the temperature and magnetic field required to stabilize the skyrmion phase.

Specific heat

Specific heat data of Gd_2PdSi_3 shows a clear magnetic transition near 20 K where the Gd moments order in an antiferromagnetic arrangement as confirmed from the magnetic susceptibility and magnetization measurements. Total specific heat attains a value of 150 J/mol K, at around 250 K, which is the Dulong-Petit limiting value of *3nR*.



Fig. 3. (a) Total specific heat vs temperature plot. Dotted line represents the 3nR limit, (inset) highlighted peak corresponding to magnetic transition. (b) Magnetic entropy change as function of temperature.

To calculate change in magnetic entropy we have used a non-magnetic isostructural compound Y₂PdSi₃ that gives the lattice (C_{latt}) contribution to specific heat (C_p). Subtracting C_{latt} and C_{el} from C_p , magnetic specific heat (C_{mag}) of Gd₂PdSi₃ is obtained. Change in magnetic entropy ($\int \frac{Cmag}{T} dT$) follows the rule that total magnetic entropy change (that is due to magnetic element Gd which has L=0, S=7/2) cannot exceed the maximum limit of Rln(2S+1) as shown in Fig.3(b).

To summarize, we have grown the single crystal of Gd_2PdSi_3 by Czochralski method and observed the topological Hall effect in the so called skyrmion phase or *A* phase region of the magnetic phase diagram.

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Effect of Mn concentration on the anomalous Hall effect in Mn₃Sn single crystals

Bishal Baran Maity, Souvik Sasmal, Gourav Dwari, Ruta Kulkarni, A. Thamizhavel

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Colaba, Mumbai 400 005.

*Corresponding author: bishal.maity@tifr.res.in

Abstract

In ferromagnetic conductors, a transverse voltage drop appears even in zero magnetic field. This anomalous Hall effect is generally observed to be proportional to the magnetization, and thus is not typically observed in antiferromagnets in zero field. Mn₃Sn, an antiferromagnet has been shown to exhibit a large anomalous Hall effect by Nakatsuji et al with anomalous Hall conductivity reaching the same order of magnitude as in ferromagnetic metals. Also, it has a weak and soft ferromagnetic moment which switches the sign of the Hall Effect with a small magnetic field of around a few hundred oersted. We attempted to grow the single crystal of Mn₃Sn to study its anisotropic behaviour. However, the phase diagram of Mn and Sn shows that the crystal formation is still possible when the stoichiometry is not exactly 3:1. The details of crystal growth and its anisotropic physical properties and the effects of Mn concentration has been investigated in this study.

Crystal Growth and Mobility Fluctuations Driven Linear Magnetoresistance in YSi

Vikas Saini¹ and A. Thamizhavel¹

¹Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Homi Bhabha road, Colaba, Mumbai 400 005.

*Corresponding author: vikas.saini@tifr.res.in

Abstract

Linear magnetoresistance has been studied extensively over a wide range of phases from trivial to topological materials. In this report, we present the results on YSi single crystal growth and the anisotropic transport properties. YSi crystallizes in orthorhombic crystal structure with space group *Cmcm* (SG. No. 63). Resistivity measurements have been carried out along all three principle crystallographic directions, along $J \parallel [001] B \parallel [100]$ orientation linearity in magnetoresistance is observed for above ~10 T magnetic field. The linear magnetoresistance in YSi is caused by the mobility fluctuations that is explained by the famous Parish-Littlewood (PL) model.

Introduction

Symmetry breaking phase transitions can be explained using the Landau theory of phase transitions but the topological phases of matters are protected by the natural, symmorphic, and nonsymmorphic symmetries which induces a verity of experimental and theoretical insights. Symmetry protected topological bulk and surface states manifest into novel transport phenomena such as quantum Hall effect, quantum spin Hall effect and quantum anomalous Hall effect along with various other novel features of weak-antilocalization, topological superconductivity and ultrahigh magnetoresistance. Although linearity in the magnetoresistance appears from the classical and quantum roots in both trivial and topological compounds. Recently, YSi has been studied as a Dirac metallic phase which is protected by nonsymmorphic crystalline symmetries [1, 2]. Magnetoresistance (MR) is defined as the appearance of resistance in applied magnetic field at a constant temperature. Quantum model proposed by Abrikosov for the linear magnetoresistance (LMR) appears in an extreme limit when the system is imposed into lowest Landau level such as this model explained the LMR observed in the (Ca, Sr)MnBi₂, Bi₂Se₃ thin films etc. [3-5]. From one of the classical approaches guiding center contributed linear magnetoresistance is observed where linearity in MR is associated with the Hall signal which is explicitly shown in the TlBiSSe and Na₃Bi systems [6, 7]. Secondly, Parish and Littlewood proposed a model, where mobility fluctuations are induced from the scattering centers of disorders, attribute to the linearity of the MR in the strong limit of inhomogeneities. Disordered semiconductors Ag (2-x) (Se/Te) and other semimetals such as n-doped Cd₃As₂ and PtBi2 show the linear magnetoresistance which are explained from the PL model [8-10].

Methods

Single crystal of YSi is grown by the Czochralski method. The stoichiometric ratio of high purity elements Y (3N, Alfa Aesar) and Si (5N, Alfa Aesar) was used for the synthesis. First the polycrystalline sample of about 10 g was prepared by repeatedly melting Y and Si in a tetraarc furnace under a partial pressure of argon gas atmosphere. A polycrystalline seed crystal was cut from the melted ingot and carefully inserted into the molten solution and gradually pulled. In the beginning of the growth, crystal was pulled with the rate of ~50 mm/hr for necking and once the steady state was achieved the regular pulling rate was set to ~10 mm/hr. A small portion of the grown crystal was used to confirm the phase purity using x-ray diffractometer at room temperature. The crystallographic directions of an orthorhombic system have been identified from the back diffraction pattern of Laue diffraction pattern. Aligned directions were isolated using the erosion copper wire machine. Electrical transport experiments are performed in the Quantum designed PPMS. Resistivity measurements are carried out from four probe method where the contacts are made from the 50µm diameter gold wires using the mixer of silver epoxy paste. The resistivity contacts were cured at 100°C for 1hr.

Results and Discussions

YSi crystallizes in orthorhombic crystal structure with the space group *Cmcm*. The conventional unit cell consists of of Y and Si atoms occupying the 4c Wyckoff position as depicted in Fig 1(a). The lattice parameters a = 4.260 Å, b = 10.530 Å, c = 3.830 Å are estimated from the Rietveld refinement using Fullprof package where the refined pattern is shown in Fig 1(b), the red circles represent the observed pattern and black solid fit is corresponding to simulated pattern. Observed Laue x-ray pattern of all the three crystallographic directions viz., (100), (010) and (001) directions are shown in Fig. 1(c-e).



Fig. 1. (a) Crystal structure of YSi single crystal. (b) Powder x-ray pattern. (c-e) Laue diffraction pattern for (100), (010) and (001) planes.

Electrical resistivity measurements are performed along all the three principal crystallographic directions. Resistivity measurements up to 14 T magnetic field at various fixed temperatures are carried out. With increasing temperature MR decreases because of dominating temperature dependent scatterings which reduce the transport scattering time, as a consequence MR decreases, which is clearly observed from Fig. 2(ac).

For $J \parallel [001]$ and $B \parallel [100]$ orientation in low field regime MR is quadratic and above ~10T magnetic field, linear MR is observed, where the solid red line is the linear fit to the MR data at 2 K for in the 10 –14 T regime. The derivative of MR with magnetic field for 2 and 50 K is shown in Fig. 2(e). The crossover magnetic field (B_c) is estimated from the intersection of red and blue fits associated with quadratic and linear MR as plotted in Fig. 2(e). Temperature dependency of MR and crossover field is depicted in Fig. 2(f), which shows the crossover field increases with the increasing temperature and MR drops with increasing temperature.



Fig. 2. (a-c) Temperature dependency of MR for $J \parallel [100]$, [010], [001] directions. (d) For $J \parallel [001]$; $B \parallel [100]$ configuration MR at T=2 K. (e) Derivative of MR against magnetic field for T = 2 and 50 K. (f) Temperature dependency of the MR and crossover magnetic field.

The crossover field (B_c) is defined as $B_c \sim 1/\mu$ or $B_c \sim 1/\Delta \mu$ for $\Delta \mu/\mu < 1$ and $\Delta \mu/\mu > 1$ cases. Where μ is average mobility and $\Delta \mu$ is width of mobility distribution. Based on the PL model of linear MR the crossover field (B_c) is proportional to $1/\mu$ and dMR/d**B** is proportional to μ . For YSi, it has been observed that hole mobility is more than the electron mobility in entire temperature range from 1.8-300 K thus mobility of hole carriers is used for the PL model analysis. Fig. 3(a) suggests the identical behavior of inverse mobility and crossover magnetic field against inverse temperature further the B_c shows linear dependency with $1/\mu$ as observed from Fig. 3(b). In the second scenario, derivative of magnetoresistance and mobility is plotted against temperature which decrease in the identical way as shown in Fig.3(c) and the direct linear dependency of dMR/dB and mobility is shown in Fig. 3(d). The previous study of YSi suggests the shifting of Fermi energy level upward from the pristine value [2] arises because of disorders, which supports the presence of disorders in YSi.



Fig. 3. (a) Inverse mobility and B_c versus inverse temperature. (b) Linear dependency of B_c with $1/\mu$. (c) dMR/dB and mobility (μ) against temperature. (d) dMR/dB against μ plot for various temperatures.

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Crossover from Linear to Quadratic Magnetoresistance in NiTe2

Indrani Kar^{1,*} and Setti Thirupathaiah¹

¹Condensed Matter Physics and Material Sciences Department, S N Bose National Centre for Basic Sciences, Kolkata, West Bengal-700106, India

*Corresponding author: karindrani.physics@gmail.com

Abstract

We have performed electrical transport and magneto-transport measurements on NiTe₂ single crystals and calculated the Debye temperature $\Theta_D \approx 230$ K using the extended Bloch-Grüneisen (BG) formula. The resistivity data fitting with BG indicates that resistance in this system is dominated by s-d electron-phonon scattering. Also, from the magnetoresistance (MR) measurements we observe a crossover from the linear magnetoresistance dependance on B (MR \propto B) to a quadratic magnetoresistance dependance on B (MR \propto B²) at applied magnetic fields of B \approx 3.5 T and B \approx -3.5 T.

Transport Properties of Sb₂X₂Te₆ (X=Si, Ge, Sn): A DFT Study

Rajeev Dutt^{1,2}* and A. Pandey³

¹Theory and Simulations Laboratory, HRDS, Raja Ramanna Centre of Advanced Technology, Indore-452013 ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai-400094 ³Metallurgical Engineering and Materials Science Department, Indian Institute of Technology, Mumbai-400076

*Corresponding author: <u>duttrajeev35@gmail.com</u>, <u>duttrajeev@rrcat.gov.in</u>

Abstract

Aim of this work is to probe the effect of isoelectronic substitution on $Sb_2X_2Te_6$ (X = Si, Ge, Sn) on the Seebeck Coefficient (S). We have optimized the structure of $Sb_2X_2Te_6$ (X = Si, Ge, Sn) by using the density functional theory based first principles calculations. Seebeck Coefficients of the probed systems have been calculated using the semi-classical Boltzmann Transport equation. Further, we have compared the S values of $Sb_2X_2Te_6$ (X = Si, Ge, Sn) for p-type doping.

I. Introduction

Combustion of the conventional sources of the energy leads to threat like global warming, further limited availability of these sources motivated researchers towards searching for unconventional sources of clean energy¹. Thermoelectric materials (TEM) which can directly convert the heat into electricity, gathered global research interest as the clean energy materials. Different variety of TEMs such half Heusler alloys (HHAs), Chalcogens, as Skutterudites, etc. show promising nature in the thermoelectric applications. Different materials have their advantages, as HHAs have promising nature at high temperatures¹, Skutterudites and Chalcogens in the room temperature region¹. Owing to a low value of thermal conductivity, different layered structure like PbTe, SnSe and Bi₂Te₃ show high values of ZT (Figure of merit)².

Recently predicted and experimentally grown $Sb_2Si_2Te_6$ (SST) layered structure shows promising TE properties with a peak value of ZT up to 1.65 at $825K^3$. Owing to these features of SST, it is worth to probe the system further. In the present work, our aim is to study the effect of isoelectronic substitution at the Si site by Ge and Sn on the Seebeck coefficient (S).

II. Methodology:

Structure optimization and ground state electronicstructure calculations have been carried out using the Vienna Ab-initio Simulation⁴ Package. For exchangecorrelation functional, generalized gradient approximation (GGA)⁵ given by Perdew, Burke, and Ernzerhof (PBE) has been used. Lattice constants and atomic positions have been obtained from experimental results. Further for each element, i.e., Si, Ge and Sn structure, full geometry optimization has been done using conventional and primitive structures.

Planewave cut-off of 500 eV with a k-mesh of 10x10x10 has been used for the structure optimization. Transport properties have been calculated by using the semi-classical Boltzmann transport theory based on relaxation time approximation, as implemented in the software, BoltzTraP2⁶. In order to calculate the transport properties, 16x16x16 k-mesh has been used for the self consistent field cycle, which is further interpolated on a 25 times dense k-mesh by using BoltzTraP2 software in the irreducible Brillouin zone.

III. Result and Discussion:

A. Geometric Structure

Conventional and primitive crystal structure are shown in Fig. 1(a,b), respectively. There are 10 atoms present in the primitive cell with 6 atoms of Te and 2 atoms of Sb and X (Si, Ge, Sn) each. Optimized lattice parameters corresponding to the conventional and primitive structure of $Sb_2X_2Te_6$ (X = Si, Ge, Sn) have been reported in Table 1.



Fig. 1. (a) Conventional, and **(b)** Primitive structure. Yellow, blue and purple color ball represent the Te, Si and Sb atoms, respectively.

It has been found that in case of primitive structure the lattice constant of the primitive structure decreases from Si to Ge and increases from Ge to Sn. Angle between the axis of the primitive lattice (α) increases from Si to Sn. In case of the conventional structure lattice constant 'a' increases from 7.27 Å to 7.50 Å from Si to Sn.

Table 1. Lattice parameters of Sb ₂ X ₂ Te ₆				
Primitive :				
	Lattice constant (a)	Angle (α) (in		
System	(Å)	degree)		
$Sb_2Si_2Te_6$	8.83	48.68		
Sb ₂ Ge ₂ Te ₆	8.63	50.42		
Sb ₂ Sn ₂ Te ₆	8.74	50.81		
Conventional :				
	Lattice constant (Å)			
System	a	С		
Sb ₂ Si ₂ Te ₆	7.27 (7.223)	23.295 (21.236)		
Sb ₂ Ge ₂ Te ₆	7.35 (7.302)	22.546 (21.010)		
Sb ₂ Sn ₂ Te ₆	7.50 (7.433)	22.778 (21.467)		

On the other hand, lattice constant 'c' shows the trend similar to the lattice constant of the primitive structure. Calculated values of the lattice constants follow the trend as reported in the literature (values given in the bracket in Table 1)⁷.

B. Seebeck Coefficient

Fig. 2 shows the variation of S with respect to the carrier concentration (n) of p-type doping. The upper panel shows the result for X = Si, which is consistent with the literature⁸. For X = Si, S value decreases with the increase in the p-type carrier concentration at T = 300 and 500K. For 700K, maxima has been obtained at 10^{18} of p-type carrier concentration.



Fig. 2. Variation of the Seebeck coefficient (S) with respect to the p-type doping charge carrier concentration (n/cm³).

Moreover, X = Si has a maximum value of S (780 μ V/K) at a very small doping concentration. Among the studied systems, X = Si shows the highest value of S followed by Ge and Sn, respectively. In comparison to

Si, maximum value of S for Ge and Sn has been observed at higher doping concentration. As in case of Sn, highest value of calculated S has been obtained around 10^{20} n/cm³, in comparison to the 10^{17} n/cm³ for Si. For each system, maximum value of S at a particular temperature is also subject to the carrier concentration. From Fig. 2, it is quite clear that calculated value of S for X = Si has an edge over X = Ge and Sn. However, it is to be noted that all the calculations are done using the PBE (GGA) exchange-correlation functional which is known to underestimate the band-gap value. A detailed study by using different exchange-correlation functional of electronic and thermoelectric properties of Sb₂X₂Te₆ is under way.

Conclusion:

Using first principle calculations based on DFT, along with the semi-classical Boltzmann transport theory, variation of S with respect to the p-type carrier of $Sb_2X_2Te_6$ (X = Si, Ge, Sn) has been calculated. We observed that with PBE (GGA), among $Sb_2X_2Te_6$ (X = Si, Ge, Sn), X = Si has highest value of the calculated S. A high S value of $Sb_2X_2Te_6$ systems, motivate us to tune it in future by using band-engineering and stress-strain effects.

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Strain-induced Anomaly And Chirality-dependent Planar Hall Effect In Type-II Weyl Semimetals

Suvendu Ghosh^{1,*}, and A. Taraphder¹

¹Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur-721302, India

*Corresponding author: suvenduphys@iitkgp.ac.in

Abstract

Application of strain in Weyl semimetals (WSMs), quite remarkably, generates pseudo-electromagnetic fields and various novel anomalies. The planar Hall effect, (PHE) occurring in regular WSMs, is one of the fundamental manifestations of chiral anomaly. A major quest, therefore, is whether PHE could still arise in a strained type-II WSM without chiral anomaly. Using Boltzmann transport theory, we show that PHE does indeed appear in type-II WSMs solely from strain. The pseudo-magnetic fields couple to the Weyl nodes of opposite chirality with opposite sign, leading remarkably to a finite chirality-dependent planar Hall effect (CPHE). We predict that a pure CPHE is possible even when PHE is absent for a particular strain configuration. We also discuss possible experimental detections of CPHE using circular dichroism.

Introduction

Strained Weyl semimetals (WSMs) show remarkable physical effects owing to the generation of strain-induced pseudo-electromagnetic fields [1]. However, robust transport signature for such pseudofields in a type-II WSM [2] is still lacking. In a time reversal symmetry (TRS) broken but inversion symmetric WSM, there is a pair of Weyl nodes separated in momentum space, each having a definite chirality. Strain-induced variation in the hopping amplitudes results in spatial modulation of the separation (b(r)) of Weyl nodes. This may, in turn, generate chiral pseudomagnetic field ($\mathbf{B}_5 = \nabla \times \mathbf{b}$) [1,3,4,5,6], which couples to Weyl nodes of opposite chirality with opposite sign. Consequently, novel strain-induced anomalies emerge in presence of an external electromagnetic field represented by the covariant anomaly relations [1,6]: $\partial_t \rho_5 + \nabla_{.j5} \sim \mathbf{E}.\mathbf{B}$ and $\partial_t \rho + \nabla_j \mathbf{v} = \mathbf{E} \cdot \mathbf{B}_5$, where ρ and ρ_5 are the total electric and chiral charge density, respectively, and j and is are current densities associated to ρ and ρ_5 respectively. The first relation describes chiral charge non-conservation due to chiral anomaly (E.B). However, the second relation suggests nonconservation of total charge due to E.B₅. To fix the non-conservation, j must be supplemented by the topological Chern-Simons current [1,7,8], jcs ~ -b×E which describes the strain-induced anomalous Hall effect. This can easily be delineated from planar Hall current through its distinct field-dependence and chemical potential dependence.

Semiclassical Formalism

The momentum space Hamiltonian (linearized) for a tilted Weyl node can be expressed, in natural unit, as $H_{\chi}=v_F(\chi \mathbf{k}.\boldsymbol{\sigma}+t_x k_x)-\mu$, where v_F is the Fermi

velocity, $\boldsymbol{\chi}$ the chirality of a node and t_x the tilt parameter along k_x-direction. For a type-II WSM, the Weyl nodes are overtilted [2] and $t_x > 1$. In presence of B and B₅, chiral charges feel different effective fields, $\mathbf{B}_{\chi} = \mathbf{B} + \chi \mathbf{B}_5$, according to their chiralities [1,6,9]. We use Boltzmann transport equation in low field regime (B, $B_5 \sim 0.3$ T) to calculate the planar Hall conductivity (PHC)[10]. We apply uniform external electric and magnetic fields as $\mathbf{E}=\mathbf{E}\hat{\mathbf{x}}$ and **B**=B cos $\theta_{\rm b} \hat{x}$ + B sin $\theta_{\rm b} \hat{y}$. Strain is applied such that $\mathbf{B}_5 = \mathbf{B}_5 \cos \theta_s \, \hat{x} + \mathbf{B}_5 \sin \theta_s \, \hat{y}$). Here, $\theta_b \, (\theta_s)$ is the angle between E and B (B5). The PHC for a single Weyl node is calculated [9] as $(\sigma_{yx})^{\chi} = \frac{\tau e^2}{(2\pi)^3} \int d^3 \mathbf{k} \, \mathbf{D}_{\mathbf{k}}^{\chi}$ $[\mathbf{v}_{\mathbf{x}}\mathbf{v}_{\mathbf{y}} + \mathbf{e}\mathbf{v}_{\mathbf{y}} \ (\mathbf{B}_{\boldsymbol{\chi}})_{\mathbf{x}} \ (\mathbf{v}_{\mathbf{k}} \ . \ \boldsymbol{\Omega}_{\mathbf{k}}^{\boldsymbol{\chi}}) + \mathbf{e}\mathbf{v}_{\mathbf{x}} \ (\mathbf{B}_{\boldsymbol{\chi}})_{\mathbf{y}} \ (\mathbf{v}_{\mathbf{k}} \ . \ \boldsymbol{\Omega}_{\mathbf{k}}^{\boldsymbol{\chi}})$ $+e(\mathbf{B}_{\chi})_{x} (\mathbf{B}_{\chi})_{y} (\mathbf{v}_{k} \cdot \mathbf{\Omega}_{k}^{\chi})^{2}](-\frac{\partial f_{eq}}{\partial \epsilon_{k}}),$ where \mathbf{v}_{k} is the group velocity and $\mathbf{D}_{\mathbf{k}^{\chi}} = [1 + e \ \mathbf{B}_{\chi} \ . \ \mathbf{\Omega}_{\mathbf{k}^{\chi}}]^{-1}$ depicts the phase space volume correction in simultaneous presence of **B**, **B**₅ and Berry curvature $\Omega_{\mathbf{k}^{\chi}}$. Now, total PHC and chirality-dependent PHC (CPHC)[9] are defined as $\sigma^{T}_{yx} = (\sigma_{yx})^{\chi^{=}+1} + (\sigma_{yx})^{\chi^{=}-1}$ and $\sigma^{C}_{yx} = (\sigma_{yx})^{\chi^{=}+1} - (\sigma_{yx})^{\chi^{=}-1}$, respectively.

Results and Discission

We present the results of the angular ($\theta_{\rm b}$) dependence of $\sigma_{\rm yx}$ in Fig.1 for $\theta_{\rm s}$ =0 (in the above panel) and for $\theta_{\rm s}$ = $\pi/2$ (in the below panel). In both cases, total PHC shows a slightly distorted sin $\theta_{\rm b}$ variation with 2π -periodicity. It can further be seen that the total PHC is enhanced [1,9] compared to a normal WSM. This happens as the strain-induced anomaly (**E.B**₅) triggers the generation of a current flowing along the direction of **B**₅, by creating a charge imbalance at the Weyl nodes. We also find that PHE does not vanish even when external **B**=0, contrary to what happens in a normal WSM, where PHE emerges as one of the fundamental manifestation of the chiral anomaly (**E.B**). But in a strained WSM, the chiral anomaly is absent with B=0 and **E.B**^s interplays with **B**^s and the tilt velocity of Weyl nodes to give rise to a finite current, i.e., a strain-induced planar Hall effect.



Fig. 1. Type II WSM. σ^{T}_{yx} (blue line), σ^{C}_{yx} (green line) for a strained WSM and σ^{T}_{yx} for a normal WSM (orange line) are plotted with θ_{b} . We fix $\theta_{s}=0$ (above) and $\theta_{s}=\pi/2$ (below). Other parameters: t_x=1.5, |**B**|=|**B**s|=1T, μ =50 meV. All conductivities are normalized by σ^{T}_{yx} for $\theta_{b} = \pi/4$ in a normal WSM.

In a normal WSM, each node makes the same contribution to PHC, irrespective of their chirality, as E and B cannot differentiate chiralities of Weyl nodes. However, in a strained WSM, a Weyl node feels the pseudomagnetic field either as B_5 or as $-B_5$, depending on its chirality. As a onsequence, $(\sigma_{yx})^{\chi=+1} \neq (\sigma_{yx})^{\chi=-1}$. The difference between the contributions coming from a pair of Weyl nodes can then be captured through CPHC, σ^{C}_{yx} . Interestingly, CPHC can be tuned by the angle θ_b for any strain configuration. It shows 2π -periodicity in its θ_{b} variations (see Fig.1). Astonishingly, for $\theta_s = \pi/2$, PHC is zero at $\theta_{\rm b}=0$, π and 2π whereas CPHC remains nonzero. This indicates that a pure chiralitydependent planar Hall effect (CPHE) is possible in a type-II WSM, for a particular strain configuration.

However, a pure CPHE does not exist for $\theta_s=0$. As the CPHE results in the separation and accumulation of left and right chiral fermions in opposite surfaces of a WSM. This chirality polarization leads to a difference of absorption of left- and right-circularly polarized light at opposite surfaces. This remarkable fact may be utilized to detect CPHE through circular dichroism. Recently discovered TRS-breaking type-II WSM in YbMnBi₂ [8] may be an appropriate system to verify above-discussed novel effects.

Conclusion

Using Boltzmann transport theory, we show that PHE appears in type-II WSMs solely from strain. **B**s couples to the opposite chiral Weyl nodes with opposite sign, leading remarkably to a finite CPHE. We predict that a pure CPHE is possible for a particular strain configuration. We also discuss possible experimental detections of CPHE using circular dichroism.

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Double Dielectric Relaxations in Pr0.5Ca0.5Mn0.9V0.1O3 Perovskite

Mintu Debnath and Sudipta Pal*

Department of Physics, University of Kalyani, Kalyani, West Bengal, India, 741235.

*Corresponding author:sudipta1@klyuniv.ac.in

Abstract

We present the dielectric permittivity and electric modulus analysis of $Pr_{0.5}Ca_{0.5}Mn_{0.9}V_{0.1}O_3$ (PCMVO) perovskite compound, synthesized by solid state reaction method. Dielectric permittivity (ϵ') (also $d\epsilon'/dT$) portrays the charge ordering and magnetic transitions behavior. Two relaxations are found around 45 K and 85 K. Arrhenius fitting revealed that, the low temperature relaxation is associated with the polaron hopping and the high temperature one is related to Maxwell-Wagner relaxation.

Magneto-transport properties of compensated metal PrSb

Shubhankar Roy¹, Prabhat Mandal¹

¹Experimental Condensed Matter Physics Division, SINP, Kolkata-700064

*Corresponding author: shubhankar.roy594@gmail.com

Abstract

We present the magneto-transport properties of PrSb single crystals. Magnetic-field-induced turn-on behavior and low temperature resistivity plateau have been observed. At 2 K and 9 T, a large, non-saturating transverse magnetoresistance (MR) 3.5×10^5 % has been obtained. MRs followed Kohler's scaling. From the semiclassical two-band fitting of Hall resistivity, high carrier mobilities and almost equal electron and hole densities are deduced, which may result in large MR.

Role of Anions in Microscopic Dynamics in Acetamide Based Deep Eutectic Solvents

H Srinivasan^{1,2*}, V K Sharma^{1,2}, and S Mitra^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai – 400 085 ²Homi Bhabha National Institute, Mumbai – 400 094

*Corresponding author: harishs@barc.gov.in

Abstract

Deep eutectic solvents (DESs) have been extensively studied over the last couple of decades owing to growing interest in their industrial applications. The structure-dynamics relationship in these systems have shown interesting insights on the emergence of transport properties. Unraveling the correlation between hydrogen bond structure and microscopic dynamics of these systems can be a useful to tailor their bulk properties. In this study, we use quasielastic neutron scattering to explore the modulation diffusive dynamics of acetamide in various DESs. The results of the study show that the identity of anions in the DES, significantly alters the diffusion of acetamide, establishing the varying strengths of hydrogen bonding in the presence of different anions.

Growth of ultra-smooth molecular semiconductor and its structural analysis Alex Sam and Abhay A. Sagade*

Laboratory for Advanced Nanoelectronic Devices, Department of Physics and Nanotechnology, SRM Institute of Science and Technology, SRM Nagar, Kattankulathur 603 203, Tamil Nadu, India.

*Corresponding author: abhaya@srmist.edu.in

Abstract

High performance of organic thin film transistors (TFT) requires uniform and ultra-smooth surfaces and interfaces. Here, we deposited Dinapthothienothiophene (DNTT) molecular film by effusion cell at high vacuum on a SAM functionalized dielectric. The SAM layer reinforce oriented growth of molecules and create ultra-smooth films of roughness 0.4 nm. X-ray diffraction revealed that molecules are oriented perpendicular to the substrate surface in (001) direction, which is required for the speedy motion of the charge carriers.

Optimization of Post-Treatment Annealing Conditions for RF Sputtered CIGS Thin Films

Sachin Desarada¹, Kalyan Chavan², and Nandu Chaure^{1*}

¹Department of Physics, Savitribai Phule Pune University, Pune, 411007 ²Department of Physics, Ahmednagar College, Ahmednagar, 414001

*Corresponding author: n.chaure@physics.unipune.ac.in

Abstract

A new approach was adopted for the post-processing of CuInGaSe₂ (CIGS) thin films deposited using single target sputtering method. The as-sputtered samples were annealed in muffle furnace and rapid thermal processing (RTP) chamber with successive higher and lower temperature cycles at 450 $^{\circ}$ C for 10 minutes. The samples were analyzed for structural and optical properties. RTP treated samples revealed better results compared to the annealed sample. Rietveld refinement gives the c/a value 2.005 (close to the ideal tetragonal crystal) in RTP treated sample. Optical measurement shows the increased absorbance values in RTP treated sample than furnace annealed sample. The bandgap was estimated to be 1.34, 1.22 and 1.18 eV for as-sputtered, annealing and RTP treated sample. Our experiment shows, however, the similar parameter used for annealing, RTP treated sample shows better results.

Influence Of Different Ion Fluence On The Structural And Optical Properties Of Bi₅In₃₀Se₆₅ Thin Films

P. Priyadarshini^{1*}, S.Sahoo², Ramakanta Naik¹

¹Department of Engineering and Material Physics, ICT-IOC, Bhubaneswar, 751013, India ²Institute of Physics, Bhubaneswar, 751004, India *Corresponding author: priyanka.priyadarshini2019iocb@gmail.com

Abstract

The paper reports the effect by different fluence of proton ion irradiation on the optical and structural properties of $Bi_{5}In_{30}Se_{65}$ thin film. The thin films were prepared by the thermal evaporation technique from bulk material and characterized by X-ray diffraction for structural analysis, UV-Visible for optical study, and Atomic force microscopy for topographical study. The amorphous nature retains with different fluence however, decrease in bandgap and transmission were observed with an increase in the fluence. This decrease in optical bandgap indicates an increase in the lattice defects with proton irradiation. The surface of the film structure was also changed as observed from the AFM images.

INTRODUCTION

Ion irradiation is one of the distinctive external energy input techniques that modifies the structural, morphological, and optical properties of the system. The different doses of ion irradiation in Ge₂₃Se₆₂As₁₅ thin films showed modification in surface morphology and optical properties that are useful for telecom and sensing applications [1]. The ion implantation in Bi/GeSe₂ films induces significant alteration in optical bandgap with the appearance of topological Bi₂Se₃ phase in the structure [2]. The proton irradiation on Bi2Te3 film successfully enhances the defects content which results in the enhancement of thermoelectric properties [3]. In this regard, the Bi-In-Se films were considered as the prototypical semiconducting materials having many useful applications. However, there is no study on the influence of proton ion irradiation on Bi-In-Se system and related changes in different properties.

The energetic ion beams with energy up to a few hundreds of KeV is considered as low energy ion beams which results in the generation defects and disorders in the system. Low energy ion beams basically interact with the target at the atomic level. As a consequence of those elastic collisions, the ions lose all their energy and are implanted inside the target materials, thereby results in the modification of several properties [4]. Thus, studying the effect of ion irradiation on various properties of Bi₅In₃₀Se₆₅ thin film is the main objective of the present study.

EXPERIMENTAL PROCEDURES

Bulk sample of $Bi_5In_{30}Se_{65}$ was prepared by conventional melt quenching method from the stoichiometric mixture of high purity (99.999% Sigma Aldrich) Bi, In, and Se with a slow heating rate (~3 4^{0} C/min) till 500⁰C for 20h.The melt was quenched with ice-cooled water to get the bulk. Then thin films were prepared by thermal evaporation technique from the prepared bulk sample under high vacuum (~10⁻⁵ Torr). The thin films were irradiated with 30 KeV proton using the low-energy ion implanter. The proton irradiation was performed at three different influence (5 x 10¹⁵ ions cm⁻², 1 x 10¹⁶ ions cm⁻², 5 x 10¹⁶ ions cm⁻²) under high vacuum (~10⁻¹¹ Torr) in the chamber.

The structural characterizations of proton irradiated $Bi_5In_{30}Se_{65}$ films were carried out by X-ray diffraction (XRD) with Cu K_a line (λ =1.54Å). The scanning range was 5⁰-80⁰ at step size of 0.05⁰/sec with grazing angle 1⁰.The topographic changes were investigated by atomic force microscope (AFM). The optical transmission data of the films were recorded by using UV-Vis spectrophotometer over the wavelength range of 450-1100 nm.

RESULTS AND DISCUSSION

The XRD patterns of proton ion irradiated $Bi_5In_{30}Se_{65}$ films at different fluence are shown in fig.1. The absence of any sharp peak and the presence of broad humps implies that the films retain amorphous nature under proton irradiation as compared to its asprepared form [5]. The ion irradiation-induced surface morphological change has been noticed from the 5µm x 5µm three-dimensional AFM images (fig.2). The RMS roughness for $5x10^{15}$, $1x10^{16}$, and $5x10^{16}$ ions/cm² fluence films were found to be 13.58nm, 1.44nm, and 2.12nm respectively. Different roughness after irradiation indicates the projectile ions possesses sufficient energy to induce surface modification and create disorders inside the material.

The optical transmission spectra of different ion irradiated films are shown in fig.3. It is observed that the transmittance (T) decreased with the increase in

the influence doses of the film. This decrease in the transmittance is due to an increase in lattice defects and the creation of localized states within the valence and conduction band [6].



Fig. 2. AFM pictures of the proton irradiated films The appearance of fringes is caused by the interference phenomenon between light, substrate, and film interfaces medium. The absorption edge shifted to higher wavelength region with an increase in the fluence.

The absorption coefficient (α) provides the estimation of light absorbed by the film which was calculated by using T data by the formula [7],

$$\alpha = (1/d) \ln [(1/T)]$$

where d represents the film thickness (~800nm). The absorption coefficient increased with ion fluence as shown in fig.3(inset). The calculated ' α ' value is of the order of 10⁴ cm⁻¹ and decreased with wavelength. The effective bandgap of the studied films was calculated from Tauc relation as given by,

$$(\alpha h \nu)^{1/2} = B^{1/2} (h \nu - E_g)$$
 (2)

(1)

where h, v, E_g and B are the Planck's constant, frequency, optical bandgap, and Tauc parameter respectively. The extrapolation of the straight-line portion of the $(\alpha hv)^{1/2}$ vs photon energy (hv) gives E_g values of the corresponding films such as 1.01eV (5x10¹⁵ fluence), 0.92 eV (1x10¹⁶ fluence), 0.79 eV (5x10¹⁶ fluence) respectively. The reduction in E_g is due to the increase in localized states over the mobility gap. In other way, the increase in the carrier concentration as a consequence of ion irradiation reduces the bandgap values [2].This reduction of bandgap is well explained by Davis-Mott model [8]. The B^{1/2} represents the degree of disorder, which decreased from $333 \text{cm}^{-1/2} \text{eV}^{-1/2}$ (5x10¹⁵ fluence) to 264 cm^{-1/2} eV^{-1/2} (5x10¹⁶ fluence) with increase in fluence. This decrease shows the rise in the degree of disorder as Tauc parameter varies inversely with disorder.



Fig. 3. Optical transmission and ' α ' (inset) variation.

CONCLUSION

The above analysis shows the influence of low-energy proton irradiation on the structural, surface morphology and optical behavior of $Bi_5In_{30}Se_{65}$ thin film. Though the films are found to be amorphous with different fluence, but there is significant change in the optical bandgap and absorption values. The reduction in bandgap is due to the increase in density of defect states and decrease in optical transmittance is for the increase in lattice defects due to proton irradiation.

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Depth Profile Analysis of Gold Ions in Silicon <100> Substrate

Md. Akhlak Alam^{1, 2}, Ayushi Trivedi¹, and M. K. Tiwari^{1, 2*}

¹Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore, 452013 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400094

n Bhaona Fational Institute, Philippiakanagar, Manibar, 100

*Corresponding author: <u>mktiwari@rrcat.gov.in</u>

Abstract

Ion implantation is a popular method for introducing foreign species into a target material. It transforms the structural, optical, electrical, and magnetic properties of the target materials, resulting in the creation of a new material. The implantation of gold ions in silicon results in improved sub-band gap characteristics, which has a wide range of applications in the field of optoelectronic devices and infrared detectors. Miniaturization of semiconductor devices often necessitates an exact and precise depth distribution of implanted ions within the crystalline silicon substrate. In the present work, we have used a non-destructive approach to analyse the depth distribution of gold ions implanted in silicon <100> substrates using combined X-ray reflectivity and grazing incidence x-ray fluorescence measurements.

INTRODUCTION

Ion implantation is a procedure that allows a foreign impurity element (e.g. As, P, Al, In, B etc.) to be introduced into a target material in a controlled manner. The procedure enables creation of novel materials with modified physical and chemical properties [1]. The technique has a wide range of applications, the most prominent of which is in the fabrication of traditional semiconductor devices. Gold implanted crystalline silicon material offers sub-band gap properties that are widely used in the production of optoelectronic devices and tunable infrared detectors [2], operating at room temperature. Though the usage of gold is restricted in silicon based IC/CMOS devices yet it finds a few interesting applications. The performance of such devices is greatly influenced by the distribution of implanted ions as well as surface alterations generated by the incident energetic ions. We present a methodology for obtaining a reliable depth distribution profile of implanted ions using X-ray reflectivity (XRR) and grazing incidence angle X-ray fluorescence (GIXRF) investigations. We have also used atomic force microscopy (AFM) to examine the surface modifications of implanted silicon substrates.

EXPERIMENTAL

Single crystal p-type silicon <100> substrates of dimension $\sim10\times10$ mm² were implanted with Au⁻ ion fluence of 5×10^{16} ions/cm² at implantation energy of 80 keV. Ion implantation was performed at the inter university accelerator centre (IUAC), New Delhi. Implantation was performed at room temperature under vacuum environment of $\sim10^{-7}$ mbar, for the time duration of 5 hours. During the implantation, the

incident ion beam was fixed at 90° with respect to the sample surface and the beam current was limited to ~ $1 \mu m$.

incidence Grazing X-rav fluorescence measurements were performed at beamline BL-16 of Indus-2 synchrotrons facility [3]. An X-ray beam of energy of 15 keV, monochromatized by a double crystal monochromator, was used to excite the implanted samples. Beam size of incident X-ray beam was set to $\sim 0.1(v) \times 10(h)$ mm² and the fluorescence Xray emitted from the sample were recorded using a silicon drift detector system. In order to obtain the direct depth distribution of the implanted Au ions, spectrometry secondary ion mass (SIMS) measurements were performed using Hiden analytical SIMS instrument. During the SIMS investigations, primary ion beam of O_2^- comprising of size $30 \times 30 \,\mu\text{m}^2$ and energy of 5 keV was permitted to impinge on the implanted sample. The implanted samples were sputtered for time duration of 25 minutes under the vacuum of order 3.6×10^{-8} Torr.



Fig. 1. 2D ion distribution obtained from SRIM simulations.

RESULTS AND DISCUSSION

Prior to the ion implantation experiment, we performed calculations for stopping and range of ions in matter (SRIM) [4], to simulate the in-depth travel range of Au ions inside the Si substrate. We employed ~ 99999 incident gold ions with an implantation energy of 80 keV during the simulations. The distribution profile of the Au ions estimated from SRIM analysis is shown in Fig. 1. The projected range of Au ions was found to be ~ 39 nm. The SIMS measurements were also carried out to visualize the distribution of Au ions directly inside the silicon substrate. Normalized concentration profiles of Au atoms as a function of depth have been depicted in Fig. 2. As can be observed, the technique provides nearly identical distribution profiles that of obtained from the GIXRF technique.

During the GIXRF investigation, a thin film model was used to estimate the exact distribution profile of the implanted gold atoms inside the Si substrate. The implanted region was divided into 11 sub-layers, each with a thickness of ~ 10 nm. The effective electron density profile (EDP) of Au atoms was then calculated as a function of depth using the best fitted GIXRF data. The EDP profile of Au ions was eventually converted to the atomic concentration (atoms/cm³). To compare the findings of the two methodologies, normalized distribution profiles of Au atoms were obtained after dividing with their corresponding maximum values (refer to Fig.2). Further, from Fig. 2, it can also be noticed that the Au ions are located near to the substrate surface, with a peak depth of ~ 30 nm. This near surface distribution of Au ions mainly arises due to the strong amorphization of the crystalline silicon substrate. The high dose of Au ions has a strong effect on the crystallinity of Si material, converting it to an amorphous phase. This mechanism is also strongly influenced by the energy of the incident ions.



Fig. 2. Distribution profile of Au ions in Si substrate obtained from the GIXRF and SIMS measurements.

The two dimensional micrographs of the bare and implanted Si substrates obtained from AFM measurements are shown in Fig. 3. These images were generated by scanning ~ $5 \times 5 \mu m^2$ area of the Si substrate in tapping mode with a silicon cantilever (Keysight 5600LS) instrument. By comparing these figures, it can be noticed that there is significant surface alternation on top of the silicon surface due to ion implantation. The surface roughness value obtained from the AFM measurement was found to be in close agreement with the roughness value obtained using the GIXRF measurement.

CONCLUSION

It was realized that Au ion implantation in silicon exhibits near surface distribution and results in significant surface change, particularly at high ion dose and long implantation time period.



Fig. 3. 2D micrographs generated from AFM measurements. (a) For bare Si substrate and, (b) for Au implanted Si substrate.

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Structural and dielectric properties of SrSnO3 and SrSn0.98Ti0.02O3

Aditya Kumar¹, Nitish Kumar¹, Manoj K Singh¹, Upendra Kumar²*

¹Centre of Material Sciences, University of Allahabad, Prayagraj - 211002, Uttar Pradesh, India

²Department of Applied Sciences, Indian Institute of Information Technology (IIIT) Allahabad, Prayagraj-211015,

U.P. INDIA

*Corresponding author: <u>upendra.bhu512@gmail.com</u>

Abstract

The sample $SrSnO_3$ and $SrSn_{0.98}Ti_{0.02}O_3$ are synthesized using chemical route followed by heat treatment at 1173 K. Rietveld refinement analysis performed on XRD data of samples has been indicated that the samples are crystallized into orthorhombic phase under space group Pbnm. The lattice constants and X-ray density are decreased with Ti^{4+} . The dielectric properties indicate the existence of interfacial and orientation polarization in samples. The dielectric constant and tangent loss are found to be thermally stable up to 300°C that makes it potentially application for thermally stable capacitor and electrical device applications.

Bi-functional behaviour of ZnO/RGO/Au device: Photodetector as well as light induced memory device

Priyanka Banerjee¹ and P. Dey^{1,2*}

¹Department of Physics, Kazi Nazrul University, Asansol, W.B. 713340, India

²Center for Organic Spintronics and Optoelectronics Devices, Kazi Nazrul University, Asansol, W.B. 713340, India *Corresponding author: pujaiitkgp2007@gmail.com

Abstract

We have investigated photo-response as well as resistive switching behaviour in hybrid zinc oxide (ZnO)/reduced graphene oxide (rGO) bilayer thin film, prepared through sol-gel process on an ITO coated glass substrate under dark and illumination condition of light. It has been observed that impedance value decreases with the increase in light intensity. Real and imaginary part of impedance are observed to maintain saturation up to a knee frequency which decreases with further increase of frequency up to the highest experimental limit. These results indicate the higher generations of photo generated carriers at the interface between rGO and ZnO layer and an enhancement of the charge transport process due to the increment of the mobility of charge carriers in the system.

Introduction

Graphene is a monolayer of sp²-bonded carbon atoms with a two-dimensional having high carrier mobility and electrical conductivity, high optical transparency [1]. Zinc Oxide (ZnO) is a compound semiconductor with a wide and direct band gap of ~3.37 eV and large exciton binding energy of 60 MeV. Recently, researchers have focused on rGOmodified ZnO nanostructures for light detection. In this framework, we have fabricated ZnO/rGO bilayer thin film to investigate the electrical and optical effect [2]. The current voltage characteristics of the ZnO/rGO bilayer thin film indicated the significant photo response under the illumination of red laser light. This device also exhibited the resistive memory characteristics. Light dependent complex impedance spectra of the bilayer thin films have been carried out at room temperature (RT). The value of impedance is found to decrease with the intensity of light. So, ITO based ZnO/rGO bilayer thin film device exhibits photoresponsivity as well as resistive switching device.

Experimental Details

The ZnO/rGO thin film was synthesized employing chemical sol-gel process. 20 mg ZnO nano powder was dissolved in 10 ml ethanol solution at RT and stirred with a magnetic stirrer at 60°C for 2 hours. 50 mg graphene oxide (GO) was dissolved in 10 ml ethanol. The prepared GO solution was ultrasonicated for 2 hours at RT to obtain homogeneous solution. Then first ZnO solution was spin coated over the ITO coated glass substrate with 1000 and 3000 rpm for 10 s and 30 s, respectively. The ZnO coated substrate was then dried at 100°C for 10 minutes. Then, rGO solution was spin coated by same process. Finally, 10 nm gold (Au) electrode as an anode was deposited on the top of rGO film using shadow mask. ITO/ZnO/rGO/Au bilayer device was prepared.

I-V measurement has been performed using a source meter (model no-B2902A) under dark and illuminated conditions. For illumination, 650 nm red laser (Thor labs) has been used, and the red laser of intensity (5.44 mW/cm²). Photosensitivity has been carried out using a source meter (model no-B2902A) under dark and illuminated red laser light of intensity 5.44 mW/cm².

Results and Discussions

Current-Voltage (I-V) characteristics

The current-voltage (*I-V*) characteristics of ITO/ZnO/rGO/Au bilayer photodetector were first measured under dark condition and then under illumination of 650 nm red and white light at biasing sweep -0.5V to 0.5V and -1V to +1V, are shown in Figs.1(a) and (b). At dark condition slight non linearity has been observed and under the illumination of red laser light with power 5.44 mW/cm² clear non linearity is observed and the current is also found to increase. When the bias voltage is increased to 1V, electrical hysteresis has been observed which indicates the coexistence of its photo response as well as memory effect.

From *I-V* characteristics of ITO/ZnO/rGO/Au device, rectifying behaviour seems to be originated the Schottky junction between the ZnO and rGO.



Fig. 1. Current-voltage characteristic of the ITO/ZnO/rGO/Au bilayer photodetector under (a) dark condition, white light illumination and illumination of 650 nm red (5.44 mW/cm^2) and white light at bias sweep of (0.5 V). (b) dark condition and illumination of 650 nm red (5.44 mW/cm^2) and white light at bias sweep of (0.5 V).

Due to irradiation of white light valance electrons in ZnO were excited to the defect levels and electronhole pairs were formed. Then, generated electric field in ZnO/rGO layer separate electron-hole pair which reduces the gap between conduction and valance band. Consequently, photocurrent of ZnO/rGO bilayer structure significantly heightened likened to that from dark to red laser light illumination [3,4].

Light dependent Impedance Spectroscopy

The light vulnerable impedance spectra have been carried for ITO/ZnO/rGO/Au at RT. The variation of the impedance Z as a function of frequency, with the variable light intensities white light, red laser light of 6.4μ W/cm², 24.04 μ W/cm², 58.66 μ W/cm², 5436.61 μ W/cm² and dark are shown in the figs.2(a) and (b). It is very prominent that Z' is maximum in the law frequency range and found to decrease rapidly with the increase in frequency [5].



Fig. 2. Real and Imaginary part of impedance vs. frequency at different illuminations of red laser, white light and dark condition.

Conclusions

In summary, we have prepared ZnO/rGO bilayer thin film which shows its photo response characteristics as well as resistive switching behaviours and also an enhancement of the charge transport process due to the increment of the mobility of charge carriers in the system.

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Electric field-induced hysteresis observed in thiol-ene-epoxy based polymeric devices

Sonatan Das^{a†}, Akanksha Singh^b, V. Ramgopal Rao^{a,b}, Tapanendu Kundu^{a,c}

^aCentre for Research in Nanotechnology and Science, ^bDepartment of Electrical Engineering, ^cDepartment of Physics, Indian Institute of Technology Bombay, Mumbai 400076. India

Corresponding author: sonatan2010@gmail.com

Abstract

In this work, an off-stoichiometry thiol-ene-epoxy polymer based metal-semiconductor-metal device was fabricated on planar interdigitated electrodes. The presence of ferroelectric dipoles was observed at room temperature when electric field-assisted current-voltage (I-V) was measured. The hysteresis loop in I-V was measured to understand the effect of dipoles. The presence of ferroelectric dipoles in OSTE+ polymer is beneficial for memory applications.

Influence of Buffer Layer on Physical Properties of RF Sputtered ZnO:Mo Films on Flexible Substrate

Santanu Pal and Durga Basak*

School of physical sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata, 700032, India *Corresponding author: sspdb@iacs.res.in

Abstract

Mo doped ZnO thin films (MZO) have been prepared by RF sputtering technique on PET substrate to study the influence of substrate temperature and buffer layer on the physical properties. With an increase in the substrate temperature, the crystallinity of the films has been improved. All the films show average 85% transparency in the visible region. The buffer layer helps to grow the film along <002> orientation resulting in better electrical property with the lowest and stable sheet resistance of 760 Ω /sq.

Grain Size Dependent Thermoluminescence Characteristics Of Beta-Irradiated Diamond Films

K. Ganesan^{1,2,*}, N. Mohasin Sulthana^{1,2}, P.K. Ajikumar¹, O. Annalakshmi^{2,3}, G. Mangamma^{1,2} and S. Dhara^{1,2}

¹Surface and Nanoscience Division, ²Homi Bhabha National Insitute, ³Envirnmental Assessment Division, Indira Gandhi Centre for Atomic Research, Kalpakkam - 603102, Tamil Nadu.

*Corresponding author: kganesan@igcar.gov.in

Abstract

We report on the effect of grain size on the thermoluminescence (TL) characteristics of diamond films. The diamond films with different grain sizes in the range of 0.02 - 1.5 μ m are grown by hot filament chemical vapour deposition. The graphitic carbon content in the diamond films increases with reduction in grain size as evidenced by Raman spectroscopy. Upon beta-irradiation, the TL glow curves of these diamond films display two prominent peaks ~ 100 and 290 $^{\rm O}C$ corresponding to two different trap and recombination centers. The TL characteristics are discussed in terms of structural defects in diamonds.

Development of CsI (Tl) Coupled GaAs Detector for γ-ray Detection

Payal Taya¹, Geetanjali Vashisht^{1,2}, S. K. Khamari¹, G. Haridas³, Mohit Tyagi^{2,4}, V. K. Dixit^{1,2}, and T. K. Sharma^{1,2}

¹Semiconductor Materials Lab, Materials Science Section, RRCAT, Indore 452013,
 ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094,
 ³Health Physics Unit, Indus Operations Division, RRCAT, Indore 452013,
 ⁴Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400085.

*Corresponding author: payaltaya@rrcat.gov.in

Abstract

In this work, the performance of an indigenously developed γ -ray detector is presented. The detector consists of a CsI (Tl) single crystal scintillator optically coupled to GaAs photodiode. The single crystal of CsI (Tl) and GaAs photodiode structures are grown by Bridgman technique and MOVPE respectively. The measured optical response of the individual components confirms their suitability for device integration. At 300K, measured dark current of the developed detector is 1.14 nA. Exposure to a γ -photon flux of 10^7ph/s/mm^2 on CsI (Tl) led to the generation of 10^{11}ph/s/mm^2 visible photons of 2.27 eV which produced nearly 32.44 nA electrical signal at an applied reverse bias of 3V.

Introduction

With the advent of nuclear science and technology, there exists a need for robust radiation detection systems for a wide variety of ionizing and nonionizing radiations. Such detectors find important applications in synchrotron facilities, nuclear reactors, and medical imaging etc. Although, Si & Ge have been established as detection standards for y-ray spectroscopy but their field applications are impeded by the need for bulky cryogenic cooling systems and inferior radiation tolerance. Compound semiconductors have advantage over their elemental counterparts since their bandgap and electrical properties can be tuned as per the desired applications. The basic properties to be considered while choosing a semiconductor that would serve as a γ -ray detector are mainly, atomic number and bandgap of the material. Out of possible compound semiconductor materials configurations available for γ -ray detection, a scintillator coupled to semiconductor offers several advantages including compact size, room temperature operation, radiation tolerance and excellent quantum efficiency. In this article, the development of an indigenous γ -ray detector consisting of CsI(Tl) scintillator which is optically coupled to GaAs detector is reported. Subsequently, the bias dependent electrical signal of the developed detector is measured.

Experimental Details

Growth conditions: The GaAs based multilayer epitaxial structure was grown on n⁺-GaAs substrate by AIX200 Metal Organic Vapour Phase Epitaxy. In this technique, tri-methyl gallium and arsine were used as

precursors for growing GaAs layers while silane and diethylzinc were used for n and p-type doping respectively. The detector structure consists of an undoped 5.5 μ m thick intrinsic layer embedded between a 600 nm n-type (1x10¹⁸/cm³) and 20 nm p-type (2x10¹⁸/cm³) GaAs layers. Furthermore, the single crystal CsI(Tl) which is the main scintillating material was grown by Bridgman technique at Technical Physics Division, BARC.



Fig. 1. (a) Schematic diagram of the p-i-n layer structure. (b) Energy band diagram of the GaAs p-i-n structure, simulated by using BandEng software.

Energy band diagram: The energy band diagram for p-i-n structure is shown in Fig. 1(b). It also provides a schematic representation of how photogenerated charge carriers would navigate inside the depletion region under the effect of internal electric field.

Device fabrication: The photodetector was fabricated by implementing several device processing steps. Initially, thermally evaporated Au-Ge/Ni/Au multilayer for n-electrode formation is deposited. Next, the active area of detector was defined by photolithography process. Furthermore, 120 nm SiO₂ layer was deposited by e-beam evaporation for surface passivation, which also served as an anti-reflection coating. Now, Ti/Pt/Au multilayer was deposited on top p-layer for p-electrode formation, followed by metal lift-off and rapid thermal annealing. For efficient coupling of scintillator with the active area of detector, a distinct annular ring geometry was chosen with extended contact-pads, enabling adequate placement of crystal. This completed the fabrication of a single detector chip, followed by bonding of 25µm thick Au wire by ball-wedge bonding and then mounted on an indigenously designed Teflon header.

Device testing: The response of the scintillatordetector assembly was measured using Keithley-2450 source measure unit, while irradiating the device with 333 GBq ⁶⁰Co source in the Radiation Instrument Calibration Facility at RRCAT. The device was placed in a manner so that the active area of device was entirely exposed to the γ -rays emanating from source.

Results and Discussion

The interaction of γ -photon with matter predominantly occurs via three mechanisms i.e. photoelectric absorption, Compton scattering, and pair production. When γ -rays are incident on the CsI(Tl) scintillator, the high energy photons cause ionization, atoms are excited to higher energy states followed by relaxation and emission of visible photons. The trace amounts of impurity atom (Tl) intensify the emission of visible photons which are easily absorbed by the GaAs detector. It is then optically coupled to the active area of detector. Moreover, the scintillation photons incident on the GaAs detector further generate electron-hole pairs inside depletion region of device which is then measured as an electrical signal.



Fig. 2. (a) Schematic diagram of the γ -ray detection process in Scintillator-GaAs detector, (b) Photograph of the scintillator-detector assembly, (c) Spectral overlap of CsI(Tl) scintillator's emission profile with the photoresponse of the GaAs detector, inset shows photograph of the scintillator emission upon interaction with high energy

photons, (d) Response of the scintillator coupled GaAs detector upon exposure to 333 GBq $^{60}\mathrm{Co}$ source.

In such detection applications, one of the foremost requirements for efficient detection of γ -rays is the spectral overlap of the scintillator's emission band with the spectral photo-sensitivity of the detector material. Fig. 2(c) shows the scintillation spectrum of CsI(Tl) crystal peaking at 545 nm and photosensitivity of the detector is significant in the range 450-870 nm. An appreciable spectral overlap of the CsI(Tl) scintillator's emission profile with the spectral photo-sensitivity of the GaAs confirms their suitability for the measurement of γ -radiation. One of the most important parameters for the qualification of any photosensitive device is dark current (I_0) which was 1.14 nA at 300K. For an incident γ -photon flux of the order of 10⁷ph/s/mm² and CsI(Tl) crystal having scintillation yield of 65 ph/keV, 10¹¹ photons/sec of energy 2.27 eV are generated. Considering that the full energy of scintillation photons is absorbed inside GaAs detector, the upper-limit on the photogenerated current would be approximately

 $I_{ph} \approx nE\mathcal{R} \approx (7 \times 10^{11} \text{ s}^{-1})(2.27 \text{ eV})(0.5 \frac{\text{A}}{\text{W}}) \approx 127 \text{ nA}$ where n is number of photons incident per second, E is energy of one photon and \mathcal{R} is the responsivity of detector. Since, complete absorption of the incident photons is not practically possible, a slightly lower value of photogenerated current is observed in real devices. Furthermore, these scintillation photons are optically coupled to the GaAs detector and biasdependent response is measured. At zero bias, output current (I-I₀) of 1.74 nA is measured, upon irradiation. The output current increases to 32.44 nA at -3V because intrinsic region gets more depleted as reverse bias is increased as shown in Fig. 2(d).

Conclusion

In conclusion, room temperature coupled scintillatorsemiconductor detectors are ingeniously developed and the detection of γ -rays is successfully demonstrated with a good signal to noise ratio. This detector along with a custom made preamplifier can be used in γ -ray spectroscopy and also for the detection of high-energy charged particles.

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Temperature Dependence Of Band Gap Of β-(Al_xGa_{1-x})₂O₃ Alloys From Optical Reflectivity

Jayanta Bhattacharjee^{1,2*}, and S. D. Singh^{1,2}

¹Synchrotron Utilization Section, Raja Ramanna Centre For Advanced Technology, Indore, 452013 ²Homi Bhabha National Institute, Anushakti Nagar, Mumbai, 400094

*Corresponding author: jayanta@rrcat.gov.in

Abstract

Band gap variation of β -(Al_xGa_{1-x})₂O₃ alloys with temperature has been studied to investigate the electron-phonon interactions. The obtained value of mean phonon temperature lies in between 473 K - 488 K, which corresponds to the involvement of phonons mainly related to deformation of [GaO₄]/ [AlO₄] tetrahedrons and [GaO₆]/ [GaO₆] octahedrons (300-500 cm⁻¹) group.

Introduction

 β -Ga₂O₃ has wider band gap (~4.8 eV), high breakdown voltage (~8 MV/cm), larger dielectric constant (~10), and moderate electron mobility (~300 cm²/V-s). These remarkable physical properties make β -Ga₂O₃ a potential candidate for UV detector and other high-power devices.¹ The absorption edge of β -Ga₂O₃ has been tailored to deep UV by substituting Al atoms.¹ The temperature dependence of the band gap for a semiconductor provides information about electron-phonon (e-ph) interactions, which are mainly responsible for the carrier dynamics. There is no information available in literature regarding e-ph interactions for β -(Al_xGa_{1-x})₂O₃ alloys. This has motivated us to determine the band gap of β -(Al_xGa₁- $_{\rm X})_2O_3$ alloys as a function of temperature from optical reflectivity (OR) and obtain the information regarding the e-ph interactions.

Experimental details

 β -(Al_xGa_{1-x})₂O₃ alloy samples with two Al compositions x=0 and x=0.35 were prepared using solid state reaction method as reported elsewhere.² The unpolarized light from deuterium (D₂) lamp was dispersed using a monochromator of focal length 320 mm with grating having groove density of 2400 lines/mm. Dispersed light was chopped at a frequency of 190 Hz. The reflected light from the sample was measured using lock-in technique with PMT as the detector. The samples were mounted in a Close Cycle Refrigerator for temperature dependent (10 K to 300 K) OR study.

Results and discussions

The β -(Al_{0.35}Ga_{0.65})₂O₃ alloy is found to be in single phase with monoclinic crystal structure similar to that of β -Ga₂O₃ as confirmed from x-ray

diffraction experiments reported elsewhere.² The OR spectra measured at 10 K for β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ have been shown in Fig. 1(a). In addition to defect related features appearing at 3.2 eV, 3.7 eV and 3.9 eV, a sharp feature observed at 4.8 eV in the OR spectrum of β -Ga₂O₃. This can be related to



Fig. 1. (a) Optical reflectivity (OR) spectra for β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ at 10 K (b) OR spectra for β -(Al_{0.35}Ga_{0.65})₂O₃ at different temperatures.

the absorption edge of β -Ga₂O₃ as its energy position is in corroboration with the reported value of the band gap of β -Ga₂O₃.^{1, 2} It is also noted that the band edge related feature blue shifts for β -(Al_{0.35}Ga_{0.65})₂O₃ sample confirming its assignment to the band edge feature of β -(Al_xGa_{1-x})₂O₃, because the band gap of the alloy is known to increase with Al substitution.² The band gap has been determined by fitting the numerically calculated derivative of OR spectra with Aspen's line shape function of the following form.³

$$\frac{dR(E)}{dE} = R_x Re \left[\frac{e^{i\theta} \{E_x - E + i\Gamma_x\}^2}{\{(E_x - E)^2 + \Gamma_x^2\}^2} \right]$$
(1)

where R_x , θ , E_x , E, and Γ_x correspond to the amplitude, phase factor, band gap energy, incident photon energy and broadening parameter of the band edge feature respectively. The values of band gap at 10 K for β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ are thus determined to be 4.81 eV and 5.40 eV, respectively.

The temperature dependent OR spectra from one alloy sample with Al composition of x=0.35 is shown in Fig. 1(b) as a representative. The absorption edge is found to red shift and broadens with increasing temperature, which is a typical characteristic of a semiconductor material. This has been attributed to the e-ph interactions.⁴ The band gap values as a function of temperature have been determined from



Fig. 2. Band gap (symbols) as a function of temperature for β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ samples as well as fitted data using equation (2) shown

the fitting of numerically calculated derivative of OR spectra with equation (1), which are plotted in Fig. 2 as shown by solid symbols. The two samples show usual red shift with increase in temperature. In order to determine the parameters of the e-ph interactions like mean phonon temperature (θ_B) and strength of e-ph interaction (a_B), the temperature dependent band gap is fitted with Bose-Einstein (BE) empirical relation of following form⁴

$$E_g(T) = E_B - a_B \left(1 + \frac{2}{\exp\left(\frac{\theta_B}{T}\right) - 1} \right) \quad (2)$$

where, $E_B - a_B$ is the bandgap energy at 0 K, a_B is the strength of e-ph interaction, θ_B is the mean phonon temperature and T is the temperature of measurement. The temperature dependent band gap of β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ have been fitted with BE equation (2), where the fitted data has been shown by the solid line in Fig. 2 and the corresponding values of fitted parameters have been listed in the Table 1. For β -Ga₂O₃, the mean phonon temperature θ_B is obtained to be 488 K, which corresponds to phonons with average energy of ~42 meV (~336 cm⁻¹). Three

different groups of phonons like libration and translation of [GaO₄] chains (100-200 cm⁻¹), deformation of [GaO₄] tetrahedrons and [GaO₆] octahedrons (300-500 cm⁻¹), and stretching and bending of [GaO4] tetrahedrons (> 500 cm⁻¹) have been reported in the Raman spectrum of β-Ga₂O₃.⁵ The value of θ_B for β -Ga₂O₃ corresponds to the involving deformation phonons of [GaO₄] tetrahedrons and [GaO₆] octahedrons (300-500 cm⁻¹) group. Thus, these phonon modes are found to be mainly interacting with the electrons. The value of $\theta_{\rm B}$ does not show any appreciable change with Al substitution. However, the strength of e-ph interaction shows a slight decrease with Al substitution. Hence, it can be concluded that the similar phonon modes interact with electrons for β- Ga_2O_3 and β -(Al_{0.35}Ga_{0.65})₂O₃ samples. However, the strength of e-ph interaction for β -(Al_{0.35}Ga_{0.65})₂O₃ is slightly lower than that for β -Ga₂O₃.

Table 1. Fitting parameters for different samples.

X	$\theta_{\rm B}({\rm K})$	$a_{\rm B}({\rm eV})$
0.00	488 ± 57	0.50 ± 0.10
0.35	473 ± 25	0.33 ± 0.04

Conclusion

The temperature dependent band gap of β -Ga₂O₃ and β -(Al_{0.35}Ga_{0.65})₂O₃ alloy are measured using optical reflectivity at various temperatures. The determined values of mean phonon temperature suggest that the phonons modes involving deformation of [GaO₄]/[AlO₄] tetrahedrons and [GaO₆]/[AlO₆] octahedrons mainly interact with the electrons. Additionally, the strength of e-ph interaction for β -(Al_{0.35}Ga_{0.65})₂O₃ is found to be slightly lower as compared to that of β -Ga₂O₃.

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Transfer Matrix Method for Reflectivity Simulation of Distributed Bragg Reflector (DBR)

Deepali Keskar¹, Sandesh Jaybhaye², Madhavi Thakurdesai¹

¹Thin Film Research Laboratory, Department of Physics, B.K. Birla College (Autonomous), Kalyan ²NTRL, Department of Chemistry, B.K. Birla College (Autonomous), Kalyan

*Corresponding author:madhavi.thakurdesai@bkbirlacollegekalyan.com

Abstract

Distributed Bragg Reflector (DBR) is multilayered structure comprising materials having different refractive indices. Reflectivity of DBR depends on the difference between the refractive indices (RI). Therefore, selection of suitable materials is challenge in construction of DBR. In this paper reflectivity of DBRs constructed using various II-VI compound semiconductors is simulated using Transfer Matrix Method (TMM). The simulation is carried out for ZnTe/ZnSe, ZnTe/CdSe, ZnTe/CdTe, ZnSe/CdSe, CdTe/ZnSe using MATLAB software. The reflectivity is simulated for 20 periods and at an incident angle of 0° and 45°.

Introduction

Recently lot of research has been carried out in developing Distributed Bragg Reflector (DBR). DBR exhibits very high reflectivity in comparison with metallic mirrors. Therefore, DBR is widely used in the field of optoelectronic devices such as Novalux Extended Cavity Surface Emitting Lasers (NECSEL), Vertical Cavity Surface Emitting Laser (VCSEL), Light Emitting Diode (LED), semiconductor microcavities, Fabry-Parrot modulator resonant cavity etc. [1-2]. Semiconductor based DBR is a multi-layered structure of materials having low and high refractive indices (RI). Many researchers have explored various combination of compound semiconducting materials from III-V group such as GaAs/AlAs, AlAs/InAs, GaAs/InAs, GaAs/GaSb, GaSb/InSb, InAs/InSb, InAs/InP, InSb/InP to construct high reflectivity DBR [3]. However, it has been reported that DBR based on III-V group shows minimal light absorption in the visible region [4]. Therefore II-VI compound semiconductors are recently explored to construct DBR. This DBR exhibits absorption in yellow wavelength range therefore can be used in the field of data transfer, adoptive optics astronomy, medicine etc. [5].

Theory

DBR consists of multi-layered stack of alternating high and low RI materials. Difference in RI of materials used in DBR determines width of stopband. Stopband is a band at which light is forbidden to pass through DBR. Thickness of each layer in the stack is quarter to wavelength of light used. A schematic diagram of typical DBR consisting of N layers is shown in Fig.1, where n_H , n_L , n_S , n_o , t_H , t_L are high RI, low RI, RI of substrate, RI of incident medium,



Fig.1 Schematic of DBR

thickness of high RI material, thickness of low RI material respectively. When light is incident on multilayer stack of DBR it undergoes reflection from each interface with phase change of π . The thickness of both the materials used is chosen to be $t = \frac{\lambda}{4n}$. As a result, reflected light gives constructive interference. Reflectivity of DBR depends on various parameter like angle of incidence, periods(pair of layers), sequence of layer, incident medium and mainly material used etc [5].

Transfer Matrix Method

As the number of layers in DBR are large, reflectivity calculation is done using Transfer Matrix Method (TMM). [6]. The characteristic matrix M for two different layers is given by 2×2 matrices which is as follows

$$M_{1} = \begin{bmatrix} \cos\phi_{1} & \frac{i\sin\phi_{1}}{\mu_{1}} \\ in_{1}\sin\phi_{1} & \cos\phi_{1} \end{bmatrix}$$
(1)
$$M_{2} = \begin{bmatrix} \cos\phi_{2} & \frac{i\sin\phi_{2}}{\mu_{2}} \\ in_{2}\sin\phi_{2} & \cos\phi_{2} \end{bmatrix}$$
(2)

Where μ_1 , μ_2 is optical admittance and ϕ_1 , ϕ_2 are phase change for each layer respectively. For periods 'N', characteristic matrices is given by equation 3 [7]

$$M = (M_1 M_2)^{N/2}$$
(3)

reflectivity R of DBR is given by $R = |r|^2$

Where
$$r = \frac{\mu_{sub}[M_{11} + (M_{12} \times \mu_{sub})] - [M_{21} + (M_{22} \times \mu_{sub})]}{\mu_{sub}[M_{11} + (M_{12} \times \mu_{sub})] + [M_{21} + (M_{22} \times \mu_{sub})]}$$

For simulation of reflectivity MATLAB software is used.

Reflectivity simulation of II-VI compound semiconductor based DBR

The reflectivity of five types of DBRs based on II-VI compound semiconductor simulated for 20 periods at wavelength of 570 nm for 0° and 45° incident angle. Figure 2 and Figure 3 shows the reflectance of 5 combinations chosen. Our simulation result indicates that the reflectivity of ZnTe/ZnSe, ZnTe/CdSe, CdTe/ZnSe is more than 99% for both the incident angles (Table.1). The reflectivity of ZnSe/CdSe combination is found to be 15% and 38.6 % at incident angle 0° and 45° respectively. Stop band shifts slightly towards the lower wavelength when angle of incident is 45° for all the combinations.







Fig. 3. Reflectivity Vs wavelength for various combination used for 20 periods and incident angle 45°

Table 1.	Reflectivity (R) For Different DBRs With	l
Incident	Angle 0° and 45° for 20 Periods at 570nm.	

mendent Angle 0 and 45 101 201 chods at 570mm.				
Material	'R'at 0°	'R' at 45°		
ZnTe/ZnSe	99.54%	99.50%		
ZnTe/CdSe	99.70%	99.68%		
CdTe/ZnSe	99.24%	99.04%		
ZnTe/CdTe	18.4%	65.53%		
ZnSe/CdSe	15%	38.6%		

Conclusion

The simulation study indicates that DBRs constructed using ZnTe/ZnSe, ZnTe/CdSe, CdTe/ZnSe exhibit high reflectivity (greater than 99%) for 20 periods and at angle of incidence 0° and 45°. ZnSe/CdSe and ZnTe/CdTe exhibit low reflectivity at both the incident angles therefore these combinations are not desirable for DBR construction.

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Study of Thermal Decomposition of Sb₂Se₃ Crystal

H. M. Patel^{1,2}, S. P. Sikligar¹, P. D. Patel¹, P. B. Patel², H. N. Desai², J. M. Dhimmar¹, B. P.

Modi^{1*}

¹¹Department of Physics, Veer Narmad South Gujarat University, Surat,395007 ² C. B. Patel Computer College and J. N. M. Patel Science College, Bharthana, Surat

*Corresponding author: <u>bharatpmodi@gmail.com</u>

Abstract

Sb₂Se₃ crystal has been grown by direct vapour transport (DVT) technique. The elemental composition of the grown crystal was analysed by energy dispersive X-ray analysis (EDAX). The kinetic decomposition parameters of the crystals have been studied by thermogravimetric analysis (TGA). The TGA thermogram shows single stage decomposition. The activation energy of kinetic degradation has been determined by Broido, Coats-Redfern and Horowitz-Metzger approximation methods. The analysis shows that the grown crystals have excellent thermal stability and it is also applicable in thermoelectric generator.

Introduction

 V_2 -VI₃ group semiconductor compounds are nontoxic and earth-abundant materials with high absorption coefficient [1]. Also, Antimony selenide (Sb₂Se₃) is a wide band gap semiconductor with orthorhombic crystal structure [2]. So, it is widely used in photo detector as well as is viable for thermal applications.

Here, Antimony Selenide (Sb₂Se₃) crystal was grown by direct vapour transport (DVT) technique. The elemental composition was analysed by EDAX. TGA has been used to study the thermal stability of material for device fabrication within definite temperature range. The percent weight loss and degradation kinetics of the grown crystals have been studied to evaluate activation energy and thermal stability.

Methodology

DVT technique was used to grow Sb₂Se₃ crystal in a dual-zone furnace. Selenium (Se) and antimony (Sb) (4N pure) powders were mixed and sealed in a cleanse quartz ampoule at a pressure of 10^{-6} mbar. The ampoule was placed in a dual-zone furnace, and the temperatures of the hot and cold zones were elevated to 650°C and 570°C, respectively, at a rate of 0.5°C/min. This process was continued for 48 hours. Finally, the temperature of the furnace was reduced to room temperature at a slow rate (0.5°C/min). After the growth process, black-grey, shiny and needle-like crystals were obtained. The grown single crystals were used for compositional and thermal analysis. The elemental composition of grown crystals was studied by EDAX (JEOL JSM-5610 LV). The TGA curve was recorded from 25 °C to 950 °C at a heating rate of 10 °C/min in inert N₂

atmosphere using Pyris-6 TGA Perkin-Elmer control unit.



Fig. 1. TGA curve for Sb₂Se₃ crystal

Results and discussion

The atomic % of grown crystal along with standard values shown in bracket are Sb: 38.81% (40%) and Se: 61.19% (60%). The data clearly states that the DVT grown Sb₂Se₃ crystals are nearly stoichiometric and free from impurity. The TGA thermogram for Sb₂Se₃ is shown in Fig. 1. revealed the total weight loss (Δ m). The TGA curve confirm that the grown crystal is stable between 25 °C and 570 °C. After that, the material begins to decompose and lose weight. The kinetic parameter was calculated from the maximum weight loss seen between 600 °C and 950 °C in the TGA curve by the standard relations; Broido [3], Coats-Redfern (C-R) [4] and Horowitz-Metzger (H-M) [5]. In these

models, the fractional weight loss (α) of the samples can be determined as follows;

$$\alpha = \frac{W_T - W_F}{W_0 - W_F} \qquad a)$$

Where, W_0 , W_T , W_F are the initial weight, weight at temperature T and final weight respectively. In the Broido model, the thermal activation energy (E_{TH}) related to respective stage was determined using the following equation;



Fig. 2. (a) Broido plot (b) C-R plot (c) H-M plot for Sb₂Se₃ crystals

$$ln\left[-ln(1-\alpha)\right] = -\frac{E_{TH}}{RT} + C \qquad b)$$

Where, $(1-\alpha)$ is the weight of the residual materials, T is the temperature and R is the gas constant with a value of 8.314 J/K mol. The value of E_{TH} can be determined from the plot of $\ln[-\ln(1-\alpha)]$ versus 1/T, as shown in Fig. 2 (a). The obtained value of E_{TH} is 235 kJ/mol.

Coats and Redfern calculated the activation energy (E_{TH}) using the following relationship;

$$ln\left[-\frac{ln(1-\alpha)}{T^2}\right] = ln\left[\frac{AR}{\beta E_{TH}}\left(1-\frac{2RT}{E_{TH}}\right)\right] - \frac{E_{TH}}{RT} \quad c)$$

Where, A and β are the frequency factor and heating rate, respectively. The slope of ln[(-ln(1- α))/T²)] versus 1/T gives activation energy as shown in Fig. 2(b). The calculated value of E_{TH} is 254 kJ/mol. According to Horowitz-Metzger model, activation energy is obtained by the following equation;

$$ln\left[ln\left(\frac{W_{0}}{W_{T}}\right)\right] = -\frac{E_{TH}\theta}{RT^{2}} \qquad d)$$
$$= -\frac{E_{TH}(T-T_{s})}{RT^{2}}$$

Where, T is the peak temperature and T_s is the temperature of particular weight loss; also, $\theta = T-T_s$. The plot of $\ln[\ln(W_0)/(W_t)]$ verses θ gives an estimate to a straight line as shown in Fig. 2(c). The slope of this plot gives the activation energy having value of 149 kJ/mol. High activation energy leads to better thermal stability [6].

Conclusion

The DVT method has been successfully employed to grow high-quality crystals of Sb₂Se₃. The TGA curve characteristics indicates that the decomposition takes place in single stage. The obtained value of activation energy is close to each other point out the good thermal stability of the grown crystals. Therefore, Sb₂Se₃ crystal can be utilized to high performance of various thermoelectric devices with suitable thermal stability.

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Role of precursor parameter on structural and optical studies of sol-gel grown GaN

P. Muzammil¹, S. Munawar Basha², and G. Shakil muhammad³

^{1,3}Department of Physics, Islamiah College (Autonomous), Vaniyambadi, Tamil Nadu, India. 635752. ²Department of Physics C. Abdul Hakeem College (Autonomous), Melvisharam, Tamil Nadu, India

*Corresponding author: muzammil.p@hotmail.com

Abstract

GaN has been grown by varying precursor concentrations using the sol-gel technique. The influence of varying concentrations on structural, morphological, and optical characteristics was studied. X-ray diffraction and Transmission Electron Microscopy shows the wurtzite structure and highly crystalline nature of the GaN nanostructure. SEM image shows the hexagonal structure for lower concentrations and nanorod for 1M concentration. The photoluminescence study shows the optical band gap of 3.3 eV to the grown GaN nanostructure.

Introduction

Gallium nitride (GaN) semiconductors have acquired much attention in academic and found commercial interest due to their exceptional physical properties at room temperature such as direct bandgap of 3.39 eV, strong bond strength, high thermal and chemically stability, high electron drift velocity makes it a promising material for power applications[1]. High optical transition probability makes the material ideal for optoelectronic devices operating in the ultraviolet region[2]. GaN nanostructures such as nanorods, nanofibers are an intrinsically attractive material for nanoscale electronic and optoelectronic devices as they possess a large surface to volume ratio. Various techniques have been employed for the synthesis of one dimension GaN nanostructure such as nanorod and nanobelt. Lei Zhang et al., grown free standing, large area single crystalline GaN membranes by a single step high temperature method and fabricated the GaNPM based supercapacitor which shows excellent electrochemical performances [3]. Tae-Hee Kim et al., synthesized GaN in powder form using a thermal plasma process. Additionally, melamine was used to avoid the oxidation of the source material. It was observed that the joint process of thermal plasma and annealing treatment enhanced the structure quality of grown GaN nanopowder with an average crystallite size of 30 nm[4]. In order to understand the effect of different precursor concentrations, we synthesize GaN for a different mole of precursor say 0.25M, 0.5M, and 1M using the sol-gel technique.

Experiment

Required amount of Gallium (III) nitrate hydrate (Ga $(NO_3)_3$. xH_2O) dissolved in deionized water and

PVP (Polyvinylpyrrolidone) solution was prepared separately. The gallium nitrate solution was added to generate a homogeneous and clear precursor solution after stirring constantly for 24 hrs. The obtained solution was calcined in the air for three hours at 500°C. The resulting product was placed in the quartz reactor for ammonization. The liquid ammonia was carried to the reaction zone using nitrogen gas, and the flow rate was kept constant for 6 hours while the temperature was maintained at 950°C. The system was gradually cooled to room temperature in the nitrogen atmosphere after the synthesis was completed [5]. The obtained powders were subjected to structural and optical characterizations.

Result and Discussion

X-ray diffraction



Fig. 1. XRD pattern for three different moles of precursor

The X-ray diffraction peak reveals the hexagonal wurtzite structure of GaN, which agrees well with the JCPDS data. It is observed that the peak intensity increases when the precursor concentration varies from 0.25 M bto 1 M, from this it is evident that the crystal quality of the grown GaN increases with the mole concentrations of precursor. The crystallite size of the grown GaN is about 23nm for 0.25 M, 21 nm for 0.5M, and 26nm for 1M precursor concentration.

SEM Analysis



Fig.2. SEM image for two different moles of precursor

(a) 0.25 mole (b) 1 mole

The SEM images of the synthesized GaN nanostructure are shown in figure 2. It appeared that hexagonal shape like grains with different sizes (larger than 1μ m) formed for 0.25 and 0.5 mole concentration, But for 1M concentration of GaN, the morphology changed to the plain nano rod like structure with different orientations. Lower precursor concentration results in hexagonal like shapes with limited dimension compare to higher precursor concentrations for which nanorod with width above 200 nm and length of 3μ m were obtained.

Transmission Electron Microscopic Analysis



Fig.3. HRTEM image of 1 M concentration of GaN, the inset figure shows SAED pattern of GaN.

TEM image with SAED pattern of GaN nanostructure confirms the polycrystalline nature of GaN. It's found that the lattice separation of 2.79 Å corresponds to (101) interplanar distance slightly decreases due to compressive stress as the molar concentration increases from 0.25M to 1M.

Photoluminescence Study



Fig. 4. Room temp. PL spectrum of 1M Concentration of GaN nanostructure.

Room temperature PL spectra exhibit two major peaks. The lower intensity peak related to the direct bandgap emission located at the wavelength 368 nm corresponds to the hexagonal structured GaN. Emissions from (~480 nm) are due to some other transition, which depicts the defects in the powder form of GaN nanostructures.

Conclusion

GaN nanostructure was synthesized by varying precursor concentrations using the sol-gel method. The XRD result exhibits the high crystalline nature of the GaN structure. FESEM image corroborates the honeycomb and one dimensional nanorod structure. HRTEM image exhibit wurtzite structure with polycrystalline nature The bandgap of the grown GaN was obtained using Photoluminescenes at room temperature, Thus, it is concluded that the different mole of precursor determines the quality of GaN nanostructure.

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Micro Raman Studies on HVPE Grown GaN epi-layers Irradiated with Light Ions

P Atheek¹, P Puviarasu^{2*}, S Munawar Basha³ and MD Kannan⁴

^{1, 2, 4}Department of Physics, PSG Collge of Technology, Coimbatore, 641004.

³Department of Physics, C Abdul Hakeem College, Melvisharam, 632509.

*Corresponding author: puv.phy@psgtech.ac.in

Abstract

The hydride vapor-phase epitaxy (HVPE) grown GaN epi-layer was irradiated with 100 MeV O⁷⁺ for different fluences. In this paper, the structural aspects of pure and irradiated sample has been investigated using micro Raman Spectroscopy by the Lorentz peak fitting method. The allowed Raman modes E_2^H and A₁ (LO) for wurtzite structure is observed for all the samples. The Carrier Concentration (n), biaxial stress (σ) are calculated for the pure and irradiated samples and the results are compared. On increasing the fluences the carrier concentration increased and the biaxial stress decreased. The wurtzite structure of GaN has been ascertained from the X-ray diffraction (XRD) analysis though it was found that the intensity of the peak reduced for their irradiated sample.

Introduction

In Group III - Nitride materials Gallium Nitride (GaN) is one of the best material to use in the space for solar cells. LED's and high temperature electronics because of its wide band gap (3.4eV), high breakdown voltage (3 Mev cm⁻¹), thermal stability and other properties. In space application, there are lot of high energy radiation which can affect the properties of materials and thereby affecting its desired application. Hence, it's important to study the irradiation effect on the application material to analyze the defect creation. GaN films has been grown by various method like Metal-Organic Chemical Vapour Deposition (MOCVD)¹, Molecular-Beam Epitaxy (MBE)², high-pressure solution growth (HPSG)³ and are studied by exposing to different ion irradiations. As per the knowledge of authors, the effect of ion irradiation on HVPE grown film has not been extensively studied yet. In this paper, the HVPE grown thin film were irradiated with 100MeV O⁷⁺ ions by varying ion fluences. The bombarded ion can create stress in the film by removing nitrogen or gallium ions. Raman spectroscopy is one of the useful technique to study the strain related phenomena and to find the crystallite quality. In the current report, the biaxial stress(s) and carrier concentration (n) were calculated from the Raman spectra

Experimental Methods

The samples were grown by HVPE method on the sapphire (Al₂O₃) substrate and irradiated with 100 MeV O^{7+} ions by 1×10^{12} and 1×10^{13} fluences at room temperature. The material's crystallite structure was confirmed by Empyrean, Malvern Panalytical X-ray

Diffraction instrument by Cu k_{α} source, the micro Raman studies were taken by "WiTech alpha 300" at room temperature.

Results and Discussion



Fig. 1. XRD Pattern of pure and irradiate with 1×10^{12} and 1×10^{13} fluences.

Fig.1 shows XRD graph for the pure and irradiated samples. The crystallinity grown in the unique c-direction as shown by (0002) and (0004) planes confirms the wurtzite structure of grown film. After irradiation, the crystal structure has not changed. Instead, the intensity of (0002) peak and (0004) peak has decreased. The substrate peak intensity almost suppressed after irradiation. This may be due to the destruction of Al₂O₃ in the interface area of GaN-Al₂O₃ which could lead to the formation of other compound like aluminium nitride (AlN).

Fig.2 shows the Raman spectrum of pure and irradiated samples. The allowed frequencies of E_2^{H} and A_1 (LO) were present in both pristine and irradiated samples.



Fig. 2. Raman spectrum of pristine and irradiate with 1×10^{12} and 1×10^{13} fluences samples measure at room temperature.

The pristine sample shows E_2^H at 569.5 cm⁻¹ and A₁ (LO) at 739.4 cm⁻¹. The area under the peak, peak position, full width half maxima (FWHM), biaxial stress (s) were calculated by the Lorentz fitting method for E_2^H peak and these values compared in the table 1. The carrier concentration (n) calculated from the A₁(LO) peak is shown in table 2.

Table 1. Area under the peak, FWHM, Stress (σ) for $E2^{H}$ mode

Fluences (ions/cm ²)	Area Under the Peak (cm ²)	FWHM (cm ⁻¹)	Stress (GPa)
1x10 ¹²	11.79	8.06	1.09
1x10 ¹³	9.99	7.06	0.91

The Biaxial stress was calculated by the following relationship⁴ (Eq.1).

$$\Delta w = -2.62 \sigma \tag{1}$$

 Δw is the difference between pristine and irradiate Raman shift in E_2^H frequency. σ is the biaxial stress. The biaxial stress decreased for 1×10^{13} ions/cm², this stress decreases due to due to recovery of crystallinity disorder or stress liberation from the lattice site.

The carrier concentration was obtained from the expression⁵ (Eq.2)

$$n = 1.1 \times 10^{17} \, \omega^{0.764} \, \text{cm}^{-3} \tag{2}$$

 ω is the difference between pristine and irradiate Raman shift in A₁(LO) frequency. The carrier

concentration increases for the high fluences (1×10^{13}) this due to the creation of point defect such as gallium ion or nitrogen ions vacancies induced.

Fluences (ions/cm ²)	Area Under the Peak (cm ²)	FWHM (cm ⁻¹)	Carrier concentration (n) x10 ¹⁷ (cm ⁻³)
1x10 ¹²	4.08	10.08	1.01
1x10 ¹³	2.02	7.46	1.84

Table 2. Area under the peak, FWHM, Carrier concentration (n) for $A_1(LO)$ mode.

Conclusion:

Micro Raman spectra of pristine and 100MeV O^{7+} irradiated with fluences of 1×10^{12} , 1×10^{13} ions/cm² were studied. The pristine sample showed good crystal quality by E_2^H at 569.5 cm⁻¹ and $A_1(LO)$ at 739.4cm⁻¹. The biaxial stress was found to be high for the lowest fluencies and lowest for high fluencies. The biaxial stress decrease maybe due to recovery of crystallinity disorder. The Carrier concentration increases for increasing the fluencies. Hence, it is concluded that the irradiation damaged the material and the damage is dependent on the magnitude of fluencies.

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Site Selective Non-Stoichiometry Study Of LaAlO₃

Minal Gupta^{1*}, Pankaj R. Sagdeo¹

¹Material Research Laboratory, Department of Physics, Indian Institute of Technology Indore, Khandwa Road, Simrol Indore 453552 India

*Corresponding author: phd1801251001@iiti.ac.in

Abstract

Sol-gel synthesis method has been used to synthesize $LaAlO_3$ with non-stoichiometry at Lanthanum (La/A-site) and Aluminum (Al/B-site) sites. The pure phase of samples has been optimized at 900°C and confirmed by X-ray diffraction technique and Rietveld refinement analysis. Decrement in the lattice parameters has been observed in non-stoichiometric samples compared to pure LaAlO₃ systems. Interestingly, decrease in band-gap values has been observed with the non-stoichiometric approach. This study demonstrates that slight disturbance at La and Al sites can enhance the physical properties of the pristine LaAlO₃ system.

Introduction

Lanthanum Aluminate (LaAlO₃) is a versatile material widely used as substrate material for high-temperature multiferroic thin films and superconducting films. LaAlO₃ is attracted for its interesting features such as wide bandgap (5.5-6.5 eV), high dielectric constant (23–25) at room temperature, and thermally stable nature at an annealing process of metal-oxide-semiconductor field-effect transistor (MOSFET). Different types of laser-induced applications have been explored in crystalline LaAlO₃ because of its wide energy gap.¹ The interfacial study of dissimilar material like LaAlO₃/SrTiO₃ are a great topic of research.² Also, LaAlO₃ is well known for its high oxygen ion conductivity at high and intermediate temperature range.³

LaAlO₃ belongs to the ABO₃ type perovskite oxide, which is stable as rhombohedral $(R\overline{3}c)$ structures at room temperature. At 540°C, LaAlO₃ undergoes a structural phase transition to cubic ($Pm\bar{3}m$) structures.⁴ Synthesis of pure phase and cost-effective bulk LaAlO₃ at a lower temperature is one of the challenges. Also, very few research groups have explored different physical properties in bulk pure and doped LaAlO₃ systems.^{5,6} To overcome this, we have presented a non-stoichiometric approach at La and Al sites to examine the physical changes that can occur after disturbing La and Al sites. Stoichiometric and nonstoichiometric LaAlO₃ (LAO), La_{0.995}AlO₃, and LaAl_{0.995}O₃ have been synthesized by the sol-gel synthesis route. Phase purity analysis has been done using the X-ray diffraction technique. Lattice parameters have been obtained by Rietveld refinement. Further, Optical absorption spectroscopy (OAS) in diffused reflectance mode has been performed to calculate the optical band-gap of the synthesized samples.

Experimental Method

The sol-gel method was used to prepare stoichiometric and non-stoichiometric LAO samples. The aqueous solution was prepared by dissolving lanthanum (III) nitrate hexahydrate $La(NO_3)_3.6H_2O$ (99.99%, Merck) and Aluminum (III) nitrate nonahydrate $Al(NO_3)_3.9H_2O$ (98.00%, Loba) in distilled water with continuous stirring. Further, citric acid and ethylene glycol have been added after forming a transparent solution. This solution was heated at 150°C with continuous stirring till the foam-like gel formed. The next step involves the combustion of gel at 350°C in the muffle furnace. The prepared solid solution was heated at 700°C for 12 hours with the interval of intermediate grinding at 550°C for 6 hours. Cylindrical-shaped pellets of 10 mm diameter have been prepared and sintered at 900°C for 12 hours to characterize the samples.

Results and Discussion

The phase purity of the prepared samples was confirmed by comparing them with JCPDS file no. 820478. **Fig. 1.** shows the room temperature X-ray diffraction data with Rietveld refinement pattern for $La_{0.995}AlO_3$ carried out on Rigaku automated multipurpose X-ray diffractometer equipped to Cu target. Rietveld refinement has been done with space group R3c to obtained lattice parameters and the values have been listed in **Table 1**. Non-stoichiometry at both La and Al sites leads to a decrement in the lattice parameter compared to the pure LAO system. This suggests that both A and B sites are sensitive and affect the structural properties of the pure LAO system. But, slightly large changes occur at the La site than at the Al site as the lattice parameter decreases more in $La_{0.995}AlO_3$ than $LaAl_{0.995}O_3$.





Fig. 1. Rietveld refinement pattern for $La_{0.995}AlO_3$ at room temperature in the angular range $2\theta=20^{\circ}-80^{\circ}$.

Fig. 2. Optical absorption spectra for LaAlO₃, La_{0.995}AlO₃, and LaAl_{0.995}O₃ in diffused reflectance mode. **Inset** shows the Tauc plot for band-gap calculation for LaAlO₃.

OAS has been performed in diffused reflectance mode of absorption as shown in **Fig. 2.** within the range of 200-300 nm, where F(R) is related to reflectance R by Kubelka-Munk equation $(1)^{7.8}$ which is given by,

$$F(R) = \frac{K}{S} = \frac{(1-R)^2}{2R}$$
 (1)

Here, K and S are the Kubelka-Munk absorption and scattering functions, respectively. For diffused reflectance of powder samples, it has assumed that reflected light scatters in a perfectly diffuse manner, and for such case, the scattering function S is nearly constant with wavelength, and the Kubelka-Munk function, which is related to the absorption coefficient (α) and represented as,

$$F(R) \propto \alpha \propto \frac{(hv - E_g)^{1/n}}{hv}$$
(2)
(αhv)ⁿ=A(hv - E_g)(3)

In Eq. (2), 'n' has the value of 2 and 1/2 for direct and indirect band-gap transitions, respectively. LAO shows an indirect band-gap transition at room temperature in rhombohedral (R $\overline{3}$ c) structure.¹ To calculate optical band-gap, the Tauc equation has been used. The graph is plotted in the inset of **Fig. 2.** and the band-gap values are listed in **Table 1.**

The band-gap of ~4.85 eV has been obtained for the bulk LAO pellet sample sintered at 900°C. Further, nonstoichiometry at La and Al site decreases the band-gap of the pure LAO system, which suggests that both the La and Al site are sensitive to any perturbation in the system. But, disturbance at La (A site) site in LAO shows lesser band-gap than non-stoichiometry at Al (B site) site. In the theoretical study by Murtaza et al.¹ and Asmara et al.², total and partial density of state (DOS) plot calculation of La, Al, and O (Oxygen), respectively, have been reported. Looking into these theoretical calculations of DOS, it has been noticed that the conduction band of La dominates more compared to Al and O in the total DOS plot, whereas the valence band of O ruling in total DOS calculation. Thus, it has been assumed that perturbation at the La site can give rise to other levels near conduction bands through which lowering of the band-gap can happen. Also, introduction of oxygen vacancies can occur due to nonstoichiometry, which can also be responsible for creating new defect states. These theoretical reports somehow resemble our study of OAS and suggest that both La and Al sites are sensitive to any disturbance in the pure LAO system, which can also enhance its physical properties. Perhaps, La site has been found more sensitive than the Al site in the optical absorption study.

Table 1. Information regarding different parameters.

Sample	Lattice parameter (Å)		Band-gap
Name	a=b	с	(eV)
LaAlO ₃	5.368(0)	13.13(1)	4.85±0.01
LaAl _{0.995} O ₃	5.361(8)	13.11(2)	4.77±0.01
La _{0.995} AlO ₃	5.359(9)	13.10(9)	4.36±0.01

Conclusion

In summary, we have successfully synthesized stoichiometric and non-stoichiometric LaAlO₃ samples using the sol-gel technique at 900°C. Phase purity analysis has been confirmed by X-ray diffraction technique and Rietveld refinement. Non- stoichiometric slight disturbance at La and Al site indicate the structural and optical properties changes. Thus, it has been concluded that the doping approach at La and Al sites in the pure LaAlO₃ system may enhance the physical properties in which the La site can be more sensitive. Also, lowering of band-gap by doping approach in LaAlO₃ can be used at wide band-gap semiconductor material.

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Robust P-type Conduction in Oxychalcogenides CuAlOS: A DFT Study

Nikunj Joshi^{1*}, Deepak Upadhyay², Ankur Pandya³, and Prafulla K. Jha⁴

¹ Institute of Science, Nirma University, Ahmedabad-382481, Gujarat, India, ²Department of Applied Physics,

Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara-390001, Gujarat, India

³Institute of Technology, Nirma University, Ahmedabad-382481 Gujarat, India, ⁴Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara-390002 Gujarat, India

*Corresponding author: nikunj_joshi2104@yahoo.com

Abstract

The study reveals the structural, electronic and optical properties of oxychalcogenide compound CuAlOS using first principles calculations based on density functional theory (DFT) implemented in quantum espresso code. This compound possesses the same crystal geometry $(R\bar{3}m)$ like most of the delafossite compounds. The calculated electronic band structure reveals the semiconducting nature of the considered compound having electronic band gap of 0.27 eV. Furthermore, we have calculated partial density of states (PDOS) to see the contribution of 3d and 2p orbitals, which are mainly responsible for the lower electronic band gap. Additionally, the optical properties such as dielectric constants, absorption spectra and refractive index were calculated to confirm the applicability of the nominee compound in the optoelectronics.

Introduction

The delafossites with the chemical formula $A^{1}B^{11}O_{2}$ (Where A and B are the monovalent and trivalent cations respectively) have been accepted as a p-type transparent conducting material since last several decades ^[1]. The production of highly effectual optoelectronic devices with these delafossites (p-type) seem very difficult due to their low electrical conductivity compared to n-type oxides ^[2]. This difficulty arises due to the localization of holes in the valance band. However, several tactics have been made to enhance the electrical conductivity by the researchers, one of the effective approaches is to change the position of the O by the N or chalcogen (S, Se, Te) in the chemical formula of delafossite ^[3].

Moreover, the above approach of chemical modulation i.e. replacing O with N or S is not sufficient enough to enhance the conductivity. So, the mixed delafossite phase, which includes one oxygen and one chalcogen atom (oxychalcogenides) alternatively occupy the same position can be the effective approach to get the enhanced conductivity. This area is not yet widely explored and very few studies were reported for these oxychalcogenides ^[4-5].

In this study, we have adopted the same approach by replacing one oxygen atom with one Sulphur atom in the Al based conventional delafossite (CuAlOS). In the p-type transparent conducting oxides, CuAlO₂ is a most promising p-type conductor with notable optical transparency, with a band gap of 3 eV ^[1]. Herein, we have nominated the above mentioned material and replaced only a single oxygen atom by chalcogen atom i.e. Sulphur (S), which results in a drastic change in the band gap. This sudden change in the band gap motivated us to scrutinize this CuAlOS oxychalcogenides for optoelectronic applications. In this article, we have calculated structural, electronic and optical properties of a CuAlOS compound.

Computational methods

All the calculations were performed using first principles calculations based on density functional theory (DFT) as implemented in Quantum espresso code ^[6]. Generalized gradient approximation (GGA) is used for exchange correlational functional. The irreducible Brillouin zone (BZ) is sampled by $9 \times 9 \times 9$ Monkhorst-pack mesh. The energy cut-off is 80 Ry. All the optical parameters were calculated using random phase approximation (RPA).

Results and discussion

The CuAlOS compound crystallizes in rhombohedral $(R\overline{3}m)$ structure (see Fig. 1). The geometry of the considered compound is same as the delafossite, which means the layers are interconnected by the linear-linkages of O-Cu-S.



Fig. 1. (a) Unit cell and (b) Crystal geometry CuAlOS

The calculated electronic band structure of CuAlOS is, which depicts an indirect band gap of 0.28 eV (Fig. 2). The valence band maximum (VBM) and the



Fig. 2. The calculated electronic band structure of CuAlOS

conduction band minimum (CBM) lies at T and Γ points respectively, suggesting an indirect band gap of CuAlOS. The dispersion of bands is more near the Fermi level, indicating the low hole effective mass due to the replacement of one S atom over O, which delocalized the holes in the valance band. To understand more precisely the dispersive nature of VBM, we have calculated partial density of states (PDOS) of CuAlOS (see Fig. 3).





Fig. 4. Real (ε_1) and Imaginary (ε_2) part of a dielectric constant of CuAlOS

As can be seen from Fig. 3, the contribution of Cu (3d) and S (2p) orbitals near VBM is more, which is mainly responsible for the reduction in the band gap. The S (2p) orbital has maximum contribution near the VBM accountable for the delocalization of holes near the fermi level, reducing the band gap. Thus, very small band gap 0.28 eV of CuAlOS observed (see Fig. 2). To confirm the electronic properties, ε_1 and ε_2 are calculated. The sharp peaks in ε_1 is due to the transition between VBM and CBM. The fundamental absorption edge arises at 0.28 eV in ε_2 spectra, confirming the electronic band gap of CuAlOS.



Fig. 5. Absorption spectra of CuAlOS The threshold occurs at 0.28 eV, which corresponds to its PBE-GGA bandgap. The absorption occurs in the visible region and notably in ultraviolet (UV) region, confirming the applicability of CuAlOS in optoelecronics.

Conclusions

To sum up, we have analyzed the structural and opto-electronic properties of CuAlOS using DFT. This compound is semiconducting with indirect band gap of 0.28 eV. The PDOS indicates the strong p-d hybridization near VBM, suggesting delocalized holes and enhancement in p-type conductivity. The optical spectra are analyzed to confirm the electronic band gap of considered compound. The absorption spectra suggest the application of CuAlOS in optoelectronics.

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A Facile Approach to Improve ON/OFF Ratio and Uniformity of Low-power HfO_x based RRAMs

Swathi S. P.^{1,2} and S. Angappane¹

¹Centre for Nano and Soft Matter Sciences (CeNS), Shivanapura, Bangalore-562162, India, ²Manipal Academy of Higher Education (MAHE), Manipal-576104, India

*Corresponding author: angappane@cens.res.in

Abstract

The resistive switching performance of hafnium oxide-based devices with transparent conducting oxides as bottom electrodes is investigated. The sputtered HfO_x film exhibits a typical clockwise-bipolar resistive switching with lower forming voltage, SET/RESET voltages, appreciable ON/OFF ratio, and self-compliance effect. Further, a simple method inspired by the hot-forming technique to suppress the current overshoot and better control the conductive filament formation and dissolution inside HfO_x films of Al/HfO_x/ITO devices is proposed. By implementing this method, the ON/OFF ratios of Al/HfO_x/FTO and Al/HfO_x/ITO devices are improved. Moreover, the ON/OFF ratio and temporal variability could be further tuned by the modulation of the thickness of HfO_x layer.

Introduction

Hafnium oxide is considered a promising dielectric material for resistive random access memory (RRAM) applications due to its excellent performance, including higher endurance and ultra-high switching speed [1]. Although significant efforts are being made to further improve the resistive switching (RS) performance, the critical issue with HfO_x based devices is the extremely high forming voltages for initiating the reversible switching operation, including large operating voltages and currents [2]. Moreover, to address another issue of current overshoot in a memory device, and achieving a more reliable and controlled conductive filament (CF) formation, various forming techniques, such as constant voltage forming, hot-forming, current sweep forming, and multi-step forming have been studied [3]. In this study, a simple heating step, inspired by the hot-forming technique, is employed to improve the ON/OFF ratio and uniformity of HfO_x based RS devices.

A 50 nm thick HfO_x film was deposited by RF magnetron sputtering using a ceramic HfO_2 target under Ar atmosphere on commercially available indium tin oxide (ITO) and fluorine-doped tin oxide (FTO) substrates [4]. The substrate temperature and RF power were maintained during the deposition at 200 °C and 80 W, respectively. Finally, a circular, 200 µm diameter and 100 nm thick Al layer was deposited as a top electrode (TE) by thermal evaporation through a shadow mask. The RS measurements of Al/HfO_x/FTO (AHF) and Al/HfO_x/ITO (AHI) devices were carried out by biasing the TE, as shown in Fig. 1 (a).

Results and Discussion

All the devices were highly resistive in the pristine states. The current abruptly increases at a certain voltage during the electroforming process, and the device enters the low resistance state (LRS) from the high resistance state (HRS). Fig. 1 (b) displays the forming curves in the pristine AHF and AHI devices. The AHF device formed at 2.46 V as compared to 5.39 V in the AFI device. The lower forming voltage in the AHF device could be primarily due to the higher surface roughness of the FTO electrode compared to that of ITO.



Fig. 1. (a) Schematic of $AI/HfO_x/BE$ (BE: FTO, ITO) devices. (b) *I-V* curves showing the electroforming process. (c, d) *I-V* curves depicting typical cF8 BRS.

After the forming process, the device enters HRS from LRS on the application of a positive bias (reset process). Subsequently, when a negative bias is applied, the device switches back to LRS (set process). Fig. 1 (c, d) shows the typical clockwise or counterfigure-of-eight (cF8) bipolar RS in AHF and AHI devices obtained under DC voltage sweep for several cycles. The cF8 bipolar RS (BRS) is characterized by applying a positive bias for the reset process and a negative bias for the set process [5]. More importantly, these devices exhibited self-compliance property, which is highly desirable for developing high-density RRAMs, as it simplifies the additional circuitry. Such a self-compliance phenomenon indicates the existence of the interfacial layers (HfO_x/FTO and HfO_x/ITO interfaces) during the switching operation. Further, consistent distribution of set/reset voltages with the average of $-0.84 \pm 0.09/0.73 \pm 0.08V$ was observed for AHF devices, whose values are much lower compared to $-1.24 \pm 0.32/1.08 \pm 0.21$ V for AHI devices (typically five devices each were considered).



Fig. 2. Endurance characteristics of AHF and AHI devices at room temperature read at 0.5 V for several cycles (**a**, **b**) before and (**c**, **d**) after heat treatment. Inset of (**d**) shows the endurance characteristics of AH(30 nm)F device.

As shown in Fig. 2 (a, b), HfO_x based devices exhibited stable, uniform, and reproducible switching characteristics up to 100 consecutive cycles; however, the memory window (ON/OFF ratio) is small. The main reason for the lower ON/OFF ratio could be the insufficient supply of oxygen ions during the reset process, which eventually leads to a decrease in the resistance of HRS. One of the best approaches to tackle this issue is by the heat treatment at a certain high temperature (~150 °C) for 30 minutes before carrying out the electrical measurements at room temperature. This approach is found to suppress the current overshoot efficiently while improving the memory window, spatial variability, and significant reduction in the input power. Fig. 2 (c, d) shows endurance data of AHF and AHI devices after the heat treatment. Interestingly, the ON/OFF ratio increased to about 10 in AHI devices and 30 in AHF devices. The resistance of HRS has significantly improved after the heat treatment; thereby, an enlarged ON/OFF ratio was obtained.

The role of HfO_x/FTO interface was further studied by reducing the thickness of HfO_x film down to 30 nm to get AH(30 nm)F structure. Though the switching patterns of AH(50 nm)F and AH(30 nm)F devices in terms of uniformity and operating voltages are similar, the dramatic increase in the ON/OFF ratio ($\sim 10^2$) with lower temporal variability in resistance states is observed. As shown in the inset of Fig. 2 (d), the stable endurance was observed for many cycles.

During the forward bias, the oxygen ions migrate from HfO_x film towards the Al TE, then their oxidation at the Al/HfO_x interface, and the device switches to HRS. During the negative bias, these oxygen ions oxidized with Al TE at the interface are driven back to the HfO_x layer and lead to the formation of oxygen vacancy-rich filaments. Thus, the device switches back to LRS. However, the decrease in the resistance of HRS can be observed after several RS cycles due to the insufficient oxygen ions to recombine with the oxygen vacancies in the switching layer. This results in the shrinkage of the ON/OFF ratio. The heat treatment has effectively increased the resistance of the HfO_x laver by providing atmospheric oxygen and enhancing the ON/OFF ratio. When the thickness of HfO_x film was reduced to 30 nm, the atmospheric oxygen can diffuse further into the switching layer and make the film more resistive, resulting in an increase in the resistance of HRS and significant improvement in the ON/OFF ratio.

Conclusion

Typical cF8 bipolar resistive switching characteristics of Al/HfO_x/FTO and Al/HfO_x/ITO devices including lower operating voltages and self-compliance effect were observed. The switching mechanism has been explained on the basis of oxygen ion migration under the electrical bias. To improve the RS properties in terms of ON/OFF ratio and uniformity, a simple method inspired by the hot-forming technique was employed, providing better control over the CF formation. Hence, this collective approach offers an effective way to address the cycling-induced shrinkage of ON/OFF ratio in low-power oxide-based RS devices.

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Light Stimulated Artificial Synapses Based on Polymer Semiconductors PBTTT and PFO

Bishwajit Mandal¹ and Samarendra Pratap Singh^{1*}

¹Department of Physics, Shiv Nadar University, Gautam Buddha Nagar, UP-201314, India

* <u>samarendra.singh@snu.edu.in</u>

Abstract

The development of synaptic devices with polymer semiconductor has drawn great attention to meet the requirement for fabricating human brain like computing and soft robotic system for artificial intelligence-related research. Taking advantage of the properties of organic semiconductors like low cost, easy solution possible, large area fabrication and biocompatible are attractive features for artificial synapses. In this study, two terminal synaptic devices are fabricated using the PBTTT and the PBTTT: PFO system. Biological synapse like nature, short-term plasticity (STP), pulse pair facilitation (PPF) and memory-forgetting-rememorizing (MFR) behaviour are successfully carried out. We attribute the behaviour of this device of charge trapping mechanism in PBTTT:PFO material system.

Introduction

The neurons and synapses of our human brain, responsible for the process of learning, computing and thinking, function more effectively than the supercomputer. But the energy consumption is much less in our human brain than the supercomputer [1]. Developing an artificial neuromorphic synaptic device using polymeric materials has the potential to realize the next generation computation system for artificial intelligence. The external stimulus (optical, electrical, chemical and mechanical) can be converted to electrical signals by selecting the right material and structure for the device. We noticed the STP, PPF and MFR capacity under a slight stimulus.

Experimental

The glass substrates were ultrasonically cleaned in a soap solution, deionized water, acetone and IPA sequentially for 20 minutes each. The substrate was subsequently treated with ultraviolet ozone for 30 minutes at 100°C. To prepare the PBTTT solution in 1,2-dichlorobenzene, 1 hour, stirred at 300 rpm and 110 temperatures. Then an easily soluble PFO solution in chloroform was mixed with a PBTTT solution. After that, only PBTTT and PFO doped PBTTT solution was spin coated onto the clean glass substrates at a speed of 800 rpm for 1 minute and then followed by an annealing at 150 °C for 15 minutes to remove the extra impurities. Finally, 7 nm and 70 nm of molybdenum oxide and silver were deposited respectively on the semiconductor layer by a thermal evaporator on a shadow mask to fabricate the respective electrodes.

Results and Discussions

Figure 1a) and 1b) illustrates the memorizing, forgetting and re-memorizing nature of the device of PBTTT and PBTTT: PFO system respectively. From the figure, it is cleared that the rememorizing process takes less number of pulses or time than the memorizing process to memorize the forgotten messages. Thus the human brain learning nature has been explained using light stimulated two terminal synaptic devices.



Fig. 1. a) Memorizing-Forgetting-Re-memorizing behavior of only PBTTT device b) Memorizing-Forgetting-Rememorizing behavior of PFO doped PBTTT device.

Figure 2. shows the EPSC behavior after one second interval in between two consecutive pulses. After the application of two successive light pulses (2.635 mW/cm2) at an interval of 1 second, the second EPSC (3.72 μ A for PBTTT and 5.82 μ A for PFO doped PBTTT) is higher than the first one (3.67 μ A for PBTTT and 5.76 μ A for PFO doped PBTTT) which indicates that the synapse retains the previous stimulus even if the stimulus is ended. This is like the retention property of human brain. The PPF index of our light stimulation synaptic device can be computed using the following formula: PPF= 100 % × $\frac{A_2-A_1}{A_1}$.



Fig. 2. EPSC response of two successive pulses of 1 second after 1 second interval a) PBTTT device b) PBTTT: PFO device.

Table1. Photo response parameters with maximum value for our devices are following:

PARAMETERS	PBTTT device	PFO doped PBTTT device
Photoresponsivity	0.99 A/W	0.45 A/W
Detectivity	3.85×10^7 Jones	5.91×10^8 Jones
Photo current/Dark	1.34	1.67
current		DAE

R is used to find the optical response efficiency of the device and D signifies that how much device is sensitive under weak light.

Conclusion

In conclusion, the artificial synapses PBTTT and PBTTT: PFO based artificial synapses were produced. The PPF, STP and MFR abilities as well as the biological nervous system are successfully performed. The electrical and optical behavior has been researched and explained.

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Low-temperature Solution-processed ZrO₂ and Ta₂O₅ for Highperformance Solution-processed Organic Field-effect Transistors

Yogesh Yadav¹ and Samarendra Pratap Singh¹

¹Department of Physics, Shiv Nadar University, Gautam Budh Nagar, Uttar Pradesh, India - 201314

Corresponding author: samarendra.singh@snu.edu.in

Abstract

Low-voltage operation of solution-processed organic field-effect transistors (OFETs) is very important for the integration of these devices into complex integrated systems. Owing to low dielectric constant and high density of trap centers, the use of conventional dielectric SiO₂ generally leads to large operating voltage in organic field-effect transistors. Here, we have demonstrated low-temperature solution-processing of zirconium oxide (ZrO₂) and tantalum oxide (Ta₂O₅) for their use as gate-dielectric in solution-processed organic field-effect transistors. ZrO₂ and Ta₂O₅ have significantly larger dielectric constant than SiO₂. The field-effect mobility in PBTTT-C14 improves from 2.73×10^{-3} cm² V⁻¹ s⁻¹ for SiO₂-gated OFETs to 1.65×10^{-1} cm² V⁻¹ s⁻¹ and 3.02×10^{-1} cm² V⁻¹ s⁻¹ for ZrO₂ and Ta₂O₅ gated OFETs respectively. The threshold voltage decreases significantly from ~ 24 V for SiO₂-gated OFETs to ~ 0.15 V and ~ 0.03 V for ZrO₂ and Ta₂O₅ gated OFETs respectively. The low-temperature processing enables this technique to be used for flexible substrates also.

Study of Interface phonons in InAs/GaAs_{1-x}Sb_x Quantum Dot Heterostructures by Low-temperature Polarized Raman scattering Jhuma Saha¹, Sudip Kumar Deb^{*2}, and Subhananda Chakrabarti¹

¹Department of Electrical Engineering, ²Centre for Research in Nanotechnology &Science,Indian Institute of Technology Bombay, Mumbai-400076, India

*Corresponding author: sudip51@gmail.com

Abstract

An experimental study of interface phonons in bilayer strain-coupled $InAs/GaAs_{1-x}Sb_xquantum dot(QD)$ heterostructure has been presented by means of low temperature Raman scattering. The effect of Sb content on the frequency position correlates with the simulated strain. The interface Raman peaks show a higher frequency shift in the heterostructure with higher Sb content in the capping layer. This shift is attributed to the strain relaxation, bigger size of the QDs and type II band alignment.

Optical Coherent Transient Effects in Core-Shell Quantum Dots

Bhupendra Kumar^{1,*} Ravi Solanki¹, and P. K. Sen¹

¹Department of Applied Physics, Shri G S Institute of Technology & Science, Indore - 452 003. *bhu.msu@gmail.com

Abstract. We present the results of the numerical analysis of the third order optical non-linearity and optical coherent transient effects like optical nutation in various Type-I core-shell quantum dots at low temperature and in ultrafast, moderate power coherent excitation regime. We have considered the role of Wannier-Mott excitons since they are more pronounced in semiconductor nanostructures. The dephasing and relaxation mechanism of excitons is also incorporated in the theoretical model.

Keywords: Semiconductor, Quantum dots, Screened Columbic electron-hole interaction PACS: 68.55.ag, 68.65.-k

INTRODUCTION

Core-shell quantum dots have many improved electrical and optical properties over spherical quantum dots and can be used in many biological imaging techniques and in designing of various ultrafast opto-electronics devices, which are the basic need of present opto-electronics communication system [1].

The various photo-induced coherent transient's effects in core shell quantum dots can facilited the designing of the ultrafast communication system. We propose to make analytical studies of the nonlinear optical processes viz, nonlinear refraction and nonlinear absorption in core-shell quantum dots of direct band gap semiconducting materials belonging to III-V or II-IV direct gap crystal classes [2-3].

THEORETICAL FORMULATIONS

The ensemble average of induced excitonic transition dipole moment is defined as [2,3],

$$\langle \hat{\mu}(t) \rangle = \frac{4\mu\Omega_R}{|\beta|^2} [-|\sin\theta|^2 X + i\beta\cos\theta\sin\theta^*] e^{i\omega t} e^{-\Gamma t}.$$

On the premises of the effective mass approximation, the 3-dimensional Schrodinger equation for electron in the spherical coordinate system can be written as,

$$\nabla^2 \Psi(r,\theta,\Phi) + \frac{2m_e^*}{\hbar^2} [E - V(r)] \Psi(r,\theta,\Phi) = 0,$$

The total Energy eigenvalue for core-shell QD, having core radius r_1 and m_{e1}^* , m_{h1}^* as electron effective mass and hole effective mass respectively in core region,

and m_{e2}^* , m_{h2}^* as electron effective mass and hole effective mass respectively in shell region, can be calculated using

$$E_{nl} = E_{nle} + E_{nlh}$$

The effective bandgap is given by $E_{g\,eff} = E_g + E_{nl}$ and used for the calculation of the effect like optical nutation in various Type-I core-shell quantum dots.

RESULTS AND DISCUSSION

The optical nutation signal inside the well in core-shell QD, for different shell thickness has been shown in Figure 1. The shell thickness can be calculated by subtracting core radius from shell radius i.e. $r_2 - r_1$.





The core radius of 3 nm is kept constant for all cases. From Figure 1, we can see that the optical nutation signal changes when we grow shell on the core. If we compare the change in Rabi time, of equivalent change in core radius and shell thickness; we can find that the change of the signal's Rabi time is more sensitive to the size of the core than to that of the shell see Figure 2. Figure 2 illustrate that Rabi time of 3 nm core radius bare QD is more than that of 3/6 nm core–shell QD. Since the core radius is same for core-shell QD and bare QD, the area of absorption of input power is equal, as shell acts as a transparent region for the incoming light.



Figure 2: Comparison of Rabi time on variation of core radius with variation of shell thickness having core radius 3 nm.

This suggest that core-shell QD responds faster than bare QD of equivalent core radius at the same input optical power. So core-shell QD are more efficient than bare QD of equal core radius.



Figure 3: Comparison between variations of transition dipole moment due to change of core radius and change in shell thickness keeping core radius 3 nm.

The cause for this is same as given for bare QD that is the increase of electric transition dipole moment with the change of shell thickness which is shown in Figure 3.

The reason for the small change in Rabi time, on the growth of shell can be due to the energy spacing or the transition frequency changes very small with the growth of the shell and the change is only noticeable for QD having small core radius [4].

The variation of transition dipole moment due to change in core radius is compared with the change in shell thickness keeping 3 nm core radius constant, in Figure 3. It can be noticed that, variation from change of shell thickness is small compared to the variation due to change in core radius.



Figure 4: Excited state occupation probability of electron in core-shell QD.

In Figure 4, we have compared the excited state occupation probability of the QD having core radius 3 nm, and shell thickness 0 nm (no shell), 3 nm and 6 nm. Due to the growth of shell, the probability of electrons presenting at the excited state enhances. As we grow shell on the bare QD, the confinement effect inside the core reduces. Due to which the energy separation reduces and the probability of occupation of excited state enhances.

From these results, the nonlinear optical properties of the QDs nanoparticles are dependent on its size and structure. The QDs attain its maxima at early times, on increasing the electric field amplitude of the incident light pulse. Thus core-shell QDs can be utilized for devices which demands high energy efficiency and quick response like optical memory devices and photovoltaic solar cells.

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Improving the Magnetic Properties of Neodymium Doped CoFe₂O₄ Film by Nebulizer Spray

A.M.S.Arulananatham^{1*}, M. Maria Stephy², M. Antony³ and K.V.Gunavathy⁴

¹St. Joseph College of arts and science, Veikalipatti, Tenkasi 627808,

²PG & Research Department of Physics, Arul Anandar College, Karumathur, Madurai, Tamil Nadu 625 514, ³Thin Film Research Centre, Department of Physics, Kongu Engineering College, Perundurai 638060.

*Corresponding author: amsarul@gmail.com

Abstract

Doping of rare earth element with $CoFe_2O_4$ thin films can make significant changes on the structural and magnetic properties, which makes it suitable for magnetic and other device applications. Undoped and neodymium doped $CoFe_2O_4$ thin films were deposited using Nebulizer Spray Pyrolysis (NSP) on glass substrates by varying Nd doping level from 0% to 5%. From X-ray diffraction pattern, crystallite size is calculated and is found that the crystallite size decreases with the doping concentration. The calculated optical band gap values exhibits an increasing trend and shifted from 1.82 to 1.95 eV on increasing Nd doping concentration. The magnetic and the saturation magnetization of the films obtained at 0% and 5% showed a strong dependence on the Nd doping concentration.

High Temperature Structural Properties of Bi_{1-x-y}La_xSr_yMnO₃ (x = 0.0, 0.1; y = 0.3, 0.4)

A. D Souza¹, M. D. Daivajna¹, S. Bhattacharya² and S. Rayaprol³

¹Department of Physics, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal 567104
 ²Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085
 ³UGC-DAE Consortium for Scientific Research, Mumbai Centre, BARC Campus, Trombay, Mumbai 400085

*Corresponding author: rayaprol@gmail.com; sudhindra@csr.res.in

Abstract

High temperature X-ray diffraction studies have been carried out on a series of substituted $BiMnO_3$ samples. With the changes in the composition of Bi and Sr, it is found that though there is no change in crystallographic structure, there are subtle changes in the unit cell parameters and lattice distortions which could be responsible for the differences or modifications in the physical properties of these compounds.

Introduction

Perovskite manganites, having generic formula, $AMnO_3$ (where A = rare earth; transition or posttransition metal ion) have been under intense study by experimentalists and theoreticians for their unique structural, magnetic, electrical, and thermal properties [1, 2]. These compounds have become unique example of functional materials due to their electrical, magnetic and other physical properties such as colossal magnetoresistance, multiferroicity, thermoelectric power etc. over a wide temperature range. One of the most efficient methods of engineering or manipulating the properties of AMnO₃ compounds is by changing the external conditions such as temperature, applied magnetic or electric fields, and isostatic pressure. Another popular method of controlling the structural and physical properties is by chemical substitution. Depending upon the substituent and site, electron count can also be altered leading to the modifications in their physical properties. Hence, by controlling the composition structural and physical properties can be easily controlled in the perovskite compounds. Among the various types of perovskite manganites studied over decades, BiMnO₃ based systems are fascinating owing to interesting structural, electrical and magnetic properties exhibited and influenced by the lone pair electrons of bismuth. BiMnO₃ is a FM with $T_C = 100$ K. By substituting Sr for Bi in BiMnO₃, ferromagnetic order gives way to antiferromagnetic/charge order and Bi0.67Sr0.33MnO3 has a robust charge-ordered (CO) state above room temperature which is stable even in presence of strong magnetic fields up to 30 Tesla (T). [3 and references therein]. However, the increase in Sr content drives the charge ordering temperatures towards room temperature. Therefore, it will be rewarding to understand the implications of Sr substitution in BiMnO₃ on the crystallographic structure and the corresponding changes in the physical properties. In the present work, we have carried out high temperature X-ray diffraction measurements on powdered samples of three compositions of the Bi_{1-x-y}La_xSr_yMnO₃ (x = 0.0, 0.1; y = 0.3, 0.4) series. The compositions thus chosen are, Bi_{0.6}Sr_{0.4}MnO₃, Bi_{0.7}Sr_{0.3}MnO₃ and Bi_{0.6}La_{0.1}Sr_{0.3}MnO₃, which helps in comparing the influence of Sr and La substitution at *A* site in the parent BiMnO₃ compound.

Results and Discussions



Fig. 1. XRD of $Bi_{0.6}Sr_{0.4}MnO_3$, $Bi_{0.7}Sr_{0.3}MnO_3$ and $Bi_{0.6}La_{0.1}Sr_{0.3}MnO_3$ measured at 300 and 650K.

Well-grounded powders of these samples were taken up for high temperature X-ray diffraction experiments in argon atmosphere on the M/s. Proto AXRD using Cu-K α radiation. Rietveld refined room temperature XRD data for all the three samples under study is shown in Fig. 1. XRD profiles of all the samples, at all temperatures could be refined using the orthorhombic structure, space group *Imma*. The values of unit cell parameters are plotted as a function of temperature in Fig. 2. The figure clearly shows that there is no structural transition as a function of substitution nor temperature variation.



Fig. 2. Variation of unit cell parameters of $Bi_{0.6}Sr_{0.4}MnO_3$, $Bi_{0.7}Sr_{0.3}MnO_3$ and $Bi_{0.6}La_{0.1}Sr_{0.3}MnO_3$ as a function of temperature.

However, it is interesting to note that for $Bi_{0.6}Sr_{0.4}MnO_3$ sample, there is a clear step in cell parameters b and c at around 475 K, which indicates towards some kind of ordering in the system. Overall, there is sluggish variation as a function of temperature in other samples studied here.

In order to understand this behaviour in better detail, we have plotted the orthorhombic lattice distortion, δ given as:

$$\delta = \frac{(b-a)}{(b+a)} \tag{1}$$

where *a* and *b* are the unit cell parameters.

The plot of δ vs. T (Fig. 3 – left panel), clearly shows that there is some kind of ordering in Bi_{0.6}Sr_{0.4}MnO₃ sample around 475 K, where as the other two samples exhibit a broad peak with maxima at 625 K

(Bi_{0.7}Sr_{0.3}MnO₃) and 575 K (Bi_{0.6}La_{0.1}Sr_{0.3}MnO₃). As delta reflects the distortions in a-b plane only, we have also plotted the distortion along *c* direction as $\sqrt{\frac{c^2}{ab}}$, which is akin to $\frac{c}{a}$ ratio, in Fig. 3 (right panel). This plot also confirms the observations made in the plot of δ vs. T, which means that the distortion along the ab plane as well as *c*-axis is signifies ordering in the system at the plot of maxima / anomaly.



Fig. 3. Variation of orthorhombic distortion for $Bi_{0.6}Sr_{0.4}MnO_3$, $Bi_{0.7}Sr_{0.3}MnO_3$ and $Bi_{0.6}La_{0.1}Sr_{0.3}MnO_3$ as a function of temperature is shown in different forms (δ and $\sqrt{\frac{c^2}{ab}}$).

Conclusions

Temperature variation of structural parameters of $Bi_{0.6}Sr_{0.4}MnO_3$, $Bi_{0.7}Sr_{0.3}MnO_3$ and $Bi_{0.6}La_{0.1}Sr_{0.3}MnO_3$ show that along with marginal changes in the average *A*-site radius, there are changes in electron count resulting in the changes in the electronic structure, which thus in turn would affect the magnetic and transport properties. Details studies on the physical properties of these compounds at high temperatures are in progress.

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Influence of Slow Cooling and Magnetic Properties of Fe-Ga Alloy

V. Vijayanarayanan¹, Himalay Basumatary², M. Manivel Raja², V. Aravindan¹, R. Sarathkumar¹ and M. Mahendran^{1*}

¹Smart Materials Laboratory, Department of Physics, Thiagarajar College of Engineering, Madurai – 625015. ²Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad 500 058.

*Corresponding author: manickam-mahendran@tce.edu

Abstract

The structural and magnetic properties of F_{77} -Ga₂₃ alloys were investigated after they were arc melted and heat treated at 900 °C. for 5 hrs followed by furnace cooling. The results of X-Ray Diffraction study confirm the alloy's Body Centered Cubic structure and the presence of the A2 phase. Optical microscopy study also confirm the presence of equiaxed grains of only single phase (A2). Additionally, differential scanning calorimetry confirms the existence of the A2 and DO₃ phases. Vibrating sample magnetometer was used to determine the saturation and remanent magnetization.

Introduction

Magnetostrictive materials are found in a wide variety of applications, including sensors, actuators, and energy harvesting devices. These materials should have a large saturation magnetostriction, a low coercivity, high Curie temperature, a broad operating temperature range, and a low saturation field. In comparison to other magnetostrictive materials such as Terfenol-D, Fe-Ga has garnered considerable interest due to a favourable combination of required properties. Terfenol-D (Tb-Dy-Fe) is brittle and should not be used in tensile or shear-stressed environments. Although it has a single-crystal magnetostriction constant of up to 1200 ppm, its application is restricted due to its low Curie temperature, high saturation fields, high coercivity (Hc), and narrow operating temperature range [1].

Terfenol-D is also expensive due to the costs of terbium and dysprosium. Galfenol alloys have a lower single-crystal magnetostriction constant (400 ppm), are ductile, and possess all required properties, including resistance to tensile or shear stresses. The Fe–Ga alloy is mechanically strong, robust, and a ductility of 1.6 percent with a tensile strength of 500 MPa. Additionally, Fe–Ga alloys have a excellent corrosion resistance, a low temperature dependence, high permeability, and the ability to be welded to other ferrous materials [2].

Extensive research has been conducted to clarify the relationship between structure and magnetostriction in order to deduce the source of the varied magnetostriction in Fe-Ga alloys. A significant experimental difficulty in studying the compositiondependent change in magnetostriction is the presence of similar structures in Fe-Ga alloys, such as the A2 phase, the ordered DO_3 phase, and the ordered B2 phase [3].

Experimental Condition

The elemental metals Fe (99.95 %), Ga (99.99 %), and Fe₇₇-Ga₂₃ were prepared using a vacuum arc melting furnace. For further studies, the prepared alloys were heat treated at 900 °C for 5 hours followed by furnace cooling and sliced using an EDM wire cutter. At room temperature, the alloys were characterised structurally using X-ray Diffraction (XRD) technique. Optical Microscopy (OM) was used to examine the particle morphology. Thermal properties were determined using a Differential Scanning Calorimeter (DSC), and magnetic properties were determined using a Vibrating Sample Magnetometer (VSM).



Fig. 1. X-Ray diffraction pattern of Fe₇₇-Ga₂₃ alloy.

Results and Discussions

The X-Ray diffraction pattern of Fe₇₇-Ga₂₃ alloy is shown in Fig.1. The XRD pattern confirms the existence of disordered A2 phase with Body-Centered Cubic (BCC) structure, there were no additional peaks observed for the superlattice. The inset shows the A2 crystal structure of the Fe-Ga alloy. XRD calculations of Fe₇₇-Ga₂₃ alloy is shown in Table 1. As a whole, the findings demonstrate that the phase distributions in Fe–Ga alloy change from a single-phase A2 to a mixture of A2/DO₃, and finally DO₃ into A2 Phase[4].

Table 1. ARD Calculations of Fe77-Ga23 alloy.	f Fe77-Ga23 alloy.	of Fe77-	Calculations	XRD	Table 1.
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Parameters	Calculated results
Crystallite Size (D) nm	20.59 nm
Lattice Constant	2.885 Å
Micro-strain	3.90×10 ⁻³
D-Spacing	1.4214 Å



Fig. 2. Optical Microscopy image of Fe77-Ga23 alloy.

The optical microscopy image of Fe₇₇-Ga₂₃ alloy with the average grain size of 22µm is shown in Fig.2. In the OM image equiaxed grains of single (A2) phase is observed. It is also observed that the grains close to the surface exhibit a greater degree of deformation than those in the centre^[5]. The Differential scanning calorimetry curve shown in Fig.3. reveals the existence of DO3 and A2 phase. Many peaks are found in DSC curve indicates the alloy is in disordered state. The steep peak around 420 °C indicates the DO₃ phase at the particular temperature. Around 500 °C the drastic increase in the peak indicates DO₃ phase transformed to A2 phase [6]. The inset in Fig.3. shows the hysteresis loop of Fe₇₇-Ga₂₃ alloy. The saturation magnetization of is proportional to the grain size. Notably, the magnetic properties of Fe-Ga alloys are influenced significantly by their structural ordering and microstructure [7].



Fig. 3. Differential scanning calorimetry curve and inset hysteresis loop of Fe₇₇-Ga₂₃ alloy.

Conclusion

The Structural, thermal and magnetic properties of Fe_{77} -Ga₂₃ was observed. The XRD pattern confirms the presence of disordered A2 and DO₃ phases with a Body-Centered Cubic (BCC) structure; no additional superlattice peaks were observed. The average grain size of the Fe_{77} -Ga₂₃ alloy was determined to be 22m using optical microscopy. The steep peak near 420°C indicates the presence of the DO₃ phase at that temperature. Around 500°C, the abrupt increase in the peak indicates the transition from DO₃ to A2.

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Hierarchical Relaxation In The Vortex Matter Of Superconducting Nb99Zr01 Alloy

Jagdish Chandra and M. A. Manekar

FEL & Utilization Section, Raja Ramanna Centre For Advanced Technology, Indore, 452013

*Corresponding author: jagdishchandra@rrcat.gov.in

Abstract

We report experimental studies on relaxation dynamics in the superconducting state of $Nb_{99}Zr_{01}$ as-cast alloy. Magnetization was measured as a function of time at a fixed temperature of 2K under various magnetic field values. The non-exponential relaxation of magnetization is described within a framework of interacting clusters that leads to hierarchical relaxation. Our work reported here suggests that clusters of flux lines (flux bundles) which interact with each other, participate in the relaxation process instead of single isolated flux lines. The observation of hierarchical relaxation indicates a continuously evolving landscape of the underlying pinning potential.

Synthesis and characterization of sugar coated superparamagnetic Zn_{0.5}Fe_{2.5}O₄ nanoparticles

Sudeep Tiwari, Ganesh Lal and Sudhish Kumar

Magnetism Laboratory, Department of Physics, Mohanlal Sukhadia University, Udaipur-313001

Presenting author: phd_tiwarisudeep@mlsu.ac.in

Abstract

Magnetic and optical properties of green sol gel synthesized $Zn_{0.5}Fe_{2.5}O_4$ nanoparticles using sugarcane juice as fuel and capping agent have been investigated. The prepared ferrite has found to been surface functionalized by sugar coating as confirmed by FTIR and difference in average crystallite size and size of magnetic particle. Sugar coated $Zn_{0.5}Fe_{2.5}O_4$ nanoparticles absorb considerable light in the visible and UV region and display semiconducting behaviour ($E_g = ~1.7eV$). ESR study provided g factor=2.08, which is attributed to presence of Fe^{+3} in high spin state. Room temperature M-H curve fitted with Langevin function revealed that sugar coated $Zn_{0.5}Fe_{2.5}O_4$ nanoparticles display superparamagnetism with saturation magnetization of 37 emu/gm (1.58µB/f.u.).

The ΔH -M and ΔM -H techniques to understand the magnetic biasing in magnetic composite

Murli kumar Manglam^{1*} and Manoranjan Kar¹

¹ Department of Physics, Indian Institute of Technology Patna, Bihta, Patna-801106, India

*Corresponding author: murli.pph17@iitp.ac.in

Abstract

Composite of BaFe₁₂O₁₉ (BHF) and CoZn_{0.25}Fe_{11.75}O₄ (CZFO) exhibits magnetic biasing, i.e., the influence of two magnetic phases on each other. This magnetic biasing in magnetic composites is the center of discussion for the last few decades to tune the magnetic parameters for technological applications. But there is no direct method to understand the magnetic interaction between two phases in the composite. This magnetic interaction is mostly due to surface interaction between two magnetic materials if they are below their spin coherence length. In the present study, the loop width (ΔH)-Magnetization (M) and switching field distribution (a derivative of demagnetization with respect to applied field, ΔM -H) techniques have been employed to understand the magnetic biasing between BHF and CZFO in the composite. The present study opens a new window to understand the magnetic interaction between different magnetic phases in the composite.

Introduction

The composite of magnetic materials is widely used in various fields [1-2]. Spinel ferrite is generally soft magnetic materiel, which has moderate saturation (M_s) , low coercive field (H_c) , high permeability, and low anisotropy. Hexaferrite has a large coercive field, moderate saturation magnetization, and high anisotropy field [1-3]. The combination of these two ferrites (spinel+ hexaferrite) gives a novel magnetism. These composite can be applied as a filter, shifter, microwave absorber, circulator, and hyperthermia agent [1]. The 0-3 type of composite is leading in the research area, due to inexpensive in production, high corrosion resistance, and chemical reaction between two phases can be negligible [2].

In the present study, the $BaFe_{12}O_{19}$ (BHF) was chosen as the hard magnetic phase due to large coercivity (~3.5 kOe), and CoZn_{0.25}Fe_{11.75}O₄(CZFO) was chosen as soft magnetic phase due to low coercivity (~0.5 kOe), and saturation magnetization (\sim 70 emu/g) [2,3]. The hardness of magnets depends on saturation magnetization, and anisotropy constant (K). The hardness parameters are defined in terms of k, $k=4K/\mu_o M_s^2$. If k<<1, i.e., soft magnetic phase, in this case, magnetic static energy dominated, and if k >> 1, i.e. hard magnetic phase, in this material, magnetic anisotropy is dominated factor [4]. Researchers have observed the magnetic biasing (kink) at the center of the M-H loop between two magnetic phases (hard and soft). proposed the They were magnetic interaction/biasing of two magnetic phase ΔH -M

curves. If there is a hump observed in ΔH -M curve, that gives evidence of biasing between two magnetic phases. The hump changes with different weight percentages of hard/soft and with different heat treatments [3,5]. The kink in M-H loops is also analyzed by derivative of magnetization versus field (ΔM -H). M.A. Almessiere et al. [1] have analyzed the kink present in M-H loops through the ΔM -H curve. In the present study, the composite of (30) %BHF+(70) %CZFO has been prepared to analyze the magnetic biasing between soft/hard magnetic phase with the help of ΔH -M and ΔM -H curve.

Experimental detail

The individual phase of BHF and CZFO have been prepared by using the sol-gel method [3,5]. The obtained sample through the sol-gel method was annealed at 850 °C at 5 h for BHF and 650 °C at 2 h CZFO. The composite (30) % BHF + (70) % CZFO was prepared by the ball mill method [3]. The crystal phase of this sample were characterized by XRD patterns (Rigaku X-Ray Diffractometer TTRX III,CuK_a with λ ~ 1.5418 A°). The *M*-*H* curve was traced using a VSM (vibrating sample magnetometer, Quantum design versa lab).

Result and discussion

The XRD pattern of composite (30) %BHF + (70) % CZFO is shown in Fig. 1a. The XRD peaks of BHF and CZFO are indicated by *(for BHF) and @ for (CZFO) by using space group P63/mmc and Fd-3m,



Fig.1: (a) XRD pattern, (b) *M*-*H* loop, (c) *ΔH*-*M* curve, (d) *ΔM*-*H* curve, for (30) % BHF+(70)% CZFO composite.

respectively [3].The XRD patterns of the sample confirm the presence of two independent crystal symmetries in the sample. The calculated average crystallite size is 23 (\pm 1) nm and 21 (\pm 1) nm for BHF and CZFO, respectively, by using Scherer's formula [6]. Due to the presence of two different crystal phases, there is a strain created at the interface between the two phases. This strain enhances the physical properties of composites.

The magnetic hysteresis of (30) %BHF+(70) %CZFO composite is shown in Fig. 1b. The M-H loop of this sample is also plotted to employ Vegard's law of magnetization points of BHF and CZF as shown in Fig. 1b. Vegard's law is an established method to analyze the magnetization data in the magnetic composite [3]. The obtained saturation magnetization (M_s) are 63 emu/g and 61 emu/g and coercive field (H_c) are 0.7 kOe, and 0.85 kOe for experimental and calculated M-H loop, respectively. The magnetic interaction present in the composite is due to superexchange interaction (Fe-O-Fe) in BHF(H) and CZFO(S), and also between magnetic particles S/S, *H/H*, and *S/H*. There is a kink observed at the center of the M-H loop. It occurs due to individual spin interaction over interface interaction, i.e., the dipolar interaction between individual grain is greater than exchange interaction at the interface. In that case, the interaction between H/H and S/S is dominated over H/S interaction at the interface. The individual reversing of the hard phase exhibits compare to a high magnetic field than the soft phase. Due to the spin torque influence on each other, the kink indicates at the demagnetization plot [7]. At the saturation state of magnetization, the magnetization of composite is not only due to applied field but also because of contribution by magnetic interaction of BHF and CZFO. If the reverse field is applied, the spin of CZFO and BHF are aligned in the direction of filed. This coherent rotation of spin could break after reaching the anisotropy barrier, and it can reduce the magnetization [3]. The magnetic biasing can be understood by loop width (ΔH) - magnetization (M) curve as in Fig. 1c. If there is a hump observed in the ΔH -M curve, it gives the idea about magnetic biasing between two soft-hard

magnetic phases. The magnetic biasing between two phases in the composite is also analyzed by switching field distribution (a derivative of magnetization with field) (ΔM) versus H) [1]. If there are two maxima present in (ΔM) versus H plot, there is magnetic biasing present between the two magnetic phases. This proves that soft/soft and hard/hard grains (dipolar interaction) are present in this sample. There are two maxima present in the ΔH -M plot, which is indicated by the arrow in Fig. 1d. The kink in the hysteresis loop can disappear, if the coupling constant $J_{critical} \leq J$, which rely on saturation magnetization, coercive field, and diameter of both magnetic phases [8].

Conclusion

The composite of (30) %BHF + (70) %CZFO was successfully synthesized by ball mill method. The crystal phase of both phase confirm by XRD. The kink observed at the center of *M*-*H* loop suggests the magnetic biasing between two magnetic phases. The magnetic biasing is analyzed by ΔH -*M* and ΔM -*H* curves. There is a dip observed in the ΔH -*M* curve, and two maxima observed in the ΔM -*H* curve, suggesting the magnetic biasing between two magnetic phases in the magnetic composite.

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Doping Induced Band-Renormalization in 122-type Fe-based Superconductor

Ram Prakash Pandeya¹, Sawani Datta¹, Anup Pradhan Sakhya¹, Rajib Mondal¹, Tanushree Saha², Giovanni De Ninno^{2,3}, Paolo Moras⁴, Matteo Jugavoc⁴, Carlo Carbone⁴, A Thamizhavel¹, and Kalobaran Maiti^{1*}

¹Department of Condensed Matter & Material Science, Tata Institute of Fundamental Research, Mumbai, 400005, India,

²Laboratory of Quantum Optics, University of Nova Gorica, 5001 Nova Gorica, Slovenia, ³Elettra-Sincrotrone Trieste, Area Science Park, 34149 Trieste, Italy,

⁴Istituto di Struttura della Materia, Consiglio Nazionale delle Ricerche, Area Science Park, I-34149 Trieste, Italy.

*Corresponding author: kbmaiti@tifr.res.in

Abstract

In this paper, we study the effect of doping on electronic structure of 122-type Fe-based superconductor (FeScs) using angleresolved photoemission spectroscopy (ARPES). We find significant orbital-dependent band-renormalization with doping along with an enhanced spin-orbit coupling (SOC) strength leading to an increased band separation. Experimental results could be captured well using density functional theory. We find that pnictogen height plays an important role in the electronic structure.

Temperature dependence of reciprocal susceptibility in linear Mn chains of Ti₄MnBi₂

Akariti Sharma¹

¹Theoretical Physics Division, Physical Research Laboratory, Navarangpura, Ahmedabad, India-380009

*Corresponding author: akaritisharma@gmail.com

Abstract

We applied the self-consistent renormalization theory of spin fluctuations implemented with first principles calculations for a quasi-one-dimensional system: Ti₄MnBi₂. The inverse susceptibility is calculated at finite-temperature T and compared with the experimental data (*Phys. Rev. B* **102**, 014406, 2020). A Curie-Weiss fit to our results suggests that the Mn moments are in the low-spin half configuration and the estimated Curie-Weiss moment is pointedly reduced from Hund's rule value.

Introduction

In past, magnetic properties of itinerant electron systems have been explored by using the Hubbard model and the self-consistent renormalization (SCR) theory of spin fluctuations [1]. The SCR theory excellently captures the dynamics of spin fluctuations beyond the random phase approximation (RPA). It is found that the study of spin fluctuations effects in three-dimensional (3D), two-dimensional (2D) and one-dimensional (1D) systems are equally important. However, there are many unanswered questions about how the magnetic properties are influenced in the low-dimensional (LD) systems. Such effects in 1D itinerant electron systems have been only discussed in 1D organic conductors [2] consisting of metallic spin chains. In metallic spin chains, the ratio of the Coulomb interaction and the bandwidth are almost equal. The electronic interactions and inter-chain coupling in these compounds are sufficiently strong to give rise to many-body ground states like Wigner crystallization, superconductivity, magnetic order, metal-to-insulator transitions, etc. In such systems, strong quantum spin fluctuations suppress magnetic order and show quantum effects at low-T [2,3]. In literature, very few studies are available on such systems as KCuF₃, SrCuO₂, Sr₂CuO₃, and CuSO_{4.5}D₂O. Therefore, the current need is to identify new compounds consisting of metallic spin chains which have potential applications. Here, we investigated Ti₄MnBi₂ [4] compound which having 1D character, and magnetic properties are calculated using SCR theory.

Theoretical and computational details

Starting with single-band Hubbard model, the dynamical susceptibility of quasi-1D antiferromagnetic metals in SCR theory [3] is calculated as

$$\chi(Q+q,\omega) = \frac{\chi(Q+q)}{1 - \frac{i\omega}{\Gamma_{Q+q}}} \tag{1}$$

with
$$\Gamma_{Q+q} = \Gamma_0(\kappa_s^2 + q^2); \ \Gamma_0 = \frac{A}{c};$$
 (2)
 $\kappa_s^2 = \frac{\chi_0(Q)}{\alpha_s A \chi(Q)}; \ \alpha_s = 2I \chi_0(Q) > 1$

In Eq. (1), $\chi(Q+q)$ is the static spin density susceptibility of interacting electrons, Γ_{Q+q} is the damping constant, Q being the antiferromagnetic wave vector, $q = \sqrt{q_x^2 + q_y^2}$ and $\chi_0(Q)$ is the static spin susceptibility of free electrons. The other notations are standard [3]. Therefore, the inverse spin susceptibility for quasi-1D systems takes the form as

$$\frac{1}{\chi(Q)} = \frac{1 - \alpha_S}{\chi_0(Q)} + \frac{5}{3} F_S S_L^2(t)$$
(3)

Here, Fs is the mode–mode coupling constant for the Fourier components of spin density around Q. The second term in Eq. (3) represents the effect of antiferromagnetic spin fluctuations where $S_L^2(t)$ is the mean square local amplitude of thermal spin fluctuations (spin local amplitude) and is defined as

$$S_L^2(t) = \frac{3T_0(1+\delta_S)}{\alpha_S T_A} \int_0^1 dx \left[\ln u - \frac{1}{2u} - \phi(u) \right]$$
(4)
where $\delta_S = \frac{\chi_0(Q)}{\alpha_S \chi(Q)};$ (5)

$$u = \left(x^2 + \frac{1}{2\alpha_S T_A \chi(Q)}\right) \frac{1}{t} ; t = \frac{T}{T_0}$$

$$T_{0} = \frac{I_{0}}{2\pi} q_{B}^{2}; \, \bar{A} = \frac{A}{2\chi_{0}(Q)}; \, T_{A} = \bar{A}q_{B}^{2}$$
$$\phi(u) = \ln u - \frac{1}{2u} - \frac{1}{12u^{2}}$$

In Eq. (4), $(1 - \alpha_s)^{-1}$ is the Stoner enhancement factor. Next, q_B is the cut-off value of q. Therefore, in low-T limit Eq. (3) takes the form as

$$\frac{1}{\chi} = \frac{1-\alpha}{\chi} + \frac{5F_S T_0}{\alpha T_A} \frac{t^2}{24y^2} \left\{ \left\{ \frac{y}{1+y} - \ln(1+y) \right\} + \left\{ \frac{y}{x_c+y} - \ln\frac{x_c+y}{x_c} \right\} \right\}$$
(6)

With $y = 1/2\alpha T_A \chi$ and $x_c \neq 0$ is the cut-off wavenumber of the lower bound in the integral. Computationally, the first principles calculations were done using the projector augmented-wave (PAW) method implemented within the VASP (Vienna Ab-initio Simulation Package). Generalized Gradient approximation (GGA) was used with Perdew-Burke-Enzerhof (PBE) exchange-correlation functional. Structure relaxation of Ti₄MnBi₂ was done with density functional theory (DFT) calculations while magnetic properties were investigated with DFT+U+SOC (spin-orbit coupling) method. The structure optimization was done with the gamma-centered Monkhorst-Pack of 6×6×6 k-point mesh within an energy cut-off of 300eV. The crystal structure of Ti₄MnBi₂ (although not shown here) having linear chains of Mn atoms with a very small inter-atomic spacing in comparison to inter-chains spacing emphasizes its 1D character.

Results and discussion

In Fig. 1, numerical results from DFT calculations are presented for density of states (DOS) which are implemented within the SCR theory to calculate spin susceptibility in Ti₄MnBi₂ compound. In Fig. 2, the T-dependence of the inverse magnetic susceptibility χ_0/χ is plotted in comparison with the experimental data [4]. Our results are in good agreement with experimental data and best fitted to Curie-Weiss (CW) behavior. For the fitting, CW plot is obtained from its conventional expression i.e $\chi = C/(T-T_P)$, where C is the Curie constant and T_P is the paramagnetic Weiss temperature. After linearizing the CW plot the estimated value of CW moment μ_{CW} is 1.77 μ_B/Mn . This reduction of the Mn moment from its maximal Hund's rule value i.e $5\mu_B$ can be associated with the itinerant nature of Mn moment in Ti₄MnBi₂. The negative value of T_P (\approx -9K obtained by extrapolating the CW plot) indicates that the dominant interaction is antiferromagnetic. To compare our results with experimental data exchange constant (α =2I χ_0) can be estimated using T_P as T_P = -J_c/2k_B for spin-half configuration, which leads to $J_c \approx 18K$ (1.3meV). In our calculations, we take $J_c=I$ and $\chi_{Pauli} = \mu^2_B \rho_{\gamma}(E_F) = \chi_0$. Here μ_B is Bohr magneton and $\rho_{\gamma}(E_F) = (\pi k_B)^2 / 3\gamma$ is the DOS at E_F deduced from the experimentally calculated γ (57mJ/molK²)[4]. Therefore, we take $\gamma_0=7.89\times10^{-4}$ cm³/mol and

I=1.3meV to calculate α =2I χ_0 . The set of Eqn. (3), (4), and (5) are solved numerically in an iterative manner within a predefined tolerance of 10^{-7} to obtain the self-consistent spin density susceptibility by taking an initial guess for δ -value from the RPA.



Fig. 1. The density of states $(\rho_{bnad}(E_F))$ vs Fermi level.



Fig. 2. χ_0/χ vs T/T_F (T_F is Fermi-Temperature).

Conclusions

We have studied the magnetic properties of Ti₄MnBi₂ that contains 1D chains of Mn atoms. Our results are in agreement with experiments and lead to a CW magnetic moment of 1.77 μ_B/Mn . From CW fit, the negative value of T_P suggests that it is antiferromagnetic. Our predictions indicate that d-electron based compounds like Ti₄MnBi₂ are itinerant magnets and demands future investigations.

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Characterization of unusual vortex-velocity fluctuations above unjamming threshold in 2*H*-NbS₂ superconductors

Biplab Bag^{1,†}, A K Sood², and A K Grover³, S S Banerjee^{1,*}

¹ Department of Physics, Indian Institute of Technology, Kanpur-208016, India ² Department of Physics, Indian Institute of Science, Bengaluru 560012, India

³ Department of Applied Sciences, Punjab Engineering College, Chandigarh 160012, India

*Corresponding author: satyajit@iitk.ac.in

Abstract

Here, using 4-probe transport measurement, we investigate the unusual voltage (V) fluctuations above a non-equilibrium (NE) jamming/unjamming transition for a driven vortex matter in 2*H*-NbS₂. Analysing the time (t) series of voltage fluctuations (V(t)) at the unjamming threshold, we reveal signatures of negative vortex velocity events, where vortex flow seems to occur in a direction opposite to the drive. And we show that these unusual V-fluctuations obey Gallavotti-Cohen non-equilibrium fluctuation relations.

Introduction

Generic depinning phenomenon is a NE transition from a pinned to sliding state under the influence of an external drive. In the context of vortex state depinning in superconductor, recently, in 2H-NbS₂, two distinct depinning thresholds (I_c) have been reported [1,2,3]. While driving, the conventionally pinned static vortex state depins at a lower $I_c (\equiv I_c^l)$, and the driven vortex state reaches a free-flux-flow (FF) state beyond a characteristic drive, I_{cr} [1,2]. In this FF state, the vortex matter exhibits a negative differential resistance transition and falls into a dynamically repined zero velocity state or jammed state [1,2]. Depinning from the jammed state (unjamming) occurs at a higher threshold (I_c^h) [1-3]. Further, the depinning these characteristics across thresholds are characteristically different, for example, (a) while I_c^l decreases with increasing magnetic field (H) or temperature (T) (conventional behaviour), $I_c^h(H,T)$ is insensitive to variations in H or T [1-3]; (b) scaling analysis of the current (I) – voltage (V) curves across I_c^l and I_c^h shows that the *I-V* curves across I_c^l and I_c^h scale satisfying different scaling forms [1]. Additionally, unlike smooth depinning near I_c^l , unjamming is associated with large fluctuations in V(I)[2,3]. Here, analysing the V(t) data, we show how the V-distribution changes at different drives and reveal signatures of negative V-distributions (events associated with vortices drifting opposite to the drive with unusually large velocities). We have analysed these negative V-fluctuations using Gallavotti-Cohen non-equilibrium fluctuation relation (GC-NEFR) theorem [4] and from GC-NEFR we estimate a NE temperature scale associated with the unjamming of vortices which is large.

Experimental Details

The electrical transport measurements are performed using four probe geometry in 2*H*-NbS₂ crystals ($T_c =$ 5.8 K) at 2.5 K and 0.7 T (in zero field cooled (ZFC) mode) with $H \parallel c$ and $I \perp c$. From V(t), we calculate the probability distribution (PDF) of V by binning voltage in intervals of 0.50 μ V.



Fig. 1. (a) *I-V* data at 2.5 K and 0.7 T (ZFC) showing unjamming at I_c^h . The stars indicate *I* values at which V(t) is recorded. (b)-(e) Insets shows the V(t) data (captured at 2.5 K and 0.7 T) at I = 40, 49.8, 55.2 & 80 mA respectively and the main panels presents the corresponding P(V) distribution. The thick black line in (c) represents P(V) for FC state. (f) Main panel and inset present $R(W_t)$ at 2.5 K & 0.7 T for ZFC & FC states respectively, with I = 49.8 mA.

[†]Present address: Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai– 400005, India.

Results & Discussions:

Figure 1(a) presents a I-V curve (measured at 2.5 K and 0.7 T (ZFC)) showing unjamming of the jammed vortex matter at $I_c^h \approx 43$ mA. At $I > I_c^h$, V(I) exhibits unusual fluctuations and increases slowly with I. To investigate how this unusual feature changes with drive, we have captured long time series data of the Vat 2.5 K and 0.7 T for various currents (constant). Inset of Fig. 1(b) shows V(t) response measured for 3000 s in the jammed vortex state at $I = 40 \text{ mA} (< I_c^h)$. It shows an initial fall in V(t), which thereafter continues to fluctuate about mean $\langle V \rangle \sim 0$. For the vortex configuration at I = 40 mA in the jammed state, the mean $\langle V \rangle$ is small and the V fluctuations about the </i>are also small. The main panel of Fig. 1(b) shows the PDF of V(t) at 40 mA which shows a perfectly Gaussian distribution with the very small $\langle V \rangle$ and FWHM ~ 3 μ V. At $I \approx I_c^h$, the fluctuations increase significantly. The Fig. 1(c) inset presents the V(t)series at 49.8 mA (just above I_c^h), showing highly fluctuating V(t) response. The corresponding PDF at I = 49.8 mA (main panel of Fig. 1(c)) shows a multipeak non-Gaussian distribution, having peaks with significant probability at positive and surprisingly negative values of 0.02 mV, which are well above the electrical noise (similar features in PDF of V(t) have been observed for driven field cooled (FC) vortices as well (Fig. 1(c)). The peak in PDF profile at V = -0.02mV indicates unusual negative V-fluctuations associated with flow of vortices in a direction opposite to the direction of drive, which are mainly entropy consuming events. Hence, the PDF at I = 49.8 mA indicates that close to the unjamming threshold, the vortex motion is highly inhomogeneous. However with increase in drive, as shown in main panel of Fig. 1(d) at I = 55.2 mA (corresponding V(t) has been shown in inset Fig. 1(d)), the peak at the negative V diminishes and the overall distribution shifts towards positive V, with the $\langle V \rangle$ being positive ~ 0.03 mV (with FWHM ~ 68 μ V). This elucidates that away from the depinning threshold ($I \sim 55.2$ mA), the vortex motion becomes relatively uniform and elastic in nature. However, the PDF at I = 55.2 mA (cf. main panel Fig. 1(d)) also shows finite probability of observation of negative events. Inset of Fig. 1(e) shows the V(t) data at I = 80 mA. It shows a fluctuating

V(t) response with monotonically increasing $\langle V \rangle$ upto t = 1030 s. Beyond t = 1030 s, the V(t) jumps to a higher value and becomes smooth which indicates a transformation from a fluctuating to FF state. The main panel of Fig. 1(e) shows the PDF distribution of V(t) response at I = 80 mA. It exhibits bimodal character with appreciable weight at two positive voltages (at 0.14 mV (with FWHM ~ 69 μ V) and 0.4 mV (with FWHM $\sim 2.6~\mu V)$). The bimodal nature of PDF indicates a mixed driven phase of slower and faster moving vortices. We have already shown in Fig. 1(c) that PDF close to the unjamming threshold indicates large probability of negative voltage fluctuations. To investigate this, we have analysed the V-fluctuations at 49.8 mA using GC-NEFR [2]. GC-NEFR state that for microscopic systems, there exists finite probability of observation of entropy consuming events, though the probability is very small compared to events, inough the probability is very small compared to events in which entropy increases. Using a normalized variable, $W_{\tau} = \frac{1}{\tau} \int_{t}^{t+\tau} V(t') dt' / \langle V \rangle$, the GC-NEFR can be restated as, $R = \frac{1}{\tau} \ln \left(\frac{P(+W_{\tau})}{P(-W_{\tau})} \right) = W_{\tau} \langle s(t) \rangle$ where $\langle s(t) \rangle = H \langle t(t) \rangle / t_{t} T$, and a fix the three time time. $\langle s(t) \rangle = I \langle V(t) \rangle / k_B T_{\text{eff}}$ and τ is the observation time. Hence, if GC-NEFR is valid the $R(W_{\tau})$ must be linear. For the PDF in Fig. 1(c), we have estimated the $R(W_{\tau})$ values (for ZFC and FC states) and the response has been plotted in Fig. 1(f) for different τ . It elucidates a linear $R(W_{\tau})$ response suggesting validity of GC-NEFR relations (for both ZFC and FC states) close to the unjamming threshold at 0.7 T and 2.5 K. Further, from the slope of $R(W_{\tau})$, we estimate an effective temperature scale for the unjamming transition, $T_{\rm eff} \approx$ 10¹⁶ K is overwhelmingly large. It is interesting note that similar large values of T_{eff} have been reported for jammed sheared micellar cells where $T_{eff} \sim 10^{11}$ - 10^{13} K [5]. We believe unjamming corresponds to highly agitated vortex flow trajectories. The high effective temperature corresponds to fluctuations in dissipation in the vortex state associated with vortex flow in this agitated flow regime.

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Ion Beam Mixing of Mn/Al Bilayer Thin Films: Structural and Magnetic Properties

H. Khanduri¹, Mukesh C. Dimri², Prashant Kumar^{1,3}, J. Link⁴, R. Stern⁴ and R. P. Pant^{1,3}

¹Indian Reference Materials Division, CSIR-National Physical Laboratory, New Delhi – 110012, India ²Jaypee University of Engineering and Technology, Guna, M.P.- 473226, India ³AcSIR – CSIR-HRDC Campus, Ghaziabad, Uttar Pradesh- 201002, India ⁴National Institute of Chemical Physics and Biophysics, Tallinn-12618, Estonia

*Corresponding author: himani.khanduri@gmail.com

Abstract

The ferromagnetic τ -phase was achieved in the Mn/Al bilayer thin films by Xe ion irradiation. Mn/Al bilayer thin films were deposited on Si substrate by evaporation technique for the total thickness of 95 nm. These as-deposited films were irradiated by 400 keV Xe ions with the fluences of 5×10^{16} and 1×10^{17} ions/cm². The enhanced ferromagnetic properties of the irradiated films are confirmed from the XRD, MFM, and VSM results.

Introduction

The Mn/Al thin films have gained much attention in recent years due to its perpendicularly magnetized τ -phase with large magneto crystalline anisotropy and high coercivity [1-4]. Among the various phases of MnAl alloy, only one phase is ferromagnetic which is known as τ -phase [1-2]. The tau phase is metastable at room temperature and it is difficult to deposit it on silicon substrates. Previous studies suggest that the formation of alloy films can be achieved by ion beam mixing of alternate metal layers [3]. Therefore, in the present study, we aimed to achieve the τ -phase by ion beam mixing of Mn/Al bilayer thin films deposited on Si substrate by evaporation technique. The structural and magnetic studies are presented in this paper.

Experimental

Thin films of Mn/Al bilayer were deposited on Si substrate by evaporation technique at a pressure of ~10⁻⁷ mbar. First, we deposited Mn layer on Si substrate by electron beam evaporation using a pellet of Manganese (99.99%). Then Al layer was deposited on Mn layer by a thermal evaporation method using an Al wire (99%) as a target. These as-deposited thin films were irradiated by Xe ions having the energy of 400 keV at room temperature with the irradiation fluences of 5 \times 10¹⁶ and 1 \times 10¹⁷ ions/cm². These samples were named F516 and F117 according to the irradiation fluences, 5×10^{16} and 1×10^{17} ions/cm², respectively. The XRD measurements were carried out by using a Rigaku Ultima IV with CuKa (1.5406 Å) target. The thickness and composition of the asdeposited Mn/Al bilayer thin film were measured by Rutherford backscattering spectrometry (RBS). The atomic force microscopy (AFM) and magnetic force

microscopy (MFM) images were studied by using Bruker Multimode NanoScope IIIa. The magnetic hysteresis curves were measured at 300 K by Vibrating Sample Magnetometer (Quantum Design 14 T-PPMS).

Results

The SIMNRA simulation of the RBS spectrum reveals that the total thickness of the as-deposited film was observed ~ 95 nm, [Mn (42 nm)/Al (53 nm)] and the atomic composition of Mn and Al were calculated 54% & 48%, respectively, which is a good Mn/Al ratio for the τ -phase formation [2].



Fig. 1. XRD patterns of as-deposited and irradiated Mn/Al bilayer thin films.

The XRD patterns are shown in Fig. 1. It exhibits only ε -phase for the as-deposited Mn/Al bilayer thin film. The τ (101) peak appears in film F516, whereas F117 film exhibits τ phase with (001) and (111) peaks and ε -phase peaks [2]. The XRD results



suggest that the ferromagnetic τ -phase enhances in the film irradiated at higher irradiation fluence.

Fig. 2. AFM images of (a) as-deposited (b) F516 (c) F117 thin films and MFM images of (d) as-deposited (e) F516 (f) F117 thin films.

The AFM and MFM images for each film were taken simultaneously for the scan area of $5\times5 \ \mu\text{m}^2$ at room temperature and zero magnetic fields (figure 2). The average grain size was observed around 80 nm,170 nm, and 100 nm for as-deposited, F516, and F117 films, respectively. The larger grain growth in the F516 film as compared to as-deposited film can be attributed to the modified microstructure of the Mn/Al bilayer thin film due to the coalescence of the smaller grains, which results in larger grains [4].



Fig. 3. Magnetization and coercivity of as-deposited and irradiated Mn/Al bilayer thin films.

Further increase in irradiation fluence causes the splitting of the grains which reduces the average grain size of the F117 film [5]. The surface roughness was observed as 2, 18, and 40 nm for the as-deposited, F516, and F117 films, respectively. The AFM results suggest that the increase in the

irradiation fluence enhances the surface roughness of the Mn/Al bilayer thin film. The MFM results show that the as-deposited film does not exhibit any domain pattern. The domain patterns appeared in the irradiated films F516 and F117 due to the enhancement of the ferromagnetic τ -phase which is consistent with the XRD results.

The magnetic hysteresis loops measured at 300 K revealed that the saturation magnetization M_S decreases gradually from as-deposited (30 emu/cc) to F516 (3 emu/cc) and then to F117 (2 emu/cc) film with the increase in the irradiation fluence (figure 3), which can be attributed to the increased defects /roughness of the film irradiated with higher fluence [1-2]. Also, the higher magnetization of the asdeposited film can be attributed to the bilaver structure, in which the deformation in Mn lattice near the interface may cause ferromagnetism [6]. The coercivity (H_C) of the F516 film (240 Oe) increases as compared to the as-deposited film (35 Oe) due to enhanced ferromagnetic τ -phase. Further increase in the irradiation fluence leads to a decrease in the coercivity (120 Oe) might be due to the increased defects and disorder in the τ -phase [2].

Conclusions

In conclusion, Mn/Al bilayer thin films were deposited on Si substrate by evaporation technique. These films were irradiated with 400 keV Xe ions at the fluences of 5×10^{16} and 1×10^{17} ions/cm². The ferromagnetic τ -phase gets enhanced in the irradiated films with the increase in the irradiation fluence which is confirmed from the XRD, MFM, and magnetic studies.

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Fe-Based Half Metallic Fe₂MnSi Heusler Alloy For Spin-Injection Devices

R. Chellakumar¹, G. Karthik¹, R. jayashire¹, and K. Ravichandran^{1*}

¹Department of Nuclear Physics, University of Madras, Guindy Campus, Chennai – 600 025, India.

*Corresponding author: ravi21068@unom.ac.in

Abstract

The Fe₂MnSi Heusler alloy was synthesized by solid state reaction method. X-ray diffraction pattern represent the formation of $L2_1$ phase with cubic structure. The surface morphology of the sample was carried out using High resolution scanning electron microscope. The presence of Fe, Mn and Si in the alloy was confirmed using Energy dispersive x-ray spectroscopy. Magnetic property was studied using Vibrating sample magnetometer. The prepared alloy exhibiting soft ferromagnetic property with low coercivity (H_C) of 8.13 Oe. Hence it is suitable for spin-injection and spintronics device applications.

Introduction

Heusler alloys are ternary intermetallic alloys represented by the formula X₂YZ or XYZ, where X and Y is the transition metals and Z is the main group element. In Heusler alloys the half metallic property was first predicted by de Groot et al.¹ Half-Metallic Ferromagnets (HMFs) intent the attention towards the applications of spintronics.² Whereas in HMFs the majority spin band shows the metallic behaviour and the minority spin band exhibits semiconducting behaviour with a band gap at the Fermi level, which is leads to 100% spin polarization.³ This property make these materials optimistic for the applications of spin-injection and spin-manipulation in spintronic devices.⁴ Particularly Si containing full-Heusler alloys are promising materials for spin injector/detector of Si-based spin devices, such as metal-oxide-semiconductor field-effect transistors.⁴ In this research work we synthesized Fe2MnSi Heusler alloy by solid state reaction method. Further several synthesized sample characterised by analytical methods to study structure, surface morphology and magnetic property.

Method and Characterization

The raw materials of Fe, Mn and Si metal powder of 99.9 % purity purchased from Alfa Aesar is used as the starting material. These metal powders are taken in 2:1:1 stoichiometric ratio. Using mortar and pestle the metal powders are crushed to achieve the homogeneity in sample, it was grinded for 18 hours. In order to see the effect of annealing on the structural, morphological and magnetic studies, part of that sample was pelletized and vacuum sealed using the quartz tube with the vacuum atmosphere in the order of 10^{-3} to prevent the oxidation. Then it was subsequently annealed at 1200 °C for a period of 6 hour. Further the structure, surface morphology and magnetic properties were investigated in detail using XRD, HR-SEM and VSM.

Results and Discussion



Fig. 1. XRD pattern of Fe₂MnSi Heusler alloy.

The structural property of Fe₂MnSi Heusler alloy was characterised by using X-ray diffraction and obtained XRD pattern as shown in Fig.1. The peaks obtained at 35.01°, 40.69°, 45.31°, 58.84°, 65.98° and 83.73° corresponds to the diffraction hkl planes (111), (200), (220), (222), (400) and (422) respectively. The XRD pattern was analysed by using HighScore Plus software and it matched with standard ICSD data (ICSD No. 632574). The structure of Fe₂MnSi Heusler alloy was found to be L2₁ phase cubic structure with space group Fm-3m (Space group No.-225). The average crystallite size was estimated by using the Scherrer's formula (a).

$$\boldsymbol{D} = \frac{k\lambda}{\beta\cos\theta} \tag{a}$$

Where, D is the crystallite size, k is the Scherrer's constant, λ is the wavelength of X-ray radiation Cu K α ($\lambda = 1.5406$ Å), β is full width half maximum (FWHM) and θ is the diffraction angle. The calculated average crystallite size was obtained to be 33.18 nm.

The surface morphology study was carried out by High-resolution scanning electron microscope (HR-SEM). The synthesized Fe₂MnSi Heusler alloy found to be random in size it as shown in Fig. 2(a). The estimated average particle size was found to be in the range of $1-15\mu$ m. Elemental analysis was carried out using Energy dispersive x-ray spectroscopy (EDS) attached with HR-SEM, the composition of Fe, Mn, Si in the alloy was found in 2:1:1 stoichiometric ratio.



Fig. 2. HRSEM image of Fe₂MnSi Heusler alloy.

From the SEM-EDS elemental contrast mapping it was proven that the sample surface shows fine distribution of Fe, Mn, Si in the prepared alloy as shown in Fig. 3.



Fig. 3. Elemental contrast mapping of Fe, Mn and Si in prepared Fe_2MnSi Heusler alloy.

The magnetic property of the prepared Fe_2MnSi Heusler alloy was investigated using vibrating sample magnetometer (VSM) measurement in the maximum applied field of +/- 1.5 Tesla. The M - H curves for room temperature as shown in Fig. 4. It is interesting to note that the M - H hysteresis loop possess very small coercivity (H_C) value of 8.13 Oe with a saturation magnetization (M_S) value of 42.64 emu/g and remanence (M_R) found to be of 0.12 emu/g. It possess very low coercivity value, hence it confirms that the sample exhibiting soft ferromagnetic property.



Fig. 4. M-H hysteresis loop of Fe₂MnSi Heusler alloy.

Conclusion

In summary, Fe₂MnSi Heusler alloy was successfully synthesized by solid state reaction method. The structure, surface morphology and magnetic properties were studied. Fe₂MnSi Heusler alloy possess cubic structure with L2₁ phase and the average particle size was estimated to be in range of $1-15\mu$ m. Magnetic properties from hysteresis loop: M_S, M_R and H_C was measured and studied extensively. It exhibit very small coercivity (H_C) of 8.13 Oe. It confirms that Heusler alloy exhibiting soft ferromagnetic property. Hence it is suitable for spin-injection and spin based device application.

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Magnetic Anomalies in Cubic R_4 PtAl (R = Ho and Er)

K. K. Iyer^{*1,2,3}, Ram Kumar¹, S. Rayaprol⁴, Sanjay Mishra², S. Matteppanavar^{2,3}, K. Maiti¹ and E.V. Sampathkumaran^{4,5}

¹DCMPMS, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai – 400005
²KLE Society's Dr. Prabhakar Kore Basic Science Research Centre, KAHER Belagavi- 590010
³KLE Society's, Basavaprabhu Kore Arts, Science & Commerce College Chikodi-591201
⁴UGC-DAE-Consortium for Scientific Research -Mumbai Centre, BARC Campus, Trombay, Mumbai - 400085
⁵Homi Bhabha Centre for Science Education, TIFR, V. N. Purav Marg, Mankhurd, Mumbai - 400088

*Corresponding author: iyer@tifr.res.in

Abstract

We report the results of magnetization, and magnetoresistance (MR) measurements down to 1.8 K on Gd₄RhIn-type cubic compounds, Ho₄PtAl and Er₄PtAl. There are three crystallographic sites for rare-earth (R) ion, providing an opportunity to understand magnetism in such a complex rare-earth environment. Dc magnetization data reveal that the magnetic ordering sets in around 21K and 12K in Er and Ho compounds, respectively. In addition, there is another magnetic feature around 17 K for Ho₄PtAl. Dc electrical resistivity exhibits a weak minimum at a temperature marginally above their respective T_N . There are fascinating findings in the isothermal magnetoresistance (MR) data, the most notable one being multiple sign-crossover for Ho₄PtAl, but not for Er₄PtAl, in the magnetically ordered state, suggesting possible subtle field-induced changes in the magnetic structure of the former. The results overall suggest that these compounds exhibit interesting magnetic and transport properties.

Low temperature structural anomaly in Pr_{0.6}Sr_{0.4}MnO₃

A. D Souza¹, S. Rayaprol², and M. D. Daivajna^{1*}

¹Deptartment of Physics, Manipal Institute of Technology, Manipal Academy of higher education, Manipal 576104 ²UGC-DAE Consortium for Scientific Research, Mumbai Centre, BARC Campus, Trombay, Mumbai 400085

*Corresponding author: mamatha.daijna@manipal.edu

Abstract

The compound $Pr_{0.6}Sr_{0.4}MnO_3$ undergoes magnetic ordering from paramagnetic state to ferromagnetic state just above room temperature, at $T_C = 308$ K. In addition to room temperature magnetism, the compound exhibits another anomaly, that is drop in magnetic susceptibility at T = 89K. In order to understand the origin of this secondary feature, we carried out detailed low temperature X-ray diffraction measurements and find that the crystallographic structure changes from orthorhombic (space group *Pnma*) to mix of orthorhombic and monoclinic structure (space group *I2/a*). Our analysis shows that the transformation from *Pnma* to *I2/a* is incomplete down to 5K, resulting in phase coexistence of mixed structures below 150 K. Detailed analysis of the XRD patterns has been presented and discussed to understand the evolution of the structural transition.

Tailoring Magnetization Switching in Electrodeposited FeNi Films

Kapil Dev¹, Garima Vashisht¹, V. R. Reddy² and S. Annapoorni^{1,*}

¹Department of Physics and Astrophysics, University of Delhi, Delhi -110007, INDIA ²UGC-DAE Consortium for Scientific Research, University Campus, Indore-452001, INDIA

*Corresponding author: <u>annapoornis.phys@gmail.com</u>

Abstract

Magnetization switching modes in electrodeposited FeNi films have been tuned by providing suitable thermal agitation effects. Angular variation coercivity and magnetic microstructure analysis are used to examine the domain reversal mechanism as a result of annealing in an inert and reducing atmosphere.

Introduction:

The study of magnetic microstructures is crucial to understand the situations of domain formation and controlling their behaviour for device fabrication. Soft magnetic FeNi alloys with high permeability are extensively used for high frequency device applications [1]. The magnetic microstructure is strongly influenced by preparation and annealing conditions, composition, crystalline structure, film thickness etc. The deposition of metallic films using electrochemical deposition has attracted significant interest because of cost-effective production and faster deposition rates [2]. The synthesis of Fe₅₀Ni₅₀ alloy thin films using electrodeposition and investigation of magnetic microstructure is of great importance for the technological applications.

Experimental Details:

The electrochemical deposition of Fe₅₀Ni₅₀ alloy thin films was performed in an Autolab PGSTAT 302N having three-electrode electrochemical cell in which Ag/AgCl solution, platinum wire, and ITO coated glass substrate were used as reference, counter and working electrodes respectively. The electrolyte bath was prepared by dissolving equimolar concentrations of FeCl₂·4H₂O and NiCl₂·6H₂O salts along with boric acid (H₃BO₃) to stabilize the pH and prevent hydroxide formation [3]. Cyclic voltammetry measurement was performed at room temperature in potentiostatic mode with voltage ranging from -1.5 V to +1.5 V with scan rate of 0.1 V/s. The co-deposition of Fe and Ni on the substrate occurred between -1.0 V and -1.5 V. The deposited films were washed in distilled water and ethanol to get rid of electrolyte residues. A set of films were annealed in the presence of Ar(95%) + H₂(5%) atmosphere at 400 °C for 1 h in a microprocessor controlled tubular furnace. Asdeposited and the 400 °C annealed films were named sample S1 and S2 respectively. The thickness of these films was ~ 209 nm, measured by VEECO Dektak-150 stylus profiler. The surface morphology and elemental composition of deposited alloy was estimated by scanning electron microscopy (SEM, JEOL JSM-6610) equipped with energy-dispersive spectrometer (EDS). The crystal structures of these samples were characterized by X-ray diffraction (XRD, Bruker AXS D8-Discover) with Cu-K_{α} (λ =1.5406 Å) radiation. Bulk hysteresis loop and angular variation of coercivity were measured by vibrating sample magnetometer (VSM, Microsense EV-9, field range: ± 1 T). Magnetic microstructures were observed using magneto-optical Kerr effect (MOKE) microscope setup (M/s Evico Magnetics, Germany) in the longitudinal configuration (L-MOKE).

Results and Discussion:

SEM images confirm uniform grains distributed all over the substrate for both samples S1 and S2. The Fe:Ni allov composition of deposited material is ~ 54:46 as determined by EDS. The XRD peaks at 44.88° and 50.90° (Fig.1a) corresponding to (111) and (200) hkl planes (JCPDS No. 98-005-6386) confirms FCC phase of FeNi alloy with lattice parameter 3.48 Å. The additional peak at 41.70° in sample S2 corresponds to FeO which evolves due to interfacial diffusion of FeNi into ITO substrate after annealing [4]. To investigate bulk magnetic behaviour of asprepared (S1) and 400 °C annealed (S2) samples, M-H curves were recorded at room temperature. The inplane coercivity (H_c) of S1 is 67 Oe which increases to 123 Oe after annealing (Fig. 1b). Subsequently, the remanence ratio (M_r/M_s) decreases from 0.84 to 0.78 after annealing. The reason is attributed to diffusion of films in ITO substrate and formation of Fe-oxides at the FeNi-ITO interface. The diffusion sites act as pinning centers resulting in pinning assisted domain reversal. This behavior is also verified by angular hysteresis measurements where the plot of H_c versus angle between film plane and applied magnetic field direction well fitted with modified Kondorsky Model and Suponev [5] model for S1 and S2 respectively.



Fig.1 (a) XRD of sample S1 and S2, (b) VSM hysteresis of S1 and S2, (c) Plot of angular H_c

L-MOKE microscopy measurements were performed over the surface area of $0.5 \times 0.5 \text{ mm}^2$ to investigate the magnetic microstructure and surface magnetic behaviour to further investigate the magnetization reversal. The L-MOKE hysteresis loop of S1 depicts a low H_c of 103 Oe and high M_r/M_s of 0.96 (*Fig. 2a*). For S2, H_c increases to 219 Oe while retaining M_r/M_s. The change in surface magnetic behaviour for S1 as compared to the bulk is due to formation of thin superficial iron oxide layer on the film surface. While there is a possibility of mixed BCC-FCC FeNi phase after heat treatment [6]. The switching field for sample S1 and S2 is 103 Oe and 222 Oe respectively which is similar to H_c of corresponding samples.



Fig.2 (a) MOKE hysteresis of sample S1 and S2, MOKE microscopy image of sample (b) S1 and (c) S2

Figure 2b and 2c depicts the magnetization reversal occurring through the formation of zig-zag domains in S1 and S2. Interestingly, it is seen that the

bigger domains in S1 have small regions pointing in the opposite direction (marked in yellow in fig. 2b) which acts as pinning centers in the magnetization reversal. This is in confirmation with the pinning assisted domain reversal observed using angular variation of H_c fitted using Modified Kondorsky model. After annealing these films, the domain size becomes smaller (~ 50-100 mm) with a low contrast (as observed from the reduced gray scale intensity) compared to S1. This indicates randomness of easy axis after annealing, which is also evident by corresponding reduction in M_r/M_s of bulk hysteresis curves. This is specifically due to removal of surface oxides while increasing the thickness of oxides existing at the interface upon annealing due to diffusion.

Conclusion:

The magnetization reversal in electrodeposited FeNi films can be effectively tuned by providing appropriate thermal treatment. Annealing FeNi films in an inert reducing atmosphere result in magnetization switching with the formation of zig-zag domains with reduced dimensions compared to asdeposited films. This is essentially due to reduction of surface oxides and randomization of easy axis after annealing.

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Development of Mg Substituted Lithium Ferrite (LiFe₅O₈) for Microwave Applications

Prajna P. Mohapatra¹, Samuel Talari², Pamu Dobbidi¹,*

¹Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India. ²Physics Division, Department of Basic Sciences & Humanities, GMR Institute of Technology, GMR Nagar, Rajam-532127, A.P, India.

*Corresponding author: pamu@iitg.ac.in

Abstract

Mg substituted lithium ferrites with improved dielectric response are synthesized by the conventional solid-state route. Reitveld refinement disclosed the generation of monophase spinel ferrites (space group – P4₁32). Substituted ceramics exhibited uniform grain growth and maximum density. The dielectric constant is enhanced, and the dielectric loss is significantly reduced (10^{-3} order). A blend of low loss, high permittivity ($\epsilon_r = 3034$), and excellent permeability ($\mu_r = 28$) of LMFO made x = 0.005 specimens suitable for microwave applications.

Magnetic and Exchange Bias Properties of Bulk and Nanocrystalline La_{0.375}Ca_{0.625}MnO₃ Compound

Soma Chatterjee^{1, *}, Kalipada Das² and I. Das¹

¹ CMP Division, Saha Institute of Nuclear Physics, HBNI, 1/AF,Bidhannagar, Kolakta-700064 ² Department of Physics, Seth Anandram Jaipuria College, 10-Raja Nabakrishna Street, Kolkata-700005

*Corresponding author: soma.chatterjee@saha.ac.in

Abstract

Magnetic properties and exchange bias effect of the polycrystalline and nanocrystalline La_{0.375}Ca_{0.625}MnO₃ compounds have been presented. With reduction of the particle size, uncompensated surface spin induced ferromagnetism is pronounced in nanocrystalline sample. However, at higher magnetic field value, long range charge ordering (associated with antiferromagnetic nature) is predominant even in nanoparticles similar as bulk counterpart. Exchange bias properties of both compounds have been found at low temperature with increasing nature depending on the cooling magnetic field. Modification in exchange bias properties in nanocrystalline sample is addressed considering the disordered polymorphs developed within the charge-orbital ordered phase.

Structural and Dielectric Characterization of LiNbO₃ Substituted BiFeO₃

Manojit De^{1, 2*}, H. S. Tewari¹, and R. N. P. Choudhary³

¹Department of Pure and Applied Physics, Guru Ghasidas Vishwavidyalaya, Bilaspur, C.G.-495009
²Department of Physics, Chouksey Engineering College, Lalkhadan, Bilaspur, C.G.-495004
³Department of Physics, Siksha O Anusandhan (Deemed to be University), Bhubaneswar, Odisha

*Corresponding author: <u>manojit.manojit.de1@gmail.com;</u> <u>manojitd@cecbilaspur.ac.in</u>

A polycrystalline lead-free sample having a composition of $Bi_{0.65}Li_{0.35}Fe_{0.65}Nb_{0.35}O_3$ (namely BLFO) is synthesized by a ceramic processing route. X-ray diffraction pattern taken at room temperature was employed to verify the formation of phase and unit cell parameters of the sample. The morphological analysis suggests a dense ceramic with non-uniform grain distribution. The dielectric properties of the material were analyzed at different interval of frequencies (10^2-10^6 Hz) and temperatures (20-480 °C) using impedance spectroscopy techniques. There is a presence of combined grain and grain boundary effects analyzed from this technique. The structural properties correlated with dielectric properties.

Introduction

The group of perovskites including transition metal oxides, rare earth magnetites, rare earth ferrites and bismuth compound fall under typical multiferroics (i.e. TbMnO₃, BiFeO₃, BiMnO₃). The most commonly used term BiFeO₃ has attracted research groups due to it's technological importance [1]; it has high Neel temperature and Curie temperature more than the room temperature (i.e. 643 K and 1103 K respectively). Its symmetry is found to be as distorted perovskite structure (Rhombohedral; space group: R3c) exhibiting canted G-type antiferromagnetic (i.e. responsible for weak ferromagnetism) [2]. The limitations such as leaky ferroelectric loop and low resistivity hamper BFO's capability as device and also in the measurement of dielectric parameters. To remove such problems various types of dopants (i.e. isovalent and allo-valent) are introduced into the BFO based solid solution or thin films. The substitution of Bi³⁺ site with alkaline earth metal, rare earth elements and substitution of the Fe³⁺ site with transition metal are reported by several researchers.

In the present communication, therefore we have synthesized a non-lead perovskite structure of BLFO using high temperature ceramic processing technique. In this compound modified BFO inferred through a literature survey that not much work have been reported for double doped (Li occupied at the Bi site and Nb occupied at the Fe site) BFO is reported. In this context, we have discussed some characterizations such as structural, morphological, and dielectric properties of the prepared composition.

Sample Preparation and Experimental Techniques

The above lead free composition was fabricated using high temperature solid state ceramic processing method. The detailed of synthesis and characterizations techniques reported previously by us [3].

Results and Discussion Structural and Microstructure Analysis

Figure-1 illustrated the XRD pattern of synthesized sample. The phase of the synthesized sample (BLFN) was detected at room temperature by XRD analysis. A standard computer program POWD [4] were used for indexing all peaks. The tetragonal structure has determined and lattice parameters were refined using the least-squares refinement subroutine of POWD. The unit cell parameters (least-squares refined) are a = 6.9761 (24) Å and c = 10.3225 (24) Å and c/a = 1.4797, V = $502.35 (24) (\text{Å})^3$ (with estimated standard deviation of the unit cell parameters in parentheses).

The morphological study of BLFN ceramic is carried out by SEM which is depicted in figure 1 (inset). From the images as depicted, it has been observed that all the samples show asymmetrical shapes and sizes of grains which may be due to instantaneous high temperature calcination and sintering during the synthesis process. The irregularity in the grain size may influence the structural and electrical properties of multiferroic materials. The shape and size of grains are quite different, which shows the existence of polycrystallinity behavior of sample. SEM picture reveals that grains of different dimensions (average grain size ranges from 3-5 µm) are non-uniformly distributed over entire scan region. Due to high temperature synthesis method, a very little amount of inter-granular pores have also been detected in the SEM image [5].

Raman Spectroscopy

Figure 2 reveals room temperature Raman spectra BLFN ceramic. Group theoretical analysis has anticipated that there are 18 optical phonon modes:

 $4A_{1}$ + $5A_{2}$ + 9E for rhombohedral BFO at room temperature.



Fig. 1. Room temperature XRD of the synthesized sample. Inset image shows SEM picture of the sample.

The both A_1 and E modes represents Raman and IRactive modes, whereas the Raman and IR inactive modes is suggested by A_2 modes [6]. All the peaks are moderately coordinated with previously described Raman data of pure BiFeO₃ that's why we fit all peaks taking BiFeO₃ as paternal phase. Here we deconvoluted all the Raman modes present in the samples using Lorentzian function. The peaks near at 137, 225, 274 and 439 cm⁻¹ could be assigned as A₁-1, A₁-2, A₁-3 and A₁-4 phonon modes of BiFeO₃, respectively. The range of 250–850 cm⁻¹ suggests other phonon modes. The Raman peaks below 250 cm⁻¹, assigned to A₁ modes, suggests Bi–O vibrations [7]



Fig. 2. Deconvoluted Raman spectra (room temperature) of the sample.

Dielectric

The figure 3 (a, b) depicts the trend of dielectric permittivity (ε_r) and tangent loss (tan δ) with respect to frequency and temperature. The graph of frequency dependent ε_r , can precisely determine the contributions of different type of polarization in the experimental frequency range at selected temperatures. From the plot, it is seen that both ε_r and tand rises with an increase in temperature while with increase in frequency both the value falls which is reliable with the dielectric material behavior. There is a significant role of a variety of polarization such as ionic, dipolar, space charge act in the compound at room temperature, which is responsible for enhancement of permittivity magnitude at the lower frequency region [8]. The magnitude of permittivity falls at higher frequency and becomes temperature independent due to the influence of electronic polarization over another one. From the graph it is observed that the permittivity value is constant up to (250 $^{\circ}$ C) and further there is a sharp rise of dielectric constant at lower frequency.

Figure 3(b) tells about temperature dependent dielectric parameters. A dielectric anomaly is observed in BLFN near 340 °C at low frequencies. However, at higher frequencies this anomaly disappears, which suggests that this anomaly corresponds to the lowfrequency relaxation process, which rise due to the oxygen vacancies [9]. Thus, this dielectric anomaly does not correspond to ferroelectric phase transition. The T_c disappears for other frequencies or shift towards higher temperature may be due to space charge polarization, diffusion of ions takes place with a rise in temperature. The increase in the value of the dielectric constant may also be related to thermal energy assisted overcoming of the activation barrier for the orientation of polar molecules in the field direction. The nature of dielectric loss at higher temperature is due to some factors like (i) defects created during sintering, (ii) unknown impurity phase and (iii) charge carriers [10].



Fig. 3. Frequency and temperature dependent (a) dielectric constant (b) dielectric loss

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Magnetic Transition in LaVO₃/LaTiO₃ superlattice: A DFT+MC study

Mukesh Sharma and Tulika Maitra

Department of Physics, Indian Institute of Technology Roorkee, Roorkee, 247667, Uttarakhand, India

*Corresponding author: msharma1@ph.iitr.ac.in

Abstract

Magnetic phase transitions have been explored in a superlattice formed by stacking monolayers of LaTiO₃ and LaVO₃ alternately, using *ab-initio* density functional theory (DFT) and Monte-Carlo (MC) simulations. DFT derived intra-layer and inter-layer exchange interaction parameters were used for the MC simulations on a Ising spin model Hamiltonian. Two sharp peaks observed in specific heat without the interlayer exchange coupling indicate two independent magnetic ordering in LaTiO₃ and LaVO₃ layers at different temperatures. Inclusion of interlayer coupling leads to one sharp peak at higher temperature with a broad hump like feature at lower temperature in specific heat indicating a single magnetic phase transition *to C-type* antiferromagnetic phase in the superlattice.

Introduction

Magnetic multilayers, where layers of different magnetic materials are stacked along a particular direction, are a part of a very active area of research because of their huge potential for applications in magnetic switch, memory devices, spintronics etc. Another important area of recent interest is oxide heterostructures where two different oxide perovskite materials (few layers of each) are grown on top of each other to form a heterointerface. These interfaces often show various exotic phenomena like superconductivity, metal-insulator phase transition, magneto resistance, etc¹, which are not present in their bulk counterparts. Such engineered structures formed by combining two different materials of varying properties to generate novel phenomena, is one of the major goals for the research community.

In this work we have studied the magnetic phase transition in a magnetic multilayer formed by two different transition metal oxide perovskite materials LaTiO₃ (LTO) and LaVO₃ (LVO). Oxide perovskites have general chemical formula ABO3, where A and B are cations and O is the anion. The structure is shown in Fig. 1(a) where one can see that B^{3+} ion is surrounded by 6 O²⁻ ions in an octahedral geometry. In Fig. 1(b) we present the unit cell of LTO/LVO heterostructure we have considered here where we have stacked monolayers of LTO and LVO alternately along c-direction. With periodic boundary condition along all three directions we construct the multilayer LTO/LVO. Since both Ti³⁺ and V³⁺ are magnetic with spin S=1/2 and S=1, this system is a magnetic multilaver.



FIG. 1. (a) Perovskite ABO3 structure where yellow, green, and red spheres represent A, B, and O ions respectively, (b) Unit cell of heterostructure LaTiO3/LaVO3 (c) J_1 , J_2 , J_3 showing the exchange coupling between Ti-Ti, V-V, Ti-V ions. In (b-c) green, blue, red, and yellow spheres represent La, Ti, V, and O ions respectively.

Method

To explore the magnetic phase transition in our system, we have first estimated various magnetic exchange coupling (J) using Density Functional Theory (DFT) calculations. Vienna Ab-initio Simulation Package (VASP)² has been used for DFT calculations within the Local Density approximation (LDA) with finite Hubbard repulsion terms (on-site Coulomb(U), exchange energy(J)) using Dudarev³ approach with U_{eff} =(U-J) of values 8eV, 3eV and 3eV applied on La(f), Ti(d) and V(d) orbitals. We estimated three J values (J₁, J₂ and J₃) corresponding to the Ti-Ti, V-V and Ti-V interactions as shown in Fig. 1(c) as per the method suggested by H. J. Xiang et al⁴.

To investigate the finite temperature magnetic phase transitions in our system we performed Monte-Carlo simulations on the following Ising spin Hamiltonian

$$H = \sum_{\langle ij \rangle} J_1 S_{Ti}^i S_{Ti}^j + J_2 S_V^i S_V^j + J_3 S_{Ti}^i S_V^j$$
(1)

where the sum runs over the nearest neighbor sites i and j, and J₁, J₂ and J₃ are the exchange coupling energies between Ti-Ti, V-V, Ti-V ion pairs, and **S** is Ising spin with value 0.5(1.0) for Ti(V) ion.

For the MC, metropolis algorithm has been used. We used cubic lattice of size LxLxL (varying $8 \le L \le 30$ to reduce the size effects⁵) with periodicity along all directions. Out of 10^6 Monte Carlo steps per spin (MCS), $5x10^5$ MCS has been considered for thermal equilibration and next $5x10^5$ MCS are used for calculating the observables like E(energy/sites), specific heat, etc. The specific is calculated by the formula $C_V = L^3T^{-2}(<E^2 - <E>^2)$.



FIG. 2. Specific heat curves as a function of k_bT/J_2 shown here for lattice size (LxLxL).

Results and Discussion

Using the lattice parameters from Eylem et al⁶ who had studied the metal-insulator transitions in doped LaTi_{1-x} V_xO_3 bulk system, we have calculated J₁, J₂ and J₃ using DFT total energy calculations. Calculated J₁ and J₂ are observed to be antiferromagnetic (AFM) in nature with strengths +33.07 and +40.45 meV respectively whereas J₃ is found to be ferromagnetic (FM) in nature having strength -11.83 meV and suggests a C-type AFM ordering at interface region. We have used these J values estimated from DFT in eq (1) to perform the MC simulations to explore the finite temperature properties. In the MC simulations we have normalized all the energy scales by J₂ which is the largest exchange coupling obtained and define $c=J_3/J_2$. We present in Fig 2 specific heat (Cv) as a function of normalized temperature (kbT/J2) for various lattice

sizes without (c=0) and with interlayer coupling c. When there is no interlayer coupling (c=0) we observe two sharp peaks in the specific heat curve at K_{c1} and K_{c2} indicating two independent magnetic ordering in Ti and V layers at two different temperatures with V layers ordering at higher temperature K_{c2} (~2.33) and Ti layers are ordering at lower temperature K_{c1} (~0.47).

However, at finite interlayer exchange coupling $(c\neq 0.0)$, we observe that the specific heat has one broad peak at lower temperature range which remains unchanged with respect to *L* whereas the higher temperature peak is pushed to slightly higher temperature \mathbf{K}_{c} (~2.37) and gets sharper as we increase *L*. This sharp peak at higher temperature represents the critical temperature where the phase transition takes place in the LTO/LVO multilayer system whereas the broad peak indicating short range correlations. Our findings are consistent with previous results in other bilayer systems reported by L. Veiller et al⁷.

Conclusion

In summary, we have studied LTO/LVO magnetic multilayer system using a combination of DFT and MC calculations. We have calculated the intra-layer Ti-Ti and V-V as well as inter-layer Ti-V exchange interactions from DFT calculations. Using those exchange parameters, we have studied the magnetic phase transition in the multilayer system using MC simulations on a Ising type spin Hamiltonian. We observe that with finite interlayer exchange coupling two independent magnetic phase transitions in Ti and V layers are converge into a single phase transition for the entire system.

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Structural and low temperature magnetic studies of M-type barium hexaferrite

Hodam Karnajit Singh, Prajna P. Mohapatra, and Pamu Dobbidi*

Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India.

*Corresponding author: pamu@iitg.ac.in

Abstract

Barium hexaferrite (BaFe₁₂O₁₉) with hexagonal structure has been prepared by conventional solid-state method and calcined at 1000°C. XRD pattern confirmed the formation of single-phase, whereas EDX and elemental mapping reconfirmed the formation of barium hexaferrite. The obtained crystallite size (34.04 nm) is below < 50nm, making it suitable for magnetic recording. High coercivity is observed at both 300 and 5K. The giant coercivity ($H_c = 2.19$ kOe) and high saturation magnetization ($M_s = 62.06$ emu/g) are observed at 5K. Temperature variation ZFC and FC curve is also measured up to 300 K.

Effect Of Magnetic Field On Thermodynamic Properties Of Anderson Lattice Model: An Application To Colossal Magnetoresistive Manganites (Re_{1-X} Ax MnO₃)

Sunil Panwar

Department of Applied Science, Faculty of Engineering & Technology, Gurukula Kangri (Deemed to be University), Haridwar-249404, India * Corresponding author: <u>dr.sunilpanwar66@gmail.com</u>

Abstract

In the present investigation, by using variational method we have studied the effect of magnetic field on various thermodynamic properties like specific heat (C $_v$) & magnetic susceptibility (χ_s) etc. of rare earth manganites doped with alkaline earths namely Re_{1-x} A $_x$ MnO₃ (where Re = La, Pr, Nd etc., and A= Ca, Sr, Ba etc.) exhibiting colossal magnetoresistance (CMR) phenomena. We have used a two band (1-b) Anderson Lattice model Hamiltonian to study these materials in the strong electron-lattice Jahn- Teller (JT) coupling regime an approach similar to the two- fluid models. We find that both the quantities C_v & χ_s increase with increasing magnetic field 'h'& 'm' parameters showing the peak at intermediate values & finally decreases at higher values of h, m parameters. We have shown the curves at temperature 100 K & 300 K only. We have also observed the effect of doping concentration ' x ' on both C $_v$ & χ_s . Both the quantities reduce as we increase the doping 'x'. The peak occurs near x=0.3 which shows the optimum value of x. Our results are in good agreement with the available experimental data.

Introduction

The study of perovskite manganites is undergoing intensive development, not only because of these materials have considerable potential in technological applications related to colossal magnetoresistance effect (CMR) & magnetocaloric effect (MCF) but also because they have many fascinating magnetic & electronic properties. In particular, manganites owe their fame to CMR effect where resistivity of a material is appreciably suppressed by applied magnetic field. It has been discovered that these systems have a rich variety of electronic & magnetic phases, such as ferromagnetic metal (FM-M), antiferromagnetic insulator (AFM-I), ferromagnetic insulator (FM-I), orbital order (OO) & charge order (CO) ground states. The origin of ferromagnetism & anti-ferromagnetism, as well as the transport properties in these systems has been explained well by a double exchange (DE) interaction between the Mn^{3+} & Mn^{4+} ions & a super exchange (SE) interaction between the Mn $^{3+(4+)}$ & Mn $^{3+(4+)}$ ions. Previous studies have shown that the strength of DE & SE interactions in doped manganites is very sensitive to varation in the Mn-O-Mn bond angle & the carrier concentration determined by the Mn $^{3+}$ / Mn $^{4+}$ ratio [1].

In a recent review, Ramakrishnan et. al [2] have presented a new theoretical model of coexisting localized JT polarons and broad band electrons for doped rare earth manganites $Re_{1-x}A_xMnO_3$ and argued that it arises inevitably in the presence of orbital degeneracy and strong JT coupling and claimed that it explains a wide variety of characteristic properties of manganites.

Some time ago, Panwar et al. [3] have developed a variational method to study the ground state and thermodynamic properties of heavy fermion systems using Anderson lattice model. Recently, Panwar et al. had used this variational method in the study of the magneto- transport properties like electrical resistivity & magnetic susceptibility etc. of doped CMR manganites over a fairly wide temperature range at zero &different magnetic fields [4]. In this paper, we continue to use this variational method to study the specific heat & magnetic susceptibility of rare earth manganites doped with alkaline earths at different magnetic fields.

Basic formulation

We start with a model Hamiltonian H_{lb} in the presence of magnetic field **H** which includes ℓ -b hybridization effects and thus can address the low temperature properties of manganites (e.g. resistivity ,Hall effect) [2,4] given by- $H_{lb} = -\sum_{\langle ij \rangle \sigma} \bar{t}_{ij} (b^+{}_{i\sigma}b_{j\sigma}) \sum_{i\sigma} E_{jt} l^+{}_{i\sigma} l_{i\sigma} + U \sum_{i\sigma} n^l{}_{i\sigma} n^b{}_{i\sigma} - J_H \sum_i s_i \cdot$ $S_i - J_F \sum_{\langle ij \rangle} S_i \cdot S_j - \sum_{k\sigma} V_K (l^+{}_{k\sigma}b_{k\sigma} +$ $h.c.) - \mu B \sum_i S_i \cdot h$ and h= g $\sigma \mu B$ H. (1) The detrike of the combala model in Eq.(1)

The details of the symbols used in Eq.(1) are given in ref [4].

Results and Discussion

In our calculations, we have taken the unperturbed band of three dimensional solid represented by simple semi-circular density of states N^c $_{\sigma}$ (ϵ_k) = (2/ π) $\sqrt{(1 - \epsilon_k^2)}$ (which is centred around zero energy) with band width W=2.0eV, *U*=5.0, E _{jt}=0.5, *J_F*= 0.1, *V*= 0.1, ϵ_F = -0.238 eV (for x =0.3) and *J_H* = 1.0 eV. Doping *x* is varied from 0.1 to 0.5. Fig. 1 shows the variation of magnetic susceptibility (χ S) with parameter h& x. Here it is observed that with the application of a magnetic field, χ S (T) values increase at low temperature. This indicates that spin ordering which occurs under field H, increases the χ S (T) of these systems. χ S (T) also



Fig 1: (a)Variation of magnetic susceptibility (χ_s) with doping 'x' at h=0.03, m=0.3 (b) with magnetic parameter 'h' at x=0.3 for U=5.0,E_{jt}=0.5, V=0.1, J_H=1.0, J_F=0.1

reduces as doping x is increased. The peak occurs near x=0.3 which shows the optimum value of x.

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Doping effects in Heusler superconductor, ScAu_{2-x}M_xAl (M: Cu, Pt)

Rajendra Loke, Biplab Bag, A. Thamizhavel and S. Ramakrishnan*

Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai 400005, India

*Corresponding author: ramky@tifr.res.in

Abstract

Here, we report the effect of doping on lattice parameter (a) and superconducting transition temperature (T_c) in Heusler superconductor, ScAu_{2-x} M_x Al (M: Cu (iso-valent doping) and Pt (hole doping)) with x = 0.1 and compare the T_c and a values with that of the parent compound. Rietveld refinement of the powder x-ray diffraction (XRD) shows decrease in lattice parameter (a) with doping. Further, from temperature (T) –dependent susceptibility measurement, we show decrease in T_c in doped compounds. We argue that the negative effects of doping on T_c are associated with change in phonon spectrum with doping.

Introduction

The Heusler family is composed of the intermetallic compounds, having stoichiometric composition, AB_2C (A: a transition metal or rare-earth element, B: a transition metal and C: a main group element) and cubic L21 crystal structure (space group $Fm\bar{3}m$ (225)) [1]. Recently, Heuser compounds have attracted enormous research interest due to their potential applications in spintronic devices. Superconductivity has been reported in various Heusler compounds with T_c ranging from 1.1 K to 5.5 K [2,3,4,5,6]. The superconducting property in these compounds is characterized by weak to moderate electron-phonon coupling and earlier reports suggest that the T_c increases significantly with electronphonon coupling constant (λ_{e-ph}). Generally, in Heusler superconductors, the T_c -dependence on λ_{e-ph} has been observed by replacing one element by other. However, it would be rather interesting to study how λ_{e-ph} and T_c vary with doping.

Recently, type II superconductivity (with $T_c = 5.12$ K at zero external magnetic field) has been reported in ScAu₂Al, in which T_c falls in the highest- T_c regime in this class of materials [7]. Further, it has been reported that among the other Heusler compounds, the λ_{e-ph} is highest in this compound [7]. Hence, it would be interesting to systematically investigate the doping effects in this compound.

Here, we report the variation of lattice parameter and T_c by doping the Au-site with Cu ((iso-valent doping, ScAu_{1.9}C_{0.1}Al) and Pt (hole doping, ScAu_{1.9}Pt_{0.1}Al). For this study, we use only 5% of the dopant concentration and compare the T_c and a values with that of the parent (undoped) compound. We show that in this compound doping has negative effects on T_c and a and these values decrease in the doped compound.

Experimental Methods:

We prepared the polycrystalline samples of ScAu₂Al, ScAu_{1.9}Pt_{0.1}Al and ScAu_{1.9}Cu_{0.1}Al by arc melting the constituents in stoichiometric ratios on a water-cooled copper hearth under excess argon pressure. To obtain homogeneous materials, the ingots were flipped and re-melted 4-5 times. Finally, the ingots were annealed at 973 K for 6 days (wrapped in tantalum foils and sealed in quartz tube under partial pressure of argon).



Fig. 1. Powder XRD data for ScAu₂Al, ScAu_{1.9}Pt_{0.1}Al and ScAu_{1.9}Cu_{0.1}Al

The phase homogeneity of these materials was checked by measuring the room temperature powder XRD pattern using a PANalytical X-ray diffractometer equipped with a monochromatic Cu-K α source (wavelength, λ = 1.5405 Å). The lattice parameter of the materials were obtained via Rietveld refinement of the powder XRD data (using the FullProf software package). We estimated the T_c of the compounds by measuring the *T*-dependent zero field cooled (ZFC) magnetization response at H = 25 Oe in a commercial superconducting quantum interference device (SQUID) magnetometer (MPMS 7, Quantum Design, USA).

Results and conclusions:

Figure 1 presents the powder XRD pattern for the compounds. Absence of any impurity peaks in XRD pattern confirms homogeneous single phase in all the compounds. Here, we would like to mention, we tried to synthesize electron doped compound also, by doping Al site with Si, but we could not grow homogenous compound. From the Rietveld refinement of the XRD patterns in Fig. 1, we estimate the cubic lattice parameter (a) for the compounds and the avalues are listed in Table 1. We show that the lattice parameters in doped compounds are smaller than that of the parent compound. Further, in the Rietveld refinement analysis, by varying the occupation no. of the dopant, we find that the occupation no. corresponding to best fitting yields x = 0.01 for ScAu_{1.9}Pt_{0.1}Al and ScAu_{1.9}Cu_{0.1}Al, suggesting uniform doping in all the compounds.

In Fig. 2, we present the *T*-dependent dc susceptibility (χ) response (demagnetization factor corrected) in the ZFC state with *H* = 25 Oe for all the compounds.



Fig. 2. *T*-dependence of $4\pi\chi$ in ScAu₂Al, ScAu_{1.9}Pt_{0.1}Al and ScAu_{1.9}Cu_{0.1}Al.

The $\chi(T)$ response for all the samples in Fig. 2 exhibits identical features. For ScAu_{1.9}Pt_{0.1}Al, with decrease

in *T*, the $\chi(T)$ exhibits a sharp transition at 4.57 K and becomes negative (i.e. onset of diamagnetic shielding response). We determine the T_c of the materials from the onset of diamagnetic transition and the estimated values of T_c are 4.99 K, 4.57 K and 4.17 K for ScAu₂Al, ScAu_{1.9}Pt_{0.1}Al and ScAu_{1.9}Cu_{0.1}Al respectively. Further, from Fig. 2 we observe that deep in the superconducting state ($T << T_c$), $4\pi\chi = -1$ for all the samples, suggesting complete expulsion of magnetic flux in the interior of the samples (strong superconducting response).

Table 1. T_c and lattice parameters of ScAu_{2-x} M_x Al compounds

compound	<i>a</i> (A)	<i>T_c</i> (K) at 25 Oe
ScAu ₂ Al	6.5301 (2)	4.99 ± 0.05
ScAu _{1.9} Pt _{0.1} Al	6.5285 (3)	4.57 ± 0.15
ScAu _{1.9} Cu _{0.1} Al	6.5214 (5)	4.17 ± 0.10

From Fig. 2, we observe that doping in ScAu₂Al compound has negative effects, i.e., T_c decreases with doping. It is interesting to observe that the decrease in T_c is smaller in hole (Pt) doped sample than that of isovalent (Cu) doping. Since T_c in this class of materials depends on the electron-phonon interaction, it is possible that the doping significantly modifies the phonon spectrum in ScAu₂Al system. However, for better understanding of doping effects on T_c , it is important to investigate the specific heat of this materials for various doping concentrations. Further, it is important to study the doping dependence on the phonon spectrum using inelastic neutron diffraction to observe how the phonon spectrum gets modified with doping, which may lead to the decrease in T_c , observed in Fig. 2.

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Two-dimensional Short-range Magnetic Correlations in the Geometrically Frustrated Maple Leaf Lattice (S= 3/2) compound Na₂Mn₃O₇

Bikash Saha^{1,2}, A. K. Bera^{1,*}, S. M. Yusuf^{1,2,*}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: <u>akbera@barc.gov.in</u>, <u>smyusuf@barc.gov.in</u>

Abstract

Two dimensional (2D) geometrically frustrated quantum magnets having new class of maple leaf lattice (MLL) are of current interest because of their novel magnetic behaviours. In the present study, microscopic understanding of the magnetic properties of $Na_2Mn_3O_7$ having MLL spin system have been investigated by using neutron diffraction study. The present compound exhibits pronounced quantum effects by showing absence of long-range magnetic ordering. In-depth understanding of spin-spin correlations are obtained by comprehensive Reverse Monte Carlo (RMC) analysis, which reveals that the magnetic spin-spin correlations are confined within the 2D MLL lattice planes in $Na_2Mn_3O_7$. The present study provides an insight on the magnetic correlations having new class of frustrated 2D maple leaf lattice geometry.

Growth temperature induced modifications in structure and magnetic anisotropy of magnetron sputtered FeCoB alloy thin films

Neha Gupta^{1,2}, Chanchal³, M. Gupta⁴, D. Kumar⁴, P.N. Rao¹, S.K. Rai¹ and Pooja Gupta^{1,2,*}

¹Synchrotrons Utilization Section, Raja Ramanna Centre for Advanced Technology, Indore 452013, India ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai 400094, India ³Central University of Haryana, Mahendergarh-123029, India

⁴UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452017, India

*Corresponding author: pooja@rrcat.gov.in, drgpooja@gmail.com

Abstract

We report on the evolution of the structure and magnetic anisotropy of magnetron sputtered Si(100)/SiO₂/W/FeCoB thin films prepared at different substrate temperatures (Ts). Film deposited at Ts=300 K exhibits amorphous structure with well-defined uniaxial magnetic anisotropy (UMA) in the film plane. At Ts \geq 673 K, FeCoB films have partially crystalline microstructure, where bcc-FeCo nanocrystalline grains are dispersed in remaining amorphous matrix. Increase in Ts leads to gradual disappearance of in-plane magnetic anisotropy. Coercive field (Hc) shows an increase from ~5 Oe to 63 Oe with growth temperature, though crystallite size remained in the range of 5-6 nm i.e., well below the ferromagnetic exchange correlation length. The disappearance of UMA and increase in Hc with the growth temperature can be ascribed to change in the magnetisation reversal process with increasing surface roughness.

1. Introduction

Amorphous FeCoB thin films have attracted recent research interest due to their applications as electrodes in spintronics devices e.g., magnetic tunnel junctions (MTJs) [1]. Thermal instability of such electrodes leads to decrease in TMR ratio when annealed above ~698 K [2]. FeCoB films having magnetic anisotropy are also being used for magnetic sensors and magnetic data storage devices. Within this framework, in the present study, FeCoB films with different microstructures were prepared and subsequently, the evolution of structure and magnetic anisotropy were studied so as to understand the possible mechanism of decreased performance of the FeCoB based spintronics devices at high temperatures.

2. Experimental

Thin film layer structure Si (100) (sub)/SiO₂/ W (25 nm)/ FeCoB (50 nm) was deposited using a direct current magnetron sputtering system (Orion-8, AJA Int. Inc., USA). Films were prepared at three substrate temperatures (Ts) viz; RT, 573 K and 773 K. All the films were characterized for structural and magnetic properties using complementary techniques of Xray reflectivity (XRR), grazing incidence X-ray diffraction (GIXRD) and Magneto optical Kerr effect in longitudinal geometry (L-MOKE).

3. **RESULTS AND DISCUSSION**



Fig. 1. (a) XRR patterns along with fitting of FeCoB films prepared at different Ts. Inset shows fitting model and SLDP of the films depicting the four-layer model. AFM image of the films prepared at (b)Ts= 300K and at (c) Ts=773 K.

The measured XRR patterns along with fit-todata are shown in Fig. 1. The fitting was done using Parratts's formalism. For all the films the electron density of the FeCoB layer is ~ $2.10 \pm$ 0.05 e/Å^3 , which is close to the electron density of bulk FeCo. The surface roughness of the film increases from 0.8 to 2.3 nm with increasing growth temperature. AFM results also corroborate this observation (Fig. 1 b and c). The average film thickness is ~73 nm for the films deposited at different substrate temperatures.



Fig. 2. GIXRD data of Si/SiO₂/W/FeCoB films with Ts

GIXRD data of film grown at 300 K exhibits only the peaks corresponding to W buffer layer (W- β phase) and a broad halo at ~ 44° corresponds to FeCoB phase. This suggests that FeCoB film has grown in amorphous phase at 300 K. Further increase in growth temperature to 573 K results in appearance of additional peaks corresponding to bcc-FeCo nanocrystalline phase (crystallite size ~6nm). Amorphous halo is still present with ~57% volume fraction, as calculated from the relative area of amorphous to crystalline peak. This suggests that at Ts=573 K, the film structure is partially nanocrystalline, where bcc-FeCo nanocrystalline grains (having size ~5 nm) are dispersed in B rich amorphous matrix. At Ts = 773K, crystalline volume fraction increases from 43% to 47%, whereas grain size remains almost constant (~5-6 nm). It may also be noted that W buffer layer exhibits β -phase, α -phase and mixed $\alpha+\beta$ phase when grown at 300 K, 573 K and 773 K (Fig.2), respectively. The growth of the W film (α or β phase) depends on preparation conditions [3] and needs to be explored in detail.

L-MOKE measurements suggest that films grown at 300 K exhibit well defined in-plane uniaxial magnetic anisotropy (UMA) (Fig.3), which may be due to quenched-in long range anisotropic stresses produced during film growth [4]. With increasing substrate temperature, magnetic anisotropy gradually decreases and film growth at Ts=773 K results in complete disappearance of UMA (Fig.3). The coercive field (Hc) as calculated from the easy axis hysteresis loop is ~5 Oe, 22 Oe and 63 Oe for the films prepared at Ts= 300 K, 573 K and 773 K, respectively. The initial increase in coercivity from 5 Oe to 22 Oe can be correlated with increase in grain size upon nano-crystallisation and can be explained in terms of random anisotropy model [4]. Further, the magnetically isotropic nature and simultaneous increase in Hc (~63 Oe) for the film grown at Ts=773 K (having



Fig. 3. Azimuthal angle (ϕ) dependence of remanence for FeCoB prepared at different Ts (right) The MOKE hysteresis loops at 0° and 90° (left).

grain size and crystalline volume fraction similar to the films grown at 573 K) can be understood by the increase in surface-interface roughness to ~ 2.3 nm for this film. As the films roughened, the domain-wall pinning dominates the magnetization reversal process. Additionally, increase in dispersion of the easy axis with the increase in surface roughness results in averaging of UMA in such polycrystalline films. At 773K, the formation of secondary boride hard magnetic phases is also expected, which may also contribute in increase in Hc by weakening the exchange coupling among the bcc-FeCo grains. Synchrotron based XRD measurements (not shown here) using beam energy of 19 keV were done and no additional peaks were observed, which rule out the possibility of the presence of such secondary phases.

Conclusion

FeCoB Films grown at Ts=300 K exhibits amorphous structure with a well-defined uniaxial magnetic anisotropy in the film plane, which may be due to anisotropic stresses built up during deposition. In the partially nanocrystalline state (Ts=573 K and 773 K) the anisotropy gradually disappears with simultaneous increase in Hc value and surface roughness. With increase in surface roughness domain wall pinning sets-in, which dominates the magnetisation reversal over magnetisation rotation.

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Ni Induced Ferromagnetism in Mn₃Ga

S.V. Malik¹, A. K. Nigam², K. R. Priolkar^{1,*}

¹School of Physical and Applied Sciences, Goa University, Taleigao Plateau, Goa, 403206 India. ²Tata Institute of Fundamental Research, Mumbai, 403005 India.

*Corresponding author: krp@unigoa.ac.in

Abstract

Structure and magnetic properties of Mn_3Ga are dependent on annealing temperature. The high temperature (850°C) annealed Mn_3Ga is antiferromagnetic with a disordered fcc structure, while the tetragonal structure of the low temperature (400°C) annealed Mn_3Ga induces a ferrimagnetic ground state. Ferromagnetic interactions can also be induced by replacing Mn by Ni in the 850°C annealed alloys. A comparative study of the local structures of constituent atoms in these undoped and Ni doped Mn_3Ga alloys indicate structural distortions induced by Ni to be responsible for the ferromagnetism in the cubic alloy.

Influence of Annealing Temperature on Structural and Magnetic Properties of Nanoscale Fe, Mn: SnO₂ and Cr, Mn: SnO₂

Manikandan Dhamodaran^{1*}, Ramaswamy Murugan², Ramesh Karuppannan¹

¹Department of Physics, Indian Institute of Science, Bangalore-560012, India.

²Department of Physics, Pondicherry University, Puducherry 605 014, India.

*Corresponding author: <u>maniphysics.mani0@gmail.com</u>

Abstract

The influence of Fe and Mn co-dopants, Cr and Mn co-dopants and annealing temperature on the structural and magnetic properties of nanoscale SnO_2 were investigated via complementary experimental techniques. $Sn_{0.96}Fe_{0.02}Mn_{0.02}O_2$, $Sn_{0.92}Fe_{0.04}Mn_{0.04}O_2$, $Sn_{0.96}Cr_{0.02}Mn_{0.02}O_2$ and $Sn_{0.92}Cr_{0.04}Mn_{0.04}O_2$ were prepared by high pressure microwave synthesis technique and annealed at 500 °C for 2 h and 450 °C for 6 h. Powder X-ray diffraction (PXRD) pattern of both as-synthesized and annealed samples indicated the single-phase tetragonal rutile structure of SnO_2 . Magnetic studies of as-synthesized samples revealed the paramagnetic nature at 300 K. The prepared $Sn_{0.96}Fe_{0.02}Mn_{0.02}O_2$, $Sn_{0.92}Fe_{0.04}Mn_{0.04}O_2$, $Sn_{0.96}Cr_{0.02}Mn_{0.02}O_2$ and $Sn_{0.92}Cr_{0.04}Mn_{0.04}O_2$ samples annealed at 500 °C for 2 h unveiled the room temperature ferromagnetism (RTFM). In addition, $Sn_{0.96}Cr_{0.02}Mn_{0.02}O_2$ and $Sn_{0.92}Cr_{0.04}Mn_{0.04}O_2$ annealed at 450 °C for 6 h exhibited the RTFM with high saturation magnetization of 4.91×10^{-3} emu/g for the $Sn_{0.92}Cr_{0.04}Mn_{0.04}O_2$. The origin of observed RTFM in the annealed samples was related to the defects based bound magnetic polaron model.

Introduction

Diluted magnetic semiconductors (DMS) have drawn considerable attention in recent times due to their applications in interesting spintronic and optoelectronic devices [1,2]. In particular, diluted magnetic oxide semiconductors (DMOS) showed richness in optical transparency and high spinpolarization at room temperature [2]. Among the various DMOS systems, SnO₂ has been explored much due to interesting properties like wide bandgap (3.6 eV), electrical conductivity, tunable optical and magnetic properties at nanoscale regimes [3,4].

In the present study, we have systematically investigated the influence of Fe and Mn co-doping, Cr and Mn co-doping, and annealing on the structural and magnetic properties of nanoscale SnO_2 via powder X-ray diffraction (PXRD) and physical property measurement system-vibrating sample magnetometer (PPMS-VSM) to reveal the origin and control of RTFM.

Experimental

 $Sn_{1-x}Fe_xMn_xO_2$ and $Sn_{1-x}Cr_xMn_xO_2$ (x = 2 and 4 at.%) were prepared using a high pressure microwave synthesis technique (Anton Parr Multiwave PRO). Required stoichiometric amounts of Sn, Fe, Cr and Mn precursors were dissolved in 200 ml of ethanol and double distilled water premixed in a 1:1 ratio. The pH of the transparent solution was increased to 12 by gradually adding the ammonia solution and then

transferred to the Teflon-lined PTFE vessels of the microwave system. The microwave system was resumed with the following reaction parameters for the temperature-controlled reaction: 200 °C; reaction time, 60 min; microwave power, 900 W. During the reaction process, the pressure builds up in the vessels were measured as 28 bar for all the prepared samples.

To investigate the influence of annealing, a set of as-synthesized samples were annealed at 450 $^{\circ}$ C for 6 h and 500 $^{\circ}$ C for 2 h in a furnace with an air atmosphere.

Results and Discussion



Fig.1 PXRD pattern of (**A**) as-synthesized and (**B**) annealed samples.

PXRD pattern of as-synthesized and annealed samples at 500 °C for 2 h are shown in Fig. 1. The

observed diffraction planes of both as-synthesized and annealed samples revealed the tetragonal rutile structure of SnO₂. The average crystallite size (estimated using Debye-Scherrer formula) of assynthesized and annealed samples were in the range of 2.59-3.25 nm and 6.38-11.96 nm, respectively. The observed changes in average crystallite size demonstrated the substitution of Fe/Mn and Cr/Mn at In site in the host lattice.



Fig. 2 M-H hysteresis loops of as-synthesized samples measured at 300 K. Inset of bottom right indicates the temperature-dependent magnetization (M-T Curve) of Sn0.96Cr0.02Mn0.02O2.

Field dependent magnetization of the assynthesized samples is shown in Fig. 2. The M-H hysteresis loops of the as-synthesized samples indicated the paramagnetic nature at 300 K. Temperature-dependent magnetization (Fig. 2e) of Sn_{0.96}Cr_{0.02}Mn_{0.02}O₂ disclosed no bifurcation in field cooled (FC) and zero field curves (ZFC), demonstrated the dominating typical paramagnetic behaviour. Conversely, the as-synthesized samples annealed at 500 °C for 2 h (Fig. 3) exhibited a weak RTFM at the lower field and dominating paramagnetic behaviour at the higher field. Interestingly, annealed $Sn_{0.96}Cr_{0.02}Mn_{0.02}O_2$ sample showed the high saturation magnetization of 2.12×10^{-3} emu/g with the coercivity and remanent magnetization of 51.33 Oe and 7.62×10^{-5} emu/g, respectively. ZFC and FC curves of Sn_{0.96}Cr_{0.02}Mn_{0.02}O₂ sample were in accordance with M-H hysteresis loops and indicate dominating paramagnetic behaviour. Further, M-H hysteresis loops (Fig. 3) of as-synthesized Sn_{0.96}Cr_{0.02}Mn_{0.02}O₂ and Sn_{0.92}Cr_{0.04}Mn_{0.04}O₂ samples annealed at 450 °C for 6 h exhibited the well-defined M-H hysteresis behaviour at 300 K. In particular, Sn_{0.92}Cr_{0.04}Mn_{0.04}O₂ sample revealed the high saturation magnetization of 4.91×10^{-3} emu/g with coercivity and remanent magnetization of 27.35 Oe and 1.3775×10^{-4} emu/g, respectively.



Fig. 3 M-H hysteresis loops of annealed samples measured at 300 K. Inset of annealed samples ($500 \degree C$ for 2 h) indicates the temperature-dependent magnetization (M-T Curve) of $Sn_{0.96}Cr_{0.02}Mn_{0.02}O_2$.

The comprehensive investigations established the observation of RTFM in annealed samples and the paramagnetic behaviour in as-synthesized samples. The observed RTFM in the annealed samples might be correlated with the defects based bound magnetic polaron exchange mechanism.

Conclusions

The structural and magnetic properties of assynthesized Fe and Mn co-doped SnO_2 and Cr and Mn co-doped SnO_2 of different doping concentrations prepared by high pressure microwave synthesis technique were investigated. The observed RTFM in the annealed samples was merely originated from the intrinsic property and not from the impurity and secondary phases. The RTFM with high saturation magnetization suggested for the room temperature spintronic device applications.

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Structural And Magnetic Properties Of a New High-T_c Heusler Alloy Rh₂FeAl

Sudip Chakraborty^{*}, Shuvankar Gupta and Chandan Mazumdar

Condensed Matter Physics Division, Saha Institute of Nuclear Physics, HBNI, 1/AF, Bidhannagar, Kolkata 700064,

India

*Corresponding author: sudip.chakraborty@saha.ac.in

Abstract

In this work we report a new Heusler compound Rh₂FeAl. XRD analysis confirms presence of B2 type of disorder, while magnetization study reveals high temperature magnetic ordering. Isothermal magnetization study shows the deviation of saturation moment from the theoretically predicted Slater-Pauli value indicating the presence of structural disorder in the system.

Structural and magnetic properties of a new quaternary Heusler alloy CoFeVAl

Shuvankar Gupta^{*}, Sudip Chakraborty, and Chandan Mazumdar

CMP Division, Saha Institute of Nuclear Physics, HBNI,1/AF-Bidhan Nagar, Kolkata-700064,India

*Corresponding author: shuvankar.gupta@saha.ac.in

Abstract

Powder X-ray diffraction and magnetic measurement for a novel quaternary Heusler alloy CoFeVAl reported for the first time. The single-phase and quaternary Heusler alloy structure of the compound established from diffraction pattern taken at room temperature. Temperature dependence of magnetization and isothermal magnetization measured at 2 K reveal the magnetic transition temperature and saturation magnetization to be 58 K and 0.58 μ B/f.u., respectively.

Transient Reflectance Ultrafast Spectroscopy (TRUS) in PLD grown Y3Fe5O12/Gd3Ga5O12

S. Satapathy^{1, 2*}, Mahesh Kumar^{1, 2}, Ravinder Kumar³, Z. Hossain³, G. A. Basheed^{1, 2}, R. P. Pant¹, K. K. Maurya^{1, 2*}

¹CSIR- National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi-110012, India ²Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India ³Department of Physics, Indian Institute of Technology, Kanpur 208016, India

*Corresponding author: <u>kkmaurya@nplindia.org</u>, subhashreenpl059@gmail.com.

Abstract

Magnetization dynamics control at picosecond timescale is of great technological importance from research as well as industrial perspective. In this report we present a detailed study on structural as well as transient ultrafast spectroscopy study on PLD grown YIG thin films. The HRXRD study reveals the growth of film epitaxially on GGG <110> and the XRR study confirms the thickness and quality of the deposited film. Further, high crystallinity is defined by very narrow FWHM values of 0.0047° for YIG obtained from the ω scan. To study the ultrafast photomagnonic phenomena we excited the film with 2.81eV (440nm) pump energy at a different average power and recorded the differential reflectance through pump-probe method. This study develops a link between photonics and magnonics and results in generation of terahertz frequency from a room temperature ferrimagnetic garnet YIG.

Impedance Spectroscopy Of Metamagnetic Eu₂CoMnO₆

Mohd Alam and Sandip Chatterjee*

Department of Physics, Indian Institute of Technology (BHU), Varanasi - 221005 (U.P.), India

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

We report on impedance spectroscopy of polycrystalline Eu_2CoMnO_6 . The structural analysis shows that the Eu_2CoMnO_6 crystallized in a single orthorhombic phase. The cole-cole plot shows single semicircle. The analysis of cole-cole plot and imaginary part of impedance shows semiconducting nature of Eu_2CoMnO_6 . The real part of impedance shows a high value at low temperature and frequency while it decreases at higher temperature and frequency due to increased mobility of charge carrier at higher temperature.

Magnetic Property Of Double Perovskite EuPrCoMnO₆

Satya Vijay Kumar, Mohd Alam, Sandip Chatterjee*

Department of Physics, Indian Institute of Technology (BHU), Varanasi - 221005 (U.P.), India

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

We report on structural and magnetic study of polycrystalline EuPrCoMnO₆. The structural analysis shows that the EuPrCoMnO₆ crystallized in a single orthorhombic phase with a space group Pnma. The temperature dependent magnetic study shows multiple magnetic transition below 160 K. The bifurcation between ZFC/FC magnetization curve shows presence of spin frustration in system. Inverse DC susceptibility shows presence of clustered phase in paramagnetic matrix.

Magnetic and Magnetocaloric Properties of Polycrystalline Bulk and Nanocrystalline Sm_{0.5}Ca_{0.15}Sr_{0.35}MnO₃ Compound

Amanulla Karikar¹, Kalipada Das², and I. Das¹

¹ Condensed matter physics division, Saha Institute of Nuclear Physics, 1/AF, Bidhannagar, Kolkata 700064, India ²Department of physics, Seth Anandram Jaipuria College, 10 Raja Naba Krishna Street, Kolkata 700005, India

*Corresponding author: aman.karikar@saha.ac.in

Abstract

The magnetic and magnetocaloric properties of $Sm_{0.5}Ca_{0.15}Sr_{0.35}MnO_3$ compound reveals that the disordered ferromagnetic and charge ordered antiferromagnetic counterparts present in bulk sample are drastically modified in its nanocrystalline form. The signature of the inverse magnetocaloric part (arises due to kinetically arrested antiferromagnetic phase) at low temperature is vanished with the development of the ferromagnetic correlation in nanocrystalline form of the sample.

Longitudinal Spin Seebeck Effect on Li_{1.02}Fe₅O₈

K. K. Kumawat¹, A. Jain^{1, 2}, and S. M. Yusuf^{1, 2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India **Corresponding author: ajain@barc.gov.in, smyusuf@barc.gov.in*

Abstract

Longitudinal spin Seebeck effect (LSSE) refers to the generation of pure spin current parallel to applied temperature gradient in a magnetic material. In this paper we report LSSE measurements on inverse spinel lithium ferrite compound Li_{1.02}Fe₅O₈ having ferrimagnetic structure (determined using the neutron diffraction technique). The LSSE measurement were performed using the indigenously developed LSSE measurement setup. The observed LSSE voltage (V_{ISHE}) depends on the direction of external magnetic field, following the relation $E_{ISHE} = (\theta_{SH}\rho)J_{SX}\sigma$ where J_s and σ are spin current density and spin polarization vector, respectively.

Emergence of Magnetic Moment by Doping of 3d Transition Dopant in BeP₂ Monolayer

Niyati Gajjar¹, Shivam Kansara^{1, 2}, Sanjeev K Gupta³, Dereje Seifu² and P N Gajjar⁴

¹Department of Physics, SMMPISR, Kadi Sarva Vishwavidyalaya, Gandhinagar 382015, India. ²Department of Physics, Morgan State University, Baltimore, MD 21251, USA ³Department of Physics, St. Xavier's College, Ahmedabad 380009, India ⁴Department of Physics, University School of Sciences, Gujarat University, Ahmedabad 380009, India

*Corresponding author: shivam.smmpisr@ksv.ac.in

Abstract

In this work, we have reported the nature of BeP₂ monolayer by doping of 3d, 4d, and 5d transition metal atom with replacing a single atom of Be and P atom in the supercell of BeP₂ monolayer. We have focused on the magnetic properties of BeP₂ monolayer using density functional theory. As we found that 3d transition metals (Fe, Co, and Ni) are a good candidate for emerging magnetic moments in the system. The pristine BeP₂ monolayer behaves as a non-magnetic system with Dirac code at the Fermi level. There are few previously reported works, who declare the stability of pristine BeP₂ monolayer. The magnetic moments for Fe (Be & P), Co (Be & P), and Ni (Be) doped to BeP₂ monolayer as 2.96, 3.04, 1.65, 1.41, and 1.07 μ B, respectively. These doped systems could be used for a spin diode.

Introduction

Nowadays, low dimensional materials are showing interest of researchers where two dimensional (2D) have special interest for device applications due to cost-effective and reduced size. 2D materials are expected to be good candidates in optoelectronics, spintronics, batteries, sensors, catalysis, energy storage, and other future applications [1]. 2Dmonolayer shows a variety of properties. Materials consisting of a single layer of atoms play an important in expanding new technologies and in such as semiconductor devices, memory storage devices, etc [2].

Beryllium di-phosphide (BeP₂) has recently gotten a lot of attention because of its Dirac semimetal condition, good environmental stability, heat stability and high mobility of the carrier. Here we focused on an atomic sheet P and Be as Be is typically used in two-dimensional binary compounds as a component. [3,4].

Here, the electrical and magnetic characteristics of the BeP₂ monolayer have been described. in which two calculations for the Be and P vacancy and the other calculation with the doping of 3d (Fe, Co, Ni, and Cu), 4d (Pd and Ag), and 5d (Pt and Au) transition metals in 2×2 supercell of BeP₂ monolayer, respectively.

Methodology

We performed ab initio DFT calculations, which were carried out using the Quantum Espresso (QE) [5]. We have done this calculation with the projector

augmented wave (PAW) type of pseudopotential and the exchange-correlation function type is Perdew– Burke–Ernzerhof (PBE) [6] to investigate the BeP₂ monolayer's overall characteristics.



Fig. 1. (a & b) and (c & d) represent the top view of Be and P vacancy as well as doping of 3d, 4d, and 5d transition metals in 2×2 supercell of BeP₂ monolayer, respectively.

We investigated a kinetic power reduction of 400 Ry for the plane-wave foundation. The conjugate gradient approach is used to fully optimise lattice constants and atomic locations without any symmetry-related restrictions, with energy and force convergence requirements of 10^{-5} eV and 10^{-3} eV/, respectively. Integrations of the Brillouin Zone (BZ) were tested $6 \times 6 \times 1$ and $8 \times 8 \times 1$ special *k*-point sampling for the geometry optimizations, electronic and magnetic properties.

Table 1. Lattice constants a, b (Å), magnetic moment (μ_B) , and the binding energy per atom BE (eV/atom) of all presented BeP₂ configurations.

Atoms	Site(s)	a and b (Å)	M.M.	B.E. (eV)
Be- Vac.		19.4 and 13.9	<u>(µв)</u> 0	-0.32
P-Vac.		19.0 and 13.9	0	-0.44
Fe	Be	19.3 and 14.0	2.96	-5.48
	Р	18.8 and 13.8	3.04	
Co	Be	19.3 and 14.0	1.65	-6.39
	Р	18.8 and 13.8	1.41	
Ni	Be	19.3 and 13.9	1.07	-7.39
	Р	19.2 and 13.9	0	
Cu	Be	19.4 and 13.9	0	-3.54
	Р	19.6 and 13.8		
Pd	Be	19.4 and 14.0	0	-4.10
	Р	19.4 and 13.9		
Ag	Be	19.6 and 14.0	0	-2.07
	Р	19.6 and 13.9		
Pt	Be	19.4 and 14.0	0	-3.52
	Р	19.4 and 13.9		
Au	Be	19.4 and 13.9	0	-4.52
	Р	19.6 and 13.8		

Result and Discussion

Structure and stability

The various structural properties of the BeP₂ monolayer with the vacancy of Be and P as well as doping of 3d (Fe, Co, Ni, and Cu), 4d (Pd and Ag), and 5d (Pt and Au) transition metal atom with replacing single atom of Be and P atom in the 2×2 supercell of BeP₂ monolayer in **Fig. 1**. The blue circle is showing the doping of 3d, 4d, and 5d transition metal atoms in the BeP₂ monolayer. BeP₂ has a rectangular lattice with related lattice constants of a = 9.70 and b = 6.98. There are four Be atoms and eight P atoms in each unit cell. BeP₂ has Pg (plane group no. 4) plane symmetry, which means that one unit cell contains two (four) inequivalent Be (P) atoms.

By the study of binding energy, we calculated the stability of the structure as shown in **Table 1**. From **Table 1**, we can see that following Fe, Co, and Ni adatoms with BeP_2 structures have large binding energy which represents the stability of the structures.

Electronic and magnetic properties

The 3d transition metals (Fe, Co, and Ni) as when subjected to a magnetic field, ferromagnetic materials have a tendency to express or exhibit considerable magnetism in the direction of the field. The alignment patterns of these materials' component atoms are primarily responsible for their magnetic. These atoms have a tendency to act like basic electromagnets. The remaining atoms Au, Ag, Cu are diamagnetic while Pd is paramagnetic. The electronic band structures as shown in **Fig. 2** are showing the metallic nature of the complex system. The Fermi energies are -3.02, -2.91, -3.03, -2.91, -3.08 and -2.94 eV for Fe (Be & P), Co (Be & P) and Ni (Be & P), respectively.



Fig. 2. The electronic band structures of 3d transition dopant in 2×2 supercell of BeP₂ monolayer.

Conclusion

The structural and electrical effects generated by several 3d atoms were presented here as Fe, Co, and Ni embedded into Be and P vacancies of BeP₂ monolayers are assessed theoretically for the first time. We found that there is the emergence of magnetic spin as 2.96, 3.04, 1.65, 1.41, and 1.07 μ_B for Fe (Be & P), Co (Be & P), and Ni (Be), respectively with high binding energy. The reported materials are a good candidate for device application as a spin diode.

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Magnetic Properties of Triangular Lattice Pr₂NiGe₃

Soumya Bhowmik*, Sudip Chakraborty, Shuvankar Gupta and Chandan Mazumdar

Condensed Matter Physics Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata- 700064, India *Corresponding author: soumyabhowmikwb@gmail.com

Abstract

Ternary intermetallic compound Pr₂NiGe₃ has been synthesized by arc melting technique and characterized by X-ray diffraction and dc magnetization measurements. The compound crystalizes in hexagonal crystal structure with space group *P6/mmm* where the rare earth atoms are arranged in 2-dimentional triangular lattice along the c-direction. Magnetic study reveals a magnetic ordering near 12.8 K and an additional phase transition around 3.2 K. The non-saturating nature of isothermal magnetization, along with the positive but low value of paramagnetic Curie temperature ($\theta_p \sim 1.2$ K) suggest the antiferromagnetic ordering in association of dominating ferromagnetic interaction. The low temperature anomaly at 3.2 K could thus be attributed to the glassy nature of the magnetic spins due to the simultaneous presence of both the antiferromagnetic as well as ferromagnetic interaction.

Evidence for octahedral tilting in antiferromagnetic La₂TiCoO₆

Papiya Saha, R. Nithya^{*} and A.T. Sathyanarayana

Condensed Matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, HBNI Kalpakkam - 603102, Tamil Nadu

*Corresponding author: <u>nithya@igcar.gov.in</u>

Abstract

Transition metals based double perovskite: La_2TiCoO_6 was synthesized using standard ceramic method. X-ray characterization showed that this compound exhibited monoclinic structure, space group P2₁/n with two formula units per unit cell. Ordering of Ti and Co ions in rock-salt arrangement over B-sites was confirmed by the observation of super lattice reflections. Various structural parameters, bond lengths and angles were extracted from Rietveld refinement analysis. Small distortion index calculated for cobalt octahedra suggested high spin state for divalent cobalt ion. Octahedral tilt estimated from refinement is found to be ~12°. Magnetic transition around 12.5 K was observed in temperature dependent magnetization data and is ascribed to antiferromagnetic transition as inferred from the Curie temperature.

Introduction

Double perovskite materials are compounds with a chemical formula, A2BB'O6, where A site is occupied by larger size cations (Sr, Ba, Ca, etc.) having 12-fold coordination of oxygen and B sites are usually occupied by transition metals with 6-fold coordination of oxygen having lesser ionic radius [1]. B and B' cations are arranged over octahedral sites depending on their relative sizes and oxidation states. If the difference is large; then BO_6 and $B'O_6$ octahedra are ordered either in rock-salt (alternate cation octahedra) or layered (alternate layers of cation octahedra) or columnar (cation octahedra in alternate columns) arrangement with lower symmetric crystal structures (whose symmetry is lower than cubic symmetry) accompanied by octahedral tilts. Recently, double perovskites with the transition metal ions in the B sites are gaining huge interest due to their interesting magnetic and transport properties. La₂TiCoO₆ (LTCO) compound with only one magnetic ion, cobalt is reported to have an antiferromagnetic ground state with different spin arrangements [2, 3].

We have undertaken synthesis of polycrystalline LTCO compound to study detailed structural and magnetic properties to understand correlation between them. Here the A site is occupied by La^{3+} ions whose ionic size, 1.36 Å is smaller than the divalent ions: Sr^{2+} (1.44 Å) and Ba^{2+} (1.61 Å). In order to fill the space created by smaller La ion at A-site, TiO₆ and CoO₆ octahedra are tilted. In this paper, we report various parameters associated with tilting, monoclinic distortions obtained from Rietveld refinement of powder X-ray diffraction data. We also briefly discuss magnetic properties of this compound.

Experimental results

LTCO was synthesized via the conventional solid state reaction route from the raw oxides of La_2O_3 (99.999%, Alfa Aesar), TiO₂ (99.9%, Testbourne) and Co₃O₄ (99.9985%, Alfa Aesar) as per the nominal composition. The oxide powders were thoroughly mixed for several hours before each thermal treatment. The powder was heated at 900°C for 24 hours with intermediate grindings and heatings until single phase compound has formed.

X-ray diffraction data were collected using STOE (Germany) diffractometer in the reflection mode using Cu K_a radiation ($\lambda = 1.5406$ Å) from 10° to 90° with a step size 0.05°. Magnetization measurements as a function of temperature were performed using QD-SQUID magnetometer from 4 K to 300 K in Zero Field Cooling (ZFC) and Field Cooled (FC) methods under 0.1, 0.5, 1, 5, 10, 50 kOe applied fields.

Results and Discussions

Generally, the lower symmetry structures are associated with two kinds of distortions: octahedral tilts and deviations of bond lengths and angles within the octahedra. Octahedral tilts are estimated from the bond angles of \angle Co-O-Ti along *c*-axis while octahedral deviations are quantified by a parameter known as Distortion Index, DI which is calculated using the formula:

$$DI = \frac{1}{6} \sum_{i=1}^{6} \frac{|l_i - l_{av.}|}{l_{av.}}$$

where l_i is the distance from the central atom to the ith coordinate atom, l_{av} is the average bond length.

To evaluate tilt angles, distortions in bond lengths and angles, Rietveld refinement of XRD pattern is carried out using GSAS-2 package [4] for monoclinic structure with the space group, $P2_1/n$ (#14).



Fig. 1. Indexed powder XRD pattern of LTCO. Symbols: observed diffraction pattern; blue solid line: computed diffraction pattern using the structure model given in the text. magenta solid line: difference between (observed-computed); tick marks: expected Bragg positions for P2₁/n space group. *: super lattice reflections revealing rock-salt ordering of Ti and Co ions. Inset: CoO₆ and ToO₆ octahedra along *c*-axis showing octahedral distortions and octahedral tilt along *c*-axis.

La and oxygen ions occupy general position, (4e): (x,y,z), Ti and Co are in special positions, (2c): (0,¹/₂,0) and (2d): (¹/₂,0,0) respectively in the structure model used for refinement. Refinement cycles were terminated when satisfactory agreement between the observed and computed pattern with low R-factors was obtained. Refined unit cell parameters are a =5.5570(4) Å, b = 5.5655(7) Å, c = 7.8561(9) Å, $\beta =$ 89.99°(2) in dimensions of $\sqrt{2}a_p \ge \sqrt{2}a_p \ge 2a_p$ where a_p is the primitive cubic lattice parameter.

The low value of DI for cobalt octahedra, 0.0013 suggests that all the six bond lengths are almost equal ascertaining that Co²⁺ ions are in High Spin (HS). On the contrary, TiO_6 with a high DI value, 0.018 shows higher level of distortions. Inset in Fig. 1 depicts the distortions both octahedra. Furthermore, of distortions observed in the internal bond angles of CoO_6 and TiO_6 octahedra: $\angle O1$ -Co-O3 = 92.9782 and $\angle O1$ -Ti-O3 = 95.0624° imply octahedral tilting. Tilt angle is calculated from bond angle (θ_1) between Ti and Co ions along the c-axis. The octahedral tilt angle estimated from $(180-\theta_1)/2$ is found to be 12.6° which aggress with the reported value (2).

Molar susceptibility (χ) curves in the FC and ZFC modes showed an anomaly at low temperature below 15 K. Variation of external magnetic field has no effect on T_N. Representative χ_{ZFC} and χ_{FC} curves shown in Fig. 2 reveal antiferromagnetic ordering

 (T_N) of Co^{2+} spins at 12.5 K [2]. $1/\chi_{FC}$ in the paramagnetic state is fitted to Curie Weiss (CW) law, $\chi = \frac{C}{T - \theta_{CW}}$ where C is Curie constant and θ_{CW} is Curie-Weiss temperature. The values of θ_{CW} , effective magnetic moment (m.m.) calculated from the fit parameters are -54.7 K and 5.09 μ_B respectively. $\operatorname{Co}^{2+}(3d^7)$ spins in HS ($t_{2g}^5, e_g^2; S=3/2$) state possesses a spin-only m.m of 3.87 μ_B . Higher m.m. indicates that there is a significant orbital contribution due to the presence of triply degenerate ${}^{4}T_{1\sigma}$, ground term of Co²⁺. The orbital contribution to the m.m. is not quenched thus adding to total magnetic moment. The m.m. corresponding to both the spin and angular momentum calculated to be 5.20 $\mu_{\rm B}$. The unquenched orbital m.m. also indicates negligible distortion in CoO_6 octahedron as mentioned above.



Fig. 2. Temperature dependence of molar susceptibility (χ) of LTCO under 1 T and CW fit.

Summary

Phase pure LTCO was synthesized and rock salt pattern of TiO_6 and CoO_6 was confirmed by the presence of super lattice reflections in the XRD pattern. Antiferromagnetic ordering was observed ~ 12.5 K and large effective m.m. determined from CW law indicates significant orbital contribution to the total magnetic moment for divalent Co ions.

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Formation of Nickel Silicide and Appearance of Anomalous behaviour of Magnetic Anisotropy in Nickel thin films

Zainab Hussain¹, V.Raghavendra Reddy² and Subhabrata Dhar¹

¹Department of Physics, Indian Institute of Technology, Bombay, Mumbai, Maharashtra, India ²UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, India.

*Corresponding author: zaineb92@gmail.com

Abstract

In the present work, we have study the formation of nickel silicide at the interface of nickel and silicon (Si), when the nickel (~15nm) is deposited on Si substrate (Si/Ni). Further, we have determined formation of different phases of nickel silicide with temperature annealing by using X-ray reflective (XRR). Besides this, we have investigated the magnetic properties, i.e. magnetic anisotropy and magnetic domain microstructure of as-deposited nickel thin film. For the sake of comparison of interface effect and magnetic properties, we have deposited another Ni film with a buffer layer of Pt between the nickel and Si substrate (Ni/Pt/Si), and examine its magnetic and structural properties. It is found that Si /Pt /Ni is textured along (111) direction, and it has no magnetic anisotropy. However, for Ni/Si, we observed anomalous magnetic anisotropy behaviour (referred to as the collapse of hard axes), i.e., anomalous behaviour of magnetic reversal process at hard axes of magnetization due to magnetic dispersion.
Superconductivity in layered Quasi-1D Ta₂Pd_{1-δ}S₅ nanostrips

Sk Kalimuddin¹, Arnab Bera¹, Satyabrata Bera¹, Raktim Datta¹, Biswajit Das¹, Mohan Kundu², Subodh Kumar De³ and Mintu Mondal^{1*}

¹ School of Physical Sciences, Indian Association for the Cultivation of Sciences, <u>Kolkata</u>-700032, India ² Department of Physics, Acharya Prafulla Chandra College, New Barrackpore, Kolkata, 700131, India ³School of Material Sciences, Indian Association for the Cultivation of Sciences, <u>Kolkata</u>-700032, India

*Corresponding author: Mintu.Mondal@iacs.res.in

Abstract

Topological superconductors with Majorana bound states obey non-Abelian statistics that are potential candidate for quantum computation. Correlated Quasi-1D electron gas systems are known to exhibit most commonly hidden order transition Charge/Spin Density Wave (CDW/SDW) and few predictions of topological aspects. Hidden order transitions are class of slow dynamics and show strong spectroscopic signatures in conductance noise spectroscopy. Here we report the synthesis and characterization of Ta₂Pd₁₋₈S₅ (δ ~0.13) which is a Quasi-1D system. Electronic transport of TPS is insulating in nature and metallic state appears with anomaly in resistivity below 5 K. Deficiency of Pd cites leads to such phenomena.

Temperature Dependent Magnetic Studies of Ni-Zn Ferrites Synthesized by Polyol Method

Dhanyaprabha K C^{1, 2}, Bibin Jacob^{1, 2}, Manoj Mohan^{1, 2}, I.A. Al-Omari³, Hysen Thomas^{*,1, 2} ¹Research and Post graduate Department of Physics, Christian College, Chengannur, Kerala,

²University of Kerala, Thiruvananthapuram, Kerala, India

³Department of Physics, College of Science, Sultan Qaboos University, Al Khood 123, Oman

*Corresponding author: hysenthomas@gmail.com

Abstract

The effect of Nickel substitution in Zinc ferrite powder is investigated. A series of $Ni_xZn_{1-x}Fe_2O_4$ nanocrystalline powder ($Ni_xZn_{1-x}Fe_2O_4$, x = 1, 0.75, 0.5, 0.25, 0) were prepared by Polyol method and annealed at 800^oC for 12 hours. The samples were then characterized using X ray diffraction as well as Vibrating sample magnetometry (VSM). The temperature dependent magnetic properties were also studied. XRD results revealed that the prepared samples were of Cubic spinel structure and particle size falls in nano meter range. The magnetic hysteresis at room temperature and 5K was recorded. The saturation magnetisation increases gradually from X = 0.0 to 0.5 and reaches to the maximum value and then decreases gradually while Ni^{2+} composition increases. The coercivity, retentivity and its variation with Nickel concentration are studied in detail. The temperature dependent magnetic studies predicted the superparamagnetic behaviour of the samples.

Key words: Zn_xNi_(1-x)Fe₂O₄, FC-ZFC Measurements, Superparamagnetism.

Introduction

Spinel ferrites are complex transition metal oxides which are extensively used in electromagnetic devices such as hard disks, sensors and microwaves. Ferrites possess interesting twin property of electrical insulator and ferromagnetic behaviour. The structural and magnetic properties of spinel ferrites depend on the magnetic interaction and cation distribution in the two sub-lattices i.e., tetrahedral (A) and octahedral (B) lattice sites [1,2].

Ni-Zn ferrites are very important materials from the commercial point of view by virtue of its excellent properties such as low coercivity, high resistivity, high Curie temperature and high mechanical hardness. Therefore, it would be meaningful to investigate the structural and magnetic properties of Ni-Zn ferrites. In this work, we present the systematic investigations on the magnetic properties of Ni substituted Zinc ferrites synthesised by Polyol method.

Experimental

Fine particles of nickel doped Zinc ferrite were synthesized by Polyol method. Nickel nitrate, Zinc nitrate and ferric nitrate were dissolved in ethylene glycol in the molar ratio of (1-x) :(x): 2 at 60°C to form a wet gel. The gel at 120°C results in the self-ignition producing a highly voluminous and fluffy product. The product is then ground to form fine powders. They were annealed in the furnace at 800°C for 12hrs. The structural properties were studied by X-ray diffraction (XRD). The magnetic properties were determined using vibrating sample magnetometer (VSM).

Result and Discussion

The structural analysis of the synthesised samples was studied using Xray Diffraction analysis. The XRD pattern for $Ni_xZn_{(1-x)}Fe_2O_4$ is as shown. The presence of different planes confirms the spinel cubic structure.





The patterns are characteristic with one of the pure structures of $ZnFe_2O_4$ and $NiFe_2O_4$ (JCPDS: 01-089-1010 and JCPDS: 01-086-2267). The peaks indicate the fine particle nature of the $Ni_xZn_{1-x}Fe_2O_4$ particles. The particle size of the prepared samples was calculated using Debye-Scherrer formula [Table (1)]. **Table 1: Calculated crystallite size and "a"**

able 1. Calculated ci ystainte size and a				
Sample	a (Å)	D (nm)		
ZnFe ₂ O ₄	8.42	85.29		
Ni0.25Zn0.75Fe2O4	8.49	82.5		
Ni0.5Zn0.5Fe2O4	8.39	61.06		
Ni0.75Zn0.25Fe2O4	8.44	90.46		
NiFe2O4	8.32	56.47		

Magnetization of all the samples of Ni_xZn_{1-x}Fe₂O₄ was performed under the maximum applied field of 80000 Oe at room temperature and 5K by using VSM [figure (2)]. Both M-H curves confirms soft magnetic nature of the samples. The value of saturation magnetization increases gradually from X = 0.0 to 0.5 and reaches to the maximum value for X = 0.5 composition and then decreases with increasing Ni²⁺. This can be explained in terms of spin-disorder and spin canting. In Ni-Zn ferrite, the Zn^{2+} ions prefer A site and the Ni^{2+} ions prefer B site.



Figure (2): M-H Loop at room temperature and 5K **Table 2: Magnetic parameters**

SAMPLE		300K			5K	
	Ms	M_r	H _C	Ms	Mr	H _C
ZnFe ₂ O ₄	36.28	0.34	8.38	86.84	12.18	365.04
Ni _{0.25} Zn _{0.75} Fe ₂ O ₄	46.22	0.47	11.17	109.08	19.16	343.52
Ni0.5Zn0.5Fe2O4	78.33	1.79	16.76	124.36	5.98	52.08
Ni _{0.75} Zn _{0.25} Fe ₂ O ₄	69.41	3.85	38.67	87.22	6.92	71.45
NiFe ₂ O ₄	48.01	2.82	43.82	51.71	4.13	66.38

As Fe³⁺ ions in the A site is diluted by low concentration of Zn^{2+} , the net magnetization increases. But, magnetization decreases at higher level doping. The reason is that low Zn^{2+} concentration reduce the no of spins occupying the A sub lattice, resulting the increase of net magnetization. As the Zn²⁺ content increases the exchange interactions are weakened and the B spins are no longer held rigidly parallel to the few remaining A spins [2]. The decrease in B sub lattice moment, interpreted as spin departure from collinearity causes spin canting. Coercivity and retentivity of the prepared samples at room temperature and 5K is given in the table (2). Coercivity and retentivity increases at 5K. The small coercivity reveals the soft magnetic nature of the prepared samples [3]. Materials with low retentivity lose their magnetism quickly.

The temperature dependent magnetic properties were studied by FC ZFC measurements under an applied field of 300 Oe in the temperature range from 5 K to 400 K was measured [figure (3)]. In ZFC magnetization increases with temperature up to a maximum and then decreases with increasing temperature [4]. The temperature corresponding to the maxima of ZFC is called blocking temperature (T_B). The blocking and irreversibility temperature is as given in table (3). The FC and ZFC curves meet at a temperature called irreversibility temperature (T_{irr}). The particles show super paramagnetism above blocking temperature. Ferromagnetic particles having very small size and low coercivity poses super paramagnetism [4].

The blocking and irreversibility temperature coincides for uniform system. The results confirm the nonuniform sized particles and the small sized particles contributes for the room temperature super paramagnetic behaviour of the system [5].



Figure (3): FC - ZFC curves Table 3: The blocking and irreversibility temperature

Sample	Tb	Tirr
ZnFe ₂ O ₄	29.73	112.49
Ni _{0.25} Zn _{0.75} Fe ₂ O ₄	109.02	144.78
Ni0.5Zn0.5Fe2O4	28.47	369.96
Ni0.75Zn0.25Fe2O4	76.33	389.50
NiFe ₂ O ₄	160.88	387.55

Conclusion

The Ni-Zn ferrite samples are prepared successfully by Polyol method Structural and magnetic properties are studied by XRD and VSM. XRD confirms the spinal cubic structure of samples. The saturation magnetisation of the prepared samples show increase with the Ni²⁺from X = 0.0 to 0.5 and reaches to the maximum value of for X = 0.5 composition and then decreases with Ni²⁺. The temperature dependent magnetic study reveals the room temperature superparamagnetic behavior of samples.

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Clustered Phase and Meta-magnetic Transition in EuTbCoMnO6

Srishti Dixit, Mohd. Alam, Sandip Chatterjee*

¹Department of Physics, Indian Institute of Technology (BHU), Varanasi – 221005 (U.P.), India

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

We report on structural and magnetic property of polycrystalline $EuTbCoMnO_6$. The structural analysis shows that $EuTbCoMnO_6$ has single orthorhombic phase with space group Pnma. Temperature dependent magnetization study shows a ferro-mgnetic magnetic transition around 113 K. The inverse DC susceptibility shows a down-turn, showing emergence of clustered phase in para-magnetic matrix. The bifurcation between ZFC/FC shows existence of spin frustration in the system.

Topological Insulating Phase In Two-Dimensional Selenene Sulphide: A DFT Study

Raghottam M. Sattigeri¹, Bhautik R. Dhori¹ and Prafulla K. Jha¹

¹Department of Physics, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara, Gujarat – 390 002

*Corresponding author: raghottam.ms@gmail.com

Abstract. We use Density Functional Theory based *first-principles* method to investigate Topological Insulating phase in two dimensional selenene sulphide. The sulphur functionalization of selenene gives rise to dynamic stability since, selenene independently cannot exist in hexagonal lattice due to its electronic configuration. This also gives rise to orbital filtering effects leading to non-trivial topology owing to the broken spatial inversion symmetry. Such non-trivial characters are attributed to the spin-orbit coupling effects which opens a band gap of $\Delta E = 0.167$ eV. We further analyze the non-trivial topology in terms of the \mathbb{Z}_2 invariant and the robust edge states which exhibits chiral spin polarization; confirming the quantum spin Hall effect. This indicates that, Selenene Sulphide has potential room temperature spintronic and nanoelectronic applications.

Introduction

Topological Insulating (TI) phase of materials has gained significant attention in recent years owing to the exotic quantum behavior with insulating bulk and conducting surface/edge states.^[1] This phase typically arises in materials due to the strong spin-orbit coupling (SOC) effects, however, other regimes such as application of pressure, electric field etc. have also been explored to realize TI materials. In twodimensional (2D) regime this behavior was first investigated in graphene, however due to low atomic number and corresponding weak SOC the phenomena could be only realized at ultra-low temperatures making graphene impractical for applications.^[11] This was followed by search for candidate materials with potential room temperature applications.

Discovery of TI phenomena in HgTe/CdTe and InAs/GaSb quantum wells motivated research into several 2D materials since these quantum wells were operable only at ultra-low temperatures and ultra-high vacuum.^[2] Ever since, several 2D TI materials have been predicted to exhibit large-gap for potential room temperature applications.^[3]

Xene's are families of materials with graphene like hexagonal lattice which have been extensively explored from TI point of view. Typically, these materials exhibit small-gap under SOC however, partial/complete functionalization of the surfaces gives rise to non-trivial topologies characterized by SOC induced large-gap owing to the dominant orbital filtering effects (OFE) saturating the *-pz* orbitals.^[4,5]

Group-VI elemental monolayers have also gained attention in this regard. However, due to their electronic configuration; these materials cannot exist in hexagonal lattice.^[3] We previously examined this feature in one of our studies and found that, group-VI elemental monolayers are not dynamically stable in their pristine form but, can be dynamically stable when functionalized partially.

In the present study we explore the effects of functionalization on hexagonal lattice of group-VI selenene (Se) monolayer. This system exhibits non-trivial topology which is evident from the large-gap originating from the SOC effects and quantified in terms of the \mathbb{Z}_2 invariant and the corresponding robust edge states which indicate chiral spin polarization. From our study we propose a candidate 2D TI with potential room temperature spintronic and nanoelectronic applications.

Methodology

We perform *first-principles* based Density Functional Theory (DFT) calculations as implemented in the Quantum Espresso package under plane-wave self-consistent formalism with scalar relativistic, norm-conserving Matrins-Troullier pseudopotentials for calculations without SOC and relativistic projector augmented fully wave pseudopotentials for calculations with SOC. These were implemented under generalized gradient approximations with Perdew-Burke-Ernzerhof type of exchange correlation functional.^[6-8] The optimized value of kinetic energy cutoff is 80 Ry and the corresponding uniform momentum (k) Monkhorst-Pack grid is 8 x 8 x 1.^[9] The structures were fully relaxed with a vacuum of 25 Å along the [001] crystal direction. Following this, we perform projection of DFT wave functions onto the maximally localized Wannier functions using the Wannier90 code to compute the quantum properties followed by the

generation of tight-binding Hamiltonian as input to the WannierTools code to compute the \mathbb{Z}_2 invariant and edge state spectrum.^[10,11]

Results and Discussion

The optimised lattice structure exhibits buckled hexagonal lattice structure with the alternative partial functionalization of sulphur (S) on the two sub-lattice positions occupied by selenium (Se) atoms (as evident from Fig. 1(b) inset). The optimized lattice constant is 4.80 Å with a buckling height of 0.91 Å. This structure exhibits a semi-conducting gap of $\Delta E =$ 2.3 meV along the high symmetry point K in the hexagonal brillouin zone (BZ). This value is lower as compared to the thermal energy (0.0259 eV) at room temperature (= 300 K) which implies that at room temperature the system will exhibit semi-metallic nature. Under the influence of SOC and OFE this gap gets further enhanced and opens up to $\Delta E = 0.167 \text{ eV}$ as evident from Fig. 1(b) along the high symmetry point K in the BZ which is higher as compared to the thermal energy at room temperature.



Fig. 1. (a) The irreducible BZ of the hexagonal monolayer superimposed with the one for orthorhombic edge ribbon.(b) The electronic structure with and without SOC (inset side and top view of SeS).

We perform the computation of slab band structure of the nanoribbons made up of SeS governed by the orthorhombic BZ (superimposed with the hexagonal BZ presented in Fig. 1(a)). From the slab band structure presented in Fig. 2(a) it is clear that, the SOC induced gap is non-trivial in nature hosting conducting edge states with Dirac cones (indicated by arrow in Fig. 2(a)). This is further confirmed from the edge state spectrum presented in Fig. 2(b) which is obtained by using the iterative Green's function method.^[11] Clearly the Dirac dispersion is evident between the high symmetry points Γ and X (equivalent to high symmetry point K in the hexagonal BZ).

As the edge states are typically spin polarized and chiral in nature, we compute the spin density of states along the edge crystal directions; [100] and [010] to confirm the chiral spin polarization which is clearly evident from Fig. 2(c,d). These analysis qualitatively indicate towards the non-trivial topological character of SeS. To further quantify the topological nature, we compute the \mathbb{Z}_2 invariant which is $\nu = 1$ implying that, SeS is a non-trivial 2D TI.



Fig. 2. (a) – (b) Slab band structure indicating the conducting edge states and edge state spectrum of SeS respectively (arrows indicate Dirac cones). (c) – (d) Edge spin density of states indicating spin polarization along the crystal directions [100] and [010] respectively.

Conclusion

We conclude that, group-VI elemental monolayer Se can exist in hexagonal lattice structure when functionalized with S at alternative sub-lattice positions. This system exhibits non-trivial gap of ΔE = 0.167 eV characterized by the Z₂ invariant $\nu = 1$ and conducting chiral spin edge states with potential room temperature spintronic and nanoelectronic applications.

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Magnetic and Transport Properties of Co₂V_{1.4}Ga_{0.6} Shape Memory Alloy

Snehashish Chatterjee, Prabir Dutta and S. Majumdar*

School of Physical Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India *Corresponding author:sspsm2@iacs.res.in (S. Majumdar)

Abstract

In this work, we have observed a martensitic like structural transition that occurs between paramagnetic(PM) austenite and PM martensitic phases in the studied $Co_2V_{1.4}Ga_{0.6}$ alloy. Their might be a ferrimagnetic state present at temperature below about 50 K. Slight deviation of V concentration from $Co_{50}V_{34}Ga_{16}$ leads to drastic drop in magnetisation value and magnetic transition temperature. The magnetic behaviour observed in the $Co_2V_{1.4}Ga_{0.6}$ is quite different from those of previously reported conventional Ni-Mn based ferromagnetic shape memory alloys.

Introduction

Co-based Heusler compounds are potential candidates in the field of spintronics as they show half-metallic ferromagnetism with high Curie Temperature (T_c) . Apart from that, in recent times Co-based Heusler alloys with slight deviation from their stoichiometric composition (such as Co₂Cr(Ga,Si), Co₂Cr(Al,Si) and Co₂VGa), are observed to undergo martensitic transformation (MPT) behavior (first-order transition from cubic austenitic $(L2_1)$ structure to the martensitic (D0₂₂ tetragonal) structure).[1,2] Stoichiometric Co₂VGa is reported to be a half-metallic ferromagnet with $T_C = 337$ K. However, no MPT has been reported below 1970 K.[2,3] Liu et al. reported the metamagnetic MPT in V-rich Co₅₀V₃₄Ga₁₆ alloy from the FM ($T_C = 180$ K) austenitic phase with highmagnetization to the FM martensite phase with lowmagnetization along with considerable inverse magnetocaloric effect (MCE) of 9.6 Jkg⁻¹K⁻¹and magneto-strain (0.07%).[3] In the present work, we report experimental magnetic and transport study of the off-stoichiometric Co₂V_{1.4}Ga_{0.6} (Co₅₀V₃₅Ga₁₅) alloy. Interestingly, slight deviation in Vconcentration from $Co_{50}V_{34}Ga_{16}$ leads to drastic difference in magnetic properties.

2. Experimental details

Polycrystalline sample of Co₂V_{1.4}Ga_{0.6} was prepared using arc melting technique in argon atmosphere. We performed X-ray powder diffraction(XRD) which was further analysed with the help of the Rietveld refinement technique using MAUD program software .[5] Commercial Quantum Design SQUID magnetometer (MPMS XL Ever Cool model) was used to carry out magnetic measurements. The resistivity (ρ) measurement was measured on cryogen-free low temperature(*T*) high magnetic field(*H*) system (Cryogenic Ltd., U.K.) in the range 5-300 K.

3. Results and Discussions

3.1. Powder X-ray Diffraction

Inset of Fig.1(b) shows the XRD pattern of $Co_2V_{1,4}Ga_{0.6}$ alloy measured at room temperature. Good fitting using the Rietveld refinement technique suggests that the alloy is single-phase with an L2₁ cubic (space group Fm-3m) austenitic phase at room temperature. The lattice parameter obtained after fitting is a = 5.805 Å, which is pretty close to the value of *a* reported for $Co_{50}V_{34}Ga_{16}$ (a = 5.804 Å) [3]. It is to be noted that the superlattice reflection (111) is weak whereas the (200) peak is absent for $Co_2V_{1.4}Ga_{0.6}$.

3.2. Magnetization

We have measured the magnetization (*M*) vs temperature(*T*) at, *H*=1kOe [see Fig 1(a)] in field cooling (FC), field heating (FCH) and zero-field cooling(ZFCH) protocol. On decreasing *T*, *M* increases until about 250 K, and then shows a sharp drop. This drop is associated with a thermal hysteresis, as evident from the loop between FC and FCH data. By comparing with the $Co_{50}V_{34}Ga_{16}$ sample [2], we can assign this thermal hysteresis to be associated with the martensitic type structural transition. Previous studies already have reported a cubic to tetragonal (L21-D022) martensitic transformation in Co-V-Ga alloys.[4] ZFC and FC bifurcate from each other around 50 K.Fig. 3presents the M versus H curves at 2, 150, 230 and 300 K for the sample. The M(H)curves [see fig 1(b)] are found to be linear at high temperatures austensite phase (230 K and 300 K). As T decreases M lowers along with a non-linear nature and prominent hysteresis loop at T = 2 K ($M \sim 0.02$ $\mu_{\rm B}/{\rm fu}$). The sample might be a weak ferromagnet in the backdrop of a paramagnetic phase or it can be a ferrimagnet with extensive moment compensation. However, had the sample been a paramagnet, the value of M at 70 kOe will be large at 2 K. Because all the paramagnetic moment will be aligned to the field. Therefore, a small moment and a loop definitely indicates that the sample is a ferrimagnet with compensated moments.



Fig. 1. (a) M vs T curves for H = 1 kOe (b) Isothermal M-H curve at different constant temperatures. Upper inset: XRD pattern of Co₂V_{1.4}Ga_{0.6} (dark circles) using Cu Ka radiation at 300 K. The Reitveld refinement curve is shown in red lines. Lower inset shows zoomed image of M-H at T = 2 K.

3.3 Electrical resistivity

Thermal variation of resistivity (ρ) for the compound was measured in zero field as well as in presence of H= 150 kOe both in heating and cooling cycles [see Fig 2]. A clear slope change is observed around 275 K close to the magnetic transition temperature in accordance with the magnetic data. From the $\rho(T)$ data a clear signature of first order transition is observed due to presence of hysteresis in heating and cooling cycle. $\rho(T)$ data measured in the presence of 150 kOe field does not show any clear deviation from the zerofield data in the entire temperature regime ruling out the presence of large magnetoresistance.



Fig. 2. Shows the T variation of ρ at zero field and for H = 150 kOe for Co₂V_{1.4}Ga_{0.6} both in heating and cooling cycle

In conclusion, we observe martensitic like structural transition in the studied $Co_2V_{1.4}Ga_{0.6}$ alloy. We argue that a possible ferrimagnet state is present at low temperature (possibly below about 50 K) and the MPT occurs between PM austenite and PM martensitic phases.

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Observation of the Griffith like phase in Pr₂CoFe_{0.5}Mn_{0.5}O₆

Khyati Anand¹, Anita Mohan¹ and **Sandip Chatterjee^{1#}** ¹Indian Institute of Technology (BHU) Varanasi 221005, India [#]Corresponding Email: <u>schatterji.app@iitbhu.ac.in</u>

Abstract

 $Pr_2CoFe_{0.5}Mn_{0.5}O_6$ (PCFMO) system is prepared which is crystallized in orthorhombic phase with Pnma space group. The dc magnetization indicates the magnetic transition at 187 K whereas the Curie Weiss (CW) fit reveals the dominating ferromagnetic (FM) interaction in the system. Moreover, the $1/\chi$ shows the typical downturn behaviour which is the symbol of the presence of Griffith phase in present system.

Preparation And Characterizations Of Gallium Substituted X-type Strontium Hexaferrites

Ayushi Patel*, Preksha N. Dhruv, and Rajshree B. Jotania*

Department of Physics, School of Sciences, Gujarat University, Navrangpura, Ahmedabad 380 009

*Corresponding author: <u>az72ze@gmail.com</u>, <u>rajshree_jotania@yahoo.co.in</u>

Abstract

Gallium substituted X- type hexaferrites were synthesized using citrate gel auto combustion method. Prepared samples were characterized using FTIR, XRD and VSM. The XRD analysis shows formation of X, along with W and M phases. The high saturation magnetization \sim 91 A m² kg⁻¹ is observed for the sample prepared without gallium and substituted samples show variation of saturation magnetization from 90 A m² kg⁻¹ to 65 A m² kg⁻¹.

Structural and dielectric study of solid state prepared double perovskite Tb₂NiMnO₆

R. Athira and S. D. Kaushik^{*}

¹UGC-DAE Consortium for Scientific Research, Mumbai Centre, 246 C Common Facility Building, BARC Campus, Mumbai 400085

*Corresponding author: sdkaushik@csr.res.in

Abstract

Phase pure double perovskite Tb₂NiMnO₆ (TNMO) have been prepared by solid state reaction method. The earlier study on TNMO reported presence of secondary phase. The prepared sample was subjected to X- Ray diffraction (XRD) and neutron diffraction (ND) at ambient temperature. The analysis by Rietveld refinement confirmed the phase purity. The sample was found to crystallize in the monoclinic structure with $P2_1/n$ space group. The dielectric constant as a function of frequency was also studied. The Cole-Cole plot have been derived from the data and two semi-circle arc are evident which is indicating the presence of grain and grain boundary in the sample. We are in process of studying the SEM to ascertain the observation pertaining to grain and grain boundary.

Introduction

Double perovskite oxides have received much attention in recent past as they provide unique opportunities to induce and control multiferroic behavior, where electric and magnetic properties may be coupled [1]. Rare earth based double perovskites have grabbed considerable interest because of their rich physical properties such as ferroelectricity, spin-phonon coupling, dielectric properties etc. [1]. These exotic properties are achieved in double perovskites, often denoted as A₂B'B''O₆, due to wide range of crystal symmetry. Perovskites with partial/complete cation substitution at different degrees at A and B sites provides more flexibility to tailor the physical properties. Such vastness in properties is largely controlled by structural ordering, valence states and spin states of B' and B" cations.

In present work we present the preparation of single phase Tb_2NiMnO_6 by employing solid state reaction method. Earlier studies have reported small amount of secondary phase [2]. We have carried out the structural and dielectric study on Tb_2NiMnO_6 double perovskite. The prepared sample were subjected to X-ray diffraction and neutron diffraction for the structural characterization to ascertain phase purity, and room temperature dielectric has been studied as a function of frequency, to understand the dielectric behavior at room temperature.

Experimental Details

Tb₂NiMnO₆ sample was prepared by conventional solidstate reaction method. The high purity (\geq 99.9% purity) precursors Tb₄O₇, NiO, MnO₂ were weighted in stoichiometric amounts which were then ground in agate mortar for up to 6 hours for proper homogenization. The powder was sintered at 900 °C and 1250 °C with intermediate grinding for 15 hrs. Phase formation was studied by powder X-ray diffraction employing Benchtop X Ray powder diffraction (XRD) system (Bruker make D2 Phaser) using Cu K_{α} radiation ($\lambda =$ 1.5406 Å). In order to further ascertain the phase purity, the neutron diffraction pattern was recorded at focusing crystal diffractometer (PD-3) at Dhruva, India [3] using neutron beam of wavelength 1.48 Å. Towards the physical property, the dielectric measurement as a function of frequency was carried out on a circular disk on which the air-drying silver paint was applied to act as electrodes to measure the capacitance. Keysight make E4980A precision LCR meter was used for the study.

Results and Discussions

Structural Characterization: Upper layer of fig 1 shows the x-ray diffractogram of Tb_2NiMnO_6 collected at room temperature.



Fig. 1. Room temperature Rietveld refined XRD and neutron diffraction pattern of Tb₂NiMnO₆ sample in upper and lower layer.

The observed XRD pattern is fitted with Rietveld refinement by employing FULLPROF suite [4]. The observed pattern could be fitted with monoclinic structure with $P2_1/n$ space group (space group #14). The refined lattice parameters obtained from the analysis are a = 5.2699(6) Å, b = 5.5408(4) Å and c = 7.5208(5) Å and the monoclinic angle $\beta = 89.790(3)^0$. The goodness of fitting parameter χ^2 was 1.40. No unindexed peak in the XRD refinement points towards the absence of secondary phase. The lower layer shows the ND pattern in the angular range from $6^0 - 120^0$ and the refinement of ND pattern reiterates that the sample crystallizes in the monoclinic space group and cell parameters a, b, c and β are 5.2727(3), 5.5365(7), 7.5283(5) and 89.838(4) respectively with decent goodness of fitting parameters $R_p = 5.98$, $R_{wp} = 7.79$, $R_{exp} = 4.65$, $\chi^2 = 9.3$. Moreover, these values are in order in agreement with reported values [1].

The crystal structure has been drawn with the help of VESTA software from the analysis of ND pattern and shown in adjacent to the diffraction spectra in fig 1. We can observe that the Ni and Mn polyhedra are alternatively interlinked. The refinement of ND pattern relevant Mn-O and Ni-O interatomic bond distances were extracted and found to be ~2.035 Å and 1.94 Å respectively. These are closer to the reported values [5].

Dielectric Behavior:



Fig. 2. The frequency dependent (a) dielectric constant (ε') (b) loss tangent as a function of frequency at room temperature and (c) depicts the Cole-Cole plot.

Variation of real part of dielectric constant (ε) and loss tangent tan δ in the frequency region 40 Hz to 2 MHz at room temperature are shown in fig 2. Dielectric constant (ε) shows the gradual decrease with increase in frequency but loss tangent data tan δ shows gradual decrease in the sub kHz region and then increases as frequency increases and depicts a maximum at around 10 kHz. Complex impedance formalism helps in determining the inter-particle interaction like grain, grain boundary effects etc. To study the contribution due to different effects, present in the sample, Cole-Cole analysis is done at room temperature. For this we have further calculated the real and imaginary part of impedance i.e. Z' and Z" and Cole-Cole plot have been obtained as depicted in fig. 2.

We clearly obsevred the two semi circel arc in the Cole-Cole plot, which indicates the possibility of distinct grain and grain boundary conditions present in the sample.

Conclusion

In summary, we have synthesized the Tb₂NiMnO₆ via solid state reaction route. The phase purity was confirmed by the Rietveld refinement of XRD and neutron diffraction data collected in the ambient conditions No unindexed peak pertaining to any secondary phase was observed. The crystal structure was obtained from the analysis, which depicted the interlinking of Ni and Mn polyhedral. The frequency dependent (40 Hz-2 MHz) dielectric data was also studied the real part of the dielectric constant shows the gradual decrease in frequency but loss tangent data shows gradual decrease in the sub kHz region and then increase in the up to few the maximum at around 10 kHz. The Cole-Cole plot shows the presence of grain and grain boundary distinctly.

We are in process of studying the SEM micrograph to ascertain the observation from Cole-Cole plot. The detailed temperature dependent dielectric and magnetization study along with neutron diffraction will also be taken up to understand the correlation between the structural and magnetic properties in the compound.

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Quantitative interdependence of spin spirality and electric polarization in CoCr_{2-x}Fe_xO₄ spinel compounds

Amit Kumar and S. M. Yusuf

Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: amitkr@barc.gov.in

Abstract

Quantitative interdependence of spin spirality and electric polarization has been probed in $CoCr_{2-x}Fe_xO_4$ spinel compounds. These compounds undergo spiral ordering (Ts) and concomitant electric polarization below ~25 K. The Ts is seen decreasing with more Fe (*x*) substitution as observed from dc magnetization measurements. Neutron diffraction study has inferred a decrease in spirality of both *A* and *B*-sites spins with increasing the *x*. Electric polarization study, on the other hand, has suggested an increase in polarization with increasing substitution of Fe, thus revealing a direct correlation between spin spirality and electric polarization.

Evidence of Temperature-Dependent Magnetodielectric Effect in KBiFe_{1.9}Co_{0.1}O₅

K. Chandrakanta¹, D. P. Sahu¹, R. Jena¹, S. D. Kaushik², and A. K. Singh^{*1}

¹Department of Physics and Astronomy, National Institute of Technology, Rourkela-769008, Odisha, India. ²UGC-DAE-Consortium for Scientific Research Mumbai Center, BARC, Mumbai-400085, India.

*Corresponding author: singhanil@nitrkl.ac.in

Abstract

Single-phase Cobalt (Co) doped KBiFe₂O₅ (KBiFe_{1.9}Co_{0.1}O₅: KBFCO) is prepared by conventional solid-state reaction route. Rietveld refinement of X-ray diffraction data confirms the single phase of KBFCO and crystallizes in monoclinic structure with P2/c space group. Surface morphology characterization reveals the grains are randomly distributed, and the average grain size formed is in the range of ~1-5 µm. The temperature (10 K to 300 K) and frequency (500 Hz to 1 MHz) dependent dielectric permittivity value decreases approximately 50% in the presence of a 1.3 T magnetic field. Our result confirms a sizeable magnetodielectric (MD) effect (MD% \approx -50% near Room Temperature) in the entire measured temperature range. The measured MD effect is recorded at the high-frequency (20 kHz to 1 MHz) range, suggesting the intrinsic effect is dominated in the probing temperature range. These results confirm that KBFCO has an excellent MD response even for a small applied field.

Introduction

Magnetodielectric (MD) materials are characterized by the simultaneous existence of magnetic and dielectric order parameters with a certain degree of coupling between them [1]. These materials are rare due to the mutually exclusive nature of electric and magnetic order and show MD coupling below room temperature (RT). KBiF₂O₅ (KBFO) belongs to the brownmillerite (A2B2O5) class of material with high Curie temperature (T_C: 780 K) and Neél temperature (T_N: 545 K), and it has the potential to show the MD coupling at RT [2]. Here, Cobalt (Co) is doped at the iron (Fe) site of KBFO, and the effect of doping on dielectric and magnetodielectric properties are investigated over a wide temperature (10 K to 300 K) and frequency (500 Hz to 1 MHz) range.

Experimental Technique

Co-dope **KBFO** (KBiFe_{1.9}Co_{0.1}O₅: KBFCO) polycrystalline sample is synthesized via solid-state reaction route. High pure (>99.9%, Sigma Aldrich) Co₂O₃, Bi₂O₃, and Fe₂O₃ oxides are taken in stoichiometric ratios. The detailed synthesis process is reported in our previous report [3]. X-ray diffraction (XRD) measurement (RIGAKU JAPAN) having Cu-K α radiations (λ =1.5406 Å) is carried out to confirm the phase of KBFCO. A wide range of Bragg's angle (10° to 70°) with a step size of 0.02° followed by a scan rate of 3° min⁻¹ is used during the measurement. Surface morphology is examined by FEI Novanano SEM 450 field-emission-electronmicroscope (FESM). The dielectric measurement is carried over a wide frequency (500 Hz to 1 MHz) using high precession Wayne Kerr 6500B impedance analyzer. MD measurement is performed by an electromagnet (GMW 5403) with a bipolar DC power supply having a maximum magnetic field of 1.3 T. Low temperature (10 K to 300 K) measurement is performed using a closed cycle refrigerator (Cryo Industries, USA).

Results and Discussion

XRD pattern of the polycrystalline KBFCO sample is recorded at RT (Fig. 1).



Fig. 1. Room temperature Rietveld refined XRD patterns of KBFCO sample. Inset shows the FESM image.

The observed XRD pattern is fitted with Fullprof software. Rietveld refinement of XRD data reveals, KBFCO crystallizes in the monoclinic crystal structure with the P2/c space group. Over the Braggs angle, no secondary peak is observed in the XRD

pattern. The goodness of fitting (χ^2) shows a minimum of 4.49 value. The above result indicates the pure phase of the synthesized sample. The surface morphology of the KBFCO sample is depicted in the inset of Figure 1. Most of the grains are in a cylindrical shape that reflects the monoclinic crystal type. Well packed and dense microstructure with average grain size varies in the range of 1-5 μ m indicates the polycrystalline nature.



Fig. 2. Temperature and frequency-dependent dielectric constant measured at 0 T and 1.3 T magnetic field.

In a wide temperature (10 K to 300 K) and frequency (500 Hz to 1 MHz) dependent dielectric permittivity (ε') of the KBFCO sample shown in Figure 2. The inset of Figure 2 shows the temperature-dependent dielectric in the presence of a magnetic (1.3 T) field. The dielectric value of KBFCO increases with an increase in temperature and decreases with the increase in frequency. Suggests the presence of normal polar dielectric material behavior. It is observed that dielectric value decrease by 50 % (at RT) with applying a magnetic field of 1.3 T. It may be due to the reduction in the space charge polarization with Co doping in KBFO. The decrease in space charge polarization causes a dielectric value. Signature of reduction in magnetodielectric effect in KBFCO is observed in the entire temperature range of dielectric study.

The temperature frequency-dependent and magnetodielectric [3] $(MD\% = \frac{\varepsilon(H,T) - \varepsilon(0,T)}{\varepsilon(0,T)} \times 100)$ $\varepsilon(0.T)$ data is shown in Figure 3. We have fixed four (20 kHz, 35 kHz, 58 kHz, and 1 MHz) higher frequencies to present MD, excluding different extrinsic effects. Co doping at Fe site in KBFO shows a maximum of -50% MD near at room temperature. Since the dielectric value decreases with decreasing temperature, so the MD also decreases. It suggests the suppression of different contributions like dipolar, Maxwell-Wagner cum magnetoresistance, and spacecharge like origins. Co-modified structural distortion can generate such a high-value RT MD in KBFCO. Further, the temperature-dependent MD shows minimal frequency dispersion behavior for the entire measured temperature range. It reveals that intrinsic nature is dominant in the observed MD for the KBFCO sample.



Fig. 3. The temperature-dependent magnetodielectric effect is shown at selected frequencies.

Conclusion

In conclusion, Co-modified KBFO is synthesized via a solid-state reaction route. The pure phase is confirmed from the Rietveld refinement of XRD data. SEM micrographs reveal that grains are distinct and distributed over a range of 1 to 5 μ m. Temperature (10 K to 300 K) and frequency (500 Hz to 1 MHz) dependent dielectric permittivity is subjected to a magnetic field, and the signature of magnetodielectric effect is recorded. Nearly -50% MD coupling is observed at RT. Temperature-dependent MD is measured at high frequencies that exclude extrinsic effects. From the primary investigation, the observed MD seems to be an intrinsic origin.

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Magnetization Reversal and Exchange-Bias in Highly Anisotropic Intermetallic Compound, DyFe₅Al₇

Deepak^{1,2}, A. Kumar^{1,2}, and S. M. Yusuf^{1,2,*}

¹Solid State Physics Division, Bhabha Atomic Research Center, Mumbai 400085, India ² Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: smyusuf@barc.gov.in

Abstract

Intermetallic compound, DyFe₅Al₇ has been prepared by arc melting method. X-ray diffraction infers the single phase formation of the compound. DC magnetization under 50 Oe reveals that ferrimagnetic ordering sets in the compound at ~ 235 K (T_C) and magnetization reversal phenomenon below T_{COMP} (~ 93 K). Moreover, compound shows the exchange bias phenomenon below ~ 50 K. A giant exchange-bias as well as coercivity with values of ~ 2 kOe and 18.3 kOe (5 K), respectively, are observed.

Effect of Isothermal annealing on the magnetic property of

Carbon thin film

Balaram Thakur^{1, 2}, N. V. Chandra Shekar^{1, 3} & Sujay Chakravarty^{1*}

¹UGC DAE Consortium for Scientific Research, Kalpakkam Node, Kokilamedu-603104, India ²University of Madras, Chennai, Tamil Nadu – 600005, India ³Material Science Group, IGCAR, HBNI, Kalpakkam-603102, India

*Corresponding author: scha@csr.res.in

Abstract

The effect of isothermal vacuum annealing on the microstructure and magnetic property of amorphous carbon thin deposited using RF magnetron sputtering at RF power of 150W is discussed. The as-deposited film consists of both superparamagnetic and paramagnetic sites distributed throughout the film. Microstructure characterization studied using Raman spectroscopy (RS) confirms that the rehybridization of sp^3 to sp^2 bonded atoms prevails on annealing. The X-ray Reflectivity (XRR) measurement reveals that the bulk density decreases considerably with annealing temperature. The magnetic measurement indicates that the paramagnetic sites are extinct on annealing, whereas the bulk saturation magnetization of the film decreases considerably. The effect of thermal annealing on the hybridization ratio and its consequence on the amorphous carbon thin film's magnetic property is explained.

Introduction

In recent years, magnetism in carbon materials has been a topic of debate and discussion in the scientific community. The presence of moment and its origin is widely discussed for an ordered structure like graphene/graphite [1]. However, only a handful of literature is available, where the origin of magnetism in the disordered/amorphous structure is discussed. In amorphous carbon, the presence of carbon atoms in different hybridization ratio is found to sustain the magnetic moment [2], which we had confirmed experimentally in our previous work [3]. In the present work, utilizing isothermal annealing, we attempted to study the correlation between different hybridization states on amorphous carbon thin film's magnetic property.

Experiment details:

The film deposited at RF power of 150W [3] with a minimum bulk saturation magnetization of 104 emu/cc having a density of ~ 2.1 g/cc and sp²/sp³ fraction of 67.4% are subjected to isothermal annealing at 250°C (F_{250}) & 650°C (F_{650}) for 2hrs in the vacuum of ~1E-6 mbar. The details of the deposition parameters are discussed elsewhere [3]. The variation in density with the film's depth is studied using XRR measurement (M/S Bruker D8 Discover instrument with 4.5 KW Cu K α rotating anode source). The microstructure change is studied using RS (M/S inVia Renishaw with Ar+ ion laser 514 nm), whereas the magnetic measurement is carried out using SQUID VSM (M/S Quantum Design, USA).

Results and Discussion:

1. X-Ray Reflectivity (XRR):

Fig1A shows the fitted XRR profile of F_{250} as a function of the momentum transfer vector (Q_z). Fig.1B illustrate the variation of the film's physical mass density as a function of depth, calculated from the scattering length density (SLD) profile obtained while fitting the XRR profile. From the density profile, it is seen that the thickness of the film decreases on annealing. However, for F_{250} , the film's bulk density remains similar to the as-deposited film indicating that there is not much change in hybridization ratio after annealing at 250°C. While for film F_{650} , the density decreases from 2.0 g/cc to 1.8 g/cc., which implies that the rehybridization process prevails on annealing at 650°C.



Fig. 1. (A) X-ray Reflectivity (XRR) profile of carbon film annealed at 250°C.Inset shows the magnified version of the marked region (B) Density variation of the film as a function of depth calculated from SLD.

2. Raman Spectroscopy:

Fig 2 illustrates the deconvoluted Raman spectra of the as-deposited and annealed films. The peak about

1350, 1555 and 1600 cm⁻¹ are assigned as D-peak, Gpeak and D' peak, respectively [4]. The peak centred between D and G-peak is due to an amorphous related peak whose intensity decreases with increasing annealing temperature [5,6]. With increasing annealing temperature, from 250°C to 650°C, a prominent blue shift in G-peak is noticed. The blue shift in G-peak and decrease of the amorphous related peak indicates that the temperature of 650°C used in the present study initiated the rehybridization of sp³ bonded atoms to sp² bonded atoms.



Fig. 2. Deconvulated Raman spectra of the as-deposited, F₂₅₀ and F₆₅₀.

3. Magnetic Measurement:

Fig.3A compares M (H) of as-deposited and annealed samples. Similar to the as-deposited sample, the films after annealing shows the presence of superparamagnetic (SPM) particle whose saturation magnetization decreases systematically with increasing the annealing temperature.



Fig. 3. (A) Comparison between the RT-M (H) and (B) variation of saturation magnetization and density of the as-deposited and film annealed at 250°C and 650°C.

Further, on annealing, the sites contributing to the linear paramagnetic part diminishes, enhancing diamagnetic contribution. The RT-M (H) is fitted while incorporating a linear paramagnetic/diamagnetic term, and saturation magnetization of the samples is determined, using the relations discussed in our previous study [3].

Fig.3B illustrates the variation in saturation magnetization (M_s) and density of the as deposited as

well annealed film F_{250} & F_{650} . From fig.3B, it is noted that with the increasing annealing temperature, both M_s and density decreases drastically for F_{650} .

Hence, to conclude, for F₂₅₀, mutual rotation of the π -orbital of sp²-sp² atoms mainly occurs [2]. This conversion compensates for the isolated sp^2 moments, resulting in the net decrease of paramagnetic sites and promoting the film's diamagnetic contribution. The mutual rotation of the π -orbital leads to the antiferromagnetic coupling, resulting in the decrease in saturation magnetization. Further for F650. а significant blue shift in G-peak and decrease in density indicates that most of the sp³ atoms get converted to sp², resulting in the further enhancement of diamagnetic contribution as well as drastically decrease in saturation magnetization due to formation of graphitic carbon.

Conclusion:

The amorphous carbon film's magnetism is unstable against the thermally driven modifications in the microstructure and depends on the sp^2 fraction. With the increase in the annealing temperature, the rehybridization of sp^3 to sp^2 atoms prevails. Such conversion results in a decrease in both bulk saturation magnetization and the density of the film. The present work provides a better understanding of magnetic amorphous carbon film containing a significant sp^2 fraction.

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Evidence of Magnetodielectric Coupling in (1-x)Bi₅Ti₃FeO₁₅-(x)La_{0.67}Sr_{0.33}MnO₃ (x= 0.0 and 0.1) Composites

Rasmita Jena¹, K. Chandrakanta¹, and A. K. Singh¹

¹Department of Physics and Astronomy, National Institute of Technology, Rourkela-769008, Odisha, India

*Corresponding author: singhanil@nitrkl.ac.in

Abstract

Composite (1-x)BTFO-(x)LSMO (x= 0.0 and 0.1) is synthesized by sol-gel modified technique in order to study the magnetodielectric (MD) properties. Rietveld refinement of the X-ray diffraction (XRD) patterns confirm the existence of dual-phases orthorhombic ($A2_1am$) and rhombohedral (R-3c) in the composites. The systematic change in dielectric permittivity with a static magnetic field (0 T and 1.3 T) indicates the signature of the MD effect in the composite. The magnitude of the room temperature the MD effect is 0.08% for x= 0.1 composite, which is twenty times higher than that of the x= 0.0 sample with 0.004% at 1.3 T field.

Introduction

Magnetoelectric (ME) materials have immense technological applications because of the coupling between the electric and magnetic order parameters. The ME materials multifunctional characteristic adds an extra dimension that is useful for fabricating novel devices, high-density storage devices, viz. transducers, spintronic devices, and microsensors [1]. Bi₅Ti₃FeO₁₅ (BTFO) belongs to the Aurivillius family with general fomula Bi_{m+1}Ti₃Fe_{m-3}O_{3m+3}, where m corresponds to the number of corner-sharing perovskite layers in the crystallographic direction of c. The crystal structure of the Aurivillius compound can be intergrown by the alternating stacking of the perovskite-like layer (Bi₃Ti₃FeO₁₃)²⁻ and fluorite-like (Bi₂O₂)²⁺ layers. BTFO material shows good ferroelectric properties with a high curie temperature of 730 °C and a piezoelectric coefficient of value d₃₃= 66 pm/V [2]. On the other hand, the manganite-based La_{0.67}Sr_{0.33}MnO₃ (LSMO) sample exhibits superior ferromagnetic properties with a transition temperature of 370 K and a large magnetic moment at room temperature [3]. In this paper, we report on the preparation of BTFO-LSMO composite via the solgel-modified method. Here, we have observed an enhanced response of the magnetodielectric (MD) effect with the addition of 10% LSMO content.

Experimental Section

The sol-gel modified method was adopted for the synthesis of composites (1-x)BTFO-(x)LSMO (x=0.0 and 0.1). The chemical precursors used for the BTFO synthesis were bismuth nitrate, iron nitrate, and titanium isopropoxide ($\geq 99.9\%$ purity from Sigma Aldrich) as a source of Bi, Fe, and Ti, respectively. Similarly, for the synthesis of LSMO, the high purity chemicals of lanthanum nitrate, manganese nitrate,

and strontium nitrate were taken as the precursors of La, Mn, and Sr accordingly. The precursor materials of both BTFO and LSMO were dissolved in two different beakers containing the deionized water followed by the nitric acid. The solutions were constantly heated at 100 °C and stirred on the hot plate till the formation of transparent gel. After that, the proper ratio of citric acid to ethylene glycol and citric acid to glycine were added to the respective BTFO and LSMO solutions. The gel was dried under the continuous heating process to obtain the xerogel powder. The powders of BTFO and LSMO were calcined at 600 °C 2 h and 800 °C 4 h, respectively. Finally, the (1-x)BTFO(x)LSMO composite of x= 0.1 was prepared via the mechanical mixing process and subjected to sintering at 900 °C for 4 h.



Fig. 1. The Rietveld refined of the XRD patterns of (1-x)BTFO-(x)LSMO composites with x=0.0 and 0.1. The phase purity of the prepared samples was confired from the X-ray diffraction (XRD) measurement (Rigaku Japan) with Cu-k α radiation. The temperature-dependent dielectric and field variation

MD measurements were performed using the impedance analyzer (Wayne Kerr 6500B) with the closed cycle refrigerator (CCR, USA).

Results and Discussion

Rietveld refinement of the XRD patterns of the (*1*-*x*)BTFO-(*x*)LSMO composite with x = 0.0 and 0.1 is shown in Fig. 1. During the refinement, dual-phases of BTFO and LSMO are considered with orthorhombic (*A*2₁*am*) and rhombohedral (*R*-3*c*) crystal structure. The refined XRD patterns give a good fit between the experimental and simulated data points with the goodness of fit parameters $\chi^2 = 1.84$ and 4.0 for x = 0.0 and 0.1 samples.



Fig. 2. Temperature-dependent dielectric permittivity under a magnetic field of 0 T and 1.3 T for x = 0.0 and 0.1 samples.

The temperature variation of dielectric permittivity (ϵ) for the composites (x = 0.0 and 0.1) at a different static magnetic field (0 T and 1.3 T) at 58 kHz is depicted in Fig. 2. An increasing trend is noticed in ε' with the increase in temperature till 320 K. But the value of ε' decreases from 48 to 45 with a highest magnetic field of 1.3 T for the x = 0.1 sample. In comparison, a negligible change in ε' is found for the x=0.0 sample. The tuning of ε' with the variation of the magnetic field indicates the signature of the MD effect in the composite. The quantitative analysis of MD response is estimated from the field variation of MD measurement.

Fig. 3. depicts the room temperature MD response of the composites (x= 0.0 and 0.1) with the variation of magnetic field (±13 kOe) at 50 kHz. The increasing linear trend of the MD% is observed for x= 0.0 sample. This is due to dominating grain boundary contribution over the grain, causing Maxwell-Wagner and magnetoresistance in the sample [4]. The linear behavior of the MD change to a nonlinear (inverted butterfly loop) response with a small addition of the LSMO (10%) to the BTFO sample. The evolution of nonlinear MD response in x= 0.1 suggests the strain-induced coupling at BTFO and LSMO interface. The magnitude of MD effect for x= 0.0 and 0.1 composites at 1.3 T are 0.004% and 0.08%, respectively. Hence, the strength of the MD response in the x= 0.1 composites is ~20 times higher than the parent sample.



Fig. 3. Room temperature field-dependent MD effect of x = 0.0 and 0.1 composites at 50 kHz.

Conclusion

In summary, we have prepared the (1-x)BTFO-(x)LSMO (x=0.0 and 0.1) composites by considering the sol-gel modified method. The Rietveld refinement of XRD data confirms the dual-phase formation. The tuning of dielectric permittivity under a static magnetic field establishes MD effect in the composite. The observed MD effect in the composite is due to the generation of interfacial strain. The strength of the MD effect in x=0.1 composite is ~20 times higher than in the x= 0.0 sample.

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Interfacial Spin Scattering Enhanced Magnetoresistance in La_{0.7}Sr_{0.3}MnO₃/ZnO Heterostructures Integrated on (001) Si

Bibekananda Das^{1, *}, S. N. Achary², and Prahallad Padhan¹

¹Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India ²Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India **Corresponding author: bibekanandadas404@gmail.com*

Abstract

A series of $La_{0.7}Sr_{0.3}MnO_3(LSMO)/ZnO$ heterostructures with different ZnO thicknesses were grown on (001) oriented Si substrate at 700 °C using RF magnetron sputtering. The X-ray diffraction patterns indicate the (001) orientation of LSMO and ZnO films. The LSMO thin film shows positive as well as negative magnetoresistance (MR). The charge transfer induced interfacial antiferromagnetic coupling at the Si-LSMO interface and spin-orbit coupling due to the presence of non-collinear Mn ions spins at the interfaces and surfaces are responsible for the positive MR of LSMO thin film. However, the positive MR is suppressed and negative MR is enhanced by depositing a ZnO film on the Si/LSMO. The out-of-plane negative MR of LSMO/ZnO heterostructures increases with ZnO thickness. This type of MR behavior of LSMO thin film and LSMO/ZnO heterostructures integrated on Si can be used in spintronic applications.

Introduction

Sr (30%) doped LaMnO₃ (La_{0.7}Sr_{0.3}MnO₃ (LSMO)) is a ferromagnetic metal at room temperature. It has a strong coupling between lattice, spin, charge, and orbital degrees of freedom. The ferromagnetism in LSMO can be understood by the double exchange mechanism. Mixed valence (Mn³⁺/Mn⁴⁺) manganite LSMO undergoes metal-to-insulator transition close to the Curie temperature (T_C) well above room temperature. It is widely known for its colossal magnetoresistance and half metallicity. Holed doped LSMO is p-type [1].

Zinc Oxide (ZnO) crystallizes in wurtzite structure is a well-known wide band gap semiconductor. It has large free-exciton binding energy (60 meV) and a direct band gap (3.37 eV) at room temperature. The as-grown ZnO is n-type because of native defects [2].

LSMO/ZnO heterostructures show the photocarrier injection effect, UV photovoltaic effect, and rectifying behavior [3, 4]. In this article, the magneto-transport properties have been studied.

Experimental Methods

For pulsed plasma deposition in RF magnetron sputtering, the LSMO and ZnO targets were prepared using the standard solid-state reaction method. The powder of La₂O₃, SrCO₃, and Mn₂O₃ were used for making the LSMO target [5] and the high purity ZnO powder was used for making the ZnO target. First, the LSMO was grown on Si at 9×10^{-3} mbar Ar:O₂ (20:80) gas pressure and 700 °C. Then, the ZnO was grown on LSMO with 60% Ar and 40% O₂ with the same pressure and temperature. The structural

characterization and measurement of thickness were carried out using X-ray diffraction technique. The inplane field-dependent resistance R(H) for 45° oriented in-plane current with the in-plane magnetic field (i.e, growth of LSMO channel//[110] Si, H//[100] Si) was measured using a setup comprises of an Advanced Research System made closed-cycle cryostat, a Lakeshore temperature controller, a Keithley pico-ammeter, a Keysight nano-voltmeter, and a copper coil solenoid electromagnet with an upper field limit of 1.3 kG. The out-of-plane R(H) was measured using the Physical Properties Measurement System (PPMS).

Results and Discussions

The (00l) oriented growth of LSMO thin film and LSMO/ZnO heterostructures was confirmed from the θ -2 θ X-ray diffraction patterns [Fig.1].



Fig. 1. θ -2 θ X-ray diffraction patterns of (a) Si/LSMO 120 Å and (b) Si/LSMO 120 Å/ZnO 930 Å heterostructure.

The LSMO and ZnO layers experienced the strain of -0.28 % and 0.08 %, respectively. However, the presence of SiO₂ at the Si-LSMO interface generated due to thermal oxidation can't be ruled out. The thickness of LSMO and ZnO layers were obtained from the fitting of low angle X-ray reflectivity (not shown).

The in-plane magnetoresistance $\left(MR = \frac{R(H) - R(0)}{R(0)}\right)$ of 120 Å LSMO thin film exhibits positive as well as negative MR with maximum positive MR of ~11 % and negative MR of ~7 % [Fig. 2(a)]. The electron density increases through the charge transfer via Si-O-Mn at the Si-LSMO interface, reduces the charge state of Mn, which provides antiferromagnetic order driven by kinetic energy and lower spatial symmetry than the parent structure [6, 7]. Similar to field dependence of in-plane MR, the LSMO thin film exhibits positive as well as negative MR along the out-of-plane direction with maximum positive and negative MR of ~6 % and ~26 %, respectively [Fig. 2(e)]. The spin-orbit coupling in the LSMO thin film can be enhanced due to the presence of non-collinear Mn ions spins at the interfaces and surfaces [8]. Thus, charge transfer induced the interfacial antiferromagnetic coupling and the spin-orbit coupling are responsible for the positive MR.

However, the positive MR is suppressed in LSMO/ZnO heterostructures. The maximum positive in-plane MR of ~1 % and negative MR of ~15 % obtained in LSMO/ZnO heterostructures [Figs. 2(b)-(d)]. The in-plane MR is independent of ZnO thickness in this low field range.



Fig. 2. In-plane and out-of-plane MR (%) of (a), (e) Si/LSMO 120 Å and Si/LSMO 120 Å/ZnO heterostructures with different ZnO thicknesses of (b), (f) 372 Å, (c), (g) 744 Å, (d), (h) 930 Å.

The charge transfer occurring from ZnO to LSMO is very small (~0.022 e/Å²). The oxidation states of La/Sr and Mn are retained during the interface formation. The exchange coupling at (La/Sr)O-ZnO is weak, and the MnO₂-ZnO interface has strong coupling [9]. Thus, the spin-dependent scattering at the LSMO-ZnO interfaces suppressed the positive MR and enhanced the negative MR. In the out-ofplane direction, the positive MR became zero in the LSMO/ZnO heterostructures [Figs. 2(f)-(h)]. The negative MR of ~26 % of Si/LSMO increased to 50 % in the Si/120 Å LSMO/930 Å ZnO heterostructure. The negative MR of LSMO/ZnO heterostructures increases with ZnO thickness [Figs. 2(f)-(h)].

Conclusions

The thin film of LSMO and a series of LSMO/ZnO heterostructures with different ZnO thicknesses were grown Si using the RF magnetron sputtering technique. The LSMO thin film shows dual sign MR behavior. However, the positive MR is suppressed, and negative MR is enhanced in the LSMO/ZnO heterostructures. This type of MR behavior integrated on Si can be used in spintronic applications.

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Magnetization Reversal in Double Perovskite Y₂FeCrO₆ Nanoparticles

K Pushpanjali Patra¹, and S. Ravi²

Department of Physics, Indian Institute of Technology Guwahati, Guwahati-781039, India.

*Corresponding author: pushpanj@iitg.ac.in

Abstract

Here we have opted gel combustion route to prepare single phase nanoparticles of Y_2 FeCrO₆ (YFCO) sample and reported its structural and magnetic behavior. According to the room temperature (RT) XRD and Raman spectra analysis the sample comes under monoclinic phase with P_{21}/n space group. The average particle size as per microstructural image is 67 nm. Magnetization versus temperature (M-T) analysis reveals that the material exhibits negative magnetization below 143 K (T_{comp}). Magnetization versus field measurement (M-H) at 5 K indicates presence of mixed magnetic phase in the sample.

Introduction

A variety of interesting magnetic properties and potential applications, such as multiple memory elements, spin filter junctions, storage components and many more have sparked recent interest in complex perovskite oxides with the general chemical formula R₂BB'O₆ (R- rare-earth, B, B'-transition metals) [1]. The ordering of B/B' in double perovskites is crucial in establishing their structure, space group, and functional features. The magnetic ordering is determined by the Goodenough Kanamori rule [2], which governs the super exchange interactions between the B and B' ions. However, at ferromagnetic (FM)domain boundaries. а competing antiferromagnetic (AFM) interaction is detected across B-O-B and B'-O-B' ions due to antisite disorder among B and B' cations [1].

There are just a few research reports on Fe-Cr based double perovskites (A₂FeCrO₆, A- rare-earth element) in which the exchange interaction between Cr^{3+} - O^{2-} -Fe³⁺ determines the magnetic ordering. However, only Bi₂FeCrO₆ has undergone substantial research among this group. But it has a drawback of structural instability at high temperatures. Pr₂FeCrO₆, ia an unique member of the A₂FeCrO₆ family with remarkable structural stability up to 1500 K. Bulk Pr₂FeCrO₆ is a type-I multiferroic. Nanoparticle Pr₂FeCrO₆ was recently found to have a stable structure at 923 K with enhanced magnetic properties, which were attributed to surface spin canting [5]. In YFCO, magneto-dielectric behavior has recently been reported.

Experimental Details

The sample was prepared using gel combustion route by taking all the precursors in nitrate form with \geq 99.9% purity and following the procedure as described in the report [3], however here the final sintering, was done at 650^o C for 6 hours.

Results and discussion

The single phase formation of the sample with monoclinic phase with $P2_1/n$ space group is confirmed by the powder XRD pattern as well as Rietveld refined data shown in Fig.1.(a). The unit cell structure shows FeO₆ and CrO₆ octahedra sublattices placed alternately along the c axis with some octahedral tilting, which is the most common type of structural distortion in double perovskites. The table (inset of Fig.1.(b)) contains all structural parameters. A further confirmation of monoclinic phase formation comes from the peaks at 500 cm⁻¹ and 675 cm⁻¹ in the room temperature Raman spectrum (Fig.1. (b)).



Fig. 1. (a) RT XRD pattern along with its Rietveld refinement, inset shows its crystal structure and (b) Room temperature Raman spectrum, inset shows the obtained structural parameters.

The FESEM image of YFCO sample is shown in Fig.2. As can be seen from the figure, the particles are dense, with a calculated average particle size of 67 nm as shown in the inset of Fig.2.



Fig. 2. FESEM image of YFCO sample, inset shows the log-normal fitting to determine average particle size.

The M-T measurements are performed under zero field cooled (ZFC) and field cooled (FC) condition with an applied field of H = 1000 Oe (Fig.3. (a)). According to the ZFC graph, as the temperature is lowered, magnetization continues to decline. A rise in magnetization can be seen below 15 K. FC M-T measurements show a similar pattern of behaviour, but at 143 K, the magnetization drops to zero and reverses direction to produce a negative value. The magnetization then decreases with decreasing temperature and reaches a maximum negative value at around 15 K. The temperature where the magnetization has crossed the zero value is known as magnetic compensation temperature (T_{comp}). The ordering temperature (T_C) should be high based on these ZFC and FC curves. When the bond angle is close to 180° , the super exchange interaction in Fe³⁺ -O- Cr³⁺ networks is FM, as predicted by Goodenough-Kanamori rules [2]. However, the super exchange interactions are affected by the presence of surface spin disorder in nanoparticles and the deviation of bond angles from 180⁰[1]. Here the bond angles between FeO₆ and CrO₆ octahedra with O₁, O₂ and O₃ are found to be 156⁰, 135⁰ and 143⁰ respectively. This Structural distortion may also cause antisite disorders leading to AFM spin couplings across Fe³⁺-O-Fe³⁺ and Cr³⁺-O-Cr³⁺ networks. As the surface spin canting induced AFM is observed in Fe/Cr based nanoparticles [5]. The observed negative magnetization can be explained as follows, at high temperatures, the FM components dominate over the AFM components, but as the temperature drops, the AFM components begin to align themselves along the field direction. At 143 K, the magnitudes of both FM and AFM components are equal, so magnetization is zero. As T is lowered, AFM takes precedence over FM components, and this results in a negative M value. Then it reached its maximum value, and below T = 15 K, it began to rise. This can be attributed to the reorientation of the B/B' moment along the field direction, without affecting the

original AFM interaction between the B and B' site moments.

M-H measurement for YFCO nanoparticles at 5 K up to a field of \pm 6 T is shown in Fig. 3 (b). Even at 6 T, the unsaturated M-H loop indicates low-temperature uncompensated spins. It has coercivity H_C = 2.48 kOe and saturation magnetization M_S = 0.3 emu/g. According to the shape of M-H loop and the obtained H_C and Ms values, this compound is FIM. Uncompensated surface spin moments are responsible for the higher H_C and lower M_S values. The inset of Fig.3. (b) shows the loop width versus moment plot, revealing the presence of multi-magnetic phase [3].



Fig. 3. (a) M-T plots for both ZFC and FC condition and (b) M-H loop at 5 K, inset shows loop width versus moment plot.

Conclusion

The single-phase nanoparticle of Y_2 FeCrO₆ double perovskite has been successfully synthesized. Structural studies confirm the sample crystallized in the monoclinic phase with the space group P21/n. Average particle size is found to be 67 nm. Magnetization study reveals the negative magnetization and it is attributed to the spin canted AFM along with FM and AFM spin structure at low temperature. The M-H investigation confirms FIM nature and the existence of a multi-magnetic phase.

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Synthesis and Characterization of Topological Superconductor SnTaS₂

M. Singh¹, P. Saha², V. Nagpal³ and S. Patnaik^{*}

School of Physical Sciences, Jawaharlal Nehru University, New Delhi, 110067

*Corresponding author: spatnaik@mail.jnu.ac.in

Abstract

We have studied the superconducting properties of dichalcogenide compound $SnTaS_2$. We have grown single crystals using Chemical Vapor Transport (CVT) method. The single crystal structure was confirmed by XRD pattern of flake, which consists only (0 0 *l*) peaks. Critical temperature T_c was found to be 2.8K. Magnetization study indicates signature of type-II superconductor.

Impact of Heating Temperature on Structural And Dielectric Properties of Magnesium Ferrites

Hina N. Chaudhari¹, Preksha N. Dhruv², Sher Singh Meena³, Shrikanti Kavita⁴, C.B. Basak^{5,6}, Rajshree B. Jotania⁷

^{1,2,7}Department of Physics, University School of Sciences, Gujarat University, Ahmedabad, 380009, India.
 ³Solid state physics division, Bhabha Atomic Research Centre, Mumbai, 40085, India
 ⁴International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), IIT Chennai Research Park, Chennai- 600113, India
 ⁵Homi Bhabha National Institute, Anushaktinagar, Mumbai, 400 094, India
 ⁶Mechanical Metallurgy Division, Bhabha Atomic Research Centre, Mumbai, 400 085, India

*Corresponding author: heenachaudhary0506@gmail.com

Abstract

The spinel MgFe₂O₄ ferrites were synthesized using sol-gel auto-combustion technique and heated at 650 °C, 750 °C and 1050 °C for 4h. X-ray diffraction (XRD) and low frequency dielectric measurements are used to characterize MgFe₂O₄ ferrite. XRD analysis of samples heated at 750 °C and 1050 °C show pure spinel phase while the sample heated at 650 °C revealed formation of spinel with hematite. Dielectric study of all samples was carried out in the frequency lies between 100Hz-2MHz. Dielectric measurements show frequency dependent phenomena. Dielectric constant found to decrease with frequency.

Effect of Excessive Mn Doping on Electrical Properties of Skyrmionic MnSi

P. Saha¹, M. Singh², V. Nagpal³ and S. Patnaik*

School of Physical Sciences, Jawaharlal Nehru University, New Delhi -110067

*Corresponding author: spatnaik@mail.jnu.ac.in

Abstract

We report here on the synthesis and zero-field electrical resistivity measurements on the confirmed skyrmionic compound MnSi. Polycrystalline MnSi sample has been prepared through arc melting process. The phase purity and the crystal structure of the sample has been analyzed using Rietveld analysis and a secondary phase of Mn₅Si₃ is identified. Temperature dependence of resistivity shows a drop around Tc ~27.5 K which is indicative of the onset of magnetic ordering. Evidence for the dominance of electron-electron scattering mechanism in the ferromagnetic phase is provided.

Introduction

MnSi, is a cubic intermetallic which undergoes a magnetic phase transition at 29K. This transition can be observed in resistivity Vs temperature behaviour. Below T_c and at zero field, the spin moments constitute a helical structure and as the field increases to 0.1T the spins get more aligned towards the applied magnetic field and it gives a conical structure. As the field increases and exceeds 0.6T all the spins get aligned in the direction of the magnetic field and it exhibits a ferromagnetic behaviour. It is the first compound in which magnetic skyrmions were observed experimentally through neutron scattering. Skyrmions are topologically stable vortex like spin structures with ferromagnetic background. MnSi is a а noncentrosymmetric compound where the Dzyaloshinskii-Moriya interaction (DMI) gradually twist the spin arrangement to form skyrmions in a certain range of magnetic field and temperature. Many experiments have been done to study the magnetic behaviour and phase transition of high quality single crystal MnSi. MnSi is the most widely studied among many B20 compounds because it exhibits skyrmion rich phase in all crystallographic axes. Recently, it has been reported that polycrystalline MnSi show magnetic features which are similar to MnSi single crystal. We have synthesized polycrystalline MnSi and have studied the electrical transport behaviour.

Experimental Techniques

Polycrystalline MnSi was prepared by the process of arc melting. Manganese (99% purity) and Silicon (99% purity) powders were ground and cold pressed into pellets. They were then melted together in an arc vacuum chamber in the presence of argon gas. To compensate the loss of manganese in the process of arc melt, an extra amount of Mn of about 20 at.% was added to the starting materials. The ingots were flipped and melted 3-4 times to maintain homogeneity. They were then sealed in an evacuated quartz tube and annealed at 1173 K for 2 days. The structure and phase identification of the sample was done by XRD using Rigaku D/MAX 25000PC diffractometer (Cu-Ka radiation, λ =1.5406Å). The obtained ingots were then crushed and pressed into pellets. The pellets were again vacuum sealed in quartz tube and sintered at 1073K for 12 hrs. The resistivity measurements were done in Cryogenic Free Magnet (CFM) system at zero magnetic field in the temperature range 12-300 K temperature range, using a four-wire electrical resistance measurement setup.



Fig. 1. X- ray diffraction pattern of polycrystalline MnSi. The upper Bragg lines correspond to MnSi and the lower Bragg lines correspond to MnsSi₃.

The Rietveld refinement on the powder XRD pattern of MnSi is shown in Fig. 1. The refinement fit is good and confirms the phase MnSi in addition to a small impurity phase of Mn₅Si₃. The lattice



Fig. 2. Resistivity vs temperature plot at zero field. Inset shows the derivative of resistivity with temperature.

parameters derived from Rietveld refinement analysis are a = b = c = 4.563 Å. Fig. 2 shows the zero field resistivity ρ as a function of temperature from 11K-300K The resistivity increases with the rise in temperature, indicating a metallic behaviour of the sample. The residual resistivity ratio RRR $[=\rho(300K)/\rho(12K)]$ is determined to be 8.08. Furthermore, a drop is observed in the resistivity around a critical temperature Tc~ 27.5 K, which implies a magnetic phase transition. Further, this magnetic transition is also confirmed from the maximum peak observed in the plot of temperature derivative of resistivity $d\rho/dT$ against temperature as depicted in the inset of Fig. 2. This is different from the reported $T_c = 29$ K due the presence of impurity phase Mn₅Si₃.

The zero field resistivity in the two regions (T < Tc and T > Tc) is fitted with a power law equation: $\rho \sim bT^n$ (see Fig. 3), where b is a constant factor and n is a power exponent that describes the dominant scattering mechanism. In the region T < T_c, the fitted curve reveals that n = 2 i.e., T² dependence of resistivity implying the electron-electron dominant mechanism and the role of spin interaction during scattering. On the other hand, the fitting determines n = 0.22 in the region T > T_c. This kind of change in behaviour is assigned to the transition from helimagnetic to paramagnetic phase. At high temperatures electron phonon scattering also takes part along with other scatterings. This kind of phase transition has also been reported even at non zero fields.



Fig. 3. Shows the curve fit of resistivity vs temperature plot.

Conclusion

In conclusion, we have prepared polycrystalline MnSi by the process of arc melting. XRD data analysis showed an impurity phase of Mn_5Si_3 . Resistivity vs temperature data shows a clear transition at T_c =27.5 K which is different from the reported result due to the presence of impurity phase. The power law fitting of resistivity implies that the electron-electron scatterings are dominant below the critical temperature T_c .

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Effect of Mg²⁺ Substitution on Structural and Magnetic Properties of W-type Strontium Zinc Hexaferrites

Dipti D. Parmar¹, Preksha N. Dhruv², Rajshree B. Jotania^{3*}

^{1,2,3}Department of Physics, Electronics and Space sciences, University School of Sciences, Gujarat University, Ahmedabad, 380009, India

*Corresponding authors: rajshree_jotania@yahoo.co.in

Abstract

Mg- substituted W-type hexaferrites with chemical composition $SrZn_2Mg_xFe_{16-x}O_{27}$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) were synthesized using sol-gel auto combustion method, and subsequently heated at 1300 °C for 5 h. The structural and Magnetic properties of prepared hexaferrites were investigated using FTIR, XRD and VSM techniques. The FTIR analysis of all samples shows two absorption bands between wave-number ranges of 600-400 cm⁻¹. The XRD analysis of the sample x = 0.0 shows formation of pure W-type phase, while other Mg- substituted samples show W-type phase along with M-phase. VSM analysis of all samples shows that formed samples possess soft magnetic nature having multi-domain structure.

Linear And Non Linear Optical Properties of Bi0.95Sr0.05Fe0.95Mn0.05O3 Ceramic

Imran Ahmad Salmani¹, Mohammad Imran², Shafi ul Islam¹, Zeeshan Khan¹, Gaurav Saxena³, Mohd.Saleem Khan³, Mohd.Shahid Khan^{*1}

¹Laser Spectroscopy lab, Department of Physics, Jamia Millia Islamia, New Delhi 110025 India
 ²Centre for Nanoscience and Nanotechnology, Jamia Millia Islamia, New Delhi 110025 India
 ³Department of Physics, M.J.P Rohilkhand University, Bareilly, U.P. 243006 India

*Corresponding author: mskhan@jmi.ac.in

Abstract

In this study, $Bi_{0.95}Sr_{0.05}Fe_{0.95}Mn_{0.05}O_3$ ceramic sample was synthesized by conventional Solid state reaction. Thirdorder nonlinearity of multiferroic ceramic was studied by Z-Scan technique in which nonlinear absorption coefficient (β) was evaluated by the open aperture Z-Scan technique using continuous wave (CW) laser of 405nm wavelength. Prepared ceramics shows reverse saturation absorption (RSA) behaviour. XRD reveals the single-phase rhombohedral structure with R3c space group. Optical properties like absorption band, band gap and linear refractive index were analysed by UV-Visible spectroscopy. Morphology of the sample was analyzed by FESEM, represents the homogeneous agglomerated particles.

Study of Structure, Dielectric, and Magnetodielectric Properties of Polycrystalline KBi_{0.95}Ho_{0.05}Fe₂O₅

D. P. Sahu¹, K. Chandrakanta¹, R. Jena¹, S. D. Kaushik², and A. K. Singh^{*1}

¹Department of Physics and Astronomy, National Institute of Technology, Rourkela-769008, Odisha, India. ²UGC-DAE-Consortium for Scientific Research Mumbai Center, BARC, Mumbai-400085, India.

*Corresponding author: singhanil@nitrl.ac.in

Abstract

Holmium modified polycrystalline KBiFe₂O₅ (KBi_{0.95}Ho_{0.05}Fe₂O₅) having a *P2/c* space group is synthesized using a solid-state reaction route. The phase purity is characterized by X-ray diffraction measurement. The temperature-dependent dielectric permittivity is analyzed over a wide temperature range (10 K to 300 K) in the presence of 1.3 T and 0 T magnetic fields. The shifting of temperature-dependent dielectric permittivity (ε) with the magnetic field indicates the magnetodielectric (MD) signature. Variation of MD with magnetic field shows a butterfly-like MD loop. The extracted maximum room temperature magnetodielectric coupling is found to be 0.2% in KBi_{0.95}Ho_{0.05}Fe₂O₅. These results made it a prominent candidate for multifunctional device applications and provided space to investigate further the microscopic origin behind it.

Introduction

The Brownmillerite compound possesses A₂BB'O₅ crystal type, derived from perovskite structure [1]. These compounds are well in tuning the dielectric properties by an external magnetic field (Magnetodielectric effect). Among the brownmillerite, KBiFe₂O₅ is a promising material to investigate the coupling between magnetic and electric order. It possesses both Curie temperature (T_C: 780 K) and Neél temperature (T_N: 545 K) above room temperature and is less explored in the magnetodielectric (MD) field [2]. Here, holmium (Ho) is doped at the bismuth site of KBFO to investigate the structural, dielectric, and magnetodielectric properties of the KBi_{0.95}Ho_{0.05}Fe₂O₅ (KBHFO) sample.

Experimental Technique

The solid-state reaction technique is adopted to synthesized Ho-dope KBFO (KBi_{0.95}Ho_{0.05}Fe₂O₅: KBHFO) polycrystalline sample. High pure (>99.9%, Sigma Aldrich) K₂Co₃, Bi₂O₃, Ho₂O₃, and Fe₂O₃ oxides are taken in stoichiometric ratios. The detailed further process is mentioned in our previous report [3]. The phase purity is confirmed using X-ray diffraction (XRD) measurement (RIGAKU JAPAN) having Cu-K α radiations (λ =1.5406 Å) with a scanning rate of 3°/min. FEI Novanano SEM 450 field-emission-electron-microscope system is used to investigate the surface morphology (FESM). The dielectric and magnetodielectric measurement is carried out using high precession Wayne Kerr 6500B impedance analyzer. An electromagnet (GMW 5403) with a bipolar DC power supply having a maximum magnetic field of 1.3 T is also used. Low temperature

(10 K to 300 K) measurement is performed using a close cycle refrigerator (Cryo Industries, USA).

Results and Discussion

Figure 1 shows the room temperature (RT) XRD patterns of the polycrystalline KBHFO sample. The observed XRD patterns of the KBHFO sample is subjected to Rietveld refinement using the Fullprof program. The experimental data are fitted using *P* 2/*c* space group following a monoclinic structure. The absence of impurity peak with the good fitting parameter ($\chi^2 \approx 2.86$) indicates the pure phase of the prepared sample.



Fig. 1. Rietveld refined room-temperature X-ray diffraction patterns of the KBHFO sample. Inset shows the polycrystalline SEM image.

The surface morphology is analyzed by the RT FESM micrograph of the prepared KBHFO sample, as shown in the inset of Fig.1. The randomly oriented grains of different sizes reveal the

polycrystalline nature of the prepared sample. All the grains are distinct and well separated by the grain boundaries with varying sizes in the order of 1-2 μ m.



Fig. 2. Room temperature monoclinic crystal structure of KBHFO.

Figure 2 depicts the crystal structure of KBHFO, drawn by using VESTA software. The crystal structure is shown along *a*-axis to visualize the existence of Ho doping in BiO₆ octahedral. The structure is composed of alternative blocks of [Fe₂O₃] and [(K, Bi) O₂], having FeO₄ and BiO₆ polyhedral connected through corner-sharing oxygen atoms [3]. The Ho dopants (yellow color) are observed at the Bi (LT-Magenta color) position. The tilting of the crystal structure can be observed due to a mismatch of ionic radii (Ho³⁺=1.04 Å & Bi³⁺=1.17 Å), which can generate structural distortion in KBHFO.



Fig. 3. Temperature-dependent dielectric permittivity plot of KBHFO measured at 0 T and 1.3 T magnetic field. Inset shows the field variation magnetodielectric data recorded at 300 K at 10 kHz.

The temperature variation of dielectric permittivity (ε) is measured in the range of 10 K to 300 K, as shown in Figure 3. The dielectric data is subjected at

both 0 T and 1.3 T of the magnetic field at 10 kHz frequency. Both the curves differ from each other for all the temperature range. Near RT, the dielectric permittivity increases up to a marginal value in the presence of the magnetic field. This variation in dielectric data with magnetic field indicates the presence of magnetodielectric (MD) effect in the prepared sample. To further confirm the direct existence of MD, magnetic field variation dielectric measurement is carried out.

Room temperature magnetic field variation magnetodielectric [3] ($MD\% = \frac{\varepsilon(H) - \varepsilon(0)}{\varepsilon(0)} \times 100$) measurement is carried out at 10 kHz frequency as shown in the inset of Figure 3. The existence of nonlinear and symmetric variation of MD with both negative and positive magnetic field traces indicates the coupling effect. Doping of Ho magnetic ion (~10 μ_B) at the non-magnetic (Bi) position can contribute an essential part in the MD effect. The measured MD loop resembles with well-known butterfly MD loop. A maximum of 0.2% RT MD coupling is observed in Ho doped KBFO sample. The observed positive MD% variation is also reflected from the magnetic field-dependent dielectric data.

Conclusion

In summary, we have investigated the structural, dielectric, and magnetodielectric properties of KBHFO. The phase purity and structure are confirmed from Rietveld refinement of XRD data and with the help of VESTA software. The polycrystalline nature of the sample with the varying grain size of 1-2 um range is confirmed from the SEM image. The temperature and magnetic field dependence of ε' reveals the existence of the MD effect for the entire temperature (10 K to 300 K) range. The coupling (MD% $\approx 0.2\%$) between dielectric and magnetic field shows butter-fly like MD coupling. The above results of KBHFO can help in fabricating multifunctional device applications.

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SQUID based Magnetocardiographic mapping of fragmented QRS activity in a cardiac cycle using sample entropy

C Kesavaraja^{1*}, S Sengottuvel¹, Rajesh Patel¹, G Devanand Kumar², K Gireesan¹

¹Condensed Matter Physics Division, Materials Science Group, Indira Gandhi Centre for Atomic Research, HBNI Kalpakkam - 603102, Tamil Nadu

² Department of Atomic Energy Hospital, Kalpakkam – 603102, Tamil Nadu

*Corresponding author: kesavaraja@igcar.gov.in

Abstract

The term "fragmented QRS" (fQRS) refers to one or more deflections within the normal duration of the QRS complex (<120 ms). fQRS is induced by conduction abnormalities in the cardiac tissue or due to the presence of scar tissue subsequent to myocardial infarction (MI). Magnetocardiography (MCG) is a non-contact, non-invasive method to probe the electrophysiology of the heart by measuring its magnetic signals. MCG is effective in localizing myocardial areas where fragmentation occurs. Sample entropy (SE) measures the regularity or repeatability of a pattern in the time series. Fragmentation score (FS) gives a value based on the number of extrema present. The current work estimates SE and FS on the QRS complexes for a subject with an old inferior MI and for a healthy control subject. The acquired parameters are utilized to build two dimensional (2D) spatio-temporal contour maps, which hints at the possible areas of myocardial infarct. This preliminary finding implies that SE could be a useful biomarker in post MI assessments.

Introduction

The fragmented QRS (fQRS) is defined as the presence of additional deflections or notches in the nadir of the R or S wave in a cardiac cycle. The presence of heavy fragmentations within the QRS complex is an indicator of myocardial scarring. [1].

Superconducting quantum interference device (SQUID) sensors are known for their sensitivity to measure subtle magnetic fields, which are of the order of femto to pico Tesla. SQUID sensors are widely used to record cardiac magnetic fields, and the technique is called as magnetocardiography (MCG); These measurements are performed inside magnetically shielded rooms to reap the advantage of the SQUIDs in measuring the weak cardiac signals. The diagnostic information fetched by MCG in a non-contact way is complementary to that offered by the ECG with very good spatial and temporal resolution. Owing to these advantages, the evaluation of the fQRS activity using MCG has been recognized to be extremely useful in ascertaining its clinical significance, especially in the risk stratification of post myocardial infarction [2,3].

In this study, a quantitative way to automatic identification of fQRS is investigated using a new approach, namely sample entropy (SE), on the detailed coefficients of Haar wavelet transform for the interpolated QRS complex and compare it with existing quantitative parameters, i.e., fragmentation score (FS), by generating two dimensional (2D) spatio-temporal contour maps featuring the MCG measurement locations on the chest.

Data and Methods

The study was conducted on two subjects: A patient with a history of old inferior myocardial infarction therapeutically treated by coronary angioplasty and on a healthy control subject. A four channel MCG system with sensors arranged at the corners of a square of side length 4.2 cm was used to record signals for five minutes at each measurement location. The measured MCG signals were corrected for low and high frequency noises imposed during the measurement using a wavelet denoising algorithm. The signals at each measurement location were then epoched based on the time instants of occurrence of the R wave peak. They were used as a trigger to align all beats in a location synchronously and averaged to get signal averaged MCG (SAMCG) then arranged at each location as a spatial map of MCG signals at their corresponding spatial locations.

SE is the quantitative way to identify the irregularity of the signal [4]. For SE the morphology of the QRS complex could not be sufficient, so we interpolate the QRS twice the length of the original QRS complex and computes SE for detailed coefficients of the applied Haar wavelet transform [5]. Lower SE indicate a high regularity, i.e., normal QRS complexes, and higher SE for irregular patterns, such as fQRS complexes. Similarly, FS is computed for the QRS complex by counting the extrema present as in the literature [3]. The values obtained for a normal and fQRS complex are displayed in Figure 1.



Figure. 1. A cardiac cycle of (a) MI subject with fQRS complex and (b) healthy subject with normal QRS complex.

Results and Discussion

The computed values are tabulated in Table 1. The mean values are considered as the cutoff values in separating the normal and fragmented QRS complexes.

Table 1. Parameter values for subject with old MI and for a healthy control subject. The values are in mean \pm standard deviation (SD).

Parameters	Subject 1 (Old MI)	Subject 2 (Control)	
Fragmentation score (FS)	44.19 ± 7.25	38.10 ± 2.73	
Sample entropy (SE)	0.16 ± 0.23	0.12 ± 0.05	

The 2D contour maps were made by interpolating the FS values and SE values onto a regular grid and displayed in Figure 2. The maximum value of the SE (1.12) and FS (66.18) coincides in the seventh sensor location. The overall correlation between the SE values and the FS values was obtained as 0.76. The area of the dispersion in the contour maps could be an arrhythmogenic substrate after MI. The region where the fragmentation is absent, both SE and FS are low but the area of the higher SE values is less than the area of the higher FS values. The low amplitude noisy signals could contribute to the pseudo fragmentation and increase the area of the FS values in specific channels.



Figure. 2. 2D contour map of SE for (a) normal QRS complex (b) fQRS complex and FS for (c) normal QRS complex (d) fQRS complex

Summary

SE values for the interpolated QRS complex have been computed, and the 2D contour maps for the same have been obtained. These maps exhibit a consistency featuring a commonality of the feature under investigation, i.e., the fragmentation in the QRS. The areas of fragmentation in contour maps must be compared to cardiac MRI (the gold standard) to assess the efficacy of SE in detecting fQRS in MCG, which is still ongoing [6].

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Anomalous Magnetization and Magnetocaloric Effect of Co₂TiAl₁₋ _xSi_x Full Heusler Alloys

Subhadeep Datta¹, Shantanu Kumar Panda¹, Shampa Guha¹, and Manoranjan Kar¹

¹Department of Physics, Indian Institute of Technology Patna, Bihta-801106, India

*Corresponding author: papaidatt@gmail.com

Abstract

The half-metallic ferromagnets Co₂TiZ (Z= main group element) show tunable transport properties, high Curie temperatures, and high magnetic moments. The present Co₂TiAl_{1-x}Si_x (x=0.50, 0.75) alloys have been prepared by the conventional Arc melting technique and their magnetic properties have been analyzed. These alloys exhibit a wide range of transition temperatures from 285 K to 315 K near room temperature and theoretical magnetic moment between 1.50 μ B/f.u. to 1.75 μ B/f.u. with increasing Si concentration. However, experimentally it is observed that the saturation magnetization for x=0.75 slightly deviates from Slater Pauling's prediction. Also, the magnetocaloric effect study of this series reveals that these materials (specially x=0.50) can be tuned for magnetocaloric application near room temperature.

Introduction

The discovery of ferromagnetic (FM) Cu₂MnAl alloy from all non-FM atoms by F. Heusler in 1903 gives a huge breakthrough in the field of science and technology [1]. In 1983, Kubler et. al. first predicted Co₂MnAl and Co₂MnSn to be half-metallic ferromagnet, which changes the spintronics industry [2]. Heusler alloys are low cost, easy to fabricate, and easy to tune their physical properties. X₂YZ type full Heusler alloy consists of transition metals in positions X and Y, and the main group element at Z. X₂YZZ' type ternary allows allow tuning its physical properties according to the requirement. Thereafter, research is going on Co-based alloys by substituting various elements for different applications. Literature survey reveals that Co-based alloys exhibit high spin polarization, high Curie temperature, and exceptional transport properties [3]. Co₂TiAl_{1-x}Si_x series possess $L2_1$ cubic structure i.e. 4 interpenetrating fcc sublattices. Co atoms occupy the tetrahedral sites (0,0,0) and (1/2,1/2,1/2) and, Ti occupies the octahedral site (1/4, 1/4, 1/4). So, the mutual substitution between Al and Si occurs only at the (3/4,3/4,3/4) site. Co₂TiAl_{1-x}Si_x alloys undergo hysteresis-free second-order FM to paramagnetic (PM) phase transition with a large range of transition temperatures depending on composition. This allows overcoming the hysteresis loss and narrow working temperature related to first-order magneto-structural transition for magnetic cooling application. In this direction, the magnetic properties and magnetocaloric effect (MCE) of Co₂TiAl_{1-x}Si_x (x=0.50, 0.75) alloys have been explored here.

Experimental details

Ingots of Co₂TiAl_{1-x}Si_x (x=0.50, 0.75) alloys were prepared in an Arc melting furnace in the Argon atmosphere. Then the ingots were annealed in the vacuum quartz tube at 800° C for 24 hours followed by ice water quenching. The Crystal phase formation was confirmed by the X-ray diffraction technique, taken with the help of Rigaku TTRX III diffractometer with Cu K- α source. The magnetization measurements were carried out in the VersaLab, Quantum design vibrating sample magnetometer at temperatures ranging from 60 K to 400 K with a highest magnetic field of 3 T.

Results and discussion



Fig. 1. Normalized isofield magnetization curves for Co₂TiAl_{1-x}Si_x at 100 Oe.

The magnetic moment in Co_2TiZ type Heusler alloy is mainly concentrated to the tetrahedral and octahedral sites and, the Z site contributes very little or negative magnetic moment to the net magnetization of a unit cell [4]. The magnetic parameters for the present samples are enlisted in Table 1. The isofield magnetization (*M*-*T* Curves) measurements at 100 Oe reveal the second-order FM to PM phase transition for all the samples, shown in Fig. 1. The Curie temperatures (T_C) are around room temperature which has a great advantage in MCE.



Fig. 2. Isothermal magnetization curves for Co₂TiAl_{1-x}Si_x at 60 K.

The isothermal magnetization (*M*-*H*) curves at 60 K for all samples are shown in Fig. 2. Saturation magnetizations (M_s) for the x=0.75 sample slightly differ from Slater Pauling's (S.P.) prediction. The presence of magnon may be responsible for the decrease in M_s . Also, the anti-site disorder between Ti and Al in the system leads to form B_2 structure in place of $L2_1$, which has an impact on its magnetic properties. This type of anomaly was also observed for x=0.25 which has been described elaborately elsewhere [5].



Fig. 3. Temperature dependence of magnetic entropy change of for $Co_2TiAl_{1-x}Si_x$ at 3 T.

MCE has been calculated by maxwell's equation from isothermal magnetization (M-H) curves at different temperatures, given by [6]:

$$\Delta S_M = \mu_0 \int_0^{H_{max}} \left(\frac{dM}{dT}\right)_H dH \qquad a)$$

The magnetic entropy changes (ΔS_M) are plotted against temperature for 3 T field change, shown in Fig. 3. Another important MCE parameter, relative cooling power (RCP) is calculated from the maximum magnetic entropy change (ΔS_M^{max}) near T_C and the range of working temperature $(\delta T_{FWHM} \text{ of } \Delta S_M - T$ curve) by the following equation:

RCP= $|-\Delta S_M^{max}| \times \delta T_{FWHM}$ b) It is interesting to note that ΔS_M^{max} and RCP values for these alloys are quite large with large working temperatures as compared to other second-order FM to PM transition alloys and oxides near room temperature [7].

Table 1. Magnetic parameters of C02117	$IAI_{1-x}SI_{x}$.
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X	<i>Тс</i> (К)	<u>М</u> s (µв/f.u.) S.P.	<i>Ms</i> (μ _B /f.u.) Expt. at 60 K	ΔS_M^{max} (J/kgK) at 3 T	δT _{FWHM} (K) at 3 T	RCP (J/kg) at 3 T
0.50	285	1.50	1.52	0.90	71	63.8
0.75	315	1.75	1.19	0.83	58	48.1

Conclusion

In this article, the magnetic properties and MCE of $Co_2TiAl_{1-x}Si_x$ (x=0.50, 0.75) Heusler alloys have been studied. The second-order FM to PM transition temperatures are near room temperature. The saturation magnetization (M_S) slightly deviates from Slater Pauling's prediction for x=0.75 due to the presence of magnon and anti-site disorder between Ti and Al. ΔS_M^{max} is found to be a maximum of 0.90 J/kg-K at 3 T for x=0.50 near room temperature. This study opens a window to tune the physical properties of $Co_2TiAl_{1-x}Si_x$ alloys for industrial application as a magnetocaloric material.

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Magnetic and magnetocaloric properties in Al doped Ni-Co-Mn-Snbased Heusler alloy

Saheli Samanta^{1*}, Subrata Ghosh¹, and Kalyan Mandal¹

¹Magnetism Laboratory, Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, JD Block, Sector III, Salt Lake, Sector III, Kolkata 700106

*Corresponding author: saheli24.trc@bose.res.in

Abstract

Herein, the tuning of martensitic transformation and the magnetocaloric properties are investigated for the Ni₄₄Co₃Mn₃₈Sn₁₄Al₁ Heusler alloy. The alloy shows austenite phase corresponding to L2₁ cubic structure at room temperature. From magnetic measurement, the sample is found to undergo a first-order martensitic transformation (MT) from a ferromagnetic austenite phase to a weak magnetic martensitic phase. A maximum value of isothermal magnetic entropy changes of about 5 Jkg⁻¹K⁻¹ associated with a relative cooling power of ~137 Jkg⁻¹ is obtained due to field change of 5T. The material shows the large magnetocaloric response in a wide working temperature interval of 27 K which will lead this alloy as a potential magnetic refrigerant material for magnetic refrigeration.

Structure Mobilized Magnetic Transitions in Ca Doped Y₂Ru₂O₇ Pyrochlores

Soumyakanta Panda¹, Niharika Mohapatra^{1*}

¹School of Basic sciences, Indian Institute of Technology Bhubaneswar, Jatni, Odisha, 752050

*Corresponding author: niharika@iitbbs.ac.in

Abstract

We report on an experimental investigation of the structural and magnetic properties of the $Y_{2-x}Ca_xRu_2O_7$ pyrochlore system as a function of Ca doping. The structural properties show the presence of lattice expansion in the crystal structure, which we have verified from the Rietveld data of the XRD pattern. From the dc magnetization data, the decrement of effective moment and the shifting of Néel temperature has also been found with the Ca concentration.

Introduction

Pyrochlore oxides, of the type $A_2B_2O'O_6$, with corner sharing tetrahedra structure exhibit numerous fascinating physical properties owing to the geometrical frustration in both A and B sublattices. Among these pyrochlores, the Ruthenate based pyrochlores represent a unique platform to demonstrate the interplay of coulomb correlation and spin-orbit coupling along with their high structural and chemical flexibility. In particular, the intriguing properties of ruthenium pyrochlore [1] compounds include Metal-insulator transition, long range magnetic order, and spin singlet transitions. Moreover, the electronic and magnetic properties of these pyrochlores can be tuned by doping at A or B site ions. In the most stable configuration, refer A³⁺B⁴⁺ cation combination and sometimes A²⁺B⁵⁺ cation combinations.

In this paper, we present a study of the magnetic properties of $Y_{2-x} Ca_x Ru_2O_7 (Ca^{2+} doped system)$. Our results show the partial replacement of Ca^{2+} in the position Y^{3+} of $Y_2Ru_2O_7$ promotes the hybrid valency of Ru^{4+} and Ru^{5+} on the system and enhance the effective moment of the sample. In this case a relevant role from the structural point of view is also played by the Ca^{2+} ion as the radius of Ca^{2+} is greater than that of Y^{3+} .

Experimental Methods

Powdered samples of $Y_{2-x}Ca_xRu_2O_7$ (x = 0, 0.04, 0.2, 0.4) were synthesized using the conventional solid-state reaction method. Mixtures of Y_2O_3 , CaCO₃, and RuO₂ in proper molar ratios were mixed by planetary ball milling for 1 h at 300 rpm and pre-reacted at 800 $^{\circ}C$ for 12 h in air. After grinding these were pressed in to pellets and sintered

at 1150 ^oC for 48 h in air. The grinding and sintering cycle was repeated several times till a single-phase sample was obtained.

Results and discussions

The crystal structure and phase purity of the Ca doped Y2-xCaxRu2O7 samples were determined from the X-ray diffraction measurements as shown in Fig. 1. Rietveld refinement of the XRD pattern confirms that the prepared samples are in single phase with cubic structure (space group: $Fd\overline{3}m$). The obtained lattice parameters of the parent sample (x = 0) are close to the value reported previously [2]. From the inset of Fig 1, it can be clearly seen that the main peak (222) of the lattice plain shifts gradually towards a lower Bragg angle as we increase the Ca content in Y2-xCaxRu2O7. This shifting of the reflection lines in the XRD pattern towards lower angle indicates a lattice expansion in the pyrochlore structure which is also verified from the Rietveld data and given in the Table 1. The increment of lattice parameters can also be explained in terms of the ionic radii data, as the radius of Ca²⁺(114 pm) is greater than that of $Y^{3+}(104 \text{ pm})$.

The temperature dependence of dc magnetic susceptibility (χ) of all the specimens were collected in an applied field of 5 kOe under zero field cooled (ZFC) and field cooled (FC) conditions as shown in Fig 2. One may notice divergence of ZFC and FC susceptibilities in all the doped compounds similar to that of the pristine, while the irreversibility temperature (T_{irr}) is essentially same for all the compounds. However, the distinct maximum in the



Fig. 1. X-ray powder diffraction of $Y_{2-x}Ca_xRu_2O_{7,}x$ in the range from 0 to 04. Inset shows the shifting.

zero field cooled magnetization data, which apparently signifies the Neel temperature (T_N), shifts to lower temperature with increasing the Ca doping level in Y_{2-x}Ca_xRu₂O₇; $T_N = 77(2)$ K [3] for x = 0 and ~32 K for x = 0.4. Another noteworthy observation is that the peak in ZFC and T_{irr} coincide for the parent sample while the peak temperature is lower than T_{irr} for the doped samples. The size of divergence is also found to be reduced with the Cadoping indicating a disruption in the spin states and the magnetic frustration.



Fig. 2. Magnetic susceptibility as a function of temperature in both ZFC and FC conditions.

To get a quantitative idea, we have fitted the dc magnetic susceptibility data in the high temperature

range with the Curie-Weiss law as follows; $\chi(T) = \frac{C}{T - \theta}$, where θ_C is the transition temperature. The effective magnetic moment was calculated by using $\mu_{eff}^2 = \frac{3C k_B}{N_A}$ for all the specimens and shown in Table 1. It may be noticed that the Curie-Weiss constant (θ_C) and the frustration parameter (θ_C/T_N) decreases systematically with the Ca concentration, which suggests Ca-doping promotes release of magnetic frustration in YRO.

In addition, effective moment ($\mu_{eff}/f.u.$) or (μ_{eff}/Ru) also reduces with increasing x. As reported in a previous study, doping of a divalent ion (Ca²⁺, Ba²⁺ or Zn²⁺) results in mixed valent state of Ru (Ru⁴⁺ and Ru⁵⁺) [4, 5]. Substitution of Ru⁴⁺ (S =1) by Ru⁵⁺ (S =1/2, due to D_{3d} symmetry) causes the observed decrease in the effective moment and also the exchange coupling of the system.

Table 1. Variation lattice parameters, effective moment, Curie-Weiss temperature and frustration parameter with Ca doping.

Doping level	Lattice parameters	$\mu_{eff}/f.u.$	$\theta_{\rm C}$	$ \theta_{\rm C} /$ T _N
(x)	(Å)	(MD)		- 11
$\mathbf{x} = 0$	10.127	4.430	-1200	15.5
x = 0.04	10.134	4.415	-983.84	13.4
x = 0.2	10.139	4.365	-565.15	12.8
x = 0.4	10.149	3.939	-396.85	12.4

Conclusions

In summary, the paper reports the result of lattice expansion as a function of Ca concentration in pyrochlore structure. The dc magnetization data shows shifting of transition temperature towards lower temperature which suppress the spin glass behavior in highly doped Ca sample. We see an decrement of effective moment at the ruthenium site, which signifies the presence of Ru⁵⁺ ion in the sample after doping a divalent atom in the position of trivalent atom.

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Large magnetocaloric effect in Ho₁₅Si₉C

A. K. Jana¹, K. Panda¹, and A. Bhattacharyya^{1*}

¹Department of Physics, Ramakrishna Mission Vivekananda Educational and Research Institute, Belur Math, Howrah-711202, India *Corresponding author: amitaya bhattacharpya@rkmyu.ac.in

 $* Corresponding \ author: \ amitava.bhattacharyya@rkmvu.ac.in$

Abstract

The ground state magnetic properties and magnetocaloric effect (MCE) of $Ho_{15}Si_9C$ compound isostructural with $R_{15}Si_9C$ (R = Gd, Tb, and Dy) are investigated. Gd_{15}Si_9C, Tb_{15}Si_9C, Dy_{15}Si_9C, and Ho_{15}Si_9C exhibit second order ferromagnetic transitions at temperatures below 170 K, 130 K, 70 K, and 42 K, respectively. For $Ho_{15}Si_9C$, the maximum value of $-\Delta S_M$ is 11.04 J/kg K at 68 K for H = 50 kOe. The key finding of this research is that as the atomic number increases, the transition temperature of $R_{15}Si_9C$ (R = Gd, Tb, Dy, and Ho) decreases while the maximum entropy value rises. $R_{15}Si_9C$ compounds has high reversible MCE values, it could be useful for magnetic refrigeration. The presence of large MCE values is due to the large magnetic moment associated with rare earth elements.

Quasi-Two-Dimensional Magnetism in Spin-1/2 Square Lattice Compound Cu[C₆H₂(COO)₄][H₃N-(CH₂)₂-NH₃]·3H₂O

¹S. Guchhait, ²S. Baby, ³M. Padmanabhan, ¹A. Medhi and ¹R. Nath

¹School of Physics, Indian Institute of Science Education and Research - Thiruvananthapuram-695551, Kerala, India, ²Department of Chemistry, Christian College - Chengannur, Alappuzha, Kerala-689122, India, ³Department of Chemistry, Amrita Vishwa Vidyapeetham - Amritapuri, Kerala-690525, India

*rnath@iisertvm.ac.in

Abstract

We have synthesized the single crystal of of quasi-two-dimensional S = 1/2 quantum magnet $Cu[C_6H_2(COO)_4][H_3N-(CH_2)_2-NH_3].3H_2O$ and investigated it's magnetic properties. It crystallizes in a monoclinic structure with space group $C_{2/m}$. The temperature dependent molar magnetic susceptibility is well described by S = 1/2 frustrated square lattice $(J_1 - J_2)$ model with nearest-neighbor interaction $J_1/k_B \simeq 5.37$ K and next-nearest-neighbor interaction $J_2/k_B \simeq -0.37$ K. Our analysis using frustrated rectangular lattice $(J_{1a,b} - J_2)$ model also confirms almost isotropic nearest-neighbour interactions $(J_{1a}/k_B \simeq 5.31$ K and $J_{1b}/k_B \simeq 5.38$ K) in the ab-plane and $J_2/k_B \simeq -0.24$ K. Further, the molar susceptibility and the isothermal magnetization at T = 1.9 K is also well described by a non-frustrated square lattice model with $J_1/k_B \simeq 5.2$ K. Based on the J_2/J_1 ratio, the compound can be placed in the N'eel antiferromagnetic state of the $J_1 - J_2$ phase diagram. No signature of magnetic long-range order is detected down to 2K.

Structural and Magnetic Properties of Hexagonal BaMnO3

Malaya Kumar Das¹, Soumyakanta Panda¹, and Niharika Mohapatra^{1*}

¹School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Jatani, Odisha,752050

*Corresponding author: niharika@iitbbs.ac.in

Abstract

Polycrystalline $BaMnO_3$ synthesized by ethylene diamine derived sol-gel technique confirms the formation of single-phase hexagonal $BaMnO_3$ with $P6_3mc$ space group. Magnetic susceptibility measurements carried out at low and high dc fields on the compound between 5K and 300 K were identified with the appearance of canted antiferromagnetic ordering around transition temperature of 50 K. Non saturating magnetization value of M-H curve at higher applied field confirms this small canting in AFM state.

Introduction

Hexagonal perovskite oxides, similar to the cubic perovskites, have been drawing considerable attention due to their versatile structural, electronic, magnetoelectrical and magneto-elastic properties[1]. Hexagonal barium manganite (BaMnO₃) belongs to this exciting class of materials exhibiting strong interaction between highgly frustrated magnetic system and nearby localized spins in the lattice. The unusual structural, electronic and magnetic properties of BMO are shown to be highly sensitive to the preparation condition and oxygen deficiency.

In contrast to the cubic perovskites, which contains conrner-sharing metal-oxygen octahedral, the hexagonal perovskites are made up of face-shared metal-oxygen octahedra or trigonal prisms. This results in a structural framework with either dimer, trimer, or higher order chains of the octahedra. As shown by Negas and Roth BMO may crystallize in different forms of hexagonal structure (2H, 4H, 6H, 9R, 10R, and 15R etc.). They have shown a detailed study, of the preparation condition, phase relation, and crystallographic features of various crystallographic phases of BaMnO₃ [2].

The magnetic properties of the hexagonal BMO is also highly controversial, specifically the 2H-BMO. Christensen and Olliver [3] have reported the onset of antiferromagnetic ordering in 2H-BMO around the Neel temperature (T_N) of 2.4 K. On the other hand, Cussen and Battle [4] have shown the magnetic ordering below $T_N \sim 59$ K. Moreover, the AFM structure is shown to be collinear by Christensen et al., while Cussen et al have domenstrated a canted AFM phase. Additionally, the presence of short range magnetic ordering and temperature induced structural transitions have been reported by several studies. But there are no detail studies on the magnetization of 2H-BaMnO₃. Therefore, we consider it worthwhile to clarify this debatable structural and magnetic features of 2H-BMO. In this paper we report the synthesis of nanosized $BaMnO_3$ samples by ethylene derived solgel route under ambient atmospheric and low-temperature conditions. The results of our magnetic measurements confirm a magnetic ordering at ~ 50 K presumably to a canted antiferromagnetic structure.

Experimental details

A polycrystalline sample of BaMnO₃ was prepared by ethylene–diamine (ED) derived sol-gel route under ambient atmospheric and lowtemperature conditions. Stoichiometric amounts of analytical grade Ba(NO₃)₂ and Mn(NO₃)₂.6H₂O were dissolved in distilled water and stirred with nitric acid at 70 $^{\circ}$ C for 30 minutes. Citric acid and ethylene glycol were added to the solution & again stirred at 70 $^{\circ}$ C for 1 hr. PH 10 was maintained by the addition of ethylene diamine. Then temperature was increased to 300 $^{\circ}$ C and grey colour powders were obtained, which were calcined at 900 $^{\circ}$ C for one hour with a heating rate of 5 $^{\circ}$ C per minute.

Results and Discussion

The room temperature X-ray diffraction (XRD) pattern of BaMnO₃ shows well-defined reflections corresponding to hexagonal structure with space group P6₃mc indicating single phase nature of the sample. Fig. 1 depicts the Reitveld refinement of the XRD pattern with the corresponding hexagonal structure yielding the lattice parameters as a = 5.697 Å and c = 4.813 Å. Table1 lists other structural parameters obtained from this refinement.



Fig. 1. Rietveld refined XRD pattern of BaMnO₃.

Table1. Structural parameters of BaMnO₃ obtained from the refinement of room temperature XRD data.

Atom	site	X	У	Z	focc
Ba	2d	1/3	2/3	3/4	1.0
Mn	2a	0	0	0	1.0
0	6h	0.15186	0.30365	-0.2500	1.0
volume v = 135.30 Å ³ , $\chi^2 = 2.40$ and $R_{Bragg}\% = 2.523$					

Molar magnetic susceptibility of $BaMnO_3$ as a function of temperature in the range 5 – 300 K is shown in fig. 2. The data was measured under both ZFC and FC conditionas of the specimen in applied fields of 100 Oe and 5 kOe. The data shows an apparent transition at ~ 50 K. While the FC magnetization shows a sharp increase at T_N , ZFC magnetization decreases followed by a peak feature dependent on the applied field.

Though these features are quite different than the earlier reports, it indicates canted antiferromagnetic ordering. We also did not find Curie-Weiss type susceptibility behavior in the high temperature range similar to the earlier reports, which may be attributed to the one-dimensional short range ordering of the Mn^{4+} spins. To get more insight into this magnetic behaviour, magnetic isotherms were measured at temperatures below and above the magnetic ordering temperature. Below 50 K, the M-H curves exhibit a hysteresis loop but the the magnetization is non-saturating even for an applied field upto 50 kOe. Furthermore, the value of magnetization at 50 KOe is very small to account for any ferromagnetic component.



Fig. 2. Magnetic susceptibility as a function of temperature in the temperature range of 5K to 300K measure at field of (a) 5 KOe (b) 120 Oe for BaMnO3. (c) isothermal magnetization curve recorded at 2K, 10 K, and 100 K.

This clearly suggests a small canting in the AFM state. On the other hand, the high temperature M-H curves show essentially linear behavior.

Conclusion

In this paper we present the synthesis of 2H-BaMnO₃ material by using the ED derived sol-gel technique `under ambient atmospheric and low-temperature conditions. The room temperature XRD data confirms the formation of single phase of the prepared sample in the polar $p6_3mc$ space group. The susceptibility measurment indicates the antiferromagnetic ordering of BaMnO₃ around T_N at 50 K. A large deviation in FC and ZFC magnetization specifies the canted antiferromagnetic type ordering in 2H-BMO. As temperature increases, the loop collapses and shows a linear variation with the applied field.

Acknowledgement

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Study on Structural, Magnetic and Exchange Bias Properties of Mn-Ni-Co-Sn Heusler Alloy

Jyoti Sharma, K. G. Suresh and Aftab Alam

Department of Physics, Indian institute of Technology Bombay, Mumbai, India *Corresponding author: jsharma628@gmail.com

Abstract

Here, we have investigated the structural, magnetic, and exchange bias properties of a Mn rich $Mn_{50}Ni_{42-x}Co_xSn_8(x=6)$ Heusler alloy. Present alloy undergoes the magneto-structural (martensitic) transition at around 333 K, and the low temperature magnetic state of the alloy has been investigated by means of DC magnetization and AC susceptibility measurements. These measurements confirm the presence of spin glass (SG) phase at low temperatures. A large exchange bias field of 990 Oe is observed after field cooling the alloy at 10 kOe field. This is attributed to the large exchange anisotropy present at SG/FM interfaces. The temperature and cooling field effect on the exchange bias properties has also been studied in this report.

Introduction

In last decades, Ni-Mn-Z (Z= Ga, Sb, Sn and In) Heusler alloys have attracted a lot of attention of research community, due to their multifunctional properties, such as shape memory effect, giant magnetocaloric effect (MCE), large magnetoresistance (MR) and exchange bias (EB) etc [1-4]. For example, in Ni rich Ni₅₀Mn_{25+x}Sb_{25-x}, alloy, an exchange bias field (H_{EB}) of 248 Oe has been obtained. In another report on Ni_{50-x}Mn_{37+x}Sn₁₃ Heusler alloy, a H_{EB} of 377 Oe has been observed at 5 K [3-4]. Heusler alloys may be considered as potential candidates for various applications such as shape memory devices, magnetic tunnel junctions, sensors, storage and spintronic devices etc. Most of these properties have been found to be associated with their first order magneto-structural transition (i.e. martensitic transition) from high temperature austenite to low temperature martensite phase.

However in recent years, some Mn rich Mn-Ni-Z (Z= Ga, Sn and In) Heusler alloys have been explored for their various physical properties such as MCE, MR and EB etc [5-6]. In the present report, the Mn rich $Mn_{50}Ni_{42-x}Co_xSn_8$ (x=6) full Heusler alloy is studied for their structural, magnetic and exchange bias properties. The alloy is found to show the martensitic transition and large exchange bias properties. The effect of magnetic field and temperature on the exchange bias properties is also discussed.

Experimental Details

Polycrystalline sample of $Mn_{50}Ni_{42-x}Co_xSn_8$ (x=6) alloy has been prepared by arc melting method in presence of pure agon atmosphere. After that, sample was annealed at 1073 K for 72 hrs, followed by

quenching in ice-mix water. The structural analysis has been performed by collecting the X-ray diffraction pattern (XRD) at room temperature (RT) using a PANalytical X'pert PRO diffractometer. DC magnetization and AC susceptibility measurements have been performed in a superconducting quantum interference device magnetometer (SOUID).

Results and Discussion

Fig. 1 shows the RT XRD pattern for the present alloy, which shows the tetragonal structure. The estimated lattice parameters from the Lebail refinement are found to be a = b = 5.86 Å and c = 6.18 Å. Zero field cooling (ZFC), field cooled cooling (FCC) and field cooled heating (FCH), magnetization as a function of temperature (*M*-*T*) curves, recorded in presence of 100 Oe field for the present alloy is shown in Fig. 2. The alloy exhibits the martensitic transition at around 333 K, which is named as the martensitic transition temperature (*T*_M). With the decrease of temperature, a large splitting between ZFC and FCC *M*-*T* curves is



Fig. 1. RT XRD pattern for the present Heusler alloy.

observed, which has been attributed to the coexistence of ferromagnetic (FM)/antiferromagnetic (AFM) or the spin glass (SG) phase at low temperatures in the martensite phase of the alloy. To verify the presence of spin glass phase, we have recorded the frequency dependent, AC susceptibility as a function of temperature (data not shown here). The real part of AC susceptibility has been found to show a peak around 100 K, which is named as T_f (spin freezing temperature). This peak temperature is found to shift to higher temperatures with the increase in frequency, which indicates the presence of spin glass phase in the alloy.



Fig. 2. The ZFC, FCC and FCH, *M-T* curves, measured in presence of 100 Oe field.

It is reported in literature that the coexistence of spin glass/FM or AFM/FM phases gives rise to large exchange bias effect. To investigate the exchange bias effect in the present alloy, magnetic hysteresis loop has been recorded (in range of ± 20 kOe) at 2 K, after FC process at 10 kOe field, and data is shown in Fig. 3. The M-H loop is found to shift in negative field direction, which confirms the presence of EB. A large value of H_{EB} of around 990 Oe has been obtained for the present alloy, which is comparable to reported value for other Co doped Heusler alloys [6]. Value of H_{EB} has been estimated by using the formula H_{EB} = $-(H_L+H_R)/2$, where H_L and H_R are the left and right coercive fields. The observed EB is attributed to the large exchange anisotropy present at the SG/FM interfaces. To see the effect of temperature and magnetic field on EB properties, M-H loops are recorded at different temperatures after FC at 10 kOe (data not shown here), and at different cooling fields. The typical data for FC effect on EB at 2 K is shown in the inset of Fig. 3. From these measurements, it is observed that, the $H_{\rm EB}$ is found to decrease with the increase in temperature and FC strength. This decrease of EB can be attributed to the decrease in exchange anisotropy between the SG/FM phases.



Fig. 3. EB effect: *M*-*H* loop measured at 2 K after FC process at 10 kOe field for this alloy. Inset shows the H_{EB} and H_{C} as a function of cooling field strength.

Conclusions

In the present study, the structural, magnetic, and exchange bias properties of a Mn rich Mn₅₀Ni₄₂₋ $_{x}Co_{x}Sn_{8}(x=6)$ Heusler alloy has been investigated. RT structure is found to be tetragonal for the present alloy. It is found to exhibit the martensitic transition at around 333 K from austenite phase to martensite phase. The low temperature magnetic state of the martensite phase of the present alloy has been studied by means of DC magnetization and AC susceptibility measurements. These measurements confirm the presence of spin glass phase at low temperatures. A large exchange bias field of 990 Oe has been observed after field cooling the alloy at 10 kOe field. This is attributed to the large exchange anisotropy present at SG/FM interfaces. The temperature and cooling field effect on the exchange bias has also been studied in this study.

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Study of Pseudogap in YBCO:NaNbO3 NanocompositeThin Films

Mamta Dahiya¹, Rohit Kumar², Rajni Kandari¹, and Neeraj Khare^{1,2*}

¹Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016 ²Nanoscale Research Facility, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016

*Corresponding author: nkhare@physics.iitd.ernet.in

Abstract

In high temperature superconductors, the short coherence length and charge carrier concentrations are responsible for the thermal fluctuations in the resistivity curve. The effect of NaNbO₃ nanoparticles and nanorods addition on the basal-plane conductivity of YBCO thin films has been investigated. Thin films of pure YBCO and YBCO:NaNbO₃ composites have been deposited on SrTiO₃ substrate using pulsed laser deposition (PLD) technique. The growth of c-axis orientation is confirmed in pure YBCO and YBCO:NaNbO₃ thin films using the structural analysis. In the thermal fluctuations regime, the excess conductivity shows exponential dependence on temperature which is used to obtain information of pseudogap at temperatures away from critical temperature T_C . The characteristic temperature have been found higher for the Nanocomposite thin films than the pure YBCO thin film, which indicates the extended excess conductivity region.

Study of Magnetic Behaviour of Mg-Mn-Zn ferrites using Mössbauer Spectroscopic Technique

S.A. V. Prasad^{1,3}, K. Naga Praveen¹, Ch. Srinivas^{1,*}, E. Ranjith Kumar², R. Jeevan Kumar^{3,*}, Sher Singh Meena^{4,*}, T.V. Chandrasekhar Rao⁶, C. L. Prajapat^{5,6,*} and D. L. Sastry⁷

¹Nanomaterials and Nanomagnetism Research Laboratory, Department of Physics, Sasi Institute of Technology & Engineering, Tadepalligudem -534 101, India.

² Department of Physics, K. P. R. Institute of Technology, Coimbatore -643 048, India.

³Department of Physics, Sri Krishnadevaraya University, Ananthapur- 515 003, India.

⁴Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai-400 085, India.

⁵Technical Physics Division, Bhabha Atomic Research Centre, Mumbai-400 085, India.

⁶Homi Bhabha National Institute, Anushkatinagar, Mumbai-400 094, India.

⁷Department of Physics, Andhra University, Visakhapatnam-530 003, India.

*Deceased September 10, 2021

*Corresponding authors: <u>srinivas.chintoju75@gmail.com</u>, <u>ssingh@barc.gov.in</u>, <u>rjkskuphy@gmail.com</u>

Abstract

In the present manuscript structural and Mössbauer results of $Mg_xMn_{0.8-3}Zn_{0.2}Fe_2O_4$ (x = 0.1, 0.4, 0.7) nanoferrites are reported. XRD patterns revealed the formation of spinel phase along with anti-ferromagnetic phase of α -Fe₂O₃. Mössbauer spectra consist of fully resolved six line patterns along with quadruple dublets. The isomer shift values are the indicative for the existence of Fe³⁺ ions only. The higher value of line width of octahedral (*B*) site revealed the core-shell morphology of ferrite nanoparticles showing spin-glassy interactions. It is supported by marginal variation of hyperfine field (*H_f*) of tetrahedral (*A*) and octahedral (*B*) sites. The present series of ferrite samples are useful for multifunctional applications due to presence of fine ferrite nanoparticles.

Ultrasonically assisted wet-chemical synthesis of Lu doped BiFeO₃

Rakesh Solanki, Mayuri Kamble, and *Paresh Salame

Department of Physics, Institute of Chemical Technology Mumbai, Mumbai, INDIA-400019

*Corresponding author: ph.salame@ictmumbai.edu.in

Abstract

Lu doped BiFeO₃ (BFO) was successfully prepared via a wet-chemical route with assistance from high power ultrasound (150W). The synthesis process was further hastened by utilizing the power of uniform microwave heating. X-ray powder diffraction data and Rietveld refinements of XRD data revealed that the phase formed compound has a rhombohedral structure with R3c space symmetry. A minor secondary phase was identified as Bi₂Fe₄O₉ in the range between $2\theta \sim (25^{\circ} - 30^{\circ})$, which usually occurs while synthesizing BFO.

Introduction

Bismuth ferrite is one of the rarest compounds which manifest both ferroelectricity and magnetism properties simultaneously at room temperature. However, its antiferromagnetic and ferroelectric transition temp are high compared to room temperature (643K and 1100K, respectively) [1]–[4]. Bismuth ferrite has been given considerable attention because of its fundamental coupling of multiple order general practical application and its for magnetoelectric devices, which are electrically controlled [5]. Because of this, BFO provides a wide range of opportunities in information storage, magnetic recording media, spintronic devices, sensors, etc. [6]. Whether in ceramic or film, pristine BFO suffers from large leak current density and remanent polarization. This is due to the presence of impurity phases present in BFO prepared by conventional synthesis route. These impurities are responsible for apparent high electrical conductivity in BFO, which can be unsuitable for its application to the above-mentioned devices. To tackle this problem, researchers around the globe have been synthesizing rare-earth-doped BFO, as they are very effective in reducing leakage current in BFO [4]. BFO is a widely researched compound for its electric and magnetic properties [7]. In this paper, we propose an efficient sonochemical synthesis route for the synthesis of (Lu) lutetium doped BiFeO₃ (BLFO) in rhombohedral perovskite structure with space group R3c to be used as an effective multiferroic material at room temperature.

Experimental

To synthesis $Bi_{0.95}Lu_{0.05}FeO_3$, the precursors used for the synthesis were bismuth nitrate ($Bi(NO_3)_3 \cdot 5H_2O$), ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and Lutetium(III) oxide (Lu₂O₃). Lu₂O₃, in stoichiometric amount, dissolved in dilute nitric acid, and remaining precursors were dissolved in di-ionized (DI) water and kept on a magnetic stirrer at 400 rpm for 20 min for proper homogenization. This solution was then kept in an ice bath for ultrasonic treatment using probe sonification. For this, the solution was treated at 30% (150 W) amplitude for 30 mins (with 15 mins on/15 mins off-cycle). After ultrasound treatment, the aqueous solution of ethylene glycol (5x mol%) and critic acid (2x mol%) was added to it. The pH of the solution was maintained between 5.5-6 by dropwise adding ammonia solution so that to form a stable colloidal suspension. This colloidal suspension was kept on a magnetic stirrer at 80 °C, forming a thick gel. Later, the temperature was raised to 120 °C, so that a fluffy dry mass was obtained. This dry mass was self-combusted at a higher temperature and kept in a vacuum oven overnight to let form a xerogel. The dried mass/powder was then calcined at 350 °C for 3hrs, powder X-ray diffraction (XRD) was taken for phase identification of this calcined powder.



Fig.1. Schematic for the synthesis of BPFO powder.



Results and Discussions

Fig. 2. Rietveld refined XRD pattern of BLFO powder.

XRD pattern for Lu doped BFO synthesized using a sono-chemical assisted wet chemical method calcined at 350 °C/3h is shown in fig.2. Diffraction peaks obtained were intense and sharp, which indicates the highly crystalline nature of the synthesized powder. The Rietveld analysis of XRD data was carried out using 'Fullprof' software. The Rietveld refinement gave goodness of fitness value with $\chi^2 \leq 5$. Observed XRD pattern for Lu doped BFO is successfully indexed to the Rhombohedral symmetry (R3c) space group. Along with R3c space symmetry, cell volume, lattice parameter and structure factor are listed in table 1. Effect of Lu doping on bismuth site of BFO is clearly seen in XRD pattern, as some distortion and shifting in XRD of BFO pattern is seen. Rietveld refinement of synthesized compound was matched with pure BFO in which all the prominent diffraction peaks were identified and indexed to its (hkl) values and matched with BLFO powder; however, some low-intensity peaks were observed between $2\theta \sim (25^{\circ} - 30^{\circ})$, which are identified as secondary phase Bi₂Fe₄O₉ which on doping of Lu more than 10% can be removed [8].

Table 1. Rietveld refined structural information ofBLFO powder.

Structural	Pure BFO	BLFO	
Information			
Lattice parameters	a=5.57817	a=5.58000	
(Å)	c=13.8625	c=13.8710	
Volume (Å ³)	373.557	374.03	
R_{f}	3.6377	3.7948	
Crystal structure	Rhombohedral	Rhombohedral	
Space group	R3c	R3c	

Conclusions

Lu doped BiFeO₃ was synthesized by ultrasonically assisted wet chemical route. Rietveld refinement of XRD data reveals BLFO powder having Rhombohedral structure with R3c symmetry space group. A secondary phase Bi₂Fe₄O₉ was observed between $2\theta \sim (25^{\circ} - 30^{\circ})$. Using this method, we were able to synthesize BLFO at reduced temperature (350 °C) and time (3hrs).

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Structural Study of Samarium and Gallium Co-Doped Multiferroic Bismuth Ferrite

Farha Jabeen^{1*}, Raza Shahid¹, M. Shahid Khan¹, Raghvendra Pandey²

¹Department of Physics, Jamia Millia Islamia (Central University), New Delhi 110025, India ²Department of Physics, ARSD College, University of Delhi, New Delhi 110021, India

*Corresponding author: fjabeenjmi@gmail.com

Abstract

Samarium (Sm) and Gallium (Ga) co-doped on A and B-site of Bismuth Ferrite (BiFeO₃ or BFO) sample was synthesized using solid state reaction method by quenching technique. This is then followed by investigations into the influence of Sm and Ga co-doping on the structural and morphological properties of Bi_{0.95}Sm_{0.05}Fe_{0.975}Ga_{0.025}O₃ using XRD, Rietveld refinement and SEM with EDS. X-ray diffraction analysis reveals the crystalline structure of doped BFO and its phase formations. The rietveld refinement reveals that the A and B-site co-doping of Sm and Ga lead to the transformation of its crystal structure from a rhombohedral with a space group of *R3c* to an orthorhombic with a space group of *Pbam*. The phase fraction of 69 % was obtained for the BSFG and the rest was converted into its secondary phase Bi₂Fe₄O₉. The Field Emission Scanning electron microscope (FESEM) image and EDS study depicts the grain size and elemental composition of the sample.

Introduction

Multi-ferroic materials are those which exhibit more than one primary ferroic properties in the same phase and are known for their wide variety of applications such as their use in logical and tunable devices, multistate memories and sensors. Among the multiferroics, the bismuth-based ferrite is the one of the widely studied systems and very promising materials possessing rhombohedrally distorted perovskite structure with R3c space group at room temperature and exhibiting strong ferroelectric properties having Curie temperature of about 830 °C and possessing G-type anti-ferromagnetic ordering at room temperature with Neel temperature at around 370 °C on the account of a 6s² (Bi³⁺) lone pair-

controlled polarization directed along the (001) h axis where h-corresponds to hexagonal 001 direction, i.e., polarization is along < 001 > direction in hexagonal structure of BFO and is equivalent to < 111 > axis in pseudo-cubic notation [1,2]. Due to its narrow temperature range of phase stabilization the major secondary phase was identified as Bi₂Fe₄O₉ and Bi₂₅FeO₄₀ which is formed during its preparation [3] and these undesirable phases give on to several issues, viz. small remnant polarization, high coercive field, large leakage current etc.[4]. Thus, synthesis of pure phase BFO is difficult to achieve. However, in order to eliminate such secondary phases, some authors optimize its synthesis parameters [5] to obtain pure phase BFO.

Experimental Details

Polycrystalline Bi_{0.95}Sm_{0.05}Fe_{0.975}Ga_{0.025}O₃ (BSFG)

reaction method by quenching technique. The synthesis process was carried out using the starting reagent materials Bi₂O₃, Fe₂O₃, Sm₂O₃ and Ga₂O₃. These chemicals were mixed together in a stoichiometric ratio and ground thoroughly for 3 h with the help of a mortar and pestle using acetone. Then sample was fired at 800 °C in a pre-heated furnace and quenched in air after 30 min. X-ray diffraction was carried out with CuKa ($\lambda = 1.5415$ Å) radiation using a Bruker D8 Advance Xray diffractometer over the angular range 2θ (15–80°). Rietveld refinements on the structure were carried out by using FullProf Suite software in order to obtain an appropriate microstructural understanding about the samples from the obtained diffraction patterns. SEM with EDS investigation of BSFG pellet sample was obtained by using FEI Ouanta 200 F SEM.

Results And Discussion

The obtained XRD pattern of BSFG powder sample is depicted in Figure 1 (a). The XRD result confirms the formation of polycrystalline BSFG sample. The observed XRD pattern can be indexed to rhombohedral distorted perovskite crystal structure with the space group of R3c which corresponds with the standard crystal data in the JCPDS card No. 71-2494 with a small amount of Bi₂Fe₄O₉ possessing orthorhombic structure with space group of Pbam. The volatile nature of Bi is the major reason for the development of impurity phase [6]. It is observed that the co-doping of Sm and Ga suppressed the formation of bismuth rich impurity phase i.e. $Bi_{25}FeO_{40}$.



Fig. 1. (a) XRD diffractogram (b) Rietveld refined XRD pattern (open circle with red color) of BSFG sample compared to the Rietveld refine profile (continuous black line) and the difference curve (bottom curve) taken at room temperature. The vertical markers (blue and red) below the diffraction pattern indicate positions of possible Bragg reflections of BiFeO3 and Bi2Fe4O9 (c) FESEM image (d) EDS elemental spectrum of BSFG sample.

It is clear from the graph that the peaks (113) and (211) are suppressed. The possible reasons for this structural transformation is the replacement of smaller Bi^{3+} (1.03 Å) by larger Sm^{3+} (1.08Å) and larger Fe^{3+} (0.65Å) ions by smaller Ga^{3+} (0.62Å) ions.

 Table 1. Phase concentrations and refined unit cell

 parameters along with Bragg's factors of BSFG

 sample.

Phase	BSFG	Bi2Fe4O9
Phase Fraction (wt%)	68.77	31.23
Lattice Parameters	a = 5.529	a = 7.9661
(Å)	b = 5.529	b = 8.4083
	c = 13.858	c = 6.0038
Bragg's R-factor	3.49	6.71
R-f factor	2.41	2.68
χ2	5.25	

The Rietveld fitted curve for BSFG sample is represented in Figure 1 (b). From the rietveld refinement results the phase fraction of about 69% for BSFG was obtained and phase fraction of about 31% was obtained for $Bi_2Fe_4O_9$ as shown in the table1.

Figure 1 (c) depicts the FESEM micrographs depicting the surface morphologies of BSFG. It was noted that the obtained image shows a dense and crack-free structure with well grown grains.

Table 2. Elemental composition of BSFG.

Weight %
6.430
18.192
0.605
15.603
1d.502
4.343
53.325

The EDS image confirmed the presence of Sm and Ga in the BSFG as shown in the figure 1 (d). The chemical composition of BSFG was determined by EDS technique, as shown in the table 2.

Conclusion

This study suggests that the co-doping of Sm and Ga eliminated the Bi-rich impurity phase synthesized by solid-state reaction method using quenching technique from the BSFG sample. The phase fraction of 69% was obtained for BSFG and rest (31%) was converted into Bi₂Fe₄O₉ was reported.

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Intrinsic Room Temperature Ferromagnetism in van der Waals Fe5GeTe2 Crystal

Riju Pal^{1*†}, Satyabrata Bera^{2*}, Buddhadeb Pal¹, Mintu Mondal² and Atindra Nath Pal¹

¹Department of Condensed Matter Physics and Material Sciences, S. N. Bose National Centre for Basic Sciences, Kolkata – 700106, India. ²Indian Association for the Cultivation of Science, Kolkata – 700032, India. *Equal contributors

[†]Corresponding author: <u>rijupal07@bose.res.in</u>

Abstract

Two dimensional magnetic materials have drawn a great attention in 2D magnetism and opened up a new direction for modern spintronic applications. Here, we have synthesized a cleavable Fe_5GeTe_2 material, which shows an intrinsic ferromagnetic behaviour at room temperature (~310K). We have investigated the electronic and magnetic properties of the bulk Fe_5GeTe_2 single crystal. Our study reveals that bulk Fe_5GeTe_2 is metallic and behaves like an easy-axis ferromagnet along c-axis with a stronger inplane magnetic anisotropy compared to the out of plane. However, the magnetic state of Fe_5GeTe_2 is much complex and still unclear, hence systematic investigation may lead this material as an ideal candidate for spintronic applications.

Low-temperature magnetotransport studies on Nd_{0.6}Sr_{0.4}MnO₃ thin films

R S Mrinaleni^{1,2,a)}, **E P Amaladass**^{1,2,b)}, **S.Ganesamoorthy**^{1,2}, and **Awadhesh Mani**^{1,2}

¹Material Science Group, Indira Gandhi Centre For Atomic Research, Kalpakkam, 603102 ²Homi Bhabha National Institute, Indira Gandhi Centre For Atomic Research, Kalpakkam, 603102

*Corresponding author: ^{a)} mrina@igcar.gov.in; ^{b)} edward@igcar.gov.in

Abstract

Magnetotransport measurements performed on $Nd_{0.6}Sr_{0.4}MnO_3$ thin films having an insulator-metal transition at ~110 K reveal an upturn in its resistance in the low-temperature regime. A suppression in this resistive upturn upon application of magnetic field was observed. Further analysis using the low-temperature transport model indicates that grain-boundary or domain wall scattering, Kondo-like scattering, and strong correlation effect contribute significantly to this resistive upturn.

Superconductivity in Ir doped LaRu₃Si₂ Kagome superconductor

Subhadip Chakrabortty¹, Niharika Mohapatra^{1*}

¹School of Basic sciences, Indian Institute of Technology Bhubaneswar, Jatani, Odisha, 752050 *Corresponding author: <u>niharika@iitbbs.ac.in</u>

Abstract

In this report, we investigated the impurity induced effects on the superconducting properties of the Kagome lattice system LaRu₃Si₂ by temperature dependent magnetization measurement and electrical resistivity measurement. A downward shift of the transition temperature was observed with increase Ir(5d) doping concentration. We also note that the rate of suppression of T_c is higher than that of Co doping while it is lower than that of Fe doping. From the magnetization measurement, the diamagnetic signal in the ordered state was found close to the ideal magnitude of $-\frac{1}{4\pi}$ indicating the superconducting volume fraction of nearly 100% for all the studied samples.

Introduction

Kagome lattice compound is one of the most researched electronic system which encompasses various exotic quantum states of matter such as topological state of matter, unusual magnetism and superconductivity. [1] unconventional Another noteworthy characteristic of the Kagome lattice compound with antiferromagnetic coupled spins is the existence of high degrees of geometrical frustration, which may result in a spin liquid state. [2]There are very few Kagome compounds which show superconductivity. The rare examples include RT₃B₂ and RT₃Si₂ type family of compounds, where R stands for the rare-earth metal La, Ce, Y and T stands for transition metal Ru, Ni, and Co. Among these compounds, the highest Tc was found for LaRu₃Si₂ as 7.8K. [3] LaRu₃Si₂ adopts a distorted Kagome type structure and unusual superconducting features due to the contribution of d band electrons. Moreover, the possibility of unconventional pairing is evident from the nonlinear field dependence of electronic specific heat. Additionally, the Wilson ratio is shown to be comparatively high (near about 2.88), indicating the presence of a strong electron correlation.

Impurity induced pair breaking effects have been considered as an effective way to understand the gap symmetry of the superconducting state. The earlier studies of the substitution at different crystallographic site of LaRu₃Si₂ are shown to produce diverse results. Gupta et al. have shown that substitution of Tm at La site suppressed Tc abruptly.[4] On the other hand, substitution of magnetic impurities (Fe, Co) at Ru site induces contrasting suppression effect over T_c. While a dome like dependence of T_C was reported for Fe doped samples. Co doping suppresses T_C very slowly. These contrasting results were explained on the basis of higher localized magnetic moment of Fe (1.4 μ_B /Fe) in comparison to that of Co(0.45 μ_B /Co). [5] In this paper, we present the effect of Ir doping at the Ru site of LaRu₃Si₂ on its superconducting properties. A systematic decrease of T_c with the doping percentage was observed. The rate of suppression of T_c was found to be higher than that of Co doping but lower than that of Fe doping.

Experimental

Polycrystalline samples of La $(Ru_{1-x}Ir_x)_3$ Si₂ (x = 0, 0.05, and 0.1) were prepared by conventional arcmelting of high pure raw materials La, Ru, Si, and Ir (Purity > 99.9%) in stoichiometric ratio on a watercooled copper hearth in high pure argon atmosphere. During the melting process, the Ta ball was used as an oxygen getter. The ingots were re-melted several times by flipping upside down to get better uniformity and homogeneity of the samples. An extra amount of Ru, by 15%, was added apart from the stoichiometric mixture so that initial composition before melting was maintained as LaRu_{3.45}Ir_{0.15}Si₂. It is essential to rule out the formation of the LaRu₂Si₂ phase and to obtain the desired 132 phase. Similar stoichiometry with additional Ru was also included for the preparation of doped samples to obtain the desired phases.

Result and discussion

The phase purity and crystal structure of the prepared samples were determined from the powder X-ray diffraction (XRD) data collected at room temperature using D8 ADVANCE Bruker diffractometer with Cu K α radiation. As shown in Fig. 1, the diffraction peaks of the samples were well indexed by a hexagonal structure in the space group symmetry, p6₃/m. Minor extra peaks were observed corresponding to the extra Ru used during the synthesis process. We did not observe noticeable peak shifting for Ir-doped samples as the radius of Ir⁴⁺ is nearly comparable to radius of Ru⁴⁺.The lattice parameters of the pristine (a = 5.676Å,

c = 7.116Å) and (a = 5.679Å, c = 7.119Å), (a = 5.678Å, c = 7.12Å) for 5% and 10% Ir doped samples, obtained from the Rietveld refinement of the XRD data which shows the crystal symmetry and structural parameters remain almost unaffected by the Ir doping.



Fig.1.Room temperature powder x ray diffraction of $La(Ru_{1-x}Ir_x)_3Si_2$ (x = 0,0.05,0.1). Peaks were well indexed using hexagonal structure. Inset shows the shifting of peak at (200) position.

Magnetic Properties

Temperature dependent magnetic measurement was performed in ZFC and FC mode in 5 mT for La (Ru_{1-x}Ir_x)₃Si₂ (x = 0,0.05,0.1). The volume susceptibility vs. temperature graph reveals that superconducting volume fraction of the samples were near about 100%. The transition temperature of superconductivity was calculated from the crossing line of the extrapolated graph of the superconducting and normal state susceptibility. The transition temperature of LaRu₃Si₂ was determined at 6.5 K and it decreases to 5.6K and 5K for 5% and 10% Ir doped samples.

Electrical Resistivity

Resistivity measurement of $La(Ru_{1-x}Ir_x)_3Si_2(x = 0,0.05,0.1)$ was carried out in zero field using the Quantum Design physical properties measurement system (PPMS) in the temperature range 2- 300 K. All the samples were found to exhibit typical metal like conducting behavior followed by a transition to the zero resistive state at low temperature. A broad transition width of ~1 K was noted for all the compounds possibly caused by superconducting fluctuations. Defining Tc as the midpoint of (T_c^{onset}) and (T_c^{zero}) , a T_C of 7.4 was registered for LRS, which reduces to 6.7 K and 6 K for 5% and 10% of Ir doping Additionally, we also observed a substantial increase

in the residual resistivity and decrease in the residual resistivity ratio (RRR) with increasing the doping concentration. This may be attributed to the enhancement of impurity induced electron scatterings.



Fig.2.(a)Volume magnetic susceptibility vs. Temperature graph of $La(Ru_{1-x}Ir_x)_3Si_2$, where x is in the range from 0 to 0.1. (b) Resistivity vs. Temperature graph of $La(Ru_{1-x}Ir_x)_3Si_2$ (x = 0,0.05,0.1).

Conclusion

The impurity-induced effects on the superconducting properties of the Kagome lattice system LaRu₃Si₂ were studied by the measurement of temperature-dependent magnetization and electrical resistivity. Our results show a downward shift of the transition temperature with Ir(5d) doping concentration. The diamagnetic signal in the ordered state is close to the ideal magnitude of $-\frac{1}{4\pi}$ indicating the superconducting volume fraction of nearly 100% for all the studied samples. We also note that the rate of suppression of T_C is higher than that of Co doping while it is lower than that of Fe doping. A detailed analysis of the superconducting states of the doped samples will be published elewhere.

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Large Magnetic Entropy Change in van der Waals CrBr₃ Single Crystal

Suchanda Mondal^{1*}, and Prabhat Mandal¹

¹Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Calcutta 700064, India

*Corresponding author: suchanda.mondal@saha.ac.in

Abstract

Atomically thin intrinsic magnetic van der Waals (vdW) systems open a new platform in nanoelectronics as well as in fundamental physics in recent years. We have investigated magnetic and magnetocaloric properties of CrBr₃ single crystal from magnetic measurement. CrBr₃, a vdW semiconductor, with out of plane magnetic easy axis shows T_c around 33K. A large magnetic entropy change of 9.3J/kg-K is observed in CrBr₃ for a field change of 7T close to transition temperature. This indicates that CrBr₃ can draw significant attention as a magnetic refrigerant for liquefaction of hydrogen in fuel industry.

Synthesis of Pr doped BiFeO₃ via Sonochemistry assisted sol-gel method

Mayuri Kamble, Rakesh Solanki, and *Paresh Salame

Department of Physics, Institute of Chemical Technology Mumbai, Mumbai, INDIA-400019

*Corresponding author: ph.salame@ictmumbai.edu.in

Abstract

Synthesis of Pr doped – BiFeO₃ (BPFO) is successfully conducted via a wet-chemical route with additional assistance from high power(150W) ultrasound. The prepared ceramic powder was calcined at 350° C for 3hours, this was taken for X-ray diffraction (XRD) for phase analysis. Rietveld refinement of XRD data is successfully carried out by selecting the R3c space group in Fullprof software. Rietveld refinement manifest's rhombohedral structure with R3c group along with the existence of a secondary phase Bi2Fe4O9. A reduction in synthesis time and temperature using this method is reported here.

Introduction

Bismuth ferrite (BiFeO3) has demonstrated the coexistence of both the ferroelectric and ferromagnetic properties at room temperature. This makes it an exciting multiferroic material and a useful candidate for environmentally friendly and low power consumption devices.[1]-[4] Pure BiFeO3 (BFO), in ceramic or thin film-form, usually suffers from a significant leakage current density and low remanent polarization, which could lead to failure of ferroelectric random-access memory (FRAM) and other devices. However, the substitution of Bi ion with rare earth elements such as Pr could enhance ferroelectric properties [4]. Due to its extraordinary electrical, magnetic performance and dependence on its structural evolution, extensive research has been done on BFO. Phase pure BFO shows Rhombohedral perovskite structure with R3c space group. [5] This paper reports the synthesis and structural characterization of Pr doped bismuth ferrite Bi0.95Pr0.5FeO3 using the ultrasound-assisted wetchemical method..

Experimental

Synthesis of Bi0.95Pr0.5FeO3 is conducted by sonochemical assisted sol-gel method, Precursors used the synthesis were bismuth nitrate for $(Bi(NO_3)_3 \cdot 5H_2O)$, ferric nitrate $(Fe(NO_3)_3 \cdot 9H_2O)$ and praseodymium oxide $(Pr_6O_{11}).$ A measured stoichiometric amount of Pr₆O₁₁ is dissolved in dilute nitric acid kept in an ice bath for ultrasonic treatment. All the precursors were then dissolved in deionized water and kept on a magnetic stirrer for homogeneous mixing. The well-mixed precursors were then treated under high powered ultrasonic probe (150 W, 30% amplitude) for 30 mins (15 mins on/15 mins off-cycle). The solution was kept in an ice bath during this entire

process. To this sonicated solution, ethylene glycol (5x mol%) to form a polymeric network and bring the ions close together and citric acid (2x mol%) as a chealent is added. The solution was kept on a magnetic stirrer at 80 °C till complete gel formation was done. During the process, to form a stable colloidal suspension and avoid heavier ions settling at the bottom, ammonia solution was added in a drop-wise manner to maintain pH value at 5.5-6. Thus formed gel was further dried at 120 °C which gave way to fluffy dried mass, which was later self-combustion at higher temperature 150-180 °C. The powder was completely dried in a vacuum oven overnight, which gave pre calcined BPFO powder. This powder was then calcined at 350 °C/3h. For verifying the phase purity, powder x-ray diffraction (XRD) was carried on the powder.



Fig. 1. Generalised flowshet for synthesis of BPFO powder



Fig. 2. Rietveld refined pattern for BPFO powder synthesised by ultrasound assisted method.

Table 1. Rietveld	refined the	e structural	information	of
BPFO powder.				

Structural Information	Pure BFO	BLFO	
Lattice parameters	a=5.57817	a=5.58000	
(Å)	c=13.8625	c=13.8710	
Volume (Å ³)	373.557	374.03	
R _f	3.6377	3.7948	
Crystal structure	Rhombohedral	Rhombohedral	
Space group	R3c	R3c	

Results and Discussion

Synthesized Bi_{0.95}Pr_{0.5}FeO₃ powder was subjected to powder X-ray diffraction (XRD) for structural characterization. Figure 2 shows the Rietveld refined XRD plot of Bi_{0.95}Pr_{0.5}FeO₃. Characteristic sharp and clean peaks with a tiny impurity indicate that all reactants were reacted to form the desired phase of BFO. The Rietveld analysis of obtained XRD data for Bi_{0.95}Pr_{0.5}FeO₃ was refined using Fullprof software. Table.1indicates various structural parameters of BPFO, containing lattice parameters, structure factor, and (R3c) space symmetry cell volume. Rietveld refinement of synthesized Bi_{0.95}Pr_{0.5}FeO₃ material was successfully matched with pure BFO. The presence of low-intensity peaks at 2θ (25°-30°) are indicated as secondary phase Bi₂Fe₄O_{9.} [6].

Conclusions

Synthesis of Pr doped BFO is carried out by sonochemical assisted wet chemical (sol-gel) method.

Rietveld refinement of Bi0.95Pr0.5FeO3 data reveals that synthesized ceramic powder has R3c symmetry space group along with a rhombohedral structure. This method effectively produced a good quality Bi0.95Pr0.5FeO3 sample with a tiny Bi2Fe4O9 impurity phase at a low synthesis temperature (350 °C) and time (3h).

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Soft point contact Andreev Reflection spectroscopy to probe superconducting proximity effect in Nb thin films

Gorakhnath Chaurasiya¹, Sangita Bose^{1*}

¹School of Physical Sciences, UM-DAE Center for Excellence in Basic Sciences, University of Mumbai, Kalina Campus, Santacruz (E), Mumbai-400098, India

*Corresponding author: sangita@cbs.ac.in

Abstract

We report the use of soft point contact Andreev reflection spectroscopy (SPCAR) to probe superconducting proximity effect (SPE) in Nb thin films. SPCAR was carried out on Nb films with different thickness with a piece of indium pressed on it. The spectra were analyzed using the BTK model which gave the measure of the strength of the interface barrier (Z) and the superconducting energy gap (Δ). Our results show that the superconducting proximity effect (SPE) in the Nb thin films resulting in a reduction of Δ at the point contact is primarily affected by the interface barrier (Z), irrespective of thickness of the film. SPE becomes more pronounced for low Z contacts indicating that surface sensitive SPCAR technique can probe SPE also in films with thickness greater than the coherence length of Nb.

Magnetocaloric Effect in DyVO₃

Mohd Anas¹, V. K. Malik¹ and T. Maitra¹

¹Department of Physics, Indian Institute of Technology Roorkee, Roorkee-247667

*Corresponding author: anas21zuberi@gmail.com

Abstract

The orthovanadate DyVO₃ has been synthesized by the solid-state reaction method. The material crystallizes in orthorhombic crystal structure at room temperature (space group *Pbnm*). Magnetic entropy change has been calculated from the isothermal magnetization measured in the magnetic field 0-5T. At 2K, the M-H isotherm tends to saturate with the increasing magnetic field. The maximum magnetic entropy change $(-\Delta S_M^{max})$ has been estimated to be 12.9Jkg⁻¹K⁻¹ at an applied external magnetic field of 5T around 17K. The maximum entropy change occurs around the same temperature as that of the ordering of the Dy-sublattice.

Low-Temperature Magnetodielectric Effect in the Nd_{0.5}Dy_{0.5}FeO₃ Thin Film

Parvesh Chander¹, Ankita Singh³ Nagendra Prasad Pathak², and V. K. Malik^{1,*}

¹Department of physics, ²Department of Electronics and communication engineering, Indian Institute of Technology Roorkee, Roorkee-247667, Uttarakhand, India

³Department of Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

*Corresponding author: vivek.malik@ph.iitr.ac.in

Abstract

We have observed significant magnetodielectric effect in $Nd_{0.5}Dy_{0.5}FeO_3$ epitaxial thin film. The film is grown on LaAlO₃ (001) substrate by pulsed laser deposition technique. At 100 K, a variation of around 16% in dielectric constant is observed at frequencies higher than 2 MHz in the presence of 10 T and this variation in dielectric constant increases to about 50% at 2 K. To utilize the observed magnetodielectric effect, we have designed a microstrip line based resonator with the help of High frequency simulation software (HFSS). Simulations are performed for the two values of dielectric constant (in the presence and absence of external magnetic field) to observe magnetic field tunability of the resonance frequency. A shift of 27% is observed in the resonant frequency of the microstrip line based resonator on $Nd_{0.5}Dy_{0.5}FeO_3$ epitaxial thin film.

Thermomagnetic studies on Te doped Dy₂O₃ for eco-friendly cryogenic magnetic refrigeration

Meher Abhinav E^{1,2}, Jaison D¹, Anuraj Sundararaj¹, Subha Krishna Rao¹, Abhay Kumar Mondal³, Gopalakrishnan Chandrasekaran^{4,*}

¹Nanotechnology Research Centre, SRM Institute of Science and Technology, Tamil Nadu - 603203, India. ²Department of Electronics and Communication Engineering, KGRCET, Moinabad, Telangana-500075

³Institute of Microengineering and Nanoelectronics, Universiti Kebangsaan Malaysia, Bangi-43600 ⁴Department of Physics and Nanotechnology, SRM Institute of Science and Technology, Tamil Nadu - 603203,

India.

Email id- cgknano@gmail.com,

Abstract

The work aims to investigate the magnetocaloric effect (an eco-friendly and energy-efficient cooling technique) of Te doped nanosized dysprosia, which could be used as the best alternative for conventional chlorofluorocarbons-based refrigeration systems. In this work, Te doped nanosized dysprosia (TNSD) was synthesized using the sol-gel technique. Samples showed anti-ferromagnetic (AFM) behaviour at low temperatures and paramagnetic (PM) at high temperatures. The maximum entropy change (ΔS_M) of TNSD at a magnetic field of 5 T was found to be 18 ~JKg⁻¹K⁻¹. The significant magnetic transitions at low temperature and large magnetic entropy change make TNSD suitable for eco-friendly cryogenic magnetic refrigeration.

Magnetic Field Dependent Photoresponse In P-type Si(100)/NiFe₂O₄/C₆₀/ZnO-rGO Composite Heterostructure

Apurba Pal¹*, Saurabh Ghosh¹, J. N. Roy^{1,2} and P. Dey^{1, 2}

¹Department of Physics, Kazi Nazrul University, Asansol, 713340, WB, India ²Center for Organic Spintronics and Optoelectronics Devices, Kazi Nazrul University, Asansol, 713340, WB, India

*Corresponding author: apuphys@gmail.com

Abstract

We studied light (660 nm) and magnetic field dependent current-voltage (I-V) characteristics of p-type $Si(100)/NiFe_2O_4/C_{60}/ZnO$ -rGO composite heterostructure. Upon illumination of ZnO-rGO composite layer surface with 600 nm red light, photoresponse has been observed in the heterostructure. With the application of external magnetic field, current through the heterostructure is found to decrease both under dark and illumination. This decrease of current may be attributed to the positive magnetoresistance effect in the NiFe₂O₄ layer arising from the spin-dependent carrier transport through the layer. Coupled effect on the I-V characteristics of both light and external magnetic field has also been observed in our heterostructure.

Introduction

In the search for new technology in semiconductor industry for advanced information processing the potentials and opportunities in the field of Optoelectronics and Spintronics are a matter of major research interests [1]. Optoelectronics provides the opportunity to explore and enhance the processing speed, whereas, Spintronics has the advantages of ultra-low power consumption with high speed of information storing and processing. So, combination of both the fields, Optoelectronics and Spintronics, which may be called as Opto-Spintronics, provides the opportunity to utilize the advantages of both the fields in an effective way. In this direction, we have fabricated p-type Si (100)/NiFe2O4/C60/ZnO-rGO composite heterostructure and studied light and magnetic field dependent current-voltage characteristics of it.

Literatures on NiFe₂O₄ (nickel ferrite) in spinfiltering, magnetic ordering and possible use in magnetic sensor devices [2-4] showed the potential of this material to be used in spin-based devices. Material C_{60} is very common in organic photodetectors as acceptor for its suitable relative band positions with the organic donor materials as well as for relatively high mobility of charge carriers [5]. ZnO-rGO composite has been chosen to be explored for its intriguing photoresponse properties under visible light [6].

Experimental Details

Nanoparticles of NiFe₂O₄ and ZnO were prepared by pyrophoric reaction process [7]. Thin films of NiFe₂O₄ on p-type Si (100) substrate were deposited by pulsed laser deposition (PLD) technique. A 248 nm KrF excimer laser was employed for this deposition process. After that, a layer of C_{60} was deposited on p-type Si(100)/NiFe₂O₄ through shadow mask by thermal evaporation method under 3×10^{-6} mbar base pressure.

Reduced graphene oxide (rGO) was prepared by thermally reducing [6] graphene oxide nanopowder (Ultra-nanotech, 99%). Then, nanoparticles of ZnO and rGO were taken in 120:1 w/w ratio and dissolved in dimethyl sulfoxide (DMSO) in 1:16 w/v (g/ml) ratio. The solution was ultrasonicated for 2 hours at room temperature. After that, the composite solution was spin coated on top of the prepared p-type Si(100)/NiFe₂O₄/C₆₀ film. Our desired p-type Si(100)/NiFe2O4(NFO)/C60/ZnO-rGO composite heterostructure fabrication is completed by annealing the spin coated film at 250°C. Electrical contacts were made by electroplating copper wire and silver paste on NiFe₂O₄ and ZnO-rGO composite layer.

Measurement of structural property of top ZnOrGO composite layer has been performed by Field Emission Scanning Electron Microscopy (FESEM). Zeiss Sigma-300 has been used for this purpose. Current-voltage (I-V) characteristics measurement was carried out using a source meter (Keysight, B2902A) under different external magnetic fields (H) and different values of optical powers of 660 nm red light (THOR LABS) illumination.

Results and Discussion

Figures 1 (a) and (b) show high-resolution FE-SEM micrographs of the top ZnO-rGO composite layer at 20 KX and 40 KX magnification respectively. From these figures, it can be observed that ZnO nanoparticles have been agglomerated into clusters. These clusters are the result of hybridization



Fig. 1. FE-SEM micrograph of the top ZnO-rGO composite film at magnification of (a) 20 KX, (b) 40 KX.

of rGO with ZnO [8]. In this case, nanoparticles of ZnO are expected to be attached with the functional groups of rGO [9].



Fig. 2. (a) I-V characteristics of the heterojunction under dark and illumination (660 nm) of 41.1 μ W/cm² and 772.8 μ W/cm². Top left inset shows the schematic of heterostructure and illuminating surface. I-V characteristics under different external magnetic fields at (b) dark (c) 41.1 μ W/cm², (d) 772.8 μ W/cm². Top left inset of figure (b) shows a magnified portion of the same figure.

Figure 2 (a) shows the I-V characteristics of p-type Si(100)/NFO/C₆₀/ZnO-rGO composite heterostructure under dark and different optical power (660 nm). A clear photoresponse is observed in positive bias at 41.1 μ W/cm². However, when the optical power is sufficiently high, i.e., 772.8 µW/cm², photoresponse is observed in both the directions of bias. The observed photoresponse may be attributed to the generation of exciton in the ZnO-rGO composite layer under illumination. Though ZnO has a band gap of 3.37 eV, the absorption and photogeneration of 660 nm light (1.878 eV) is observed in ZnO-rGO composite. The absorption and generation of excitons by 660 nm light is expected to take place by electron transitions from one defect state to another in the bulk of ZnO [10]. In the ZnOrGO composite, rGO acts as electrons acceptor and the exciton dissociation takes place [6].

Figure 2 (b) shows the I-V characteristics under dark and at different values of H. From this figure, it can be observed that under H. current tends to decrease in both the directions of bias. The effect is more clearly visible from the inset of this figure, at positive bias voltages. This observed decrease of current, i.e., positive magnetoresistance, may be attributed to the spin dependent scattering and transport phenomena in the bulk of NFO layer [11]. As the input optical power increase to 41.1 μ W/cm², the decrease is much more prominent at positive bias voltages [Fig. 2 (c)]. With the further increase of optical power to 772.8 µW/cm², at positive bias voltages, the decrease of current at external H from the values of current at zero magnetic field can be observed clearly from Fig. 2 (d). In the negative bias direction, the decrease of current is accompanied by substantial fluctuations. So, coupling of the effect of light and magnetic field is observed.

Conclusion

In conclusion, we have fabricated and studied light and magnetic field dependent I-V characteristics of p-type Si(100)/NFO/C₆₀/ZnO-rGO composite heterostructure. The coupling effect of light and magnetic field is observed in our heterostructure which may be utilized for further research to develop efficient Opto-Spintronics devices in future.

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Magnetic Properties of As-cast Half Heusler Compound CoCrAl

Amrita Datta^{1,*} and I. Das¹

¹Saha Institute of Nuclear Physics, HBNI, 1/AF Bidhannagar, Kolkata 700064, India

*Corresponding author: amrita.datta@saha.ac.in

Abstract

Magnetic properties of polycrystalline as-cast half Heusler compound CoCrAl, prepared by arc melting, have been studied. A ferromagnetic transition is observed near $T_c = 14$ K though at 3 K non-saturating behavior is observed in field dependent magnetization (M-H) data even at 70 kOe applied magnetic field. It is found that the value of magnetization under 70 kOe field is $0.1\mu_B/f.u.$ at 3 K. Magnetic clusters within paramagnetic matrix are found to be present because of Cr-Al disorder (B2 disorder) within the compound above T_c . Above 200 K, the inverse susceptibility as a function of temperature (χ^{-1} -T) curves at high magnetic field follows the modified Curie-Weiss law in which temperature dependent higher order Pauli paramagnetism term is included. Further analysis indicates that the state at low temperature can be considered as correlated cluster glass state.

Structural and dielectric properties of Tb and Mn codoped multiferroic BiFeO₃ (Bi_{0.8}Tb_{0.2}Fe_{0.8}Mn_{0.2}O₃)

Seema Kumari¹, Anita Mohan¹, and Sandip Chatterjee¹

¹Department of Physics, Indian Institute of Technology (BHU), Varanasi – 221005 (U.P.), India

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

We have studied Tb and Mn codoping on crystal structure and dielectric properties of BiFeO₃ prepared via solid-state reaction method. There is the structural transition occur to orthorhombic (Pnma and Pn2₁a) phase from rhombohedral (R3c) phase. We have measured dielectric loss, and the dielectric constant (ε') with temperature variation at different frequencies shows relaxor-type behavior.

Anti-ferromagnetic thickness dependent Exchange Bias and Domain Wall Dynamics in IrMn (t)/ Fe₂CoSi(5nm) Bilayers

Apu Kumar Jana¹, M. Manivel Raja², J. Arout Chelvane², and S. Narayana Jammalamadaka^{1*}

¹Magnetic Materials and Device Physics Laboratory, Department of Physics, Indian Institute of Technology Hyderabad, Hyderabad 502 284, India

² Defence Metallurgical Research Laboratory (DMRL), Kanchanbagh P. O., Hyderabad-500058

*Corresponding author: surya@phy.iith.ac.in

Abstract

We report on the zero field cooled exchange bias (EB) and domain wall dynamics in IrMn (t)/Fe₂CoSi (5 nm) bilayers. We attribute the origin of EB to random domain configuration of IrMn (111) layer. Evolution of exchange bias is evidenced with the thicknesses of IrMn. The increase in exchange bias field (H_{EB}) above critical thickness ($t_{critical}$) of IrMn is explained on the basis of random field model in the Heisenberg regime. Indeed, there is perfect correlation between the bulk magnetization measurements and microscopic data obtained from longitudinal magneto optical Kerr effect (L – MOKE). These results suggest that IrMn (t)/Fe₂CoSi (5 nm) bilayers would indeed be useful in future spintronic device applications.

Introduction

Exchange bias (EB) is an interfacial phenomenon and it has been manifested as a shift of magnetization M vs. magnetic field H loop along the magnetic field axis upon cooling FM/AFM system through the Néel temperature of an AFM layer¹. In contrary, the zero field cooling EB has been demonstrated in various other systems and origin of the same has been attributed to the texture of anti-ferromagnetic (AFM) layer and canting of FM spins at the interface². Indeed, EB effect has been found tremendous applications in spin valve structures, magnetic random access memory (MRAM) and in other spintronic devices ³. In addition, materials which exhibits high spin polarization have been of great interest due to their wide applications in spin electronics.

Thin films based on Heusler alloy (HA) have been attained a great interest due to their multi – functional properties apart from their applications due to half metallic in nature ⁴. As Fe₂CoSi exhibits superior magnetic and transport properties, it would be more advantageous to induce EB effect in as deposited films. Hence, in the present work, we put our efforts in inducing EB effect in IrMn (t)/Fe₂CoSi bilayers. We choose IrMn as AFM layer since it consists high Néel temperature and ease of making (111) texture.

Experimental

Bilayers were deposited at 300 K using ultra high vacuum DC Magnetron sputtering with a base pressure of vacuum chamber (4 x 10^{-8} Torr) and sputtering pressure of 5 mtorr at 100 watts. Targets of Fe₂CoSi and IrMn (purity 99.9%) were used to deposit bilayer structure on Si/SiO₂ (150 µm) substrate and Ta (2nm) as a capping layer. Phase purity of the Fe₂CoSi is confirmed with the GI-XRD (θ =0.5°) using a Rigaku Powder diffractometer with Cu - k_{\alpha} X – ray source at room temperature in the scan range of

 $2\theta = 30^{\circ} - 55^{\circ}$. Composition of the films was confirmed with the Energy dispersive X – ray spectroscopy (EDX). A vibrating sample magnetometer (VSM) (Lakeshore 7400) was used to determine the magnetic properties and exchange bias (H_{EB}). Dynamics of domains were studied using longitudinal magneto-optical Kerr effect (L – MOKE).



Fig. 1 GI-XRD ($\theta = 0.5^{\circ}$) of IrMn (5 nm)./Fe₂CoSi (5 nm)

Results and Discussions

Fig. 1 depicts the GI-XRD (glancing angle ($\theta = 0.5^{\circ}$)) of the IrMn (5 nm)/Fe₂CoSi (5 nm) at room temperature. From the XRD we do see peaks pertinent to Fe₂CoSi phase (220) as well as IrMn phase (111) & (200). Indeed, the (111) texture of IrMn helped in establishing EB in IrMn/Fe₂CoSi bilayer as we discuss below.



Fig. 2. (a) M vs. H loops for IrMn (t)/Fe₂CoSi bilayers (b) Exchange bias and coercivity variation with IrMn thickness (c) In-plane M vs. H loop from L-MOKE of IrMn(15nm)/Fe₂CoSi(5nm) bilayer. (d) L - MOKE image at the marked magnetization reversal point.

Fig. 2(a) infers room temperature in - plane M vs. H loops for the IrMn (t)/Fe2CoSi (5 nm) bilayers without field cooling ($H_{FC} = 0$)). From our earlier reports⁵, we have seen symmetric hysteresis loops for Fe2CoSi single layer. However, the shift for M vs. H loop prevails upon depositing IrMn as bottom layer. We ascribe the origin of EB in IrMn/Fe2CoSi bi-layers to texture of IrMn layer which is in the direction of (111)⁶. In addition, the maximum EB is obtained for the IrMn (15 nm)/Fe2CoSi (5 nm) bilayer, which is estimated as 420 Oe. The variation of EB and Hc with respect to the thickness (t) of IrMn layer is shown in Fig. 2(b). We believe that the origin of EB in the present bilayer is due to the random field at the interface, which breaks the AFM layer into magnetic domains, so called "Imry-Ma domains"⁷. When the IrMn thickness is very less (5 nm), the strength of random filed is poor at the interface and leads to instability for the domain structure. Indeed, this leads to a situation that random field will not be able to cant the interfacial spins, which leads to zero exchange bias ⁷. For the films with thickness > 10 nm (t_{critical}), the random filed at the interface is enough to cant the spins, which leads to onset of the EB. The decrease in EB for higher IrMn layer thickness is due to the absence of exchange anisotropy

through random field mechanism as a result of comparable AFM layer thickness and domain wall width ⁷. Various reports have shown that this thickness is $\sim 15 \text{ nm}^8$, which is consistent with our observation. Indeed, Hc variation is also consistent with the variation that has been observed for IrMn/Co bilayer system⁹. For the lower thickness of IrMn, there exists a correlation between the EB and H_C which is due to exchange anisotropy. We do believe that there could be some microstructural change for 20 nm film, which leads to higher values of H_c . Fig. 2(c) shows room temperature in - plane (L - MOKE) MOKE measurements for the bilayer of IrMn(15nm)/Fe2CoSi (5 nm). In order to see domain wall dynamics, we have collected domain images at different positions of hysteresis loop and the image at one of the magnetization reversal point is shown in Fig. 2(d). It is clear from Fig. 2 (c) that there is a shift for M vs. H from L -MOKE and is consistent with the M vs. H from VSM. As we discussed earlier, the onset of EB exists for the bilayer IrMn (15 nm)/Fe2CoSi (5 nm) is due to pinning of the spins at the interface.

Conclusions

We have successfully demonstrated the evidenced exchange bias (EB) effect in as deposited IrMn (15 nm)/Fe₂CoSi (5 nm) bilayers using magnetization and longitudinal MOKE measurements. The increase in EB above t_{critical} is explained on the basis of random field model in the Heisenberg regime. We do ascertain that the magnetization reversal occurred through domain nucleation. We believe that the present results would indeed be helpful for the future spintronic device applications.

Acknowledgement

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Magnetization switching effect due to flipping of Ce³⁺ moment in one step synthesized CeCrO₃

Manish Yadav¹ and Chandana Rath^{1*}

¹School of Materials Science and Technology, Indian Institute of Technology (Banaras Hindu University), Varanasi,

221005, India

*Corresponding author: crath.mst@iitbhu.ac.in

Abstract

Here, we have synthesized CeCrO₃ via a facile, fast, and cost-effective one-step solution combustion method using different fuels (citric acid, urea, and glycine). As prepared compound synthesized with citric acid shows amorphous CeCrO₃, and with urea, CeCrO₃ is formed with an additional phase of CeO₂ while with glycine pure phase CeCrO₃ are found. Magnetization vs. time measurement with varying magnetic fields demonstrate flipping of paramagnetic moment of Ce³⁺ in the direction of superposition field direction, of the internal field due to Cr³⁺ and external applied field. Such flipping of moment demonstrated bipolar magnetization switching in CeCrO₃ which makes these materials potential candidates for nonvolatile magnetic memory, magnetic switching, and spintronics devices.

Phenomenological Investigations on Magnetocaloric Properties of La_{0.8}Bi_{0.05}Na_{0.15}MnO₃.

Lozil Denzil Mendonca¹, Subasa Chandra Sahoo², M S Murari³ and Mamatha D Daivajna^{1*}

¹ Department of Physics, Manipal Institute of Technology, MAHE, Manipal, Karnataka 576104, India, ² Department of Physics, Central University of Kerala, Tejaswini Hills, Periye, Kerala 671316, India, ³ DST PURSE Program, Mangalore University, Mangalagangotri, Mangalore, Karnataka 574199, India

*Corresponding author: mamata.shet@yahoo.com

Abstract

We report the structural, morphological and magnetocaloric properties of the Bismuth (Bi)-substituted manganite $La_{0.85-x}Bi_xNa_{0.15}MnO_3$ (x=0, 0.05). X-ray diffraction data implicates rhombohedral structure belonging to $R\overline{3}c$ centrosymmetric space group. The Bi₂O₃ added as substituent ensures densified compound even at low sintering temperature. The increase in grains size and decrease in magnetic transition temperature (T_C) are due to the Bi₂O₃ chemical potential. The phenomenological model is used to model the thermomagnetic behaviour of prepared samples. The sample with x=0.05 shows phenomenal increase in magnetic entropy and the maximum of magnetic entropy change is seen at room temperature (\approx 310K).

Introduction

Today most of the scientific advancements with a motive of industrial application have sought the help of century old physical phenomena to reduce the green footprint. Magnetocaloric effects (MCE) is one such phenomenon discovered a century ago by Weiss and Piccard in transition metal nickel (1917) [1]. It is change of temperature in a suitable magnetic substance upon exposure to magnetic field and laid virtue towards magnetic refrigeration (MR). The featuring of reversable thermodynamic cycle in Gd, giant MCE in Gd₅Si₂Ge₂ [2, 3], stimulated the substantial research activity for materials with large MCE at room temperature (RT). In principle a magnetic material contains two energy reservoirs: the lattice degrees of freedom leading to usual phonon excitations and spin degrees of freedom enabling magnetic excitations. Generally, these two are coupled by the spin-lattice coupling which ensures loss-free energy transfer within a small interval of time [8]. Rare earth based manganites are one such class of materials which offer a platform to elucidate spin-lattice coupling. These manganites have been extensively reviewed by M-H. Phan et al. [4] to nominate them for small and large-scale MR due to their superior magnetocaloric properties, cheap processing cost and chemical stability. A specimen for RT MR should respond to feeble magnetic field and must have T_C around the RT. The thin films and polycrystalline samples of manganites were significantly tailored in this regard over a decade optimizing the substitution content. The review showed bismuth substituted system $La_{0.62}Bi_{0.05}Ca_{0.33}MnO_3$ displays reduction in the T_C and improvement in the ΔS_M^{max} at low filed. Recently Dhahri *et al* [5]. have exploited such feature nanostructures of La0.67-xBixBa0.33MnO3 and obtained

improved ΔS_M^{max} near RT. With this motivation we synthesized the polycrystalline samples of $La_{0.85}$. $_xBi_xNa_{0.15}MnO_3$ (x=0, 0.05), and report their structural, magnetic and magnetocaloric properties.

Materials and Methods

The $La_{0.85-x}Bi_xNa_{0.15}MnO_3$ (x=0 and 0.05 viz. LB0, LB5 samples were synthesized using ceramic route with La_2O_3 , Bi_2O_3 , Na_2CO_3 , and MnO_2 precursors. The structure details were obtained using standard X-Ray Diffraction system (Bruker D8-Advance). The morphology was studied using Field Emission Scanning Electron microscope (FESEM) on Oxford Zeiss Sigma Microscope. The magnetic measurements were performed using a commercial; Quantum Design made physical property measurement system (PPMS)

Results and Discussions



Fig. 1. XRD pattern of $La_{0.85-x}Bi_xNa_{0.15}MnO_3$ (x=0, 0.1, 0.2, 0.25 and 0.3).

The samples are single phasic without any detectable impurity within the sensitivity limits of the instrument (Fig. 1). The Rietveld refinement was successful under the $R\bar{3}c$ centrosymmetric space group of hexagonal setting indicating the structure being rhombohedral. The change in cell parameter a=b, c and volume V with increse in Bi^{3+} is marginal (≈ 5.500 Å and 349.1 to 349.2 Å³). Even upon substitution of 6s lone pair dominant Bi^{3+} , the dormant variations can be asserted to local lattice distortions happening along the line connecting *Mn* and *O* against other *O* ions in a plane perpendicular to their direction without causing large changes in *Mn*-*O-Mn* bond angles. [6].



Fig. 2. FE-SEM images of LB0 and LB5 40.00KX magnifications.

The morphological development becomes evident at this stage. Though there are no structural changes, the micrographs provide clear evidence of grain growth. The particles are few micrometres in size. Bi_2O_3 is generally regarded as chemical additive which assist the sintering process. It forms a liquid phase at high temperature, which penetrates grain boundaries and enhances the grain growth.



Fig. 3. Magnetization verses Temperature plots of LB0 and LB5. Inset is variation of d^2M/dT^2 with T.

As per the magnetism, the samples have shown a single magnetic transition perhaps from paramagnetic state to ferromagnetic state. The remarkable changes upon 5% of Bi substitution are shift of T_C to low temperature (from ~323K to ~306K), significant improvement in magnetic sensitivity (dM/dT) (Inset fig. 3). T_C drop is the signature of weakened double exchange mechanism (*DE*). The reduction is caused by strong hybridization among *Bi-6s* and *O-2p* orbitals, which seizes the 2*p*-electron available for simultaneous hopping between *Mn* and *O* [5]. The variation of magnetic sensitivity with temperature at low field is due to reduced grain boundaries. The drop of T_C to RT and increased sensitivity is invokes the MCE investigations. Apparently, the MCE

investigations are carried out using phenomenological model proposed by Hamad *et al.*[]



In mangnaites the magnetic transition viz. AFM-FM and FM-PM is responsible for onset of magnetic entropy changes [4]. In addition, the large entropy changes can originate from spin-lattice [5]. Along with these factors in our case we attribute the variation in $|\Delta S_M^{max}|$ to two factors i) the grain growth and ii) weakened DE interaction due to enriched Bi^{3+} content. The increased grain size ensures the easy alignment of the magnetic spins in intra and interdomains leading to sharp FM-PM transitions in LB5. As the magnetic entropy change depends majorly on magnetic moment and magnetic sensitivity though Bismuth reduces moments, we claim there exist a critical concentration say x=0.05 where effect of grain growth is dominant over reduction in moments. This is responsible for phenomenal entropy change in La_{0.8}Bi_{0.05}Na_{0.15}MnO₃.

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Exploring Magnetic Behavior of Oxalate and Phenanthroline based 1-D Chain Like Molecular Magnet $[{Cu^{II}(\Delta)Cu^{II}(\Lambda)}(ox)_2(phen)_2]_n$

Pramod Bhatt¹, M. D. Mukadam¹, S. M. Yusuf¹

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India *E-mail: prabhatt@barc.gov.in

Abstract. The oxalate (ox) and phenanthroline (phen) ligands based single chain molecular magnet $[{Cu^{II}(\Delta)Cu^{II}(\Lambda)}(ox)_2(phen)_2]$ is hydrothermally synthesized. The magnetic properties of the compound are investigated using *dc* magnetization measurements. The room temperature x-ray diffraction measurement s a single phase formation of the compound with space group of *P*2₁. The compound exhibit 1-D chain like structure containing two different crystallographic sites of Cu metal ions (Δ - and Λ -). The Cu transition metal is bridged to oxalate ligands and phen ligand produce π - π interactions within the chain. The *dc* magnetization measurement shows transition temperature of ~75K along with ferromagnetic nature of the compound. The compound exhibit short range magnetic ordering as well over the temperature range ~20-60K.
Excess velocity of domain walls in amorphous CoFeB thin films Brindaban Ojha¹, Minaxi Sharma¹, Stanislas Rohart², Vincent Jeudy² and

Subhankar Bedanta¹*

¹Laboratory for Nanomagnetism and Magnetic Materials (LNMM), School of Physical Sciences, National Institute of Science Education and Research (NISER), HBNI, Jatni-752050, Odisha, India
²Laboratoire de Physique des Solides, Université Paris-Saclay, CNRS UMR 8502, F-91405 Orsay Cedex, France *Corresponding author: sbedanta@niser.ac.in

Abstract

Domain wall (DW) dynamics have been immensely studied for the last few decades due to rich fundamental physics and spintronics applications. Controlled DW motion has been proposed to use in DW-based race track memory, spintronic memristors, logic units, etc. Here, we have studied the DW dynamics in Pt/CoFeB/MgO multilayer thin films. The depinning field (H_d) is found to be ~15mT. We have observed the excess velocity in the film near H_d .

Tailoring Domain Wall And Relaxation Dynamics In Pd/Co/C₆₀/Pd

Esita Pandey, Brindaban Ojha, and Subhankar Bedanta

Laboratory for Nanomagnetism and Magnetic Materials, School of Physical Sciences, National Institute of Science Education and Research (NISER), HBNI, Jatni-752050, India

*Corresponding author: sbedanta@niser.ac.in

Abstract

Spin dependent hybridization at the ferromagnet (FM)\organic semiconductor (OSC) interface is very promising for fabricating highly efficient spintronic device. The hybridized interface called as 'spinterface' plays a key role in tuning the interfacial magnetism. However, the ability of such spin polarized interface on tailoring domain wall dynamics, interfacial DM interaction and magnetic relaxation mechanism is not understood well. In this context, we have studied the effect of inserting a low spin orbit coupling organic molecule (C_{60}) on the magnetic properties of PMA Pd/Co/Pd sample. The coercivity of the samples reduced systematically by increasing the thickness of the molecular layer. But a striking reduction of bubble domain size is found for a 0.5 nm thin layer of C_{60} , which again increases until the completion of the formation of spinterface. Magnetization relaxation mechanism became much faster in the Pd/Co/C₆₀/Pd samples due to the enhanced domain wall (DW) velocity measured by applying pulsed magnetic field. It reflects that the formation of a spin polarized interface (at Co/C₆₀ interface), has reduced the magnetic anisotropy of the sample and enhanced the DW velocity in the creep region. Also a decreases in depinning field has been observed in the samples prepared with C_{60} . The interfacial DM constant has been deduced for all the samples by asymmetric DW expansion method. Insertion of the molecular layer leads to an increase DMI constant and hence a reduced DW formation energy, which helps in faster DW motion. Thus our study reveals a novel way of tailoring basic magnetic properties of a PMA thin film at the molecular scale.

Enhanced Electromagnetic Interference Shielding in Magnetodielectric Layers: A Simulation Study

Athira Rajan¹, Sibi K. S.¹ and Subodh G. ^{1*}

¹Department of Physics, University of Kerala, Thiruvananthapuram, Kerala, India 695 581

*Corresponding author: <u>gsubodh@gmail.com,gsubodh@keralauniversity.ac.in</u>

Abstract

In this work, layered structures were simulated and the influence of electromagnetic parameters on the EMI shielding performance of the same was investigated. Simulation results revealed the superior shielding performance of layered structures over individual dielectric and magnetic systems. Further studies on the influence of electromagnetic properties, particularly electromagnetic losses, on the shielding of layered structures demonstrated the importance of incorporation of magnetic materials with high losses in the layered configuration. This study sheds light on the innovation of design strategy of stacked structures designated for suppressed electromagnetic reflections and enhanced microwave absorption.

Role of the Sintering Temperature on the Crystal Structural and Oxygen-Ion Conduction Properties of Y_{2.7}La_{0.3}Fe₅O₁₂

K. Parui^{1,2}, A. K. Bera^{1,*} and S. M. Yusuf^{1,2,*}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: <u>akbera@barc.gov.in</u>, <u>smyusuf@barc.gov.in</u>

Abstract

The roles of the sintering temperature on the crystal structural and oxygen ion conduction properties of $Y_{2.7}La_{0.3}Fe_5O_{12}$ have been reported. The x-ray diffraction studies confirm that the crystal structure of all the samples sintered between 1200 and 1500 °C are cubic (space group *Ia3d*), however, with an increase in the values of the lattice constant and crystallite size with the increasing sintering temperature. The complex impedance spectra, measured over the temperature and frequency ranges of 40 - 540 °C and 1 - 10⁷ Hz, respectively, reveal a thermally activated ionic conduction. The Arrhenius plots relating oxygen ion conductivity show a slope change near the magnetic ordering temperature *T*_c due to the magneto-electric coupling. With the increase in sintering temperature, the oxygen ionic conductivity increases and the activation energies decreases. Here, we have found a high ionic conductivity (~10⁻² S/m) at low temperatures (*T* < 500°C) for the samples sintered at 1500°C.

Probing structural changes in TiO₂ thin film anodes of Li ion batteries during discharge

V Bhasin^{a,b,*}, C Nayak^a, A Biswas^a, K K Halankar^c, ^dS. K. Rai, D.Bhattacharyya^a

^aAtomic and Molecular Physics, ^cChemistry Division, Bhabha Atomic Research Center, Mumbai- 400 085, India ^bHomi Bhabha National Institute, Anushaktinagar, Mumbai- 400 094, India ^dSynchrotron Utilisation Section, Raja Ramanna Centre for Advanced Technology, Indore-452013, India *Corresponding author (e-mail: bhasinvidha@gmail.com)

Abstract

Coin cell type Li ion batteries have been prepared with rutile TiO₂ thin film electrodes deposited by RF magnetron sputtering on polished stainless-steel substrates. The cell shows a significantly high specific capacity of around 1200 μ Ahcm⁻² μ m⁻¹ even after 1000 charging/discharging cycles. Investigations have been carried out on the structural changes of TiO₂ electrodes during discharge of the batteries by synchrotron radiation based grazing incidence X-ray diffraction (GIXRD) and X-ray absorption spectroscopy (XAS) measurements and it has been observed that during discharge of the Li ion battery oxidation state of Ti changes from Ti⁴⁺ to Ti³⁺ and the lattice also undergoes a structural change from rutile to monoclinic phase. Such information on structural changes in electrode materials during the charging/discharging cycles of a Li ion battery is very important in understanding the long term cyclic stability of its performance.

Studies on the screen printed CdTe thin films for photovoltaic applications

Maruti Salve and N. B. Chaure^{*}

Electrochemical laboratory, Department of Physics, Savitribai Phule Pune University, Pune 411 007

*Corresponding author: n.chaure@physics.unipune.ac.in

Abstract

We report the synthesis of CdTe powder by colloidal method and then thin films using screen printing technique. The annealed powder in Ar ambient was used to prepare the annealed samples. The optical and structural properties were studied using UV-Vis spectroscopy, X-ray diffraction and Raman spectroscopy. XRD results reveal the growth of cubic polycrystalline structure of CdTe. TeO2 phase appeared in as-prepared sample was found reduced upon annealing the sample. These results are consistent with Raman results. The intense 1LO peak reveals improved crystallinity of annealed CdTe sample. The decrease in band gap, 1.49 eV (close to bulk value, 1.45 eV) is proposed to be associated to the enhancement in particle size with uniform grain growth.

Introduction

Cadmium telluride (CdTe) is one of the promising absorber layers for thin film solar cells because of its direct band gap 1.45eV, which is close to the optimum band gap to produce high efficiency single heterojunction devices, and high optical absorption coefficient (10^4 - 10^5 cm⁻¹) in the visible range of the spectrum [1]. The highest cell efficiency, 22.1% and module efficiency 18% is reported by First solar [2]. Numerous growth techniques such as electrodeposition, pulsed laser deposition, closed space sublimation, Rf sputtering etc. have used to prepare the CdTe thin films [1-4]. Low-cost, wet chemical techniques have attracted much attention due to the less principal investment, maximum (< 95%) utilization of chemicals, fast growth rate, large area deposition etc. [3]. We have used the colloidal and screen printing techniques together to produce the CdTe thin films.

Experimental details

Initially, CdTe powder was prepared using a simple wet chemical colloidal method from aqueous solution consisting of 4:3 molar concentration ratio of cadmium acetate and tellurium oxide in presence of NaBH₄ as reducing agent. The final residue was centrifuged with double distilled water and later with ethanol and subsequently dried in hot air oven at 70°C for 6 hour.

The powder sample was annealed 300°C in Ar ambient for 15 min. The as-prepared and annealed powder was used to prepare thin films with ethanol, ethyl cellulose and terpineol. The thin film samples were characterized thoroughly using JASCO V- 770 UV-Vis-NIR Spectrophotometer, X-ray diffractometer, model Bruker D8 with Cu Kα anode (λ =0.154nm), Invia Renishaw Raman spectrometer with excitation wavelength 785nm to study the optical and structural properties.

Results and discussion



Figure 1: K-M Plot for a) as-prepared and b) annealed CdTe thin films

The energy band gap was estimated from the diffuse reflectance data using the Kubelka- Munk (K-M) Tauc plot shown in figure 1. The estimated values of band gap are 1.59 eV and 1.49 eV for as-prepared and annealed samples, respectively. The decreased band gap upon annealing could be associated to increase in crystallite size, decrease in internal strain and dislocation density [2].

XRD patterns of as-prepared and annealed CdTe thin films are shown in figure 2. The XRD pattern exhibited the peaks corresponding to (111), (220) and (311) reflections of CdTe cubic crystal structure, (JCPDS Card No. 15-0770). The diffraction peak observed at 29.88° was identified to (102) reflection of TeO₂ tetragonal structure, (JCPDS Card No. 42-1365). The presence of TeO₂ peak reveals incorporation of oxygen on surface during processing of CdTe samples. The intensity of TeO₂ peak was

found to be reduced for annealed sample. The sharper and intense diffraction peaks revealed in annealed sample could be associated to the more surface mobility of adatom due to annealing, which support an enhancement of grain size as well as the formation of ordered crystal structure [4]. These results are in good agreements with previous reported work of Sali et al. [2]. The recrystallization of sample can affect on the crystallite size and internal strain, therefore Williamson-Hall relation was used.

$$\beta \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta$$
 (1)

Where β is full width at half maxima (FWHM), K is dimensionless shape factor with value is 0.9, λ is x-ray wavelength, ε is the internal strain.

The internal strain 0.21×10^{-3} and -4.15×10^{-3} were calculated for as-prepared and annealed samples. The negative value of strain demonstrates the compressive strain upon thermal heat treatment, which could also be responsible to enhance the degree of crystallinity by decreasing lattice imperfection [4].



Figure 2: XRD pattern for a) as-prepared and b) annealed CdTe thin films

The Raman spectra of as-prepared and annealed CdTe thin films are represented in figure 3. The peaks observed around 165 and 332 cm⁻¹ were identified to first and second longitudinal optical (LO) phonon mode of CdTe respectively [1, 2]. The Raman peak observed around 121 and 140 cm⁻¹ were attributed to A1 phonon mode of Te and transverse optical (TO) phonon mode of CdTe and/or E phonon mode of Te, respectively [1, 2]. The intensity of 1LO peak for annealed sample was increased with substantial decrease in FWHM illustrates the

enhancement in the crystallinity and particle size. The Raman results support the XRD analysis.



Figure 3: Raman spectra for a) as-prepared and b) annealed CdTe thin films

Conclusion

A simple and low cost wet chemical colloidal method was employed to prepare the CdTe powder. The as-prepared and annealed powder was used to deposit the CdTe thin films by screen printing technique. The energy band gap 1.59 and 1.49 eV was estimated for as prepared and annealed CdTe thin film, respectively. The improvement in the intensity with decreased FWHM to the annealed sample observed in XRD and Raman analysis is attributed to enhancement in degree of crystallinity and grain growth. The prepared thin films could be suitable to produce the flexible CdTe solar cells on to plastic substrates.

Acknowledgement

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Investigation on the Effect of Substrate Temperature of CZTS Layers Grown by RF Sputtering

Kalyan B. Chavan^{1,2}, Sachin V. Desarada¹, Nandu B. Chaure^{1*}

¹Department of Physics, Savitribai Phule Pune University (formerly University of Pune), Pune, 411 007, India ²Department of Physics, Ahmednagar College, Maharashtra, 414001, India *Corresponding author, E-mail- n.chaure@physics.unipune.ac.in

Abstract

We report the growth CZTS (Cu₂ZnSnS₄) thin films using RF magnetron sputtering technique in Argon ambient and effect of substrate temperature. Polycrystalline samples with (112), (220) and (312) reflections were deposited at 300°C and 400°C. Thin films deposited at deposition temperature lower than 300°C shows amorphous nature. (112), (220) and (312) reflections were noticed at about 28°, 47° and 56° respectively. Microstrain shows decrement upon increasing deposition temperature. Crystallite size witnessed rise upon increasing disposition temperature. Dislocation density shows reduction upon increasing deposition temperature. Optical features were probed using UV-Vis technique. Tauc plots reveal the inverse relation of band gap with deposition temperature. Absorbance, transmittance and refractive index values were obtained using UV-Vis technique. Key words: CZTS thin films, XRD, UV-Vis etc.

Benefiting From Less Crystallinity: SnO₂ Anode

D. Lakshmi¹, M. Infanta Diana¹, P. Christopher Selvin¹*

¹Luminescence and Solid State Ionics Lab, Department of Physics, Bharathiar University, Coimbatore-46, India.

*Corresponding author: *csphysics@buc.edu.in

Abstract

Tin oxide (SnO_2) is an efficient candidate in metal oxide class of anode materials for Li ion batteries (LIB). Although SnO_2 is able to possess high theoretical capacity (1494 mAhg⁻¹), the volume disintegration issue is detrimental when employed as active participant in LIB. In the present attempt, a less crystalline SnO_2 was prepared along with a highly crystalline SnO_2 and a composite of these two were prepared. The prepared composite was checked for anodic properties and compared with regular SnO_2 material. From cycling tests, composite SnO_2 was able to deliver 220 mAhg⁻¹ whereas simple crystalline SnO_2 delivered 155 mAgh⁻¹ for 500 cycles. Also, capacity fading is very low in this composite compared to the unaltered SnO_2 sample, revealing a hopeful choice of this modified SnO_2 as anodic component in LIBs.

Introduction

Due to the everlasting thirst for Li ion battery research, exploration and development of electrode materials for this application gets fanatical focus. Tin oxide is one among such candidate possessing high theoretical capacity (1494 mAhg⁻¹) by performing conversion and alloying type redox reactions/ charge discharge cycles [1]. During the ion insertion and deinsertion in the SnO₂ matrix, the system undergoes structural expansion and compression. But repeated number of charge-discharge cycles impose huge volumetric change in the host which leads to performance deterioration.

A wide range of reports available on alleviating the structural issue of SnO_2 anode by different attempts such as doping with inter-metallics, addition of carbon based materials, morphological regulation [2, 3]. A good crystalline material is stubborn for structural changes to a certain extent which does not easily accommodate ion migration into its structure. Repeated ion migration into such a crystalline structure leads to volumetric change and ends up in performance limitation and limited life. To attempt this issue, a consideration is taken to soften the SnO_2 structure and thereby enabling the better ion migration.

In this research work, a novel attempt is proposed by extracting the virtue of amorphous/less crystalline SnO_2 in combination with crystalline SnO_2 and analyzed for anodic properties. This is completely different than doping or making composites of other alloys into the host. Composite of a single material with two different phase would be a new avenue to relieve the detrimental effects of a high crystalline anode materials whereas such an attempt can preserve the holistic properties of the host as well.

Experimental

Tin oxide nanoparticles were prepared by simple one step co-precipitation method [4]. The precipitated powders were dried in hot air oven and calcined at 200° C and 800° C. The sample treated at 200° C would hold lesser crystalline SnO₂ along with a minute trace of SnOH impurity and sample treated at 800° C was expected to be highly crystalline. Post synthesis and structural analysis of these two samples, the novel composite SnO₂ was prepared by mixing these two samples in equal volume. For naming convention, SnO₂ treated at 200° C is mentioned as SnO₂-A (amorphous/ less crystalline) and SnO₂ treated at 800° C as SnO₂-C (crystalline) and composite of these two as SnO₂-AC.

The obtained powders were analyzed for structural properties by X-ray diffraction technique (XRD) [Panalytical –XPERTPRO diffractrometer with CuK α source], SEM analysis for morphological records [SEM, JEOL-JSM 6390] and electrochemical analysis [Biologic SP-150]. The electrodes prepared for charge discharge analysis [GCD] by the process mentioned in earlier report [5] and the measurements were carried out in the potential range 0-1 V vs. Ag/AgCl reference electrode and Pt counter electrode. 0.5 M aqueous LiOH served as electrolyte solution.

Results and Discussion

XRD analysis reveals the structural aspects of the SnO_2 samples prepared in this research work, Fig. 1. As expected SnO_2 treated at low temperature, 200° C ends up in poor crystallinity with a negligible SnOH phase at 30°. The SnO_2 treated at 800° C shows sharp diffraction peaks without any impurities revealing high crystallinity of this sample. SnO_2 -AC sample

shows mixed features with less sharp peaks than SnO_2 -C indicating the impact of SnO_2 -A sample in its composition. The crystallite sizes are calculated by Debye-Scherrer formula and the values are found be 33 nm and 20 nm for SnO_2 -C and SnO_2 -AC samples.



Fig. 1. X-ray diffractograms of SnO₂ samples

Morphological records of the SnO_2 samples are shown in Fig. 2. There are no much variations seen in the grain distribution between three samples. However for composite sample, grain distribution appears as blend of both the samples. From SEM analysis, size distribution is ~17-30 nm for all the three samples.



Fig. 1. SEM micrographs of SnO₂ samples

Electrochemical analysis by means of cyclic voltammetry (CV) and GCD cycling were carried out in the potential window 0-1 V vs. Ag/AgCl. In the preliminary analysis by CV, SnO₂-C and SnO₂-AC samples found to deliver redox peaks with varied peak current values. Post CV analysis, GCD analysis was recorded at different current rates and the good performing SnO₂-C and SnO₂-AC samples were preceded for cycling studies as shown in Fig. 3.



Fig. 3. Cycling stability and GCD capacitance of SnO_2 samples

Due to the added quality by means of SnO_2 -A sample, SnO_2 -AC exhibits better stability and improved capacity than the pristine SnO_2 -C. SnO_2 -C sample exhibits specific capacitance ~155 mAhg⁻¹ for 500 cycles whereas composite SnO_2 delivers capacitance ~ 215 mAhg⁻¹ at discharge mode for 1200 cycles in aqueous electrolyte system. The novel composite attempted in this research work is absolutely a great way to alleviate the structural issues and low output capacitance of the SnO_2 anode material.

Conclusion

 SnO_2 nanoparticles prepared by co-precipitation method were calcined at two different temperatures. The less crystalline and crystalline samples were made into a composite to serve as SnO_2 anode material and analyzed for charge storage properties. Undoubtedly, SnO_2 composite sample serve better than the pristine, by means of both capacitance (215 mAhg⁻¹) and stability. This kind of SnO_2 composite will be an honest choice as anode for commercial LIB application without having any structure related issues.

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Reduced graphene oxide (rGO)/nickel sulfide nanohybrid as counter electrode in Dye Sensitized Solar Cells

Rajinder Singh, Navdeep Kaur, and Aman Mahajan*

Materials Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143005, India

*Corresponding author: aman.phy@gndu.ac.in

Abstract

In the present work, optimally decorated Ni₉S₈ nanoparticles on reduced graphene oxide (rGO) based nanohybrids were synthesized using hydrothermal method for their potential application as counter electrode (CE) in cost-effective dye-sensitized solar cells (DSSCs). The photovoltaic (PV) performance nanohybrid with 40 wt% of Ni₉S₈ based CE is found to be comparable to Pt based DSSC and is attributed to their better electrocatalytic activity provided by the synergistic effects of highly conducting rGO sheets and large number of active sites of Ni₉S₈ for efficient oxidation and reduction reactions.

Introduction

So far, DSSCs have significantly explored in the photovoltaic technology due to their flexible and userdefined design, facile fabrication process, and efficient PV performance under diffused light conditions.¹ Among various components of DSSCs, standard Pt CE is of pivotal importance as it aids in the regeneration of dye sensitizer and contributes to the charge transportation processes. However, it constitutes half of the cost of DSSCs as well as reacts with $I_3^-/I^$ electrolyte forming unwanted PtI₄.² In this context, various non-Pt based materials especially transition metal sulfides (TMSs) and their hybrids with graphene and its analogue materials have attracted remarkable attention owing to their high catalytic activity, mechanical strength, and thermal stability.^{3, 4} Individually carbon-based materials possess lower electrocatalytic activity and TMSs, poor conductivity, hence their synergistic effect would generate highly conducting efficient electrocatalytic and nanohybrids.5,6

In the present work, Ni_9S_8 nanoparticles were incorporated in graphene sheets to obtain rGO/Ni₉S₈ nanohybrids at different concentrations. They have been effectively used as Pt replacement in DSSCs and have shown comparable PV performance as that of Pt, which has been confirmed from the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies.

Experimental

All the chemicals were used as purchased from Sigma Aldrich. Modified Hummer's method was used to synthesize the graphite oxide (GO) and rGO. Here, 200 mg of GO was added to 40 ml DI water and sonicated for 40 min. Different concentration solution of Ni(NO₃)₂.6H₂O (20 wt% (N1), 40 wt% (N2), 60

wt% (N3)) in 20 ml DI water were added drop wise in the above solution and stirred continuously. A solution mixture of N₂H_{4.x}H₂O (200 μ l) and NaOH (500 μ l) were added to above solution for the reduction of GO, along with TGA (4 ml). The obtained product was transferred to sealed Teflon-lined stainless autoclave and kept in vacuum oven at 180°C (48 h). The resultant products were filtered, washed, and dried at 80°C to obtain N1, N2 and N3 nanohybrids, which were then drop-cast on pre-cleaned FTO substrates to prepare CE. The standard N719 dye sensitized TiO₂ photoanodes were prepared by doctor blading and dipping technique. The photoanodes and CE were sandwiched together along with inserting I₃⁻/I⁻ electrolyte between them to fabricate DSSCs.

PV characteristics of fabricated DSSCs were studied with a Keithley 4200A-SCS under 1 sun illumination (Intensity 100 mW cm⁻²) at AM 1.5G (OAI solar simulator). CV and EIS measurements were carried out with Autolab potentiostat/galvanostat system (PGSTAT302).

Results and Discussion

The successful formation of nanohybrids were confirmed from XRD and FESEM, which indicates the crystalline nature of nanohybrids and homogeneous attachment of Ni₉S₈ nanoparticles on rGO sheets. To investigate the electrocatalytic activity of the prepared nanohybrids, they were used as working electrode in an acetonitrile solution containing 10 mM LiI, 1.0 mM I₂ and 0.1 M LiCl₄ electrolyte and were performed at scan rate of 50 V s⁻¹. The peak current density (J_{PC}) and peak to peak separation (E_{PP}) of all the samples is tabulated in Table 1. J_{PC} and E_{PP} of N2 nanohybrid is observed to be comparable to that of Pt. It indicates that an optimal synergetic effect between Ni₉S₈ nanoparticles and rGO sheets plays a significant role to efficiently improve interfacial charge transfer by reducing I_3^- to I^- and provide more active catalytic sites. Since, N2 exhibited comparable electrocatalytic property with Pt, thus can be effectively used as CE of DSSCs.



Fig. 1. Cyclic voltammetry of (a) rGO, (b) Ni₉S₈, (c) N1, (d) N2, (e) N3 nanohybrids and (f) Pt CEs.

The PV parameters i.e., short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF) and power conversion efficiency (PCE) of fabricated DSSCs using different CEs are extracted from the current density-voltage curves (Fig. 2) and are listed in Table 1. It has been observed that among all, N2 CE based DSSC exhibited highest and comparable PCE with that of Pt and a remarkable increase in J_{SC} and FF. It is attributed to the improved electrocatalytic activity leading to faster oxidation and reduction reactions in I^-/I_3^- electrolyte.



Fig. 2. Current density-Voltage curves of (a) rGO, (b) Ni₉S₈, (c) N1, (d) N2, (e) N3 nanohybrids and (f) Pt CEs.

Fig. 3 show Nyquist plots of rGO, Ni₉S₈ nanoparticles, N1, N2 and N3 nanohybrids and their equivalent circuit model. The charge transport resistance (R_{CT}) at CE/ electrolyte interface is described by the diameter of semicircle in high frequency region and is summarized in Table 1. It is found that N2 shows the lowest R_{CT} among other nanohybrids which confirmed faster and superior charge transportation in fabricated N2 CE DSSC.

Conclusion

In conclusion, rGO/Ni₉S₈ nanohybrids have been successfully synthesized and showed comparable PV

performance when used as a replacement of Pt CE in DSSCs. The amount of Ni_9S_8 in nanohybrid effectively tune their electrocatalytic performance due to Ni content. Herein, Ni_9S_8 provide large active sites for the reduction of I_3 to I^- whereas, the conducting rGO sheets facilitates charge transportation.



Fig. 3. (A) EIS curves of (a) rGO(b) Ni₉S₈ (c) N1 (d) N2, (e) N3 nanohybrid and (f) Pt and their (**B**) equivalent circuit diagram.

Table 1. DSSCs parameters using different CEs.

53
15
78
46
01
45
5 1 7 4 0 4

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Raman scattering analysis on low energy Kr⁺ ion irradiated Y₂Ti₂O₇ and Y₂TiO₅

P. Jegadeesan^{1*}, S. Amirthapandian^{1,2}, T.R. Ravindran^{1,2}, B.K. Panigrahi³

¹Materials Science Group, Indira Gandhi Centre for Atomic Research, ²HBNI-Kalpakkam, Kalpakkam – 603 102, India, ³School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Khordha – 752 050, India

*Corresponding author: tojegadeesan@gmail.com

Abstract

Oxide dispersion strengthened (ODS) steels is considered as the most promising structural material for advanced nuclear systems. The predominant compositions of the dispersoids in the ODS steels are $Y_2Ti_2O_7$ and Y_2TiO_5 . In the present work, pellets of $Y_2Ti_2O_7$ and Y_2TiO_5 were irradiated with 70 keV Kr⁺ ions at room temperature. Irradiation induced disorder was analyzed in these systems with the help of Raman scattering and transmission electron microscopy (TEM). In the case of $Y_2Ti_2O_7$, there is no significant change in Raman scattering, except for a small change in few peaks. In the case of Y_2TiO_5 , majority of the Raman modes (associated with both Y- and Ti- bonds) have broadened upon ion irradiation. The Raman scattering results are in agreement with TEM observations, where krypton bubbles are observed in Y_2TiO_5 but not in $Y_2Ti_2O_7$. It is suggested that more of $Y_2Ti_2O_7$ oxide nanoparticles in ODS steel may improve the high temperature radiation resistance of ODS steels.

Shape-Controlled SnS Nanostructures: A Wet-Chemical Approach Privanka Jangra, Privanka Lakharwal, Hem C. Kandpal*, Pravas C. Patel

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee-247667, India.

*Corresponding author: hem.kandpal@cy.iitr.ac.in

Abstract

Present study reports the successful synthesis of highly crystalline SnS nanoparticles of various shapes/sizes via modified polyol approach. The effect of synthesis parameter (such as refluxing time, solvent, surfactant etc.) on the structural and surface properties of the particles has been comprehensively studied. The study showed that the presence of surfactant and seed based synthesis favors the growth of sheet-like or related morphologies. However, only simple refluxing based synthesis resulted in the development of rod-like feature. Study showed that with the meticulous selection of synthesis conditions with slight modifications, one can result with desired morphology.

Introduction

In recent times energy needs have skyrocketed dramatically, thereby putting pressure on conventional sources. Thus, energy perhaps is going to be the most discussed issue in near future. Harnessing solar power seems panacea to solve major part of the debate. Amongst active solar energy technologies, photovoltaic is above all and the most promising solution.¹

SnS continue to attract immense attention due to its vast potential in solar-cells application. Primarily, it is a layered p-type semiconductor with uniquely ideal parameters as required for solar cells; however it also shows n-type behavior in non-stoichiometric compositions. The dual valence nature of Sn (Sn²⁺ and Sn⁴⁺) enables tin sulfide to form many composition dependent phases.² This makes working with SnS is challenging.

Currently, efforts to establish a link between nanoparticle shapes/size and solar cell efficiency are on move.³ Particle morphologies notably tailor the charge transfer efficiency by modifying the percolating pathways of the donor/acceptor phases, thereby playing a major role in power conversion efficiency. In this context, this work presents the successful synthesis of SnS nanostructures in different shapes by systematically varying the synthesis parameters (tabulated in Table 1) in modified polyol approach.^{4, 5} Synthesis of sample S1 may be considered as model reaction for comparison. All the synthesized samples were comprehensively studied for their structural, morphological and surface properties.

Results and Discussion

The microstructural analysis from X-ray and electron diffraction (shown in Fig.1 (c) & (b), respectively) confirmed the formation of highly crystalline orthorhombic phase in all the synthesized samples. Fig. 1 (a) shows the TEM image of sample S2, depicting the formation of layered structure. The surface-scan SEM image (shown in Fig. 3) shows significant variation in shape/size of all the synthesized samples.

From Fig.2 and Table 1, it is clear that surfactant and seed based synthesis approach favors the growth of sheet like features which may further aggregate to form different morphologies. CTAB when present in the reaction, binds

with S^{2-} and slows down reaction rate, thereby leads to the differential growth of facets (stabilizing 100 plane), and hence forms sheet like structure. Similarly the sheets also get formed in presence of pyragallol, however, they further tend to aggregate to form rod like structure. The case for PVP is little different where it interacts with SnS through oxygen and nitrogen atom of Pyrollidone ring. This enables PVP to control morphology via strongly interaction with <111> facet rather than <100>, and thus leading to the growth of highly crystalline smooth edged folded sheet.

S5 showed agglomerated sheets with broken ends whereas well separated small flaked-sheets appeared in S6. Both were synthesized via seed induce mechanism where the key point was to avoid seed agglomeration. This was done by limiting the role of Na₂S (which primarily effects



ig. I. Structural analysis; (a) XRD pattern, (b) TEM image, (c) Electron diffraction pattern.

Sample	S1	S2	S 3	S 4	S 5	S 6	S 7	S 8
Surfactant		СТАВ	Pyragallol	PVP				
Seed Amt.					0.025 mmol	0.05 mmol		
Plateau time	2	2	2	2	2	2	2	10
Morphology	Nanorods	Nanosheets	Flaked Nanorods	Folded sheets	Agglomerate sheets	Flaked sheets	Bipyramidal Nanorods	Cubes

Table 1. Experimental details of the synthesized samples.



Fig. 2. SEM image of surface scan of sample S1 - S8.



Fig. 3. Pore size distribution from BET analysis; N₂ adsorption isotherms (inset).

the reaction kinetics) to the formation of seed only. Further supply of S ions was ensured by thiourea which releases S

ions in a controlled fashion. The amount of Na_2S present during the nucleation might have resulted in the development of seeds with different facets possibly due to variation in the nucleation density. Differential growth along with controlled release of S ions can be considered to be major factor for sheet-shaped growth.

Furthermore, the effect of refluxing time (plateau) was also evident in the morphology where elongated bipyramidal nanorods and cubes were formed for samples S7 and S8, respectively. The formations of such features are understood to be due to the rich abundance of both Sn and S atoms, which may have got hampered in other samples primarily due to the presence of surfactant or seed formation.

Surface pore size analysis and N_2 adsorption isotherms (shown in Fig. 3) also shows significant difference in the volume available for adsorption, however, the average pore size distribution remained same. Here both the samples shown are mesoporous and show II+III type hysteresis loop.⁶ This might have resulted in significant difference in the charge transfer capabilities of the synthesized samples, which could be a part of further subsequent studies.

All the observed shape modifications can be understood in terms of relative chemical potentials, which are themselves the function of relative abundance of the reacting atoms, temperature, reaction time etc. Conclusively it can be said that by systematically tailoring the appropriate synthesis parameters, SnS nanoparticles of various shape/size could be successfully synthesized.

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Orientation induced piezoelectric coefficients (d₃₃ and d₃₁) in aligned and random fibers of P(VDF-CTFE)

Ajay Kumar and Dipankar Mandal^{*}

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

In this work, the dipole orientation in aligned and random fibers of P(VDF-CTFE) is investigated to see the effective change in piezoelectric coefficients. The prepared random electrospinning fibers of P(VDF-CTFE) show feeble dichroism ($R\sim1$) and very low ($f_m = 0.03$) fraction of dipole orientation, while aligned fibers display varying dichroism ($R_{max} \sim 2.24$) with large fraction ($f_m = 0.29$) of dipoles oriented perpendicular to fiber axis. The oriented and uniform distribution of fibers will further enhance the value of piezoelectric coefficients (i.e., d_{33} and d_{31}).

Introduction

Out of all energy harvesting systems, piezoelectric energy harvesters are considering as one of the efficient and promising power sources for the portable and wearable electronics. Polyvinylidene fluoride (PVDF) and its copolymers are well known semicrystalline materials those possess high piezoelectric coefficients (d₃₃, d₃₁), used to prepare flexible piezoelectric energy harvesters, sensors and actuators. Piezoelectric devices are mainly operate in mainly d₃₃ and d₃₁ mode, generally d₃₃ mode generate higher output as compared to d₃₁ mode.¹ PVDF and poly(vinylidene fluoride-trifluoroethylene) (P(VDF-TrFE)) possess higher value of d_{33} in highly oriented β crystalline phase, while poly(vinylidene fluoridehexafluoropropylene) (P(VDF-HFP)) and poly(vinylidene-chlorotrifluoroethylene) (P(VDF-CTFE)) have higher values of d_{31} coefficient.² The d_{33} and d_{31} piezoelectric coefficient can be calculated from equation 1 and 2,

$$d_{33} = \frac{D_3}{X_3}$$
(1)
$$d_{31} = \frac{D_3}{X_4}$$
(2)

where D_3 is displacement polarization along the z-axis, X_3 and X_1 are the direction of applied stress along z and x-axis respectively.

The alignment of dipoles along the direction of applied stress will further increase the d_{33} coefficient of piezoelectric device. On the other hand, fraction of dipoles oriented perpendicular to applied stress will affect the d_{31} coefficient of device. Therefore, it is possible to increase the d_{33} and d_{31} coefficient of P(VDF-CTFE), which already have higher values of d_{31} coefficient as compared to PVDF.

In this study, we have prepared highly aligned and random fibers of P(VDF-CTFE) and studied the orientation of dipoles by using polarized infrared

spectroscopy (FTIR). Highly oriented and uniform distribution of dipoles have direct influence on the d_{33} and d_{31} coefficient of piezoelectric device.

Experimental section

Electrospinning solution was prepared by dissolving 6 wt % of P(VDF-CTFE) powder in 6:4 volume ratio of DMF/acetone solvent. Electrospinning process was carried out under electric field of 93 kV/m to produce random and aligned fibers on plate and drum collectors respectively.

Results and discussion

The FTIR spectra of aligned and random fibers is shown in figure 1 where different vibrational bands are marked those corresponding to crystalline phases of P(VDF-CTFE). The presence of α phase can be ruled out because of the absence of α phase characteristic vibration bands (such as 764, 796, 1209 cm⁻¹) and appearance of 841 and 1275 cm⁻¹ (symmetric stretching of CF₂, anti-symmetric stretching of CC, bending of CCC) vibrational band in FTIR spectra of aligned and random fibers confirm crystalline β phase conformation of P(VDF-CTFE). ^{3,4} The percentage of electroactive phase was calculated by using Beer – Lambert law of absorbance, as described in equation (3),

$$F_{EA} = \frac{A_{841}}{\frac{K_{841}}{K_{764}} \times A_{764} + A_{841}} \times 100 \%$$
(3)

where, A_{841} and A_{764} are absorbances at 841 and 764 cm⁻¹ respectively, $K_{841} = 7.7 \times 10^4$ cm² mol⁻¹ and $K_{764} = 6.1 \times 10^4$ cm² mol⁻¹ are the absorbance coefficients corresponding to 841 and 764 cm⁻¹ wavenumbers. The estimated percentage of electroactive phase is 81 % in both aligned and random fibers.



Figure 1. FTIR spectra of aligned and random P(VDF-CTFE) fibers.

The effect of orientation of dipoles was further studied by polarized FTIR with parallel and perpendicular orientation of polarizer axis. Polarized FTIR spectra of aligned fibers shown in figure 2 indicates that there is change in absorbance of different vibrational bands with change in polarizer axis, while no such feature is observed in random fibers. The change in absorbances of different vibrational bands was analyzed by estimating the value of dichroic ratio (R), minimum fraction of completely oriented dipoles (f_m) and range of angle δ formed by their long axis with transition dipole moment vector from equations 4-6,^{4,5}

$$R = \frac{\Delta A_{parallel}}{\Delta A_{perpendicular}} \tag{4}$$

 $if R > 1: 0^{\circ} \le \delta \le \cot^{-1}(\sqrt{R}/2); f_m = \frac{R-1}{R+2}$ (5)

if
$$R < 1: \cot^{-1}(\frac{\sqrt{R}}{2}) \le \delta \le 90^\circ; f_m = \frac{2(1-R)}{R+2}(6)$$

Table 1. The R and f_m in different vibrational bands in aligned and random fibers of P(VDF-CTFE).

Wavenumber	Aligned		Random	
cm-1	R	f _m	R	f _m
1430	0.45	0.447	0.98	0.010
1402	2.24	0.292	1.01	0.003
1280	0.64	0.270	0.95	0.033
1182	1.02	0.008	0.97	0.018
1073	2.09	0.267	0.99	0.002
883	0.91	0.061	0.95	0.027
841	0.78	0.157	0.96	0.021

It can be observed from table 1 that vibrational bands of random fibers show weak dichroism, very low (< 3 %) fraction of dipole orientation and similar range of angle δ formed by different dipoles due to uniform distribution of dipoles in parallel and perpendicular direction. While aligned fibers are exhibiting varying dichroism from 0.45 to 2.24, maximum 44 % dipole orientation and different range of angle δ formed by dipoles axis. The variation of dichroic ratio and fraction of dipole orientation indicates that dipoles are highly aligned perpendicular to long chain fiber axis and uniformly distributed in aligned and random fibers respectively. This perpendicular alignment of dipoles in aligned fibers will further leads to increase in d₃₃ piezoelectric coefficient. While uniform distribution of dipoles in parallel and perpendicular direction of random fibers will further enhance the d₃₁ piezoelectric coefficient.



Figure 2. Polarised FTIR spectra of aligned (PVDF-CTFE) fibers.

Conclusion

In this study, highly aligned and random electrospinning fibers of P(VDF-CTFE) were produced and characterized by polarized FTIR to analyze the distribution and orientation of dipoles in aligned and random fibers. The perpendicular alignment of dipoles in aligned fibers further increase the d_{33} piezoelectric coefficient and uniform distribution of dipoles in random fiber enhance the d_{31} piezoelectric coefficient, thus it may have new avenue in the device design perspective.

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External Pressure Induced Current Enhancement in Cu Salt-PVDF Composite

Dipanjan Sengupta, Sudip Naskar and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

Combination of poly(vinyldine fluoride) (PVDF) with hydrated copper (Cu) salt in definite proportion shows a drastic enhancement in current, in presence of external pressure impact. The superiority of the composite is attributed to the induced β and γ -phase in PVDF molecule after Cu-incorporation, which is evident from the Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) spectra.

Introduction

Transforming mechanical stimuli to electrical response using piezoelectric materials has been extensively investigated and administered in numerous advanced technologies. Poly(vinylidene fluoride) (PVDF) is one of the most explored polymeric materials for flexible electronics, owing to promising piezoelectric properties, costits effectiveness, easy processability and superior flexibility [1]. PVDF can exist in five different phases $(\alpha, \beta, \gamma, \varepsilon \text{ and } \delta)$ in different molecular chain conformation [2]. However, the β , γ and δ phases are the most eligible conformers of PVDF for devicebased applications due to their inherent electrical dipole moment due to their non-centro symmetric space group symmetries [3]. Incorporation of hydrated salts into PVDF matrix is an already established approach to accomplish improved performances [4]. Some of the hydrated salts, e.g. NiCl₂·6H₂O, $Mg(NO_3)_2 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$ etc., are so far reported to form composite with PVDF because of the availability of nucleation sites which is stabilized by the dipolar interactions and H-bonding in the interfacial zone which enhances the formation of alltrans (TTTT) β -phase orientation [4-6].

Herein, we have combined PVDF with $CuCl_2.2H_2O$ (Cu@PVDF) as a hydrated salt and investigated the electrical response for the hybrid energy harvesting device fabrication.

Experimental

4 (w/v) % PVDF solution is prepared by incorporating PVDF powder (industrial grade) in N,Ndimethylformamide (DMF) solvent. 20 mM copper chloride (CuCl₂.2H₂O, Merck) is prepared by mixing with the former in same solvent. The homogeneous mixture is obtained by stirring (400 rpm) at 60°C for 12 h. The PVDF solution and the Cu salt mediated PVDF (Cu@PVDF) solution in DMF are mixed in 3:1 proportion to attain the final solution (5mM) which is further used for thick film preparation by solvent casting. The films (with and without CuCl₂.2H₂O) are characterized with respect to their phase formation behavior via FTIR-ATR spectra (Nicolet iS20, ThermoFisher, USA). The composite formation is confirmed by the UV-visible spectrophotometer (UV-2600, Shimadzu, Japan). Finally, the current-voltage response is recorded by using a Keysight B2901A (USA) source current unit at room temperature.

Results and discussions

Fig. 1 shows the FTIR-ATR spectra of neat PVDF and Cu@PVDF thick film. In the neat PVDF sample, mainly the α -phase is predominant.



Fig. 2. FTIR-ATR and UV-visible absorbance (inset) spectra of neat PVDF and Cu@PVDF.

The distinguishable vibrational bands at 1212, 1152, 795 and 763 cm⁻¹ are the α -phase characteristics vibrational bands [7]. On the other hand, β - and γ - crystalline phases are found to be present in the Cu@PVDF sample.

The 1273 cm⁻¹ vibrational band authorize the presence of the β - phase and the band at 1230 cm⁻¹ is indicating the γ - phase [7]. The presence of the both electroactive phases (β and γ) are confirmed from the characteristics 837 cm⁻¹ peak [7]. The electroactive phase content, which is calculated from standard formula [8], is 73% for Cu@PVDF and 27% for PVDF film. The β and γ phases are estimated to be 28% and 45% respectively in Cu@PVDF film. Further, the loading of the sample with Cu salt is ascertained from the UV-visible absorbance study as depicted in inset of Fig. 1. The characteristics peak at 260 nm confirms the incorporation of CuCl₂ salt in PVDF matrix [9].

To further verify the accountability of Cu@PVDF film upon neat PVDF film, a response detector device is fabricated to investigate the film responses for the two different samples.



Fig. 2. I-V characteristics of pressure induced and without pressure Cu@PVDF sample; *Inset 1:* Photograph of finger pressure application; *Inset 2:* I-V characteristics of PVDF sample; *Inset 3:* I vs t plot with and without pressure.

The device has been prepared by solvent deposition of Cu@PVDF on flexible indium tin oxide (ITO) substrate under heat treatment at 120°C for 1 hour. Connections has been established by adhering Cu-wire by silver (Ag) paste. The response of the fabricated Cu@PVDF based device is shown in Fig. 2. In a

voltage (V) of 10 V, the device shows $\sim 50 \,\mu\text{A}$ current (I) response which increased by 3 times after exerting finger pressure (FP), as presented in Inset 1 of Fig. 2. On the other hand, the response of neat PVDF-based device is estimated to be in the nanoampere (nA) range in the same voltage (Inset 2 in Fig. 2). The superior performance of Cu@PVDF based device may be attributed to the better charge separation and transportation due to aligned dipole orientation in predominant β and γ phases. Parallelly, the current response with FP has also been recorded in 0 V voltage (just to ascertain the non-participation of voltage in current increment). Inset 3 in Fig. 2 shows the current (I) vs time (t) plot, which clearly demonstrates the amplification of current after exerting FP. The result confirms the existing piezoelectric properties in Cu@PVDF film.

Conclusion

In a nutshell, 4 (w/v) % PVDF and 5 mM Cu@PVDF solution is prepared and comparative study has been carried out via phase formation behavior and electrical responses. Increment in electroactive phase content leads to the performance enhancement of Cu@PVDF film-based device. The superior result is accredited to the induced β and γ phases in Cu@PVDF, which increase the dipolar nature, resulting in effective charge separation and transportation.

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Two-dimensional β-PdSe₂ Monolayer For Photovoltaic Applications: First-principles Study

Mukesh Jakhar, Jaspreet Singh and Ashok Kumar*

Department of Physics, School of Basic Sciences, Central University of Punjab, Bathinda, India

*Corresponding author: ashokphy@cup.edu.in

Abstract

By employing first principles theory, we demonstrate that two-dimensional β -PdSe₂ monolayers is promising candidates for the construction highly efficiency heterojunction solar cells. β -PdSe₂ monolayer exhibits a semiconducting nature with an indirect band gap of 1.16 eV. Subsequently, we show that β -PdSe₂ monolayer can be used to form type-II heterostructures with the other TMDs for photovoltaic cells. The PCE of β -PdSe₂/WS₂(2L), β -PdSe₂/P-PdSe₂ and, β -PdSe₂/MoSe₂ excitonic heterojunction can reach 22.8%, 21.79% and 20.3%, respectively.

Introduction

To meet society's ever-increasing energy demand, much emphasis has been placed on the use of renewable energy resources that are green, clean, and limitless, such as solar energy harvesting (i.e. photovoltaic, artificial photosynthesis). 2D materials beyond graphene, such as transition metal dichalcogenides (TMDs), MXenes have drawn considerable attention for their use in energy storage and conversion [1]. Particularly, their van der Waals heterostructures with different TMDs materials show variety of applications including photovoltaic, optoelectronics and spontaneous water splitting [2].

Among TMDs, the layered $PdSe_2$ has received much attention due to its unique ground-state puckered pentagonal structure which has also been synthesized in experiments [3]. Also, $PdSe_2$ can exist in many phases such as hexagonal T-phase and trigonal β -phase with highly efficient application in a solar cell [4] and photocatalysis [5], respectively.

In this paper, we have calculated the electronic properties of the β -PdSe₂ monolayer. Calculations based on density functional theory found β -PdSe₂ to be a semiconductor with a moderate band gap appropriate for photovoltaic applications. Subsequently, consider β-PdSe₂ we based heterostructures with different TMDs demonstrating that the calculated maximum power conversion efficiency (PCE) of such heterostructures can reach as high as $\sim 23\%$.

Computational Details

The electronic structure computations were carried out using the SIESTA simulation package in the density functional theory (DFT) framework [6]. The exchange and correlation energies were treated within the generalized gradient approximation (GGA) potential parameterized by the Perdew–Burke–Ernzerhof (PBE) functional. Numerical atomic orbitals type of basis set with double zeta polarized are used with a cutoff energy of 450 Ry in a real-space grid. The energy and force convergence requirements were chosen at 10^5 eV and 0.01 eV/Å, respectively. The Brillouin zone is sampled with a 30x30x1 k-point mesh using the Monkhorst Pack method. A vacuum distance of 20 Å in Z-direction is used to avoid interaction between periodic images.

Results and Discussions



Fig. 1. (a)Top and (b) side view of the β -PdSe₂ monolayer with its (c) band structure and (d) partial density of states.

Fig. 1. (a, b) depicts a schematic top and side view crystal structure of β -PdSe₂. The computed lattice parameters are a = 3.60 Å and b = 4.36 Å. The electronic band structure of β -PdSe₂ shows a semiconductor nature with an indirect bandgap of 1.16 eV (Fig 1(c)).

At Y (0, 0.5, 0), the valence band maximum (VBM) is observed, while the conduction band minimum (CBM) is found at Γ (0, 0, 0) point. The Pd-4d and Se-4p states contribute the most to VBM and CBM, respectively, according to the partial density of states (PDOS) analyses (Fig. 1(d)).

β-PdSe₂/TMD Heterostructure Solar Cells

The β -PdSe₂ monolayer show desirable electronic properties (moderate band gap), which can be combined with other suitable TMDs and other phases

of PdSe₂ for the designing of a heterojunction solar cell. Here, we propose van der Waals heterostructures composed of β -PdSe₂/T-PdSe₂, β -PdSe₂/MoS₂, β -PdSe₂/MoSe₂, β -PdSe₂/PoSe₂, β -PdSe₂/MoTe₂, and β -PdSe₂/WTe₂, which form type-II donor-acceptor interface band alignments, as shown in Fig. 2(a).

TMDs with a greater (lower) conduction band minimum than β -PdSe₂ operate as a donor (acceptor) for β -PdSe₂-based heterostructures. β -PdSe₂ acts as a donor (acceptor) for MoTe₂, WTe₂, 2L-WTe₂, 2L-WSe₂ (T-PdSe₂, MoS₂, MoSe₂, P-PdSe₂, 2L-WS₂), as shown in in Fig. 2(a).

In excitonic solar cells, heterostructures with type-II band alignments have effective electron-hole separation for light harvesting. The ideal band gap (1-1.5 eV) and modest conduction band offset are desired to develop highly efficient heterojunction solar cells. In particular, 2L-WS₂, P-PdSe₂, and MoSe₂ show optimal band gap values along with small conduction band offsets (0.01, 0.06 and 0.15 eV), suggesting β -PdSe₂/WS₂(2L), β -PdSe₂/P-PdSe₂, and β -PdSe₂/MoSe₂ heterostructures to be promising candidates for designing highly efficient solar cells.



Fig. 2. (a) Band alignment of β -PdSe₂ with different TMDs. (b) Power conversion efficiency (PCE) contour as a function of the donor bandgap and ΔE_c .

Next, we calculate the upper limit of PCE, which has been widely used for efficiency estimation. The maximum PCE of a heterojunction solar cell can be described as [7]

$$\eta = \frac{\beta_{FF} V_{OC} J_{SC}}{P_{solar}}$$

Here, the β_{FF} and P_{solar} is band fill factor and total incident solar power per unit area (air mass 1.5 (AM1.5) solar energy flux) respectively. The upper limits of PCE for β -PdSe₂-based heterojunction solar cells are calculated to be $\sim 2-23\%$ (Table 1). The maximum efficiency depends critically on the donor band gap and the CB offset (ΔE_c). Thus, the estimated maximum efficiencies are around

Table 1. The ΔE_c and PCEs (%	6) of heterostructure.
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System	ΔE_c (eV)	PCE%
T-PdSe ₂	0.76	2.82
MoS ₂	0.58	7.64
MoSe ₂	0.15	19.33
P-PdSe ₂	0.06	21.79
$WS_2(2L)$	0.01	22.89
MoTe ₂	0.20	17.98
WTe ₂	0.44	11.46
$WTe_2(2L)$	0.50	10.25
$WSe_2(2L)$	0.35	15.97

19.33%, 21.79%, and 22.89 %, for $MoSe_2$, P-PdSe₂ and WS₂ (2L) systems, respectively, due to the smaller CB offset in comparison to other heterobilayers.

Conclusions

In summary, β -PdSe₂ possesses a moderate band gap of 1.16 eV. This characteristic makes β -PdSe₂ a potential candidate for optoelectronic applications. Importantly, combining the β -PdSe₂ monolayer with the monolayer TMDs forms type-II heterostructures. A series of heterostructure solar cell systems containing MoSe₂, P-PdSe₂ and WS₂ (2L) are proposed, which show ~19–23% PCE. Our study reveals that PdSe₂ can be a promising candidate for the fabrication of photovoltaic devices.

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In-situ structural studies on LiNi_{0.3}Mn_{0.3}Co_{0.3}O₂ cathode-based Li ion batteries

Abharana N^{1,2,*}, Kruti K. Halankar^{2,3}, Velaga Srihari⁴, S.N. Jha¹, D. Bhattacharyya¹

¹Atomic & Molecular Physics Division, ³Chemistry Division, ⁴High Pressure & Synchrotron Radiation Physics, Division, Bhabha Atomic Research Centre, Mumbai 400 085 ²Homi Bhabha National Institute, Anushaktinagar, Mumbai – 400 094

*Corresponding author: abharana@barc.gov.in

Abstract: *In-situ* structural studies has been carried out with synchrotron radiation on Li ion batteries with Li[Ni_{0.3}Co_{0.3}Mn_{0.3}]O₂ cathode materials. While *in-situ* X-ray diffraction measurement indicates structural changes during the charging/discharging cycles, *in-situ* element specific X-ray Absorption Spectroscopy (XAS) measurements reveal site specific information. It has been found the major charge compensation at the metal site during charging or Li ion de-intercalation is achieved by oxidation of Ni²⁺ ions without any change in the oxidation state of Co or Mn ions. It is also found that coordination numbers and bond length of Ni-O coordination shells respectively increase and decrease during charging and reverse happens during discharging, while local structure around Co or Mn sites show much less variation in these parameters.

Spray Pyrolysis Synthesized Zinc Ferrite Thin Film as an Electrode for Supercapacitor Application.

S. D. Jituri¹, V. C. Pawar¹, S. M. Nikam², G. M. Lohar³ and S. H. Mujawar^{1,*}

¹ Department of Physics, Yashavantarao Chavan Institute of Science Satara, (Autonomous), 415001 ²Department of Nanoscience and Technology, Yashavantarao Chavan Institute of Science Satara, (Autonomous), 415001

³Department of Physics, Lal Bahadur Shastri College of Arts, Science and commerce, Satara, 415001

*Corresponding author: sarfrajmujawar695@gmail.com

Abstract

Abstract. Zinc ferrite thin films were deposited on nickel foam by using simple and inexpensive spray pyrolysis technique for electrochemical supercapacitor application. The structural, morphological, and optical properties of synthesized zinc ferrite film were investigated by X-ray diffraction, UV-visible, and FT-IR spectroscopy. The electrochemical measurement of the as-prepared film was carried out by using cyclic voltammetry and galvanostatic charge-discharge techniques.

Electroactive δ-phase of PVDF Based Piezoelectric Mechanical Energy Harvester

Hari Krishna Mishra and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: E-mail: dmandal@inst.ac.in

Abstract

Piezoelectric electromechanical energy conversion has been studied through poly(vinylidene fluoride) (PVDF) δ -phase film based mechanical energy harvester (MEH). The XRD and ATR-FTIR spectra confirms the formation of electroactive δ -phase in PVDF polymer which is pieo- and ferro-electric in nature. An excellent electrical response is recorded with unpoled MEH (as Voc ~ 1 V and Isc ~ 600 nA) under gentle finger imparting, but corona poling has shown the significant enhancement in electrical output (as Voc ~ 1.5 V and Isc ~ 900 nA) in the case of poled MEH comparison to the unpoled MEH. This enhancement leads to the dipole orientation upon the application of electric field.

Introduction

The rapid development of personal electronics gazettes and sensor networks have raised the urgency and challenge for portable and sustainable power sources as a continuous power supply with small and low power electronic devices such as wireless sensing, Internet of things (IoT), artificial intelligence (AI), i.e., physiological bio-medical sector signal monitoring and mechanical energy harvester.¹ There are various vibration sources such as human motion, pulse and heart breathing, wind energy, music are available in the surrounding that can be converted into electrical energy. In this regard, piezoelectric polymer poly(vinylidene fluoride) (PVDF) is a very suitable choice of polymer because of its flexibility, light weight, biocompatibility and outstanding piezo-, pyroand ferro-, electric properties. Since PVDF possess mainly four different polymorphic phases α , β , γ and δ depending on the macromolecular chain conformation. Among these β - and γ - phase has been explored strongly because of its electroactive nature but α -phase have non electroactive nature due to its alternate chain arrangements trans (T) and gauche (G) i.e., TGTG which results the net dipole moment is zero. Whereas δ -phase of PVDF also possess similar chain conformation as α -phase but it is an electroactive in nature because each second chain along c-axis is rotated at 180° therefore the net dipole moment per unit cell is non-zero.^{2,3} In last few decades, tremendous efforts have been made for most desirable electroactive phase β and γ and it has been explored for various application in piezoelectric and ferroelectric properties such as memory devices, energy storage, mechanical energy harvester, sensors and actuators etc. But δ -phase of PVDF is not explored

that much as β - and γ -phase so far. In this context, we have introduced the piezo-and ferro- electric δ -phase formation in PVDF pellets through XRD pattern and ATR-FTIR spectra.

Experimental Section

PVDF pellets ($M_w \sim 1,80,000$) were purchased from Sigma-Aldrich. PVDF pellets were characterize with fourier transformation infrared (FTIR) spectra (iS20, Thermofisher Scientific) in ATR mode and X-ray diffraction (XRD) (D8, Bruker Advance) and then customized homemade hot press machine was used for PVDF film preparation. Followed by device ($4 \times 2 \text{ cm}^2$) was fabricated by making the electrode (Copper foil) on both side and then two copper wire were taken out from both side of electrode. For the better performance and high piezoelectric response, the device was poled at 55 kV and 80°C temperature for 30 m. The electrical response voltage and current was measured with digital storage oscilloscope (DSOX1102G, Keysight) and sourcemeter (B2902A, Keysight)



Fig.1 PVDF δ -phase (a) XRD pattern with the deconvolution and (b) ATR-FTIR spectra.

Results and Discussion

The electroactive δ -phase in PVDF pellets is investigated with XRD pattern as shown in Fig. 1(a). It can be observed there are only two peaks present before 21° of 2 θ value at 18.4° and 20.1° and having reflection planes (020) and (110) respectively. Thereafter, in the range of 25-30° an asymmetric Gaussian peak has deconvoluted with 2 crystalline peaks at 26.7° and 27.4° with (021) and (111) reflection respectively. It is noteworthy to mention that, α crystallographic peaks are missing at 17.8° (100) and 25.7° (120) respectively. Therefore, we can conclude the δ -phase formation in PVDF. This diffraction pattern is similar with the δ -phase in thin film with high electric field.⁴ As a proof of concept the ATR-FTIR spectra is recorded in 600 to 1600 cm⁻¹ region as shown in Fig. 1(b). It is observed the characteristics band of PVDF are present at 840 and 1276 cm⁻¹ respectively along with the strong α -phase bands at 764, 975 and no γ -phase bands are present. Therefore, it is expected that it is neither complete β -, γ nor α phase, but due to the presence of α -phase bands in FTIR spectra there should be the 17.8° (100) peaks present in XRD pattern (which is absent in XRD pattern Fig. 1(a)). It is noteworthy, to mention that first time we observed the electroactive δ -phase in PVDF pellets which has almost similar piezo- and ferroelectric properties.



Figure 2. (a) Schematic representation of corona poling to poled MEH and (b, c) electrical output response of PNG in both condition unpoled (MEH@UP) and poled (MEH@P).

Mechanical energy harvesting

 δ -PVDF film after making the electrode was poled by corona poling as shown in schematic representation of Fig. 2(a). The piezoelectric mechanical energy harvesting properties are examined through δ -PVDF film. In this context upon the application of an external mechanical force the crystal structure is deformed thereby the positive and negative ions forms the dipoles in the material, which results the large piezoelectric potential.⁵ Thus, an open circuit voltage (Voc) and short circuit (Isc) current was measured by continuous finger imparting as shown in Fig. 2(b, c) respectively. The large change has been observed between unpoled and poled MEH, in case of unpoled MEH the Voc and Isc is found to be ~ 1 V and ~ 600 nA respectively. Whereas in the case of poled MEH, it is ~ 1.5 V and 900 nA respectively. This change is due the corona poling *i.e.*, the maximum number of dipoles are trying to reorient upon the application of electric field that gives rise to large polarization at the surface. Thus δ -PVDF MEH can be used further as a sensor, actuator and bio-medical sector applications.

Conclusion

In summary, we have introduced the electroactive δ -phase in PVDF pellets. The MEH comprises of PVDF δ -phase film prepared by hot press machine have shown the excellent electrical output response. The significant enhancement is noticed in Voc and Isc before and after corona poling MEH. Thus it is evident that the δ -phase of PVDF have piezoelectric nature.

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Poling Effect on Electrical Properties of KBT based Piezoceramic

Manish Badole¹, Sushmita Dwivedi¹, Hari Narayanan Vasavan¹, and Sunil Kumar^{1,*}

¹Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Indore 453552

*Corresponding author: sunil@iiti.ac.in

Abstract. This study explores the structural, dielectric & piezoelectric behavior of $0.97K_{0.5}Bi_{0.5}TiO_3 - 0.03BiAlO_3$ (KBT-3BA) ceramic fabricated *via* the sol-gel synthesis route. The coexistence of tetragonal (*P4mm*) and cubic phase (*Pm* $\overline{3}m$) was observed in the Rietveld refinement of X-ray diffraction (XRD) patterns of unpoled KBT-3BA sample. The temperature-dependent dielectric analysis of poled KBT-3BA sample showed an additional anomaly which suggests the possibility of electric-field induced structural variation or core-shell microstructure in the system. The ferroelectric to relaxor transition temperature (*T*_{*F*-*R*} ~ 265 °C) was obtained by the first derivative of dielectric permittivity (ε_r) with respect to temperature (*T*). Further, the resonance & antiresonance technique was used to determine the depolarization temperature (*T_d*) ~ 310 °C.

INTRODUCTION

Bismuth-based lead-free materials (especially $Na_{0.5}Bi_{0.5}TiO_3$, NBT) have shown excellent piezoelectric performance due to the presence of Bi-6s² lone pair. K_{0.5}Bi_{0.5}TiO₃ (KBT) is one of the important members in this category which shows tetragonal symmetry along with relaxor ferroelectric behavior. Despite having a higher temperature of dielectric maximum ($T_m \sim 380$ °C) and depolarization temperature ($T_d \sim 300$ °C) compared to NBT, the available reports on the nature of poled KBT ceramics are limited¹. It is well known that the functional properties of these materials can be improved by aliovalent doping at A-site and/or B-site in the perovskite structure.

The present work is the extension of our previous study where the effect of BiAlO₃ doping in KBT ceramic was systematically investigated². The thermal stability of piezoelectrics can be determined by depolarization temperature T_d that ensures the high-temperature applicability of these materials. Another important parameter is normal to the relaxor crossover temperature (T_{F-R}) at which long-range order domains convert to polar nanodomains. In this work, we report on dielectric behavior (T_m , T_{F-R} , and T_d) of poled (0.97K_{0.5}Bi_{0.5}TiO₃-0.03BiAlO₃; KBT-3BA) ceramics.

EXPERIMENTAL

Soichiometric amounts of KNO₃, Bi(NO₃)₂·5H₂O, $C_6H_{18}N_2O_8Ti$, and Al(NO₃)₃·9H₂O were used to prepare KBT-3BA via a sol-gel technique. Bismuth precursor was dissolved into nitric acid, and deionized water was used as the solvent for other precursors. These mixtures were mixed with citric acid and ethylene glycol. After vigorous stirring, the

mixture was heated at 90 °C for 8 h, then at 550 °C for 12 h, and finally at 800 °C for 6 h with intermediate grindins. The unixaily pressed cylindrical pellets were sintered at 1020 °C for 12 h in air. X-ray diffractometer (Bruker-D2 Phaser, with Cu-K α radiation) was used to perform the XRD analysis in the 2 θ range from 20° to 80°. For proper contact, the sintered pellets were electroded with fired-on silver paste on either side. Temperature-dependent dielectric measurements were carried out in a frequency range of 100 Hz to 1 MHz using a LCR meter (NF Corp., model: ZM 2376). The poling was done by applying an external DC field (40 kV/cm) in a heated (~ 160 °C) silicon oil bath.

RESULTS & DISCUSSIONS

The Rietveld refinement was performed on the room tempearure XRD data of KBT-3BA powder and the fitted curve along with experimental data is shown in Fig. 1.



A good fit indicates the coexistence of tetragonal (*P4mm*) and cubic phases ($Pm\overline{3}m$) in this sample. A dense microstructure with cuboid-shaped grains (average grain size ~ 300 nm) can be seen in the SEM image as shown in inset of Fig. 1.

The temperature-dependent dielectric behavior of unpoled and poled KBT-3BA is represented in Fig. 2. Two anomalies were observed in dielectric constant (ε_r) vs. temperature (*T*) plot of poled sample at 355 & 400 °C (at 1 MHz), suggesting two-phase transitions in this sample. It is known that the poling process can modify the structure and dielectric behavior in piezoelectrics. In several reports, an additional dielectric anomaly was observed in poled piezoceramics which was attributed to the electric field induced phase transition or core-shell type microstructure in these samples³.



Fig. 2 $\varepsilon_r vs. T$ plot of (a) unpoled (b) poled KBT-3BA sample and (c) $(d\varepsilon_r/dT) vs. T$ curve for T_{F-R} estimation

The core-shell microstructures in piezoceramics are reported to possess a tetragonal core covered with a relaxor ferroelectric shell (cubic symmetry). On the application of the DC field, the tetragonality of the core increases and some polar regions (tetragonal) are induced in the shell part. Core and shell regions undergo tetragonal to cubic transformation at different temperatures which appear as two dielectric anomalies in ε_r -T plot^{4, 5}. Similar phenomena could explain the origin of additional dielectric anomaly in poled KBT-3BA. However, detailed characterization are needed to confirm the structural inhomogenities within a grain⁶.

The temperature of ferroelectric to relaxor transition was estimated to be 265 °C from the first temperature derivative of permittivity $(d\varepsilon_r/dT)$ with temperature plot as shown in Fig. 1(c). The depolarization temperature was obtained ~ 310 °C

using the resonance–antiresonance technique as represented in Fig. 3. The occurrence of T_{F-R} below T_d also signifies a non-ergodic relaxor state in the KBT-3BA ceramics.



Fig. 3. Resonance-antiresonance curves for KBT-3BA.

CONCLUSIONS

Perovskite structured dense KBT-3BA ceramic was fabricated via a sol-gel route. XRD analysis confimred the coexistence of tetragonal and cubic phases. An additional dielectric peak was observed in poled KBT-3BA sample which was attributed to the localized phase variation or core-shell microstructure induced by DC field. The T_{F-R} and T_d were obtained at ~265 °C and ~310 °C respectively. The occurrence of T_{F-R} below T_d suggested a non-ergodic relaxor state in the KBT-3BA ceramics.

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Synthesis and Transport Properties of P2-type Na0.78Cu0.22Fe0.11Mn0.67O2 Layered Oxide

Hari Narayanan Vasavan¹, Manish Badole¹, Sushmita Dwivedi¹, and Sunil Kumar^{1,*}

¹Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore, Indore 453552

*Corresponding author: sunil@iiti.ac.in

Abstract

Abstract. Layered oxides are considered the 'holy grail' of cathode materials in ion storage batteries due to their high energy density and easier processing. In this work, a P2-type Na_{0.78}Cu_{0.22}Fe_{0.11}Mn_{0.67}O₂ sample was synthesized via a sol-gel method, and its structure and electrical properties were evaluated. Le-Bail fitting of the x-ray diffraction data confirmed the single-phase P2-type structure (space group: $P6_3/mmc$) for the sample. The room temperature bulk conductivity estimated from equivalent circuit modeling of impedance data was ~ 4.5×10^{-4} S/m with an associated activation energy ~ 0.45 eV.

Density Functional Theory investigation of Mn doped LiFePO4cathodes for Li ion batteries

ChandraniNayak* and Dibyendu Bhattacharyya

Atomic and Molecular Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, INDIA.

*Corresponding author: nayakc@barc.gov.in

Abstract

Density Functional Theory calculations have been done on Mn doped LiFePO₄ system to investigate its structural and electronic properties for differentMn doping concentrations. Effect of Mn doping has been investigated on the lattice constants and unit cell volume of LiFePO₄structure. The band gap values have been derived from the density of states calculation which gives an estimation of the electronic conductivity in the Mn doped LiFePO₄ system. Li ion diffusion has been simulated using the nudged elastic band (NEB) model and the activation barrier has been compared for the system with different Mn doping concentrations.

High Performing Triboelectric Nanogenerator Based On Biodegradable Cellulose Acetate Nanofibers

Sagar Sardana¹, Aman Mahajan^{1,*}

¹Material Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar 143005, India. *Corresponding author: aman.phy@gndu.ac.in

Abstract. The accelerated evolution of miniaturized electronics platform has been motivated the development of reliable, wearable and self-powered devices to reduce the dependence on external power source. In this work, the electrospun positive triboelectric layer of cellulose acetate nanofibers with significant triboelectric effect and biodegradable nature has been prepared and integrated with Kapton sheet to fabricate the flexible triboelectric nanogenerator (TENG). Herein, the fabricated TENG demonstrated the conversion of waste mechanical energy ranging from low to high frequency into an electrical energy.

INTRODUCTION

Recently, with the increasing demand of fiber-based miniaturized portable electronic devices, a research path to explore the applications of electrospun nanofibers (NFs) in wearable devices, sensor network, health monitoring, soft robotics etc. is opened¹. The emerging growth in novel technology of self-sustainable nanopower harvesting system creates a link between the fiber-electronic devices and ubiquitously available mechanical energy that could replace the traditional batteries². In this context, triboelectric nanogenerator (TENG) based on the principle of tribo-electrification and electrostatic induction has received significant attention due to its simple fabrication method, low-cost, diverse structural features and environment friendly nature³. It is used to scavenge bio-mechanical energy and then convert it into electrical energy for a superior and sustainable power source. Nowadays, researchers are highly interested to investigate the triboelectric properties based on flexible NFs instead of plane films⁴. High surface roughness and porous structure of NFs enhances the frictional contact area and triboelectric defects of material and hence, improves the TENG output performance.

In this work, in order to complement the benefits of NFs prepared using electrospinning technique, a flexible TENG based on cellulose acetate (CA) NFs was fabricated. Herein, electrospun CA NFs were chosen as positive triboelectric layers because of their strong triboelectricity and biodegradability. They were assembled with a Kapton sheet to obtain a triboelectric pair and further investigated under the application of different tapping frequencies and external loads. The as-fabricated flexible TENG with high output power density proposes a great potential in wearable devices to reduce the external supply dependency.

EXPERIMENTAL PROCEDURE

At first, a polymer solution was prepared by dissolving 2.85 g of CA in a 15 mL solution of acetone/DMF (2:1 v/v) under constant stirring for 2 h. Then, as-prepared CA solution was loaded into a 5-mL syringe and electrospun at high voltage supply of 17 kV, pump-flowrate of 0.7 μ L/s and drum rotation speed of 1200 rpm.

The characteristic absorption bands of NFs were observed on Perkin Elmer Frontier Fourier transfer infrared-spectroscopy (FTIR) spectrometer in the wavenumber range of 500-4000 cm⁻¹. Field emission scanning electron microscopy (FESEM) was conducted to determine the surface morphology and fiber diameter. The output electrical characteristics of TENG were measured using a home-made tapping instrument and Keysight digital storage oscilloscope (DSO1052B)

RESULTS AND DISCUSSION

FESEM image (Fig. 1) shows that the electrospun CA NFs are of 500 ± 120 nm diameter with rough surface which could result in the large frictional contact area for effective triboelectric performance.



Fig. 1. FESEM image of CA NFs

As shown in fig. 2, the FTIR spectra confirms the functional groups OH (3412 cm^{-1}), C=O (1752 cm^{-1}), C=CH₃(1372 cm^{-1}) and C=O=C (1211 cm^{-1}) of CA NFs.



Fig. 2. FTIR spectra of CA NFs

The basic structure of TENG consisted triboelectric materials, where CA NFs as positive triboelectric layer and a Kapton sheet as negative triboelectric layer due to difference in their charge densities. The influence of tapping frequency on the output performance of TENG was investigated as shown in fig. 3. The results indicate that the output voltage increases to 10 V, 19 V and 37 V as the tapping frequency changes between 3 Hz, 6 Hz and 9 Hz, respectively. The observed increase in output voltage with tapping frequency is attributed to the greater charge transfer between the triboelectric pair. Based on the results, further increase in tapping frequency i.e. 10 Hz decreases the output performance of TENG due to the surficial properties of tribo-induced charges.



Fig. 3. Dependence of output voltage of Kapton-CA NFs combination based TENG on tapping frequency.

To expand the practical working of TENG, the dependence of output performance on the external

resistance load is demonstrated in fig. 4. The output voltage increases with the rise in external load while the output loading current exhibits opposite trend due to ohmic losses. Under the application of 9 Hz tapping frequency, the instantaneous power density of TENG reached to a value ~284.44 mW/m² across the external load of 10 M Ω .



Fig. 4. Dependence of output voltage, current and power density of Kapton-CA NFs combination based TENG on resistance load.

CONCLUSION

In summary, this case study focused on a novel energy harvesting method based on electrospun TENG. Utilizing the porous structure of NFs, the influence of tapping frequency on the triboelectric performance has been evaluated. The fabricated TENG exhibits the maximum power density of ~284.44 mW/m² at the tapping frequency of 9 Hz and 10 M Ω . We believe that the as-proposed CA NFs based TENG with high flexibility holds a great significance in the development of smart, wearable and self-sustainable electronic devices.

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CdS incorporated polyaniline:High Performance Polymer Based Thermoelectric Composite for Green Energy Harvesting

Ajit Debnath¹, Krishna Deb¹, Jayanta Das¹ and Biswajit Saha^{1*}

¹Department of Physics, National Institute of Technology Agartala, Jirania 799046, West Tripura, India

*Corresponding author: biswajit.physics@gmail.com

Abstract

Improved thermoelectric (TE) performances with reduced hopping barrier potential have been achieved in hybrid system of CdS incorporated polyaniline (PANI/CdS) composites through an in-situ chemical polymerization technique, for next-generation green energy sources. For exploring the physical properties of the prepared materials XRD patterns and UV-Vis spectra were analyzed. The well-ordered chain packing of PANI and the reduction of carrier hopping barrier with CdS incorporation in the PANI system enhanced the carrier conduction and lead towards better TE properties of this composite. At 100 $^{\circ}$ C of the hot end, the highest value of TE power factor (PF) for the composite is found to be 2.61 μ W/mK². The results indicate that PANI/CdS composite can appear an effective and novel material with improved TE properties of conductive polymers.

Mechanical Energy Harvesting by Magnesium Salt-Modulated Poly(vinylidene fluoride) Electrospun Nanofibers

Biswajit Mahanty^{1,2}, Sujoy Kumar Ghosh¹, Santanu Jana³, Subrata Sarkar¹ and Dipankar Mandal^{4,*}

¹Department of Physics, Jadavpur University, Kolkata 700032, India

²Department of Electronics & Communication Engineering, Ramgarh Engineering College, Murubanda, Ramgarh,

Jharkhand 825101, India

³Department of Electronics, Netaji Nagar Day College, Kolkata 700092, India ⁴Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India ^{*}Corresponding author: dmandal@inst.ac.in

Abstract

In this work, piezoelectric nanogenerator (PNG) is fabricated by hydrated metal salt (MgCl₂•6H₂O) (Mg-salt) reinforced polyvinylidene fluoride (PVDF/Mg) nanofibers (NFs) as an active layer and interlocked conducting micro-fiber mats as top and bottom electrodes. The prepared electrospun PVDF/Mg composite NFs having higher content of electroactive phases (i.e., F_{EA} ~ 98 %) than that of pure PVDF NFs. As a result, the fabricated PNG generates ~7 V open circuit output voltage under 8 kPa of finger imparting stress.

Introduction

Now a day, in the era of Internet of Things (IoT), numerous numbers of sensors have been used for all the time. In real time applications need constant source of power supply as battery to run the sensors but battery has a limited life time and frequently recharging and replacing is required which is a tedious job and also battery contains some lead base constraints and chemicals that are also vulnerable to the environment. In this present scenario the selfpowered sensors/devices are of prime interest. This purpose is achieved using mechanical energy harvester called nanogenerators (NGs).^{1,2} In this condition, piezoelectric materials are ideal candidates as they require no external bias to operate. From materials point of view, in contrast to the several inorganic and semiconducting materials, ferroelectric polymer poly(vinylidene fluoride) (PVDF) and its copolymers are highly suitable for flexible electronics owing to their excellent properties of flexibility, light weight, chemical resistivity, large area processing feasibility and environmental friendly (lead free).¹ Normally, PVDF has got four distinct crystalline polymorphs, such as α -, β -, γ - and δ -phases.¹⁻³ Among them, the β -phase (TTTT conformation) is polar and uniaxial ferroelectric.

In this work, Mg-salts induced enhanced β -phase nucleation in electrospun PVDF nanofibers (NFs) is reported in a one-step technique. Thus, we have fabricated electrospun PVDF/Mg NFs and observed the performance of the fabricated nanogenerator (PNG).

Experimental Section

Materials:

Poly(vinylidene fluoride) (PVDF) pellets (Sigma Aldrich, USA). Magnesium chloride hexahydrate (MgCl₂. 6H₂O), N,N-dimethyl formamide (DMF, 99.5% of purity) and acetone (Merck Chemical, India).

Fabrication of PVDF/Mg NFs: In order to prepare PVDF solution, PVDF pellets were dissolved in 2:1 volume ratio of DMF/acetone at a polymer/solvent concentration of 12 % w/v and to prepare PVDF/Mg salt NFs, the 1.5 wt% of Mg-salt was added to the solution. The electrospinning process was performed under applied electric field across the metal tip and collector was 1 kVm⁻¹ and solution was injected at a constant rate of 0.6 ml h⁻¹. Finally, the NFs mats were collected onto the Al foil and the NFs generated from PVDF/Mg salt solution and pure PVDF are termed as PVDF/Mg and neat PVDF NFs respectively.

Device fabrication:

A sandwich like piezoelectric nanogenerator (PNG) is fabricated as shown in (Fig.1a). The nanogenerator fabricated from neat PVDF NFs is named as a control PNG.

Materials characterizations:

For material characterization Field Emission Scanning Electron Microscopy (FE-SEM) (FEI, INSPECT F 50) and Fourier transform infrared spectroscopy (FTIR) (TENSOR II, Bruker) was used. The open-circuit output voltage from the nanogenerator is measured using a digital storage oscilloscope (Agilent, DSO3102A).

Results and Discussions

The field-emission scanning electron microscopy (FE-SEM) image with the corresponding histogram profile of the PVDF/Mg NFs is depicted in Fig. 1b. It is found from the fiber diameter distribution plot the average diameters of the fibers are ranging from 30 to 169 nm with the maximum numbers of fibers having diameter of 56 nm. The FT-IR spectra of neat PVDF as well as PVDF/Mg NFs are shown in Fig. 1c and the respective vibrational bands are marked according to the presence of crystalline phases in the region of 1600-600 cm⁻¹. The neat PVDF NFs contains nonpolar α -phase (at 764 cm⁻¹) and polar β -, γ -phases (at 1277 and 1234 cm⁻¹ respectively.¹⁻³ However, the PVDF/Mg NFs does not contain any characteristic vibrational bands of a-phase but containing only polar β - and γ -phases. It is observed that neat PVDF and PVDF/Mg both NFs contains 841 cm⁻¹ vibrational band, which represents the existence of β and γ -phases simultaneously. The relative proportion of electroactive β - and γ -phases (F_{EA}) was estimated by Beer-Lambert law of absorbance.¹⁻³ Thus, the estimated F_{EA} for neat PVDF NFs is ~84% whereas in the case of PVDF/Mg NFs, $F_{EA} \sim 98\%$.



Fig. 1. (a) 3-D design of the prepared PNG device. (b) Surface morphology of the PVDF/Mg nanofibers and its fiber diameter distribution plot in the inset. (c) FT-IR spectra of the nanofibers. (d) Characterization of output performance of the PNG under repetitive human finger imparting force. (e) Capacitor charging performance of the PNG.

Electrical characterization of the PNG is shown in Fig.1 d and e. The repetitive finger imparting stress (σ_a) of 8 kPa is applied over 6 cm height to both the control PNG as well as PNG. As a result of that, the PNG generated more voltage (~7 V) than that of the control PNG (~ 2.8 V). The average mechanosensitivity S_M ~0.87 V kPa⁻¹ has been estimated to quantify the dynamic mechanical stimuli sensing ability^{1.4}. In the interest of demonstrating the practical application of the PNG, the device is connected externally to a capacitor (C~1.0 µF) and charging up under a periodic finger imparting stress amplitude (σ_a) of 8 kPa (see Fig.1e). Finally the capacitor has been charged to ~6.0 V in 90 sec. The power (P) and stored energy (W) are calculated as,

$$P = \frac{CV_s^2}{2t}$$
 ii)

and $W = \frac{CV_S^2}{2}$ (iii), where C is the capacitance of the capacitor, V_S is the

where C is the capacitance of the capacitor, v_s is the saturation voltage, and t is the time required to reach the saturation voltage.^{2,3} So, the estimated power and stored energy are 0.2 μ W and 18 μ J respectively. Under repetitive finger imparting, the PNG can charge a commercial capacitor of 1 μ F ~6.0 V in a short time interval of 90 s.

Conclusions

In summary, we have demonstrated Mg-salts induced enhanced β -phase nucleation in electrospun PVDF nanofibers (NFs) in a one-step technique. The fabricated device, i.e. PNG generated 7 V open circuit output voltage under 8 kPa of stress amplitude with estimated $S_M \sim 0.87$ V kPa^{-1.}

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Tailoring PEDOT:PSS passivation property by ethylene glycol for PEDOT:PSS/Si solar cells

Avritti Srivasatava^{1,2}, Deepak Sharma^{1,2}, Anjali Saini, P. Prathap^{1,2}, S.K. Srivasatava^{1,2)*}

¹Photovoltaic Metrology Section, CSIR-National Physical Laboratory, New Delhi-110012, India ²Academy of Scientific and Innovation Research (AcSIR), CSIR-NPL campus, New Delhi-110012, India *E-mail: <u>srivassk@nplindia.org; sksrivastava78@gmail.com</u> (S.K. Srivastava)

Abstract

Conductive polymer PEDOT:PSS is known as an effective hole transport layer in organic optoelectronics PEDOT:PSS/Si hybrid solar cells (HSCs). It also serves as the surface passivation layer for silicon (Si) thereby reducing the interface recombination losses in the PEDOT:PSS/Si HSCs. However, the mechanism of passivation is not fully established. For better understanding of the role of PEDOT:PSS in Si surface passivation, a systematic investigation of minority carrier lifetime (MCL) for different doping of ethylene glycol (EG) in PEDOT:PSS is performed on PEDOT:PSS/micro-textured-n-Si/PEDOT:PSS symmetric structure made by spin coating of PEDOT:PSS. The PEDOT:PSS coated Si exhibited an enhanced (~20 folds) value of MCL (~53µs) as compared to that of bare micro-textured Si (~2.5µs) for an optimum EG concentration (7wt%). Further increase in EG concentration has adverse effect on the passivation which is attributed to the segregation of PSS due to excess EG in the matrix. The passivation property of PEDOT:PSS on Si is further demonstrated by detailed quantum efficiency analysis of the Ag/PEDOT:PSS/Si/In:Ga HSCs prepared with different EG concentration.

Introduction

Contemporary organic-inorganic hybrid solar cells (HSCs) concept, particularly, PEDOT:PSS/Si (poly (3,4-ethylenedioxythiophene): polv (styrenesulfonate) as hole transport layer and n-Si as absorber) based HSCs have drawn much attention due to low-cost processing and reasonable performance. Theoretically, the HSCs have potential to achieve photoconversion efficiency (PCE) comparable to that of a conventional Si solar cell [1]. However there exists a large discrepancy in the performance of the device due to its dependency on several parameters like property of PEDOT:PSS, secondary dopants, quality of Si wafers, device design, dimensions, and so on. Tuning PEDOT:PSS electrical conductivity via secondary dopants like ethylene glycol (EG) is explored by many researchers and shown that PEDOT:PSS also act as the surface passivation layer for Si thereby reducing the interface recombination losses in the PEDOT:PSS/Si HSCs [1, 2]. However, the mechanism of passivation and the role of EG has not been explored. Tailoring the passivation property of PEDOT:PSS on Si through EG is investigated for the first time.

Here, influence of EG doping on the passivation property of PEDOT:PSS for the micro-textured n-Si (T-Si) surfaces is reported. A systematic investigation of minority carrier lifetime (MCL) is performed on PEDOT:PSS/T-Si/PEDOT:PSS symmetric structure made by spin coating of PEDOT:PSS with different doping of EG. The PEDOT:PSS coated Si exhibited an enhanced (~20 folds) value of MCL as compared to that of bare T-Si for an optimum EG doping (7wt%) and has adverse effect in case of excess EG. The passivation property of PEDOT:PSS on Si is further demonstrated by detailed quantum efficiency analysis of the Ag/PEDOT:PSS/Si/In:Ga HSCs prepared with different EG doping.

Experimental and characterization

PEDOT:PSS solution blend with different EG concentration (0, 2, 7, 12 wt%) is prepared in ultrasonicator bath with equal amount of iso-propyl alcohol (IPA). Details of fabrication of HSCs on T-Si has been discussed in our earlier work [1]. The surface passivation property of the PEDOT:PSS layer on the T-Si surface was evaluated by Sinton's tool (WCT-120). Quantum efficiency (QE) measurements of the HSCs were carried out under standard test conditions using M/s Bunkoukeiki (Model: CEP-25HS-50) make system. The HSCs made for different EG are named as HSC-xEG, where 'x' indicates the EG concentration (wt%) in PEDOT:PSS.

Results and discussion

The MCL and the effective surface recombination velocity (S_{eff}) estimated from the corresponding MCL values for micro-textured Si surfaces with different EG doped PEDOT:PSS coating and that with without PEDOT:PSS coating are presented in **Fig.1**. All the process parameters and measurements conditions are identical for both the set of samples except variation of the EG in PEDOT:PSS. The MCL measurements are performed at carrier injection of $5x10^{14}$ cm⁻³.



Fig. 1. Comparative MCL and S_{eff} for different EG doped PEDOT:PSS on micro-textured Si (inset: Symmetric structure of sample prepared for the MCL measurements)

The S_{eff} is calculated through the measured MCL value by following expression,

$$S_{eff} = \frac{W}{2*MCL}$$
(a)

Where 'W' is the wafer thickness~180µm.The unpassivated Si surface exhibits very poor MCL (~2.5µs) while it increases ~12 folds (29.2 µs) after coating PEDOT:PSS (without doping, i.e. 0-EG). The electrochemical oxidation mechanism at the PEDOT:PSS/Si interface is attributed to the chemical passivation property of the PEDOT:PSS film [3]. The MCL reaches a maximum value of ~53µs corresponding to 7wt% of EG concentration and achieve the minimum S_{eff} ~372.9cm/s value. However, on further increase in EG concentration in PEDOT:PSS (e.g. 12wt%), the MCL is reduced (~26.5us) drastically. The excess EG doping in PEDOT:PSS probably causes the segregation of PSS which affect the continuity and conformality of the PEDOT:PSS thin film on textured Si and hence the passivation. Further, Ag/PEDOT:PSS+xEG/T-Si /In:Ga structured HSCs were fabricated for different EG concentrations. The EQE of the HSCs are shown in Fig. 2. Here, the PEDOT:PSS is coated on the front side (facing the incident light) of the device and rear side is unpassivated. The QE in the low wavelength range (300-450 nm) are increased significantly for optimized EG (7wt%) based HSCs which confirm the improved front surface passivation of Si by PEDOT:PSS as compared to no EG or excess EG based HSCs (see Fig. 2). The OE in the higher wavelength ranges (>950 nm), a measure of rear surface passivation, is almost similar for all the cells irrespective of EG doping indicating unpassivation of the rear surface. The observed enhanced QE for the optimized EG doping in entire visible spectrum further indicate the efficient charge conduction and collection. Therefore, the optimum

EG in PEDOT:PSS facilitates the efficient PEDOT conducting chain for charge transfer with optimum PSS to maintain the PEDOT suspension aq. PSS while retaining its passivation property.



Fig. 2. EQE response of the PEDOT:PSS/Si HSCs with different EG doping (inset: Schematic of the Device)

Table 1	. Passiva	tion throug	h EG con	centration	variation

Sample Name	MCL (µs)	S _{eff} (cm/s)	EQE (%) (300-500nm)			
T-Si	2.53	7905.5	-			
0-EG	29.26	683.5	60			
2-EG	34.41	581.2	60			
7-EG	53.62	372.9	80			
12-EG	26.46	755.8	70			

Conclusions

Surface passivation property of PEDOT:PSS for Si surface is tailored as a function of EG doping. The surface recombination velocity as low as 370 cm/s is achieved for an optimum EG concentration (7wt%) in PEDOT:PSS. The structural rearrangement in PEDOT:PSS matrix caused by EG is attributed for EG dependent passivation properties. The enhanced passivation effect is further confirmed by the improved QE (~80%) in the low wavelength range, primarily caused by reduced recombination losses at PEDOT:PSS/Si interface (front surface).

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Fabrication of efficient PEDOT:PSS/Si hybrid solar cell with 'Back PEDOT:PSS' geometry

Premshila Kumari^{1,2}, Avritti Srivastava^{1,2}, Ruchi K. Sharma^{1,2}, Sanjay K. Srivastava^{1,2)*}

¹Photovoltaic Metrology Section, CSIR-National Physical Laboratory (NPL), New Delhi-12, India ² Academy of Scientific and Innovative Research (AcSIR), CSIR-NPL Campus, New Delhi-12, India

*E-mail: sksrivastava78@gmail.com; srivassk@nplindia.org

Abstract

Organic conjugated polymer, PEDOT:PSS and silicon based hybrid solar cells (HSCs) have drawn a significant attention towards efficient and cost effective silicon solar cells. A lot of studies have been dedicated to front PEDOT:PSS device geometry wherein the PEODT:PSS is coated on the Si surface facing the incident light (front side). The PEDOT:PSS acts as an effective hole transport layer as well as passivation layer. However, degradation of PEDOT:PSS caused by environment and the radiation (photo-induced) in such device geometry is a major concern. Here, the hybrid solar cell with inverted structure, Ag/(n-Si/PEDOT:PSS/Ag is fabricated in which PEDOT:PSS is coated on the rear side of the micro-textured Si surface. Maximum power conversion efficiency (PCE) of ~ 2.18% with open circuit voltage (V_{oc}) of 384 mV and short circuit current density of 13.08 mA/cm² is achieved. The results are preliminary yet encouraging and require extensive optimization of the parameters. Nevertheless, the 'Back PEDOT:PSS' concept has potential for high PCE and better stability as it provide easy processing with additional advantage of reduced parasitic losses of 'Front PEDOT:PSS' geometry.

Introduction

Hybrid solar cells (HSCs) are the bright candidate to make solar cell technology more cost effective and easy processing. In HSCs, the crystalline Si is used as active material and the organic layer as hole transport layer (HTL). PEDOT:PSS is a most favorable hole transport material on c-Si due to its high transparency, suitable work function and easy solution processing. Pietsch et al. investigated the planar hybrid PEDOT:PSS/n-Si solar cell interfaces with open circuit voltage (V_{oc}) upto 645 mV and power conversion efficiency (PCE) of 12.6% [1]. Although, HSCs on planar Si achieved a great PCE but it limits the performance due to poor absorption of incident light. So, the microengineering of Si surface is a promising technique for effective light harvesting to improve the PCE of HSCs. Front coated PEDOT:PSS on micro-textured Si surface has been demonstrated in our earlier work with PCE of 12.29% [2]. In this device structure, PEDOT:PSS is used as HTL and effective passivation layer. However, due to parasitic absorption of the thick PEDOT:PSS film and environment and radiation induced degradation, the 'Back PEDOT:PSS' with full coverage of the Ag contact is a promising approach. With this geometry, PCE of >16% efficient HSCs having 200 nm of PEDOT:PSS layer in back junction is reported [3].

Here, an inverted structure of HSCs with device configuration $Ag/\mu T$ -Si(n⁺)/PEDOT:PSS/Ag is demonstrated. The 'Back PEDOT:PSS' structure has potential to improve the light utilization, charge collection properties and device stability. The microtexturing of the Si surface is done by conventional KOH texturing method [2]. To facilitate the Ohmic contact of Ag with Si on front surface, front side of the n-Si wafer was diffused with phosphorus (P) to make highly doped thin n^+ layer.

Experimental

As-cut solar-grade n-Si wafers (thickness: $180\pm20\mu$ m, 1-3 Ω cm) have been used in the present work.



Fig. 1. Schematic of back PEDOT:PSS hybrid solar cell with the configuration $Ag/n^+/\mu$ T-Si/PEDOT:PSS/Ag.

The device was fabricated via following steps, (i) conventional cleaning, followed by micro-textruing in aq. 2 wt% KOH solution at ~75°C for 60 min to get symmetrical surface on both sides as shown in fig.1 (a) schematically. (ii) Making of thin n^+ layer diffusion of P on front side of the textured Si at 850 °C using the spin coated spin-on dopant (P507). (iii) Deposition of Ag grid pattern (front electrode) on

front (n^+-Si) side. (iv) PEDOT:PSS coating on the rear surface via spin coating as in fig 1(c). (v) Finally, deposition of Ag layer on rear side as back electrode (full area) by thermal evaporation. The schematic of the HSCs is shown in the fig. 1(d). The solar cell performance parameters of the HSCs were measured under the standard test conditions.

Results and Discussion

Dark and illuminated J-V characteristics of the four 'Back PEDOT:PSS' HSCs are shown in fig. 2 (a) and (b) respectively. Dark J-V characteristics indicate the formation of Schottky (rectifying) junction in all the cells. The best diode behavior was obtained for cell-2 with diode ideality factor (n) of ~3.5 and dark saturation current (J_o) is 42 x 10⁻⁶ A/cm² respectively. These values indicate that it requires further optimization of all the processing parameters to improve the diode characteristics.



Fig. 2. (a) Dark J-V characteristics, and (b) Illuminated J-V characteristics for Back PEDOT:PSS/Si hybrid solar cell.

The short circuit current density (J_{sc}) and V_{oc} of the cells are in the range of 12-15 mA/cm² and 235-385 mV respectively. The values of fill factor (F.F.) of all the cells are quite poor. The best PCE (η) of 2.18% is obtained for cell-2 with J_{sc} of 13.08 mA/cm², V_{oc} of

384 mV and F.F. of 44%. The performance parameters of all the HSCs are summarized in table 1. Such a low performance of the cells is expected to be due to the large series resistance (R_s) and very low shunt resistance (R_{sh}) (e.g. for cell 2: $R_s = 18.62 \Omega$, $R_{sh} = 476.55 \Omega$) and the recombination losses in the unpassivated front surface side caused by heavy dopant diffusion (n^+) region. The large flux of the UV and visible light are absorbed in the top few microns of the Si and an unpassivated front surface (n⁺) region can have adverse effect on the collection of generated charge carriers due to very high front surface recombination. Therefore, front surface passivation in such Back PEDOT:PSS (back junction) and high diffusion length of the charge carriers (higher quality Si wafers) are primary requirements for improving the performance in addition to optimization of the device design and process parameters. Nevertheless, the concept of 'Back PEDOT: PSS hybrid solar cell' is demonstrated here which are subjected for further investigation for high PCE.

 Table 1. Photovoltaic parameters of 'Back PEDO:PSS'

 hybrid solar cell.

Cell No.	Voc (mV)	Jsc (mA/cm ²)	FF	η(%)
1	236	10.03	0.31	0.73
2	384	13.08	0.44	2.18
3	205	10.78	0.33	0.73
4	283	8.38	0.25	0.59

Conclusions

The concept of 'Back PEDOT:PSS' based HSCs has been demonstrated with encouraging preliminary results. The concept has potential for high PCE and better stability as it provide easy processing with additional advantage of reduced parasitic losses of 'Front PEDOT:PSS' geometry. However, the front surface passivation in such back junction cell and higher quality Si wafers are the keys for improved performance in addition to optimization of the device design and process parameters.

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Tea leaf derive carbon dots for high performance Supercapacitor Debabrata Mandal¹, Lalit Bharti², and Amreesh Chandra³

¹School of Nanoscience and Technology, ²Department of Physics, Indian Institute of Technology.Kharagpur Kharagpur, West Bengal -721302, India

*Corresponding author: achandra@phy.iitkgp.ac.in

Carbon dots quantum dots (CQDs) are fast emerging as next generation nanomaterial for applications ranging from optoelectronic, biomedical to energy field. We present a novel synthesis protocol, to prepare carbon dots quantum dots (CQDs). The prepared CQDs have dimensions in the range of 10-20 nm, as confirmed by TEM and AFM analysis. The graphitic phase formation was confirmed by XRD and Raman analysis. The results clearly show that the materials can be used as electrode materials in energy devices. The electrochemical performance of CQD, in combination with 3M KOH, show that the supercapacitors with specific capacitance as high as ~ 82 F/g and low equivalent series resistance can be obtained. The fabricated symmetric device exhibited a maximum specific capacitance of 44 F/g at 1 A/g current density, with an excellent energy density of ~ 11.2 Wh/kg, along with a power density of ~ 0.5 kW/kg at 1 A/g current density. The symmetric device continues to deliver high coulumbic efficiency and excellent capacitance retention even after 3000 cycles. The results establish a new protocol for the carbon based material synthesis of CQDs from waste tea leaf.

1.Introduction

Supercapacitors have gained attention because of their high specific capacitance, long cycle life and high power density. Depending upon the charge storage mechanism and cell configuration, supercapacitor can be classified into three different categories i.e. electric double layer capacitors (EDLCs), pseudocapacitor and hybrid capacitor. Carbon based material like activated carbon, carbon sphere, graphene and carbon quantum dots (CQDs) primarily shown EDLC type behavior. In the case of EDLCs, charging process is a direct consequence of the adsorption of ions of electrolytes onto the electrode material. No Faradic reaction is involved here. Electric double layer is created due to the charge separation at the electrode-electrolyte interface and most of the charges are stored near the surface of the electrode. Though EDLC can show better performance because of fast uptake and release of charges, it has a limitation associated maximum energy density that can be obtained. CQDs have better surface area via π - π conjugated network because of the structure is based on graphite layers [1]. CQDs have shown major advantages such as lower toxicity, better resistance to photo response and better biocompatibility, in comparison to commercial organic dyes and/ or traditional semiconductor quantum dots (for example, CdS and CdTe, SnO₂). The high surface area and pore size studies clearly show that CQDs can be used as electrode materials in energy devices and it is also a low cost and environmental friendly material for supercapacitor applications.

2.Results and Discussion

Tea leaf was successfully carbonized by the pyrolysis method. The black powder was added in



Fig1. XPS and TEM image of CQDS

DMF solution, with 1:8 concentration ratio, in the solvothermal chamber for 160^oC for 10hr. The XRD of CQDs show a wide (002) peak, suggesting that carbonizing tea leaves were leading to graphite structures. Raman data shows the characteristic peaks viz., D band (1312 cm⁻¹) and G band (1420 cm⁻¹). The



Fig2. CV and CD result of CQDS in 3M KOH

ratio of the peak intensity of D band and G band was 0.85, which is a measure of the defects. XPS data showed that obtained CODs exhibit absorption of carboxyl group and hydroxyl group, as shown in Figure 1(b). The surface topography of GQDs was studied using the atomic force microscopy (AFM) in tapping mode. The heights of pristine CQDs were mostly distributed in the range of 1.0-3.2 nm, respectively. TEM micrograph of CQDs diameter are between 2 to 5.5 nm, as shown in Figure 1(a). TEM images further confirmed the formation of quantum dots. The high resolution TEM micrograph of GODs indicated highly crystalline structure with inter planar spacing of 0.34 nm, which is similar to (002) peak of graphitic carbon. The particle size of CQDs was 6 nm, which corroborated TEM results.

In this work, we used 3M KOH as electrolyte and studied electrochemical behaviour using cyclic voltammetry(CV) and charge discharge(CD) measurement in 0V to -1V stable window. The three electrode configuration measurement data is shown in Figure 2. CQDs is a showed EDLC type behavior in KOH electrolyte. It showed linear and symmetrical

shape of galvanostatic charge discharge curves, indicating excellent charge transfer process. Size effect increases the active sites for the ion diffusion between CQDs electrode and electrolyte interface [2]. The specific capacitance values for CQDs was found to be 56 F/g for 3M KOH electrolyte at 5 mV/s scan rate. In KOH solution, CQDs based electrode showed a higher EDLC capacitance value because of fast interaction between K⁺ ions and the electrode interface.In galvanostatic charge-discharge curve, linear region were observed. The linear region implies that the electrode stored the charges based on adsorption-desorption reactions at the electrode surface. Galvanostatic charge discharge curves for CQDs, with different concentration, taken at different current densities from 1A/g to 7.5A/g in 3M KOH electrolyte solutions. The maximum specific capacitance value of CQDs electrode was 110 F/g from CD curves at 1A/g current densities. The fabricated symmetric device exhibited a maximum specific capacitance of 44 F/g at 1 A/g current density with an excellent energy density of ~11.2 Wh/kg along with a power density of ~ 0.5 kW/kg at 1 A/g current density. Nearly 92.8% of the specific capacitance was retained even after 3000 chargedischarge cycles. The Coulombic efficiency was estimated to be ~91% for the electrodes, at higher current density. The calculated R_{ct} values from EIS measurements was ~ 1.30Ω . The lower charge transfer resistance could be attributed to the enhanced diffusive resistance of negative ion at the carbon based electrode.

3.Conclusions

Tea leaf derive carbon dots were successfully synthesized using pyrolysis and solvothermal methods. The CQDs were successfully characterized by different physiochemical technique and their electrochemical properties in 3M KOH were insvestigated electrolytes. CQDs delivered maximum specific capacitance of 110 F/g at 1A/g current density. The fabricated symmetric supercapacitor device with 1.2 V operating voltage window, was delivered high specific capacitance of nearly 56F/g along with specific energy of 16.48 Wh/Kg a power density of ~0.5 kW/kg at 1 A/g current density.

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Frequency dependence of dielectric properties of modified BCZT lead-free ceramic

Sapna Kumari^{1,2,*}, Amit Kumar^{1,2}, V. Kumar², and Anil Arya³

¹Department of Physics, Kurukshetra University, Kurukshetra- 136119, India ²Department of Physics, Institute of Integrated & Honors Studies (IIHS), Kurukshetra University, Kurukshetra- 136119, India ³Department of Physics, Central University of Punjab, Bathinda- 151001, India

*Corresponding author: ydvsapna37@gmail.com

Abstract

In this research work, $Ba_{0.965}Bi_{0.01}Ca_{0.02}Zr_{0.02}Ti_{0.976}Cu_{0.008}O_3$ (BCZTCuBi) lead-free ceramic has been manufactured by the solidstate reaction method, and its structural and dielectric properties were observed. SEM technique has been used to characterize the microstructural properties of the ceramic and observe a dense microstructure with non-uniform grain size distribution. Further, to understand the role of frequency and polarization contributions to dielectric properties, frequency dependent dielectric analysis of the ceramic sample has been done. Dielectric properties have been studied at different frequencies within the 18 °C to 190 °C temperature range and observed that dielectric permittivity (ε) decreases with the increase in frequency while Curie temperature remains unchanged.

A Facile Hydrothermal Route For Synthesizing Beta-NiS And Its Electrochemical Performance

M. P. Harikrishnan, Manisha Patro and A. Chandra Bose*

Nanomaterial Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli-620015

*Corresponding author: acbose@nitt.edu

Abstract

In this work, the β -NiS nanoparticles are synthesized by a hydrothermal process. The structural study of the sample is analyzed by X-ray diffraction (XRD). Apart from that, in order to investigate the electrochemical performance of the as-prepared material, we carried out electrochemical studies, that is, cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS). The XRD of the sample confirmed the formation of β -NiS. The study of CV revealed the presence of redox peaks suggesting the faradic reaction taking place at the interface of electrode/electrolyte. The GCD analysis shows that the as-prepared electrode has high specific capacity (194 Cg⁻¹ at 1 Ag⁻¹) in 1 M KOH as electrolyte. Further, the EIS analysis suggested the material has good conductivity. The better electrochemical performance of β -NiS electrode is a future aid to energy field.

Li Based Quaternary Heusler Compound LiTiCoSn: A Search of New Thermoelectric Material by First Principle Studies

Jaspal Singh¹, Kulwinder Kaur², Shakeel Ahmad Khandy³, Megha Goyal⁴, Shobhna Dhiman⁵, and SS Verma⁶

¹Department of Physics Mata Sundri University Girls College, Mansa-151505 (Pb), India ^{2,5}Department of Applied Sciences Punjab Engineering College, Chandigarh (160012), India ³ Department of Physics, National Taiwan University-Taipei 10617, Taiwan ^{4,6}Department of Physics Sant Longowal Institute of Engineering and Technology (Deemed University), Longowal-148106, Sangrur (Pb), India

*Corresponding author: jaspalsliet@gmail.com

Abstract

In the present research work we explore the structural, electronic, vibrational and thermoelectric properties of a new Li-based quaternary Heusler compound LiTiCoSn, which is recently proposed by Jiangang He et.l. [Chem. Mater. 30 (2018) 4978] that is obeying the 18-valence electron rule. Here the theoretical research work is performed within the approach of density functional theory (DFT) and the semi-classical Boltzmann transport equations at the constant relaxation time approximation. The maximum figure of merit (ZT) recorded is 0.16 at 700 K temperature. As the compound is first time reporting here; the investigations can be the fertile ground to study the material experimentally as well as in the practical era of energy conversion techniques.

Temperature dependence of Raman spectra of Halide perovskites: Cs₂AgBiCl₆ and Cs₂AgInCl₆

Bikash Sahoo, and P.A. Bhobe

Department of Physics, Indian Institute of Technology Indore, Simrol, Indore, 453552

*Corresponding author: phd1901151008@iiti.ac.in

Abstract

Halide double perovskite has been attracting attention from the researchers due to its stability and fascinating properties. The potential application of these materials largely depends on temperature of the system, studies related to this aspect are few in number. Using the temperature dependent Raman spectroscopy measurements, we study the phonon decay process of two presently popular halide double perovskites, Cs₂AgBiCl₆ and Cs₂AgInCl₆, and the preliminary results are presented here.

Introduction

Halide double perovskites (HDPs) have received significant attention from the research community due to their structural stability and wide range of optoelectronic applications. Amongst several combination of chemical formulation, the lead free inorganic HDPs are being actively investigated for its non-toxicity and environmental friendliness. In such A₂B'B''X₆, the A cation is generally Cs⁺ or Rb⁺, B' and B" constitute of monovalent (Ag⁺) and trivalent $(Bi^{3+}, In^{3+}, Sb^{3+})$ cations respectively, while $X = Cl^{-}$, Br⁻ or I⁻. Electron-phonon interaction is an important phenomenon in perovskite, which affects both electronic and optical properties [1]. Therefore, a brief study on the temperature dependent Raman spectra for two HDPs Cs₂AgBiCl₆ and Cs₂AgInCl₆ have been undertaken here and the results are discussed.

Experimental details

Cs₂AgBiCl₆ and Cs₂AgInCl₆ were synthesized by co-precipitation method and annealed at 210°C before further characterization [2]. The prepared samples were characterized by Rigaku X-ray diffractometer with Cu K_a radiation (λ =1.54°A), Raman spectrometer (Horiba Labram) using 633 nm laser source, and the UV-Vis-NIR spectrometer (Shimadzu UV-3600i) in the wavelength range 200-1000 nm.

Result and discussion

Structural refinements of the measured XRD data of the two HDPs were carried out in Fullprof suite using the Rietveld method, as shown in fig. 1. All the peaks obtained for both the compounds can be indexed to cubic structure with space group Fm-3m. The lattice parameter is found to be $10.78^{\circ}A$ and $10.48^{\circ}A$ for Cs₂AgBiCl₆ and Cs₂AgInCl₆ respectively. In order to determine optical band gap of the compounds the UV-Visible diffuse reflectance study was undertaken. The Kubelka-Munk equation is used to model the data as, $F(R) = (1-R)^2/(2R)$, R being the reflectance and F(R) is the optical absorption coefficient. A plot of $[F(R)hv]^n$ vs. hv, where n is $\frac{1}{2}$ for indirect transitions and 2 for direct transitions, is used to extract the gap. Thus a value of 2.68 eV was obtained as an indirect band gap for Cs₂AgBiCl₆, while Cs₂AgInCl₆ yields a direct band gap of 3.63 eV.



Fig. 1. Rietveld refinement of Cs₂AgBiCl₆ and Cs₂AgInCl₆ compounds.

Room temperature Raman spectra of $Cs_2AgBiCl_6$ exhibit 3 Raman active modes at 114 cm⁻¹ (T_{2g}) which corresponds to the breathing vibration of Ag-Cl bonds, 215 cm⁻¹ (E_g) due to the asymmetric stretching of Bi-Cl₆ octahedra and 283 cm⁻¹ (A_{1g}) due to the symmetric stretching of Bi-Cl and Ag-Cl bonds in the octahedral cages. Cs₂AgInCl₆ exhibit the Raman mode at 301 cm⁻¹ (A_{1g}) because of the symmetric stretching of In-Cl and Ag-Cl bonds, consistent with the other reported results [3]. Raman spectroscopy can be used to study electronphonon interaction, which is reflected in frequency shifting and FWHM of Raman modes. The temperature dependence of Raman modes can be analysed by fitting with the linear equation: $\omega = \omega_0 + \chi T$; where, ω_0 is the extrapolated peak position at 0 K, and χ is the first-order temperature coefficient.



Fig. 2. Temperature dependent Raman spectra for Cs₂AgBiCl₆ and Cs₂AgInCl₆ compounds.

Table 1. Parameters extracted from Raman shifting and FWHM of various modes of Cs₂AgBiCl₆ (CABC) and Cs₂AgInCl₆ (CAIC).

HDPs	CABC			CAIC
Mode	T _{2g}	Eg	A _{1g}	A _{1g}
ω0	110.68	221.32	285.82	303.13
(cm ⁻¹)	± 0.18	± 0.34	± 0.07	± 0.24
χ	0.0083	-0.0228	-0.0083	-0.0244
Γο	8.3 ±	10.6 ±	13.5 ±	8.7 ± 1.6
(cm ⁻¹)	0.4	0.9	1.8	
а	0.02832	-0.05114	0.02001	-0.09693
b	0.0006	0.0063	0.0124	0.0091

From table 1, it is observed that the first order temperature coefficient of T_{2g} mode of $Cs_2AgBiCl_6$ is positive, that means there is an increase in peak position towards higher frequency which denotes a contraction in Ag-Cl breathing vibration with increase in temperature. In contradiction, there is a shifting of Raman peak positions of E_g and A_{1g} modes of $Cs_2AgBiCl_6$ and A_{1g} mode of $Cs_2AgInCl_6$

towards the lower frequency which indicate that there is a stretching of bond length of B-X bonds.

The anharmonic effects of phonon decay processes can be described by the following equation: $\Gamma(T) = \Gamma_0 + a \left[1 + \frac{2}{e^{x-1}}\right] + b \left[1 + \frac{3}{e^{y-1}} + \frac{3}{(e^{y}-1)^2}\right]$ where, $x = \frac{\hbar\omega}{2kT}$ and $y = \frac{\hbar\omega}{3kT}$, and coefficients a and b represent the contributions of three and four-phonon processes, respectively [4]. The extracted parameters from the nonlinear fitting of Raman peak widths (fig. 3) using the above equation are given in the table 1. The parameter b is found to be very small which suggest that four phonon process is very weak in the compounds. The dominant contribution to the non-linear temperature dependence of the Raman spectra of various modes is thus due to the three-phonon anharmonic process.



Fig. 3. Nonlinear fitting of A_{1g} mode of (a) $Cs_2AgBiCl_6$ and (b) $Cs_2AgInCl_6$ compounds.

Conclusion

The broadening of the linewidth can be explained using the phonon decay processes. A detailed study on local crystal structure by Raman spectra has provided an idea about the thermal effect on crystal lattice and phonon decay process. The electron-phonon interaction is investigated by the temperature dependent Raman study and three phonon process is found to be significant in these HDPs that may play an important role in various optoelectronic properties.

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Triboelectric Nanogenerator Based On ZnO Nanosheet Networks For Mechanical Energy Harvesting

P. Supraja, R. Rakesh Kumar^{*} Siju Mishra, and D. Haranath

Energy Materials and Devices Lab, Department of Physics, National Institute of Technology-Warangal,

India-506004

*Corresponding author: <u>rakeshr@nitw.ac.in</u>

Abstract

In this report, we presented a simple and cost-effective method to fabricate triboelectric nanogenerator (TENG) using ZnO nanosheets. The ZnO nanosheets are grown on aluminium substrate using hot plate assisted hydrothermal method. The ZnO nanosheets film and ITO surface act as triboelectric layers in the TENG. The open-circuit output voltage of ~ 2 V and power density ~ 0.48 μ W/cm² are generated from TENG in vertical contact separation mode. Subsequently, TENG has the ability to power one Light Emitting Diode (LED) without utilization of any storage element. Therefore, the proposed TENG has potential uses in self-powered sensors and electronic devices.

3D Printed Single Electrode Based Triboelectric Nanogenerator (S-TENG)

Dalip Saini, Hari Krishna Mishra, Varun Gupta and Dipankar Mandal*

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge city, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

In this work, a S-TENG is developed using micro-patterned 3D printed poly lactic acid (PLA) film as active material with copper (Cu) as single electrode-layer. Triboelectricity depends on contact-separation induced surface charge density between active material and electrode layer that can be manipulated by altering surface chemistry of active material to enhance the performance of S-TENG. Here, 3D printed PLA film is assisted with corona poling is employed to improve surface potential, thus the fabricated S-TENG generates 2 V output voltage under gentle human finger imparting. It is also capable to charge up 1.5 μ F capacitor up to 1 V instantaneously. More importantly, S-TENG is possibly utilized as a self-powered pressure sensor which is expected to be a potential candidate for real time motion monitoring, static and dynamic pressure distribution tracing, healthcare and giant monitoring.

Introduction

Comfort and health monitoring are the prime characteristics of our society. With the support of 3D printing, data processing system and wireless communication, the smart sensors have capability to develop comfort and monitor health of living things. Mostly pressure, temperature and motion sensor are used for discussed applications. Ultra-fast responsive pressure sensor with small dimension has great importance to monitor respiratory rate, pulse rate, blood pressure, limb motion and robotic applications. Recently COVID-19 pandemic faced a new threat to health expert as contactless health care monitoring is recommended Thus physiological signal monitoring system based on wearable pressure sensor is preferred. To fulfil the above-mentioned applications the pressure sensor with high sensitivity and ultra-fast response time have gained a lot of interest in the betterment of wearable artificial gadgets, humanmachine interaction (E-skin) and healthcare.¹

Here, we fabricate a 3D printed S-TENG device from PLA filament (cost-effective, flexible, biocompatible) which possesses 2 V output voltage on gentle finger touch, 1 V capacitor charging on hand-punching, high sensitivity (0.66 V kPa⁻¹) and fast response (10 ms) on mechanical pressure, have potential application as self-powered pressure sensor, tactile sensor and energy harvester and can be utilized for continuous health monitoring, wearable pressure sensor development and in robotics as E-skin.

Experimental Section

The fabrication of S-TENG is depicted in Fig. 1. The specified fabrication process includes model design,



Fig. 1(a) Schematic fabrication of PLA film using 3D printing technique; (b) 3D printed PLA film $(2 \times 2 \text{ cm}^2)$; (C) Schematic of S-TENG e; (d) Surface potential measurement of unpoled and poled PLA film at different temperature; (e) FTIR spectra of poled and unpoled PLA film.

it's conversion in machine code, FDM 3D printing and deposition of electrode layers. A square shaped thin film model was designed by solid works (3D CAD design software), converted into machine code using Fracktory 2.0 (slicing software) and PLA thin film printed into modeled square shape film having edge dimension 2 cm and thickness 0.3 mm (Fig. 1b) from 3D printing machine (Ender 3), later PLA films were pass through from corona poling process under 1.25 kV/mm electric field for 20 minutes at temperatures 60 °C, 80 °C and 100 °C. At last Cu is used as single electrode layer on one side of unpoled and poled PLA film. Proper cu wire connection is made on electrode layer (Fig. 1c) to obtain S-TENG.

Results and discussion

Fig. 1d presents the surface potential of unpoled and poled PLA films at different temperature, indicates that PLA film poled at 60 °C have maximum surface potential (1000 kV) which revealed improvement in dipole orientation along PLA film plain direction.

The FTIR spectra of unpoled and poled PLA films are depicted in Fig. 1e. The characteristic bands at 871, 1088, 1184 cm⁻¹ are attributed to C-C backbone stretching, symmetric and asymmetric stretching of C-O-C group.² The band at 1268 cm⁻¹ appeared in poled PLA spectra corresponds to semi-crystalline nature and peak shift from 1749 to 1757 cm⁻¹ in unpoled to poled FTIR spectra,³ replicate crystallinity enhances in PLA film after poling treatment. The FTIR spectra of electrospun PLA nanofiber reported earlier² which concludes corona poling induces electroactive phase in PLA film.

The working mechanism of S-TENG is illustrated systematically in Fig. 2a. The large difference in triboelectric series motivate PLA to attracts and preserve electrons from Cu layer, leaving positive charge on Cu layer and negative charge of same magnitude on PLA layer.4 As external pressure is applied on the PLA surface, a friction act between patterned PLA layer and Cu layer which leads to electrification and triboelectric charges induces between PLA surface and cu layer as a result electron releases from Cu layer. Reverse mechanism occurs when pressure releases. Furthermore, the flow of electrons between Cu layer and ground generates AC voltage of magnitude 0.5 V and 2 V in unpoled and poled PLA device respectively under gentle human finger imparting stress of magnitude 3 kPa over 4 cm height to both unpoled and poled PLA made S-

TENGs. Fig. 2c show transient capacitor charging responses by S-TENG where different capacitor of different capacitances is employed. It indicates that up to 1 V of charging is possible to obtain within very short time interval under the gentle hand imparting, e.g., within 5 s when 1.5 μ F of capacitance is used. S-TENG also possesses excellent mechano-sensitivity (0.66 V kPa⁻¹) and fast response time (10 ms).



Fig. 2(a) Working mechanics of S-TENG; (b) The output voltage of unpoled (brown) and poled (blue) PLA film; (c) Capacitor charging performance when S-TENG is work under repeating mechanical stimuli.

Conclusion

In conclusion, we have fabricated a 3D printed S-TENG that can sense a gentle finger touch and harvest mechanical energy from human motion. The fabricated S-TENG possesses outstanding mechanical-sensitivity and ultra-fast response that can be utilized as a self-powered pressure sensor for real time motion monitoring, static and dynamic pressure distribution tracing, healthcare and giant monitoring.

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Nickel Ferrite Thin Films for Supercapacitor Application

S. M. Nikam¹, S. D. Jituri², P. B. Patil³ and S. H. Mujawar^{2*}

¹Department of Nanoscience and Technology, Yashavantrao Chavan Institute of Science, Satara, 415001

² Department of Physics, Yashavantrao Chavan Institute of Science, Satara, 415001

³ Department of Physics, New College Kolhapur, 416012

*Corresponding author: sarfrajmujawar695@gmail.com

Abstract

Abstract

The nickel ferrite (NiFe₂O₄) thin films were synthesized by chemical bath deposition (CBD) method by using nickel chloride and iron chloride as precursors of nickel and iron respectively and nickel foam as a substrate. The as synthesized thin films were characterized by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) for structural and morphological studies. The films were further tested for their electrochemical performance. As synthesized Nickel ferrite exhibits the highest specific capacitance of 1976.78 F/g and 302.67 F/g at scan rate 10 mV/s and 100 mV/s respectively. Scan rate increases specific capacitance decreases.

Ti₃C₂ based two dimensional materials for electrocatalytic activity towards methanol oxidation

Navjyoti Bhagat¹, Vaishali Sharma¹, Anshul Kumar¹, Vibha Saxena² and Aman Mahajan^{1,*}

¹Department of Physics, Guru Nanak Dev University, Amritsar, Punjab - 143005 ²Technichal Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai - 400085

*Corresponding author: <u>aman.phy@gndu.ac.in</u>

Abstract. Owing to high cost and poisonous intermediate species of platinum, developing an electrocatalyst with high activity and stability is the main concern for methanol oxidation reaction (MOR). Herein, Ti_3C_2 based two dimensional MXene has been synthesized and explored in MOR. The synthesized MXene is characterized by XRD and SEM. The electrocatalytic behaviour of samples and bare Pt has been studied using cyclic voltammogram curves. The optimized MXene sample shows higher current density (7.726 mA/cm²) and low onset potential (-0.48 V) which is almost comparable to Pt (8.186 mA/cm², -0.50 V).

Enhanced Dielectric Diffusion With Fe Doping in Eu₂Ti₂O₇

Dheeraj Kumar, Mohd Alam, Sandip Chatterjee*

Department of Physics, Indian Institute of Technology (BHU), Varanasi - 221005 (U.P.), India

*Corresponding author: schatterji.app@itbhu.ac.in

Abstract

The structural and dielectric property of the pyrochlores $Eu_{2-x}Fe_xTi_2O_7$ have been reported. The structural analysis shows that the $Eu_{2-x}Fe_xTi_2O_7$ has pure pyrochlore phase up to x = 0.2. The dielectric permittivity shows a diffused dielectric transition in $Eu_{2-x}Fe_xTi_2O_7$. The increase in dielectric transition temperature and diffuseness with Fe doping have been observed.

Effect of Temperature on Electrochemical Performance of Activated Carbon FeOOH Composite Electrode for Energy Storage Device Nirbhay Singh^{1, 2}, Shweta Tanwar², Simran Kour², B.C.Yadav^{1*}, A. L. Sharma^{2*}

¹Department of Physics, Babasaheb Bhimrao Ambedkar University, Lucknow Lucknow-226025, U.P. India

²Department of Physics, Central University of Punjab, Bathinda-151401, Punjab, India

*Corresponding Authors: <u>alsharma@cup.edu.in</u>, bcyadava@bbau.ac.in

Abstract

Low cost, environment-friendly activated carbon-iron hydroxide is synthesized via a low-temperature hydrothermal technique. The structural confirmation is done by verifying its pattern consistency with the JCPDS file. The nano rod-like morphology is revealed by the FESEM technique. The temperature variation, it confirms that temperate rise hinders the contribution of electrolyte ions, so most of them cannot operate at high temperatures may be due to the flammability or volatility of currently used aqueous electrolyte. Which results in increase in bulk resistance of the material in EIS, and decay in specific capacitance value calculated by the CV and GCD. The overall performance of the device is best at the temperature 40° C.

Introduction

The rapid demand for energy is reflected by its tremendous developed energy storage devices like secondary batteries, fuel cells, and capacitors. Among them, supercapacitor outperformed other energy storage devices with advanced cycle stability, specific capacitance, power density, and high chargingdischarging rate. [1] To see the temperature effect on device performance, we have tested the fabricated device in the range of 40 to 100°C. In present report, we found that Nyquist plot indicated bulk resistance variation on increase in temperature. CV analysis provides the highest value of specific capacitance 111 F/gm at 40°C, the same pattern is concluded by GCD too. The energy density and power density at this optimum temperature are 3.7 W/kg⁻¹ and 1000 Wh/kg⁻ ¹ respectively.

Materials and methodology

All materials were used as received, the precursors used are activated carbon (Merk, Germany), ferric chloride hexahydrate (FeCl₃·6H₂O, Sigma UK),. Here we have synthesized AC@F (0.1) via a lowtemperature hydrothermal technique. The possible growth mechanism of FeOOH nanorods embedded in activated carbon matrix is:

AC + Fe (III) $+2H_2O = AC-FeOOH + 3H^+$

Results and discussion

The structural confirmation is done by using XRD data analysis. The XRD pattern (depicted in fig. 1) is consistent with the JCPDS card numbers # 34-1266 and 41-1487. The morphological confirmation is done by FESEM analysis. The fig. 1 (a), inset depicts the nano rod-like morphology which provides enhanced surface area at the electrode-electrolyte interface. The electrochemical analysis is done with CHI 760

electrochemical work station, by making a coin cell. The electrochemical impedance spectroscopy (depicted in fig. 1 (b)) is performed to see, frequency-dependent behavior of the device with an increase in temperature. From the Nyquist plot as depicted in (fig. 1(b)) on an increase of temp, the value of bulk resistance R_b and R_{ct} increases with an increase in temperature. The inset fig. 1 (b), shows the bar-graph value of the R_b and R_{ct} . The continuous increase in Rb and Rct show the device gain resistive nature, due to loss of electrolyte (liquid electrolyte contribution).



Fig. 1. (a) XRD Pattern of AC@FeOOH composite, inset consist FESEM image (b) Nyquist plot, inset showing R_b and Rct values at different temperature.

The Cyclic voltammetry analysis is done in a potential window of 1.0 V. Fig. 2 (a) shows the CV graph at a scan rate of 100 mV/sec with temperature variation. The analysis shows at a lower temperature,

the specific capacitance $[C_{s=}\frac{1}{2mv\Delta V}\int_{Vi}^{Vf} I \, dV]$ has a higher value, which is reflected in the enclosed area of CV. To see clear behavior at 40°C, the CV pattern at different scan rates (10-100) in the inset is drawn, which concludes, the consistent device performance. Specific capacitance vs temperature at fixed scan rate is depicted in fig. 2 (b), inset shows coulombic efficiency[$\epsilon = \frac{\Delta t \, discharge}{\Delta t \, charge} 100\%$] of the device at different temperatures. At the lowest temperature of the study, device have maximum efficiency that is 97%, on after the efficiency also decreases.



Fig. 2. (a) CV graph at 100 mV/scan rate different temperature, inset shows the CV at 40° C for 10 to 100 mV/sec scan rate. (b) Presents specific capacitance at a different temperature, inset shows coulombic efficiency vs temperature.

The Galvanostatic charge-discharge analysis was done at a different current density (2-20 A/g) in the potential range -0.5 to 0.5. figure 3(a) depicts an almost symmetric charging-discharging profile at different temperatures. For fixed current density (4A/g) the devices show maximum discharge time at 40°C, after its value decreases with the advance in temp. The inset of fig.3 shows its GCD behavior at a broad range of current density varying from 2 to 20 mA. The specific capacitance $[C = \frac{I\Delta t}{m\Delta V}F/g]$, energy density $[E = \frac{C(\Delta V)^2}{7\cdot 2}$ (Wh Kg⁻¹)] and power density $[P_d = \frac{E \times 3600}{\Delta t}$ (kWkg⁻¹)] is calculated. The Ragone plots show the highest value of power density and energy density at 40 °C. The inset of fig.3 (b) presents the specific capacitance value with temperature, from here we can also conclude that the variation of temperature shows a decrease in electrochemical performance of the energy storage device. The optimum behavior is depicted at a lower temperature 40°C.



Fig. 3. (a) Charging discharging at different temperature inset at 40° C with the varying current. (b) Ragone plot, inset show Specific capacitance by GCD with temperature variation.

Conclusion

The device shows, maximum specific capacitance, energy and power density as 111 F/g, 3.7 Wh/kg and 1000 W/kg respectively. Increase in temperature hinders the contribution of electrolyte ions. It is difficult to operate the device at high temperature may be due to flammability or volatility of currently used aqueous electrolyte, the device performance is best at 40°C.

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Effect of pH on Electrochemical Performance of Molybdenum Selenide: Ultracapacitor Application

Shweta Tanwar¹, Nirbhay Singh², Simran Kour¹, and A.L. Sharma¹

¹Department of Physics, Central University of Punjab, Bathinda 151401 ²Department of Physics, Babasaheb Bhimrao Ambedkar University, Lucknow, India **Corresponding author: <u>alsharma@cup.edu.in</u>*

Abstract

The pH effect on the chemical bonding and electrochemical performance of molybdenum selenide (MoSe₂) has been reported in this paper. The samples were prepared via the hydrothermal method and further characterized via Fourier transform infrared spectroscopy (FTIR) and electrochemical workstation (CHI 760). The FTIR confirms the chemical bonds in the prepared samples. The electrochemical performance of the MoSe₂ decreases with an increase in pH value from 9 to 11. The M 9 sample exhibits a maximum specific capacitance (C_s) of 156 F g⁻¹ at current density 2 A g⁻¹. It shows an energy density (E_d) of 22 Wh kg⁻¹ at a power density (P_d) of 1015 W kg⁻¹. Hence pH 9 is an optimized condition for high electrochemical performance for MoSe₂ nanomaterial for supercapacitor application.

Introduction

The energy crisis is the major challenge in front of society due to the depletion of fossil fuels. The energyrelated problem is addressed via switching from nonrenewable to renewable energy sources like solar, wind energy so on. The issue of conservation of energy generated via renewable energy sources drives the attention of the research community towards energy storage devices [1]. Among all storage devices, ultracapacitor/supercapacitors (SC) are most popular due to their high power density. A typical SC has components like a current collector, electrode, and electrolyte cum separator. The electrode material of the SC is a major role player in better electrochemical performance. Based on the charge storage mechanism an SC is classified as an electric pseudocapacitor double-layer capacitor (EDLC) and hybrid capacitor [2]. The hybrid capacitor is receiving more popularity than others as it processes the quality of charge storage of both EDLC and pseudocapacitor.

The literature review indicated that TMDs are emerging as new trending hybrid electrode material for supercapacitor application [3]. In the paper, we have synthesized $MoSe_2$ material at different pH 9 and 11 and named as M 9 and M 11 respectively and done its analysis using FTIR and electrochemical analyzer.

Material and Methodology

All chemicals utilized for MoSe₂ preparation are of high purity and Sigma Aldrich.

Preparation of MoSe₂

 $MoSe_2$ material was synthesized via a hydrothermal route. Initially, solution A of 38 mg Se powder in 2 ml

hydrazine hydrate aged for 24 hours prepared. Meanwhile, solution B is of 51.5 mg $Na_2MoO_4.2H_2O$ in 13 ml double deionized water (DDW). Later solution A is added to solution B dropwise by maintaining pH 9 and 11 of the solution with the aid of NaOH (1M) solution. Then the solution after 30 min of stirring transferred into Teflon liner of 25 ml and subjected to 180° C for 24 h in an oven. The black colour MoSe₂ powder collected by washing and drying for 12 hours at 70° C temperature in vacuum oven.

Result and Discussion

The FTIR band assignments corresponding to MoSe₂ at pH 9 and 11 are depicted in figure 1(a) respectively. The shift of FTIR peaks with an increase of pH might be due to a change in the MoSe₂ particle size [4]. The electrochemical performance of M 9 and M 11 samples was studied in a two-electrode system using 6 M KOH as electrolyte. In figure 1 (b-c) the CV and GCD plot of M 9 and M11 is depicted which indicates that the M 9 sample shows better results. Further, the specific capacitance of M 9 sample at the different scan and current density calculated using equations

 $C_{sp} = \frac{\int I(V) dv}{mv\Delta V}$, $C_s = \frac{i\Delta t}{m\Delta V}$, where m, v, V, I, t has usual meaning and the graphical representation showed in figure 1(d). The C_s value decrease with the increase of scan rate and current density values might be due to less time available for the electrolyte ions for electrode/electrolyte interaction for charge storage. The Nyquist plot in figure 1(e) also indicates that M 9 material possesses less bulk resistance (R_b) than M 11 material. The Ragone plot for both the sample samples is presented in figure 1(f).



The various electrochemical performance analyzing parameters as calculated are presented in table 1. **Table.1**. Electrochemical performance parameters.

Sample (pH)	C _s (at 2 A g ⁻¹)	E _d (Wh kg ⁻¹)	P _d (W kg ⁻¹)	R _b (Ω)
M 9	156	22	1015	2
M 11	136	18	952	3.5



Fig. 1. (a) FTIR plot (b) Cyclic voltammetry (CV) curve at 10-100 mV s⁻¹ scan rate (inset M 9 and M 11 samples CV at 100 mV s⁻¹) (c) Galvanostatic charge/discharge (GCD) of M 9 at current density 2-5 A g⁻¹ (inset comparative GCD curve of M 9 and M 11 at 2 A g⁻¹) (d) Specific capacitance (C_s) versus scan rate (inset C_s versus current density) (e) Nyquist graph (f) Ragone plot of M 9 and M11 samples respectively.

Conclusion

The FTIR and electrochemical performance results of M 9 and M 11 samples reveal that pH 9 is the optimum condition to preparing better potential MoSe₂ material for SC application might be due to an increase in area and pore size of the material for more charge storage.

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Structural And Supercapacitor Properties Of Chemical Bath Deposited Cobalt Doped Nickel Hydroxide Thin Films

D.B. Mane¹²³, O. C. Pore¹, G. M. Lohar¹, L. D. Kadam^{*2}, R.V. Dhekale^{**3}

¹Department of Physics, Lal Bahadur Shastri College of Arts, Science and Commerce, Satara 415002, ²Department of Physics, Arts, commerce and science college, Ramanadnagar (Burli) 416308 ³Department of Physics, Kisan Veer Mahavidyalaya, Wai 412803

*Corresponding author: <u>rvdhekale2@gmail.com</u>, <u>dpkmane40@gmail.com</u>,

Abstract

In present investigation, Cobalt doped nickel hydroxide thin films were deposited on cost-effective stainless-steel substrate by simple chemical bath deposition method. The FT-IR study confirmed the presence of Ni-OH and Co-OH bonds. The electrochemical supercapacitor properties of as synthesized thin films were studied by cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) study. The overall supercapacitor study indicated that 0.6% cobalt doped nickel hydroxide electrode exhibited a maximum specific capacitance of 930 F g⁻¹ at a current density of 0.5 mA cm⁻² in 1 M KOH electrolyte.

Introduction

In our modern society due to the pace development of the global economy, various issues such as depletion of fossil fuels and rapidly increasing environmental pollution; there is necessity of efficient, environmentally friendly and sustainable energy source, as well as advanced technologies associated with energy conversion and storage [1]. Supercapacitors, also called ultracapacitors or electrochemical capacitors, are the energy storage devices which bridge the gap between batteries and capacitors [2-4]. Carbon based material, metal oxide/hydroxide, polymer used in formation of supercapacitor. Metal oxides/ hydroxide have high stability, good specific capacitance, high energy density. Nickel hydroxide attract to researchers due to high specific capacitance value.

Hu et al. [6] reported Nickel hydroxide deposited on nickel foam by simple chemical deposition method have specific capacitance 2200 F g-1 at current density 1 A g⁻¹. Enhancement of supercapacitive properties of nickel hydroxide doping of metal usually applied. Jagdale et.al [7] Prepared symmetric supercapacitor device of electrodeposited Co (OH)₂ thin film on steel archive supercapacitance 44 F g⁻¹ at scan rate 5 mV s⁻¹ along with current density and power density 3.96Wh kg-1 and 42 kW kg⁻¹ respectively. Purushothaman et.al. [8] doped cobalt in nickel oxide exhibit improved result and gain in maximum specific capacitance 1982 F g⁻¹ for scan rate 5 mV s⁻¹ in 1M KOH electrolyte. Enhancement of supercapacitive properties of nickel hydroxide doping of metal usually applied. Cobalt doped nickel hydroxide is a promising electrode for supercapacitor application due to the good synergy of Nickel and cobalt ions which provide multivalent states of Co/Ni ions and high ion-exchange capability. In present study Cobalt doped nickel hydroxide thin films were deposited on stainless-steel substrate by chemical bath deposition method. The optimized cobalt doped nickel hydroxide electrode exhibited a maximum specific capacitance of 930 F g⁻¹ at a current density of 0.5 mA cm⁻² in 1 M KOH electrolyte.

Experimental

Cobalt doped nickel hydroxide thin films were synthesized by chemical bath deposition method by using cost-effective stainless-steel substrate as a current collector. In actual experiment, 1MNiSO46H2O was used as nickel source and CoSO₄6H₂O was used as cobalt source in double distilled water (DDW). The different concentration of (0.4%, 0.6%, and 0.8%) CoSO4 6H2O was added into 1M NiSO₄ 6H₂O with constant stirring in a beaker. Then, 0.25 M K₂S₂O₈ was added into the solution. The pH of solution was adjusted to the 12 by using aq. NH₃ (30%). The precleaned substrates were immersed in the above beaker and kept at room temperature for 2h. After completion of reaction Co-Ni hydroxide thin films rinsed with DDW and dried at temperature a 100°C for 2 hrs. For 0.4%, 0.6%, and 0.8% Co doping the obtained films were named as N-0.4%, N-0.6% and N-0.8% respectively.

Result and discussion FT-IR STUDY

Fig. 1 shows the FT-IR spectra of cobalt doped nickel hydroxide thin films in the range of 4000 to 400 cm⁻¹. The peaks observed at about 3436 and 1627 cm⁻¹ are assigned to the O-H stretching and bending vibrations of water [9]. The characteristic peaks observed at 678

and 456 cm⁻¹ are attributed to Ni-OH and Co-OH Stretching vibration respectively [10]. Here the FT-IR result indicated the presence of O-H, Co-OH and Ni-OH groups which confirms the formation of Co-Ni mixed hydroxide.



Fig. 1. FT-IR spectra of different Cobalt doped nickel hydroxide (N-0.4%, N-0.6% and N-0.8%) electrodes.

ELECTROCHEMICAL SUPERCAPCITOR STUDY



Fig. 2. (A) CV curves at a scan rate of 10 mV s⁻¹ (B) GCD curves at a current density of 0.5 mA cm⁻² of N-0.4%, N-0.6% and N-0.8% electrodes (C) Specific capacitance vs scan rate (D) Specific capacitance vs current density.

Electrochemical supercapacitor properties of Cobalt doped nickel hydroxide electrodes were investigated by using CV and GCD technique. The comparative CV curves of N-0.4%, N-0.6% and N-0.8% electrodes at a scan rate of 10 mV s⁻¹ are mentioned in Fig. 2 (A). The presence of cathodic and anodic peaks in CV curves indicates the Faradic reaction and pseudocapacitive behavior of electrodes [11]. Fig. 2 (B) indicates the comparative GCD curves of N-0.4%, N-0.6% and N-0.8% electrodes at a current density of 0.5 mA cm⁻² in potential range 0-0.4 V. Fig. 2 (C) depicts the specific capacitance calculated from CV curves as a function of scan rate. Fig. 2 (D) presents the specific capacitance calculated from GCD curves at different current densities for all electrodes. Here we can observe that as current

density increases, specific capacitance decreases. This is because, at lower current density the lower charging rate provides a maximum contribution of electroactive material during redox reactions. resulting in a high specific capacitance value. But at higher current density, the utilization ratio of electroactive material gets lowered hence specific capacitance decreases. Here the overall supercapacitor study indicated that the 0.6% doped cobalt in nickel hydroxide thin film (N-0.6%) exhibited a maximum specific capacitance as compare to other thin films (N-0.4%, N-0.8%) of 930 F g^{-1} for current density 0.5 mA cm⁻².

Conclusion

In conclusion, cobalt doped nickel hydroxide thin films have been successfully deposited on stainless steel substrates by chemical bath deposition and used for supercapacitor study. The electrochemical supercapacitor study of cobalt doped nickel hydroxide thin films indicates the 0.6% doped cobalt in nickel hydroxide exhibited a maximum specific capacitance of 930 F g⁻¹ for current density 0.5 mA cm⁻². Such Co-Ni mixed hydroxide is very promising electrode for electrochemical supercapacitor application

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Effect of Molar Concentration of FeOOH on Electrochemical Properties of TiO₂/FeOOH Composite for Supercapacitor

Simran Kour¹, Shweta Tanwar¹, Nirbhay Singh¹, R. V. Pateriya¹ and A.L. Sharma^{1*}

¹Central University of Punjab, Bathinda- 151401, Punjab, India

*E-Mail: alsharma@cup.edu.in

Abstract

Transition metal oxides and hydroxides (TMOs and TMHs) have gained wide attention as pseudocapacitive materials for supercapacitors owing to their low cost, high theoretical capacitance, variable oxidation states, and vast abundance. Herein, we report the synthesis of TiO₂/FeOOH composite through a facile hydrothermal route and studied the electrochemical properties of the composite for supercapacitor application. The effect of FeOOH concentration on the performance of the composite was observed. With increasing concentration of Fe³⁺ ions, the specific capacitance of the composite decreased. The composite exhibited maximum specific capacitance of 29.28 Fg⁻¹ at 10 mVs⁻¹ and specific energy of 0.5 Wh kg⁻¹ at a specific power of 175 W kg⁻¹ in a two electrode system.

Enhanced power factor of Si₉₈B₂ added higher manganese silicide synthesized by spark plasma sintering.

Chandrakant Prajapati^{1,2}, M. Saravanan^{1,2}, N.K. Upadhyay¹, Radhey Shyam¹ and S.R. Dhakate^{1,2}

¹Advanced Material and Devices Division, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi, 110012

²Academy of Scientific and Innovative Research (AcSIR), Ghaziabad, 201002

*Corresponding author: chandrakant1097r@gmail.com

Abstract

Higher manganese silicides are being explored as the best suitable intermediate-temperature p-type thermoelectric material for waste-heat recovery. Although higher manganese silicides possess low cost, non-toxic and thermally stable constituent elements, their low thermoelectric performance restricts its application compared to other materials in the mid-temperature range. We report an enhanced power factor of higher manganese silicide synthesized using a nano-inclusion approach employing the combination of arc melting and spark plasma sintering technique. An improved power factor ~ 1.40×10^{-3} Wm⁻¹K⁻² at 773 K was achieved by Si₉₈B₂ nano-inclusion in higher manganese silicide material. This power factor enhancement is due to improvement in the Seebeck coefficient, which is imparted from the nano-inclusion composite structuring.

Introduction

The thermoelectric generators (TEGs) are the solid-state devices having ability to direct conversion of unused waste heat to electricity. TEGs are potential alternative green energy source in energy generation applications¹. The performance of thermoelectric materials is defined by the dimensionless parameter figure-of-merit (ZT). The ZT is the material intrinsic property and depends on the Seebeck $coefficient(\alpha)$, electrical conductivity(σ), and thermal conductivity(κ) of the thermoelectric material. The figure of merit (ZT) is defined by $ZT = \frac{S^2 \sigma}{\kappa}$, these transport properties are interdependent by electron scattering mechanism and energy dependent of scattering time². The nanostructuring process is useful to create energy filtering mechanism to improve Seebeck coefficient. The nanostructured thermoelectric materials are preferred than their counterpart thin film due their process easier, low cost and most suitable for commercial and The wide industrial applications. range of thermoelectric materials has been investigated such as chalcogenides, skutterudites, silicides, and Half-Heusler alloys for device applications¹⁻⁵. Among these the Higher Manganese silicides (HMS) are potential ptype thermoelectric materials at mid temperature range applications. HMS are cost-effective, non-toxic, mechanically, and chemically stable at higher temperatures. The Higher Manganese silicide are commonly represented as MnSi_X with X ranging from 1.73 to 1.75. The synthesis of single-phase HMS is complex because it is not a eutectic composition. It exists along with either Si or cubic-MnSi phase. Although Si phase is a desirable phase due to its better thermoelectric properties⁴. In this work the two-step synthesis approach is adopted here for developing nanostructured HMS and for improving the thermoelectric properties. The combination of Arc melting (AM) and Spark Plasma Sintering (SPS) techniques offers the nano-structured higher manganese silicide in simple way of fabrication.

Experimental details

Si (99.99%) and B (99.99%) powders are milled in a ball mill for an optimized time period of 100 h for nano-structured $Si_{98}B_2$ synthesis. The nano-structured $Si_{98}B_2$ powder used as nano-inclusion in HMS matrix. The HMS was synthesized by employing Arc Melting technique. The Mn (99.9%) and Si (99.9%) granules were taken in stoichiometric ratio of MnSi_{1.73} and melted in inert atmosphere Arc melting chamber.



Fig. 1. XRD pattern of the HMS and HMS- 5wt% $Si_{98}B_2$ sintered samples and Ball milled $Si_{98}B_2$ nano-structured alloy.

The 5 wt% $Si_{98}B_2$ nano-inclusions mixed in HMS matrix and ground in fine power. The fine powder transferred into graphite die with 12.7mm diameter. The Spark Plasma Sintering (SPS) was performed to consolidation of powdered sample. The sintering was held at a temperature 1273 K and 50 MPa uniaxial pressure. The XRD analysis was performed using Rigaku X-ray diffractometer at a scan speed of 5° per minute. The sintered pellet samples cut into rectangular prism shaped specimen, for electrical transport properties measurement. The electrical transport properties of the sample performed by ZEM-3 apparatus under He atmosphere.

Result and Discussion

The phase analysis of the sintered materials were carried by XRD powder diffraction technique (Fig. 1). The sintered material have tetragonal structure and the pattern shows the polycrystalline HMS phase. The synthesized samples shows no Si or elemental MnSi impurity on pristene HMS material. Fig. 1(c) shows the XRD pattern of the $Si_{98}B_2$ ball milled nano-structured alloy. The Si peak of (111) phase appers at 28.26° in XRD pattern of HMS- 5wt% $Si_{98}B_2$ samples.



Fig. 2. Temperature dependence thermoelectric properties, Seebeck Coefficient and electrical conductivity of the HMS and HMS- 5wt% Si98B₂ sintered samples.

The electrical transport properties of the synthesized sintered samples were performed at 323 K to 873 K temperature range, shown in Fig. 2. The temperature dependent Seebeck coefficient value shown in the Fig.2, indicating p-type semiconducting behaviour^{4,5}. The increase in the Seebeck coefficient of the sample is primarily due to Si₉₈B₂ nano-inclusion, and the increase is prominent at a higher temperature. The highest value of the Seebeck coefficient~234 μ VK⁻¹ is obtained at 773 K. A small decrease in the Seebeck coefficient value at higher temperature (above 600 K) is due to the bipolar effect⁴. The temperature dependent electrical conductivity is shown in the Fig.

2. The electrical conductivity decreases with the increasing temperature, showing the degenerate semiconductor nature of sintered samples. The electrical conductivity decreases with Si₉₈B₂ nano-inclusion at higher temperature, due to increase the charge carrier scattering by Si₉₈B₂ nano-inclusion. The calculated thermoelectric power factor ($\alpha^2\sigma$) was improved effectively (Table.1) and the maximum power factor is 1.41×10^{-3} Wm⁻¹K⁻² at 773 K for HMS-5wt% Si₉₈B₂ sample.

Table 1. Power factor values of the HMS and HMS-5wt% Si98B2 samples.

Composition	Max. Power factor (10 ⁻³ W m ⁻¹ K ⁻²)
HMS	1.29
$HMS+5 \ wt\% \ Si_{98}B_2$	1.41

Conclusion

The HMS was successfully synthesized by Arc melting and Spark Plasma Sintering technique. The Sintering process parameter were optimized during the sintering process. The study shows $Si_{98}B_2$ nano-inclusion are useful for improving Seebeck coefficient. The $Si_{98}B_2$ nano-inclusion is also helpful to overcome the bipolar effect at high temperature. The enhancement of thermoelectric performance via power factor increases in this study ensure the higher manganese silicide application in mid-temperature TEGs.

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Cavity and Diffusion Channel Structured MnMo₆S₈ Nanoflakes for Flexible Supercapacitor Electrode Application

R Balamurugan, S Siva Shalini, Vishal Singh, and A Chandra Bose^{*}

Nanomaterials Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli-620015, India

*Corresponding author: <u>acbose@nitt.edu</u>

Abstract

In this work, we successfully synthesized $MnMo_6S_8$ nanoflakes by the facile hydrothermal method. Cavities and diffusion channels in its crystalline structure were investigated from XRD patterns. Its nanoflakes-like morphology was scanned by the HR-SEM image. Its functional groups and purity have confirmed from FTIR and EDX spectra. Its electrochemical properties were performed in a three-electrode system. The highest areal capacity of $MnMo_6S_8$ modified carbon cloth is 37.7 mC cm⁻² at a current density of 2.5 mA cm⁻² was measured from GCD.

Introduction

Nowadays, we are all moving towards flexible and smart devices. All these flexible smart devices need flexible and fast-charging energy storage devices with high energy density.^[1,2] For providing fast charging and discharging with high storage capacity, the electrode material must need a porous channel for the diffusion of electrolyte ions and charge storage cavities.

Manganese and Molybdenum sulfides are superior materials for electrochemical energy storage devices.^[3,4] MnMo₆S₈ material has its ionic diffusion channels and internal cavities in its crystal structure.^[5] Carbon clothes are the most flexible, conductive, and have high mechanical strength. Because of these above properties, MnMo₆S₈ modified carbon cloth should furnish excellent performance for flexible energy storage devices. In this work, we synthesized and investigated MnMo₆S₈ modified carbon cloth for the flexible supercapacitor electrode application.

Experimental Section

Cavities and diffusion channel structured $MnMo_6S_8$ nanoflakes were synthesized by the facile hydrothermal method. Manganese sulfate, ammonium heptamolybdate, and thiourea were mixed into 30 mL of DD (double distilled) water at 7:1:21 molar ratio, respectively, and the solution was stirred for 1 h. The homogeneous solution was transferred into a teflon-lined SS autoclave and heated at 200 °C for 12 h in a muffle furnace. After that, it was allowed to cooldown to room temperature by itself. The precipitate was collected and washed with DD water and ethanol several times. And it was

desiccated in vacuum condition at 60 °C for overnight.

The sample's crystalline structure, functional groups, morphology, and elemental characterizations were carried out by Ultima III Rigaku powder X-ray diffractometer, Thermo Scientific NICOLET iS5 FT-IR (Fourier transform infrared) spectrometer, Thermo Scientific Apreo S HR-SEM (Hi-Resolution Scanning Electron Microscope), and EDX (Energy-Dispersive X-ray) spectrometer respectively.

Electrochemical properties of $MnMo_6S_8$ were studied by Biologic SP-200 electrochemical workstation at 2 M KOH aqueous electrolyte. As prepared sample 80%, carbon block 10%, and PVDF 10% were mixed in DMF to make a slurry, and it was coated in flexible carbon cloth by a drop coating method. And it was desiccated in vacuum condition at 60 °C. $MnMo_6S_8$ modified carbon cloth as a flexible working electrode, SCE (saturated calomel electrode) as a reference electrode, and platinum foil as a counter electrode. And the areal capacity was calculated from the GCD curve using the below equation.

$$C_A = \frac{I\Delta t}{A}$$
 a)

Where I - discharge current, Δt - discharge time, and A - the active material coated area.

Results and discussion



Fig. 1. (a) XRD pattern, (b) Crystal structure of the MnMo₆S₈.

XRD pattern of cavity and diffusion channel structured $MnMo_6S_8$ is shown in Fig.1a. It was matched with COD database ID: 4303147. Fig.1b shows the presence of diffusion channels in the c direction and cavities in between Mo_6S_8 blocks and the diffusion channel.



Fig. 2. (a) FTIR spectrum, (b, c) HR-SEM image at different magnification, and (d) EDX spectrum of the $MnMo_6S_8$.

FTIR spectrum shows the presence of H_2O and NH_3 . It's due to the precursors used for synthesis. And the fingerprint peaks of Mn-S and Mo-S are in the range of 700 cm⁻¹ to 500 cm⁻¹. HR-SEM image confirms the nanoflake-like morphology of the as-prepared sample. Nanoflake like morphology of the sample gives a high surface area for charge storage and enhances the electron conductivity. The purity of the MnMo₆S₈ was further confirmed by the EDX spectrum.

Electrochemical storage performances of the MnMo₆S₈ modified carbon cloth were characterized by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) in a three-electrode system with 2 M KOH electrolyte concentration. CV was taken at the potential range of 0 to 0.45 V with a different scan rate of 5, 10, 20, 50, 100, and 200 mV s^{-1} . The broad oxidation peak and reduction peak in the CV curve clearly says the pseudocapacitive behavior of the material. GCD was measured over the potential range of 0 to 0.41 V with a different current density of 2.5, 5, 10, 20, 30, 40, and 50 mA cm⁻². The GCD curve shows the pseudocapacitive nature of the sample, and it reflects the results of CV. Areal capacity measured from GCD are 37.7, 36.3, 34.5, 31.4, 28.0, 23.8, and 19.0 mC cm⁻² at current density of 2.5, 5, 10, 20, 30, 40, and 50 mA cm⁻², respectively.



Fig. 3. Electrochemical characterization (a) CV, (b) GCD of the $MnMo_6S_{8.}$

Conclusion

As-prepared sample of MnMo₆S₈, its crystal structure and phase has confirmed from XRD. The presence of the cavities and ionic diffusion channels in its crystal structure enhances its capacity. Its nanoflakes-like morphology was confirmed from HR-SEM. Its purity has been confirmed from FTIR and EDX spectra. It was successfully coated on flexible carbon cloth, and it exhibits the highest areal capacity of 37.7 mC cm⁻² at the current density of 2.5 mA cm⁻².

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Hydrothermal Synthesis of AgBr as Flexible Electrode Material for Effective Supercapacitor Application

S. Siva Shalini, R. Balamurugan, and A. Chandra Bose*

Nanomaterials Laboratory, Department of Physics, National Institute of Technology, Tiruchirappalli-620015, India

*Corresponding author: acbose@nitt.edu

Abstract

AgBr nanomaterial was synthesized by hydrothermal method with hexadecyltrimethylammonium bromide as bromide source (CTAB). Morphological and structural studies were investigated using SEM and XRD analysis. Electrochemical performance of the material was examined using three electrode system. The prepared material exhibits the maximum areal capacity of 56.31 mC cm⁻² at a current density of 1.25 mA cm⁻².

Introduction

Raising world's population, cost of fuels and the energy crisis led to various problems connected with the depletion of fossil fuels. Therefore, we are in need of alternative energy storage devices with higher capacity [1,2]. Batteries and capacitors are well known energy storage devices. But both batteries and capacitors are not sufficient for application requiring high energy and power density [3]. In this view, now supercapacitors are used as an alternative energy storage device for storing the charge efficiently. Supercapacitors have gained more awareness due its high-power density, long cycle stability and high specific capacitance [4]. Among numerous bromides silver bromide is proved to be prominent material due to its high electrical conductivity, high oxidative ability, low toxicity and simple preparation process [5,6].

Experimental section

AgBr nanomaterials were synthesized using hydrothermal method. In this method a suitable amount of AgNO3 and Cetrimonium bromide (CTAB) were dissolved in 30 mL DD water. CTAB was used as a bromide precursor. The complete solution was kept under vigorous stirring for 3 h. Then the solution was transferred into stainless steel autoclave and maintained the temperature at 120 °C for 15 h. Then the precipitate was collected and washed several times with DD water and ethanol and dried at 60 °C for 12h. Structural and morphological studies of the prepared sample materials were characterized using Rigaku Ultima III powder X-ray diffractometer with Cu K α_1 radiation (XRD), and TESCAN VEGA-3 LMU scanning electron (SEM) analysis. Electrochemical microscopy behavior of the prepared AgBr nanomaterial was

analyzed using Bio-logic SP-200 electrochemical workstation.

Working electrode preparation

The working electrode is prepared by making slurry in the ratio of 80:10:10 active material, PVDF and carbon black which are mixed together with few drops of dimethylformamide (DMF) and coated in carbon cloth. The coated carbon cloth is used as a working electrode. Saturated calomel is used as the reference electrode and platinum foil as counter electrode. 2M KOH is used as electrolyte medium throughout the electrochemical studies.

Results and Discussion

The surface morphology of AgBr particles shows polyhedron shaped morphology with more agglomeration. The particles were highly aggregated and distributed unevenly, hence cannot be distinguished separately.



Fig. 1. SEM images of AgBr at different magnifications.

The crystalline structure and phase purity of the prepared AgBr are studied using X-ray diffraction pattern. In Fig. 2 the diffraction peak at 20 values of 26.71, 30.94, 44.32, 52.51, 55.04, 64.49 and 73.24 corresponding to the miller indices (111), (200), (220), (311), (222), (400) and (420) respectively are

matched with the JCPDS number 79-0149. This clearly confirms the cubic crystal structure corresponding to the space group of $Fm\overline{3}m$.



Fig. 2. XRD pattern of the prepared AgBr.





Fig. 3. Electrochemical studies (a) Cyclic Voltammetry (b) Galvanostatic Charge Discharge.

The electrochemical behaviour of the flexible electrode material is analysed using three electrode system. The areal capacity for the prepared electrode is calculated using charge/discharge curve.

Cyclic voltammetry (CV) was carried out from 0-0.5 V shown in Fig. 3(a). While increasing the scan rate, there is a shift in oxidation peak towards higher potential and shift in reduction peak towards lower potential which is due to insufficient time to intercalate with electrode material. The presence of redox peak in the CV curve affirms the pseudocapacitive nature of the electroactive material. Galvanostatic charge discharge (GCD) studies were carried out in the potential range from 0.0 to 0.42 V shown in Fig. 3 (b). In GCD curve the 1.25 mA cm^{-2} take longer discharge time, exhibits the maximum areal capacity value. The GCD curve reveals the pseudocapacitive behavior and it is in good agreement with CV result. The areal capacity value is calculated using eq. (1)

$$C_A = \frac{I\Delta t}{A} \tag{1}$$

The prepared AgBr material exhibits the maximum areal capacity of 56.31, 55.12, 53.42, 52.11, 46.94, 32.34 mC cm⁻² at a current density of 1.25, 2.5, 5, 10, 25, 50 mA cm⁻² respectively.

Conclusion

AgBr nanomaterial is successfully synthesized by hydrothermal method for supercapacitor application. The crystalline structure of the prepared material is confirmed using XRD. The polyhedron structure is affirmed using SEM studies. The flexible electrode material exhibits the maximum areal capacity of 56.31 mC cm⁻² at a current density of 1.25 mA cm⁻².

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Morphology Tuning of SnO₂ Based Electrode Materials for Supercapacitors

Satvik Anshu¹, Surbhi Priya¹, Debabrata Mandal² and Amreesh Chandra^{1,2*}

¹School of Energy Science and Engineering, ²School of Nanoscience and Technology, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal-721302, India.

*Corresponding author: achandra@phy.iitkgp.ac.in

Abstract

In this work morphological dependent study of SnO_2 structures for application in supercapacitors is presented. The work revealed that the rutile tetragonal SnO_2 structure can be used as a negative electrode in supercapacitors. The materials were synthesized using two routes viz., co-precipitation, hydrothermal method. The physiochemical characterization was performed using XRD, SEM and BET measurements. The electrochemical characterization of SnO_2 indicates that the performance of particles, synthesized using co-precipitation, is limited due to the low surface area of the particles. Therefore, SnO_2 particles were synthesized hydrothermally, to counter the limiting factors. The stabilized hollow structures lead to appreciable improvement in the performance. The electrochemical properties of all the synthesized materials were investigated by cyclic voltammetry and charge-discharge measurements in 3M KOH, using a three-electrode configuration.

Introduction

Materials based on transition metal oxides (TMO) such as MnO_2 , CuO, NiO, ZrO_2 etc. show the high specific capacitance^[1,2].

Recently, there have been reports discussing the use of SnO_2 in supercapacitors but the results have remained inconclusive^[3]. The tuning of the surface morphology of SnO_2 material is discussed in this paper as ways to improve the performance for electrochemical storage applications^[1]. The importance of using hierarchical and pseudo type nanostructures of SnO_2 to make it a competitive material is unequivocally established.

Experimental

Co-precipitation method: 5.64 g of stannus chloride dihydrate (SnCl₂.2H₂O) and 25 mL of methanol (CH₃OH) were mixed together under constant stirring. 10 g of sodium hydroxide (NaOH) and 50 mL of deionized (DI) water were combined and stirred continuously. In the solution of SnCl₂.2H₂O and CH₃OH, NaOH solution was added dropwise to adjust the pH to 10, while stirring continuously at 80 °C. A milky white solution was obtained. The precipitate was centrifuged, collected, and dried at 80 °C for 24 h, before being calcined at 800 °C for 6 h and the product obtained is termed S₁.

Hydrothermal method: 0.3 M SnCl₂.2H₂O was introduced in 4:1 volume ratio of DI water and 2propanol. The solution was continuously stirred until the solute was completely dissolved. The pH was kept at 12 by dropwise adding NaOH. Subsequently, the solution was stirred continuously for 1 h. The prepared solution was transferred into a Teflon lined stainless steel autoclave and the reactor was set at 150 °C for 24 h. The obtained sample was subsequently filtrated and the filtrate was dried in the air at 600 °C for 6 h the product obtained is termed S_2 .

Results and Discussion

Fig. 1 shows a comparison of XRD patterns of SnO_2 structures. The diffraction patterns for SnO_2 particles showed sharp peaks that are in perfect agreement with the tetragonal rutile phase of polycrystalline SnO_2 . To match the diffraction pattern, JCPDS Card No. 41-1445 was used.



Fig. 1. XRD pattern of SnO₂.

The scanning electron microscopy (SEM) results depicted in Fig. 2 showed that the particle distribution was nearly uniform across the sample in both materials. Further, the average size of the particles obtained by in S_1 and S_2 methods was ~150 and 30 nm respectively.

The N_2 adsorption-desorption isotherms were recorded at 77K. It indicated that SnO_2 particles synthesized using hydrothermal had a highest surface area of 27.75 m² g⁻¹. The hysteresis loops indicated the type IV isotherms and mesoporous nature of the particles.



Fig. 2. SEM micrographs of SnO_2 prepared using (a) S_1 and (b) S_2 .

For the electrochemical investigation, the threeelectrode measurements were carried out with Ag/AgCl as a reference electrode, platinum as the counter electrode, and SnO_2 as the working electrode.



Fig. 3. Comparison of CV curves in SnO_2 at 50 mV s⁻¹ scan rate prepared using (a) S_1 and (b) S_2 method.

All the measurements were carried in 3M KOH (electrolyte) solution. The CV curves were taken at different scan rates from 5 to 200 mV s⁻¹ in -0.7 V to

0.3 V. The highest obtained specific capacitance was 23 and 15 F g⁻¹ at 5 mV s⁻¹ for S₁ and S₂ SnO₂, respectively. The observed increase in the specific capacitance was due to the increased surface area in the case of S₂. Fig. 3 shows comparison of CV curves at 50 mV s⁻¹ supporting the greater capacitance value in S₂. The galvanostatic charge discharge (GCD) were performed at various current densities from 0.5-10 A g⁻¹. Comparison of CD curves at 1 A g⁻¹ is shown in Fig. 4. The specific capacitance values decreased at higher current density values. The highest obtained specific capacitance values were 48 and 26 F g⁻¹ at 1 A g⁻¹ for S₁ and S₂ respectively.



Fig. 4. Comparison CD curves of SnO_2 at 1 A g^{-1} prepared using (a) S_1 and (b) S_2 methods.

Conclusion

Successful synthesis of SnO₂ structures via two different methods i.e. co-precipitation and hydrothermal was presented. The XRD results confirmed the formation of rutile type tetragonal phase of SnO₂. A homogeneous distribution and granular shaped morphology were observed from the SEM. The highest obtained specific capacitance was of 48 F g⁻¹ at 1 A g⁻¹ for S₂. The results confirm that morphology tuning enhances the electrochemical performance.

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Preparation of Mg ion conducting polymer electrolyte based on PVA and *Nelumbo Nucifera*

Muniraj @ Vignesh N^{1, 2*}, Jayabalakrishnan S S², Selvasekarapandian S¹, Jerlin Fati Ranjitham E³, Leena Chandra R³, Aafrin Hazaana S¹, Meera Nachiyar R¹

¹Materials Research Center, Madurai, Tamil Nadu, India. 625 009.

²Department of Physics, Mannar Thirumalai Naicker College, Madurai, Tamil Nadu, India. 625 004.
 ³Department of Physics, Fatima College, Madurai, Tamil Nadu, India. 625 001.
 **Corresponding author: naamuvi@gmail.com*

Abstract

Polymer electrolytes (PEs) based on Poly Vinyl Alcohol (PVA) and Lotus Leaf (*Nelumbo Nucifera* leaf (NNL)) added with Magnesium Chloride (MgCl₂) are prepared by simple solution casting technique. The membrane with PVA and NNL gives ionic conductivity in the order of 10⁻⁶ S/cm for 1gm PVA:300 mg NNL. This composition is optimized one based on ionic conductivity increased from pure PVA conductivity of 10⁻¹⁰ S/cm. The sample with 0.2 m.wt% of MgCl₂ highest ionic conductivity of 1.805x10⁻³ S/cm. Addition of NNL in the PVA matrix enhances its amorphous nature, in which MgCl₂ is added as Mg ion donors. A primary Mg ion battery has been constructed with highest conducting sample and open circuit voltage is 1.57V. **Keywords**: Solid Polymer Electrolytes, Mg ion batteries, Poly Vinyl Alcohol, *Nelumbo Nucifera*, AC impedance.

Crystalline Characteristics Dependent Pseudocapacitance Property of Na₂Ti₃O₇ as a Negative Electrode for Sodium Ion Supercapacitors

Puja De¹, Debabrata Mandal², Abhishek Kumar¹, Sudipta Biswas¹ and Amreesh Chandra¹*

¹Department of Physics, ²School of Nanoscience and Technology, Indian Institute of Technology Kharagpur, Kharagpur-721302, India

*Corresponding author: <u>achandra@phy.iitkgp.ac.in</u>

Abstract

Layered $Na_2Ti_3O_7$ (NTO) is investigated as a negative electrode for sodium ion supercapacitors owing to its low cost, environmental friendliness, low operating potential and less toxicity nature. Different crystalline features of NTO material were synthesized *via* hydrothermal and facile solid-state route. Solid-state synthesis based NTO material exhibited excellent electrochemical performance with a specific capacitance of 151 F g⁻¹ at 1 A g⁻¹ current density in 1 M Na₂SO₄ aqueous electrolyte. This enhanced electrochemical performance could be attributed to the higher crystallinity of NTO material. Thus, the material facilitates the intercalation of Na⁺ ions during electrochemical processes. Therefore, it is clear that solid-state synthesis based highly crystalline NTO material can be used in high performance sodium ion supercapacitors.

Introduction

Supercapacitor has been considered as a novel energy storage device with excellent power density, fast charge/discharge rate, and long cycle life. Sodium ion supercapacitors (NISs) have shown great promise as next-generation energy storage devices for large-scale applications in the field of electronic industry. However, the achieved energy density from NISs is low due to the larger ionic radius of Na⁺ ions (1.02 Å), which leads to the serious structural instability of the electrode material due to greater volume change during cycling. So, layered structured materials, with larger interlayer spacing have been attracting lot of interest. In particular, Na₂Ti₃O₇ (NTO) is being investigated as a negative electrode of NICs.

Results and discussions

NTO was synthesized by utilizing facile solidstate and hydrothermal routes. After the successful synthesis, to confirm the phase formation, X-ray diffraction (XRD) analysis was done and the collected XRD patterns are presented in Fig. 1. All the obtained diffraction peaks could be indexed using the JCPDS card no. 31-1329. In both the XRD profiles, the most intense characteristic peak situated in the vicinity of $2\theta = 10^\circ$, corresponds to the (001) plane of the NTO material. The XRD pattern clearly demonstrated that the solid-state synthesis-based material (NTO-S) possessed a high degree of crystallinity, compare to а hydrothermally synthesized material (NTO-H). This high degree of crystallinity can improve the capacitive performance of the material, as shown later. The BET

measurements were studied and the results showed the effective surface area of NTO-H was ~73 m² g⁻¹, more than six times higher than that of NTO-S (12 m² g⁻¹).



Fig. 1. XRD pattern of the synthesized NTO materials.

To explore the electrochemical performance, a conventional three-electrode assembly was used. Both cyclic voltammetry (CV) and galvanostatic (GCD) measurements charge-discharge were performed in 1 M Na₂SO₄ neutral aqueous electrolyte for better interpretation of the charge storage mechanism of the electrodes. Fig. 2 represents the evolution of CV profile of NTO-H and NTO-S at 5 mV s⁻¹ scan rate. Both the electrodes showed quasirectangular shaped CV curve along with the appearance of small pair of redox peaks. The origin of redox peaks in the material is due to the battery type intercalation/de-intercalation of Na⁺ ions into/from the lattice of the NTO during charging/ discharging processes without any permanent phase change of the electrode material. Most interestingly, the redox peaks were more prominent in NTO-S, and the area under the CV profile was also greater in comparison to the NTO-H. As a consequence, NTO-S exhibited the maximum specific capacitance of 80 F g⁻¹ at 5 mV s⁻¹ scan rates, nearly two times higher than the specific capacitance of NTO-H i.e. 47 F g^{-1} . It is well believed phenomenon that electrode material with a larger specific surface area will deliver higher electrochemical performance. Here, though the NTO-S possessed lower BET surface area, still it exhibited a higher specific capacitance in compared to NTO-H. This happens because the charge storage mechanism of NTO is based on the intercalation of the electrolyte ions. So, the appearance of intense redox peaks in NTO-S could be ascribed to the higher crystallinity of the material, which facilitates the ions transporting channel through the lattice of the electrode. Here the crystalline nature of the NTO-S enhanced the ability of Na⁺ ions intercalation/de-intercalation during electrochemical response.



Fig. 2. CV profile of synthesized NTO materials at 5 mV s^{-1} scan rate.

To further confirm higher electrochemical behaviour of NTO-S, the galvanostatic chargedischarge curves at 1 A g⁻¹ current density is shown in Fig. 3. Generally, the discharge curve comprises of three segments: the first one is IR drop, which is mainly attributed to the resistance induced by electrode materials; the second is monotonous curve, which is believed to be due to Na⁺ extraction from the NTO anode and the third one is sudden drop, implying that Faradaic and non-Faradaic reactions have been completed. The GCD profile revealed that NTO-S was capable to provide a longer discharge time in compare to NTO-H. Consequently, calculated specific capacitance was also larger as discharge time is proportionally related to the capacity of the material. At 1 A g^{-1} current density the estimated specific capacitance was 151 F g^{-1} , and 56 F g^{-1} for NTO-S and NTO-H, respectively. So, NTO-S exhibited the outstanding specific capacitance value due to the facile intercalation of the Na⁺ ions through the material leading to the larger amount of charge accumulation at the electrode. The cyclic stability measurement of the materials was also investigated as it is an important factor for the practical applications of the material.



Fig. 3. CD profile of synthesized NTO materials at 1A g⁻¹ current density

Conclusion

In conclusion, two material of NTO were constructed via hydrothermal and solid-sate routes. In comparision to NTO-H, NTO-S gave a higher specific capacitance of 151 F g^{-1} at 1 A g^{-1} current density, due to its well-defined pathways for crystallinity. The presented results make NTO an important material for supercapacitor.

Acknowledgement

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Effect Of Lithium Doping In Nickel Ferrite Based Hydroelectric Cell

Sandeep Saini^{1*}, K. L. Yadav¹, Jyoti Shah², R. K. Kotnala²

¹Department of Physics, IIT Roorkee, Roorkee, Haridwar, Uttarakhand-247667 ²CSIR-NPL, New Delhi, Delhi

*Corresponding author: ssaini.ph@gmail.com

Abstract

A hydroelectric cell is an emerging device in the field of green and clean energy generation devices. Defects play an essential role in the adsorption and dissociation of water molecules on the material's surface. We have synthesized nickel ferrite and lithium doped nickel ferrite by ball milling. Lithium doping increases the defects in the nickel ferrite, which improves the output of the hydroelectric cell. X-ray diffraction confirms the cubic spinel structure in both samples. From V-I polarization curves, we observed the maximum output current and output voltage for lithium doped nickel ferrite based hydroelectric cells as follows 40.5 mA and 0.95 volts.

Introduction

Research has recently focused on green and clean energy generation sources, energy conversion, and energy storage devices to provide a stable supply to the constant ever-increasing demand for energy worldwide. As a result, there is a thrust to develop new eco-friendly sources and devices. In the past few years, the hydroelectric cell has been a potential candidate who emerges as an outstanding alternative to clean and green energy sources. It produces electricity by adsorption and dissociation of water molecules on the defect centres of materials. Hydroelectric cell (HEC) splits water molecules at the metal oxide/ferrite surface directly in H+ and OHions initially by chemidissociation, followed by physidissociation of water molecules onto defect centres. Metal oxides and ferrites have shown many potential applications in the energy sector. Many oxides and ferrites have been used for hydroelectric cell application and have shown promising results[1-3].

Nickel ferrite has been widely used in the applications of catalysts, energy storage in a supercapacitor, gas sensors, microwave devices, magnetic fillers, magnetic recording media, magnetic fluids, magnetic resonance imaging, magnetic sensors, transformer cores, spintronics and actuators, solid oxide fuel cells, water purification methods and many others. High surface reactivity and water adsorption were reported in the nickel ferrite[4], which motivated us to fabricate nickel ferrite based HEC.

Experimental Section

Lithium doped nickel ferrite (Ni_{0.8}Li_{0.1}Fe_{2.1}O₄) was synthesized using Ball milling. All high purity precursors (NiO, Fe₂O₃, Li₂CO₃) were taken in proper stoichiometric ratios and appropriately mixed. These powders were ball-milled in ethanol with the ball to powder ratio of 5:1 for 16 h and then dried in the hot air oven at 120 °C. These powders were calcined at 750 °C for 8 hours. Pellets of calcined powder were sintered at 850 °C for 2 hours. These pellets (2.2 cm x 2.2 cm) were used to fabricate hydroelectric cells for further studies. Silver paste is used as a cathode as a comb pattern, and zinc plate is used as an anode.

Results and Discussion

XRD pattern shown in Fig.1 confirms the spinel cubic phase formation, and it matches with JCPDS no. 10-0325. Few impurity peaks of Fe₂O₃, NiO were also observed. The lattice parameter was calculated



Fig. 1. X-ray Diffraction Pattern of Li-doped NiFe₂O₄

as 8.34 Å. Fig. 2 shows the FESEM micrograph of lithium doped nickel ferrite, and it confirms the porosity. Grains are found to be spherical in shape. The average grain size was found to be 326 nm. Fig. 3 shows the FTIR spectra of lithium doped NiFe₂O₄, and two metal-oxygen vibration bands are observed at



Fig. 2. FESEM Micrograph of Li-doped NiFe₂O₄







Fig. 4. V-I polarization curve of Li-doped NiFe₂O₄

595 cm⁻¹ and at 470 cm⁻¹ due to tetrahedral and octahedral sites, respectively. Due to adsorbed water molecules' bending and stretching, two bands were observed at 1635 cm⁻¹ and 3427 cm⁻¹[5].

V-I polarization curve of lithium doped nickel ferrite based hydroelectric cell has been shown in Fig. 4. The maximum output current and open-cell voltage estimated from the V-I polarization curve is 40.5 mA and 0.95 V. In this device, Water molecules are firstly chemisorbed on the surface of the materials, which has unsaturated cations and defects and then physisorption will occur on this chemisorbed layer of hydroxide ions. During the adsorption, water molecules dissociate into hydronium and hydroxide ions. These ions get attracted towards the cathode and anode of the hydroelectric cell, and because of reduction and oxidation reactions at these electrodes, an electric current flows in the outer circuit.

Conclusion

Lithium doped NiFe₂O₄ have been synthesized using Ball milling and studied for water molecule dissociation by fabricating hydroelectric cells. Lithium doping causes strain and defect formation in the lattice of NiFe₂O₄ due to different ionic radii and valence states, which play an essential part in the adsorption and dissociation of water molecules. Lithium doped nickel ferrite gives a better current density than earlier reported magnesium and lithium ferrite based hydroelectric cells. Li doped NiFe₂O₄ HEC is a very low costly and portable device that can be very useful for electricity in rural and remote areas of India.

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The Pseduocapacitive behaviour of CeO₂ Nanostructure in Acidic and Organic electrolytes

N. Maheswari^{1*} and G. Muralidharan²

¹Department of Physics, AMET (Deemed to be University), Kanathur, Chennai-603112, India ²Department of Physics, The Gandhigram Rural Institute -Deemed to be University, Gandhigram, Dindigul – 624302, India.

*Corresponding author: nmahi.phys@gmail.com

Abstract

The CeO₂ nanoparticles have been synthesized by hydrothermal method. Cerium Nitrate and CTAB was used as the precursor and capping agent respectively. The prepared samples were annealed at 500 °C for 4 h. The structural and morphological features of the samples were characterized by XRD, FTIR and SEM. The electrochemical performance of the CeO₂ electrodes has been studied through cyclic voltammetry, charge discharge studies and ac-impedance technique using a three electrode cell. H₂SO₄ and propylene carbonate were employed as electrolytes. The highest specific capacitance of 508 F g⁻¹ at a scan rate of 2 mV s⁻¹ obtained for 1 M H₂SO₄. Further this electrode exhibits 82.6 % capacitance retention after 2000 continuous charge discharge cycles. All these electrochemical studies reveal that the prepared CeO₂ electrode to be suitable for supercapacitor applications.
Metal-Organic Framework $[Zn_2(1,4-bdc)_2(dabco)]_n$ as an efficient Electrocatalyst for H₂O₂ Production in Oxygen Reduction Reactions

Vrushali Raut¹ and Dipanwita Das*1

¹Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai 400019, India

*Corresponding author: dr.das@ictmumbai.edu.in

Abstract

Development of non-noble element-based electrocatalyst for oxygen reduction reactions (ORR) through a two-electron pathway to generate hydrogen peroxide (H₂O₂) electrochemically from O₂ reduction. We synthesized [Zn₂(1,4-bdc)₂(dabco)]_n as electrocatalysts, by using 1, 4-benzenedicarboxylic acid (H₂BDC), 1, 4-diazabicyclo[2.2.2]octane (dabco) as an organic linker and Zn(NO₃)₂.6H₂O as metal ion precursor. The structure was characterized and investigated ORR activity by cyclic voltammetry (CV) and rotating ring disk electrode voltammetry (RRDE).

Introduction

A fuel cell is an energetic energy conversion device, which is environmentally friendly. Hydrogen is considered to be the most promising fuel so far, however, the hydrogen ceiling is due to its low energy density and highly explosive nature. Hydrogen peroxide (H_2O_2) as an alternative fuel has attracted increasing attention in this field. H₂O₂ can be produced by reduction of O_2 , which is abundant in the atmosphere by using various types of reductants. H₂O₂ is generated as an unwanted by-product of the oxygen reduction reaction (ORR) in fuel cells. To date, the best-known catalyst for ORR is Pt nanoparticles supported on carbon black due to its high catalytic activity However, the high price and limited reservoir of platinum hinder its large-scale commercialization for the fuel cell.

Metal-organic frameworks (MOFs) emerged as a new class of material which is porous and crystalline, assembled by two main components of inorganic vertices (metal ions or clusters) and organic linkers. In the present work, we have successfully synthesized $[Zn_2(1,4-bdc)_2 \ (dabco)]_n$ and its successfully catalyzes oxygen reduction in a twoelectron pathway in an alkaline medium.

Experimental Details

Synthesis of [Zn₂(1,4-bdc)₂(dabco)]_n

 $[Zn_2(1,4-bdc)_2(dabco)]_n$ has been synthesized as reported by Dybtsev *et al.* using the reported procedure [1]. A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (1.0 g, 3.36 mmol), H₂BDC (0.560 g, 3.37 mmol), and dabco (0.187 g, 1.67 mmol) were dissolved in 100 mL of DMF at room temperature and heated in a Teflonlined autoclave at 120 °C for 48 h. The colourless crystalline precipitate formed was collected, washed with DMF and dried. The colourless $[Zn_2(1,4-bdc)_2(dabco)]_n$ has been prepared (Scheme 1).



Scheme 1. Synthesis of $[Zn_2(1,4-bdc)_2(dabco)]_n$ by using the solvothermal method.

Results and Discussion

Structural characterization of catalyst

The $[Zn_2(1,4-bdc)_2 (dabco)]_n$ was characterized for crystallinity using an x-ray diffractogram (XRD). Fig.1, shows the powder XRD pattern and diffraction peaks of $[Zn_2(1,4-bdc)_2 (dabco)]_n$ around 8.4, 8.2, 9.2, 12.3, 16.5, 18.4, 18.9, 21.6, 24.4° and it was matched with the reported data obtained by Dybtsev *et al.*

Fig. 2, shows the Thermogravimetric analysis (TGA) pattern of samples. The three weight losses were observed, the 1^{st} weight loss is related to the moisture and guest molecules, 2^{nd} weight loss is related to the destruction of the dabco ligand and the last one is devoted to the destruction of the H₂BDC ligand.



Fig. 1. PXRD patterns of [Zn2(1,4-bdc)2(dabco)]n.



Fig. 2. (a)TGA curves and (b) SEM image of the [Zn₂(1,4-bdc)₂ (dabco)]_n.

Fig. 2(b), exhibits a Scanning electron microscope (SEM) image of the $[Zn_2(1,4-bdc)_2 (dabco)]_n$ samples obtained in the monoclinic crystal structure.

Electrochemical Characterization

Cyclic voltammetry (CV) was performed with the $[Zn_2(1,4-bdc)_2(dabco)]_n$ modified GC electrode in 0.1 M KOH aqueous solution saturated with N₂ or O₂ (Fig. 3). In N₂-saturated solutions, no characteristic peak was observed. The O₂-saturated solution shows a noticeable reduction peak, which suggested pronounced electrocatalytic activity of catalysts for ORRs in O₂-saturated solution. The reduction peak potential was -0.41V vs. Ag/AgCl and current density -0.60 *j*(mA cm⁻²). Catalyst indicates that active performance towards ORR.



Fig. 3. CV of $[Zn_2(1,4-bdc)_2 \text{ (dabco)}]_n$ in N₂ and O₂ saturated 0.1 M KOH solution at a scan rate of 100 mV s⁻¹.



Fig. 4. (a) RRDE test of the ORR on $[Zn_2(1,4-bdc)_2 (dabco)]_n$ in an O₂-saturated 0.1 M KOH electrolyte solution with a sweep rate of 10 mV s⁻¹ different rotation

rates (c) K–L plots from –0.5 to –1.0 V (d) H_2O_2 percentage of $[Zn_2(1,4\text{-bdc})_2\,(dabco)]_n.$

To investigate the ORR activity of $[Zn_2(1,4-bdc)_2 (dabco)]_n$ in O₂-saturated 0.1 M KOH with different rotations through rotating ring disk electrode. Fig. 4 shows the measured ring currents at top panels and disk currents at bottom panels for the ORR. The onset potential and a half-wave potential were -0.24 V and -0.38 V respectively. Fig. 4c, shows Koutecky-Levich (K-L) plots [2]. The K-L plots showed good linear fitting and non-zero intercepts for each potential which indicate first-order reaction kinetics toward O₂ reduction within the potential range and the K-L equation calculated electron transfer numbers (n) various potentials. In ORR proceeding in presence of the MOF predominantly give a two-electron pathway.

The quantitative analysis of hydrogen peroxide generation ($I(H_2O_2)\%$) was determined by the ring and disk current using the equation [3].

$$I(H_2O_2)\% = \frac{200 \cdot I_r / N}{I_d + I_r / N}$$
 (a)

Where N is the current collection efficiency of the Pt ring (N = 0.2), I_d and I_r are the measured currents for the disk and ring electrodes respectively. The electron transfer number and percentage of H_2O_2 observed were 2 and ~70%, respectively.

Conclusion

 $[Zn_2(1,4-bdc)_2(dabco)]_n$ was prepared by a hydrothermal method and characterized. The ORR activity of $[Zn_2(1,4-bdc)_2 (dabco)]_n$ electrode was investigated by CV and RRDE. $[Zn_2(1,4-bdc)_2 (dabco)]_n$ is active towards a two-electron reduction pathway to produce H_2O_2 as a product in an alkaline electrolyte. The advantages of this catalyst are low price and environment-friendly behavior.

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Optimization of the texturizing process with multi-crystalline silicon wafer for increasing the optical properties <u>Madhesh Raji</u>,¹ Kesavan Venkatachalam,¹ Srinivasan Manikkam,^{*1} Ramasamy

Perumalsamy¹

¹Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai-60311

*E-mail: srinisastri@gmail.com.

Abstract

Multi-crystalline silicon (mc-silicon) ingot was grown using the Directional Solidification (DS) method. The bricks and wafers were sliced from the grown ingot. The aim of this work to analyse the mc-Silicon wafer texturizing for improving the optical properties. Lower reflectance can be obtained by the optimized etching conditions. In this work, we have used the different types of acids in different ratios for texturizing process. Here, we have used HF: H₂O₂: CH₃COOH=3:2:2 (set-1), HF: H₂O₂: KMnO₄=3:2:0.2 M (set-2) and HF: H₂O₂:KMnO₄=3:2:0.2M (set-3) for etching with the etching time of 60 sec. The HF: H₂O₂:KMnO₄=3:2:0.2M (set-2) gives the better results as obtained from optical microscope and UV- Visible reflectance studies. The etched mc-Silicon wafer surface was analyzed by the optical microscope.

Structural, morphological, ferroelectric, and dielectric properties of (0.99)BaTiO₃-(0.05)Bi₂O₃-(0.05)Nb₂O₅

Shivam Kumar Mittal^{*}, Sandeep Saini, and K. L. Yadav

¹ Smart Materials Research Laboratory, Department of Physics, Indian Institute of Technology Roorkee, 247667, India

*Corresponding author: shivam_km@ph.iitr.ac.in

Abstract

In this study, we have synthesized (0.99)BaTiO₃-(0.05)Bi₂O₃-(0.05)Nb₂O₅ -ceramic (lead-free) material via a solid-state reaction method. We have studied the structural, ferroelectric, morphological, and dielectric properties. The formation of a single-phase (tetragonal) perovskite structure with P4mm symmetry was confirmed by powder X-ray diffraction patterns and the average grain size was around the 460 nm range. From P–E loops of the sample, we have found recoverable energy storage density around $(W_{rec} \sim 31.32 \text{mJ/cm}^3)$ and efficiency ($n_{eff} \sim 48.65\%$).

Introduction

In this modern era, the researcher's main challenge is to synthesize an eco-friendly (lead-free) perovskite material because of the harmful effects of lead on human beings and nature. These lead-based ceramics contain about 60 wt% lead[1], released into the environment. That's why the need to develop leadfree perovskite ceramics (environmentally friendly) is increasing, and therefore more and more researchers are encouraged to work on environmentally friendly Another perovskite materials. challenge for researchers is to enhance the dielectric properties of these perovskite (lead-free) materials, which are beneficial for the miniaturization of electronic devices and improve their energy density (ED) for its energy storage applications[2]. use as Antiferroelectric, relaxor ferroelectrics, dielectric glass-ceramics, and polymer-based ferroelectrics have all been extensively explored and are regarded to be more likely to be utilised in energy storage applications[3]. Among the various lead-free perovskite ceramics, the BaTiO₃(BT) based ceramics have attracted considerable attention since they exhibit good polarization behaviour with suitable dielectric and ferroelectric properties[4].

Our aim to introduce high dielectric perovskite-based material and then summarize its properties.

Synthesis of BTBN ceramic

Barium titanate oxide (BaTiO₃), Bismuth oxide (Bi₂O₃) and Niobium pentoxide (Nb₂O₅) were used as raw materials. Barium titanate oxide was mixed with 0.05 wt% of Bi₂O₃ and 0.05 wt% of Nb₂O₅, and calcined in alumina crucible at 1150 °C for 2 hours hereafter termed as BTBN. This BTBN powder is grinded for 30 minutes, and then PVA is mixed

thoroughly to the calcinated powder as a binder. After that, this mixture is pressed into a disk (pellets) and then these pellets are sintered at high temperature $(1225^{\circ}C)$ for 3 hours.

Experimental results and discussion



Fig. 1 X-ray diffraction pattern of BTBN ceramic.

Fig. 1 illustrates the powder XRD pattern of the BTBN sample. From the XRD pattern, sharp peaks were observed at Bragg diffraction positions and confirmed the formation of a single-phase (tetragonal) perovskite structure with P4mm symmetry, and it matches with JCPDS No. 00-005-0626. The lattice parameters were calculated to be a=3.9762 Å, c= 4.0323 Å. Fig. 2 shows the material's morphology, with uneven grain development and the average grain size was around the 460 nm range. Fig. 3 shows the variation of dielectric constant as a function of temperature. It can be seen that the dielectric constant increases up to a particular T_m (curie temperature ~100°C), and then starts

decreasing. Above temperature T_m , the tetragonal phase transforms to a cubic phase[4]. As demonstrated in Fig. 3, polarizability, such as ionic, electronic, space charge and dipolar polarization, causes a drop in dielectric constant as frequency rises[1]. All polarization mechanisms respond quickly at low frequencies, but distinct polarization processes begin to filter out as frequency rises. As a result, the material's net polarization reduces, resulting in a fall in dielectric constant[5]. Variation of dielectric loss $(\tan \delta)$ with temperature changes, followed normal ferroelectric behaviour (Fig. not shown).



Fig. 2 FESEM micrograph of BTBN-ceramics.



Fig. 3 Variation of the dielectric constant with temperature of BTBN ceramics at different frequencies.

Fig. 4 shows the P-E loop of the BTBN sample under the fixed 11kV/cm electric field. From the P-E loop, we have calculated the recoverable energy density (W_{rec}) , energy storage efficiency (n_{eff}) and stored energy density (W_{store}) from the following expressions.

$$W_{rec} = \int_{P_r}^{P_s} E \, dP \,, \qquad W_{store} = \int_0^{P_s} E \, dP \,,$$
$$n_{eff} = \frac{W_{rec}}{W_{store}} \times 100,$$

Where P is polarization, E is applied electric field, P_r is remnant polarization, and P_s is saturation polarization. The BTBN-ceramic showed recoverable energy density of $W_{rec} \sim 31.32 \text{mJ/}cm^3$, $W_{store} \sim 64.37 \text{mJ/}cm^3$ and efficiency is 48.65 %.



Fig. 4 P–E loop of BTBN-ceramics.

Conclusion

Single-phase BTBN ceramic is synthesized via solidstate route method. The microstructure shows the average grain size to be around 460 nm. P-E loop of BTBN-ceramic showed recoverable energy density of $W_{rec} \sim 31.32 \text{ mJ/}cm^3$, $W_{store} \sim 64.37 \text{mJ/}cm^3$ with an efficiency about 48.65 %. Hence, this BTBN ceramic is particularly suitable for energy storage applications.

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Poly(vinylidene fluoride-co-hexafluoropropylene) additive in perovskite for stable performance of carbon-based perovskite solar cells

N. Santhosh*, K.R. Acchutharaman, R. Isaac Daniel, M. Senthil Pandian, P. Ramasamy

Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam - 603110, Tamilnadu, India

*Corresponding author: santhosh.10409@gmail.com

Abstract

In this study, we improved the hole-transport free carbon-based perovskite solar cells by using polymer additive to passivate the perovskite grains with large size crystals and aid in the growth of polycrystalline perovskite layer with preferred orientation. The fluoro-polymer as an additive into perovskite layer facilitated hydrogen bond with organic cation to form H-F bond, which ought to prevent degradation from moisture. The photo voltaic device with 5 wt% PVDF-HFP additives carried out ~14% enhancement in open-circuit voltage and yielded PCE of 11.1%. It is revealing that the fluoro-polymer enhances passivation of perovskite grains and gives a hope in perovskite photovoltaics.

Structural and Electrochemical properties of

Sm_{1.5}Sr_{0.5}NiO_{4-δ} Ruddlesden Popper perovskite Material

Manisha Chauhan¹, and Prabhakar Singh^{1*}

¹Department of Physics, Indian Institute of Technology (Banaras Hindu University) Varanasi, Varanasi-221005 (India) Email: psingh.app@iitbhu.ac.in

ABSTRACT

In present work, we have studied the Ruddlesen-Popper type of material $Sm_1.5Sr_0.5NiO_{4\pm\delta}$ prepared by Solid State Route and characterized by XRD and Cyclic Voltammetry. A single-phase solid solution of $Sm_1.5Sr_0.5NiO_{4\pm\delta}$ having orthorhombic structure with *Fmmm* symmetry is observed. The duck shape of cyclic voltammogram suggests the catalytic regeneration of reactants close to working electrode.

Introduction

Due to structural compatibility of Ruddlesden-Popper (K₂NiF₄) class of materials, they can accommodate excess Oxygen in their unoccupied interstitial sites. Because of this they can have large oxide ion conductivity as compared to perovskites materials. These -type of structures (Ln₂NiO₄; n = 1) consist of perovskite layer (LnNiO₃) separated by rock salt layer (LnO) [1]. A close scrutiny of literature revealed that SmSrNiO_{4- δ} material has been less investigated for electrochemical behavior compared to other RP structures [2]. so, we have chosen this material for further investigations.

2. Experimental procedure:

2.1 Synthesis Technique- The $Sm_{1.5}Sr_{0.5}NiO_{4-\delta}$ ceramic was prepared by conventional solid state reaction process with initial reagents samarium oxide (Sm_2O_3) , Strontium carbonate $(SrCO_3)$ and Nickel Oxide (NiO) of purity > 99% weighed in Stoichiometric amount and mixed thoroughly. The sample was then calcined in air at 1200 °C for 3 hr and then ground and mixed with 2% polyvinyl alcohol (PVA) and pelletized via 12mm diameter cylindrical die-set. Resulting pellets were sintered at 1425 °C temperature for 3h at the heating rate of 5°/min in air.

2.2 Characterization techniques- The phase purity of samples was determined by X-Ray powder diffraction pattern (Rigaku Miniflex II desktop) with Cu-K α radiation ($\lambda \sim 1.4506$ Å) at room temperature

in the range 20° - 70° with a step of 0.01. Electrochemical behaviour as Cyclic voltammetry was performed in Keithley 2450 source meter using three electrode system.

3. Result and analysis:

3.1 Structural analysis- The XRD graph of the sintered pallets was recorded and we found the phase pure sample with purity greater than 99%. Further to confirm the facts, Rietveld refinements was performed using *Fmmm* symmetry and value of χ^2 lies in appreciable range shown in Fig. 1. The peaks of XRD were indexed and matched with the well-reported data [PCPDF#880117].



Fig.1. Rietveld refinement of the Sm_{1.5}Sr_{0.5}NiO_{4-δ.}

3.2 Electrochemical Properties

Cyclic Voltammetry (CV) is used to understand the redox processes. The recorded voltammogram is shown in Fig.2(a). The duck shape of voltammogram indicates the catalytic regeneration of the reactants close to the electrode [3]. It is also evident from the voltammogram that there is an additional kink present in OER regime suggesting the formation of multiple oxidation states and the conversion of Ni⁺³ to Ni⁺² as a redox rection takes place.

$$2\text{NiO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Ni}_2\text{O}_3 \quad (1)$$

Further in ORR regime, we got one strong peak suggesting the reduction of ion into atom. The continuous rise in current with the scan rate is suggesting the reduction of size of the diffusion layer. We have also calculated the relaxation time by fitting the data with exponential decay equation shown in Fig.2(b) and the steady current is achieved nearly at 488 sec. To understand the electrochemical reversibility the Randles Sevcik (RS) equation was plotted (peak current versus $V^{1/2}$) in Fig.2(c) which is almost linear showing the quasi-electrochemical reversible nature of the process with freely diffusing redox species.





Fig. 2. (a) Cyclic voltammetry (b) Chronoamperometry (c) RS equation of Sm_{1.5}Sr_{0.5}NiO₄₋₈.

Conclusion Sm_{1.5}Sr_{0.5}NiO_{4- δ} was prepared using conventional solid-state route method followed by sintering at 1425°C for 3h. A single-phase solid solution of Sm_{1.5}Sr_{0.5}NiO_{4± δ} have orthorhombic structure. Electrochemical studies suggests that sample shows quasi electrochemical reversibility, relaxation time of 488 sec, and a reduction and oxidation of Ni ion with catalytic regeneration of reactants close to the electrode.

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Enhanced energy storage and dielectric properties of BaTiO₃+(0.05 wt.%)Bi₂O₃ and Nb₂O₅ ferroelectric ceramics

Aditi Rathore^{*}, Sandeep Saini, and K.L. Yadav

¹Smart Materials Research Laboratory, Department of Physics, Indian Institute of Technology Roorkee, 247667, India

*Corresponding author: a_rathore@ph.iitr.ac.in

Abstract

Lead-free ceramics of $BaTiO_3 + (0.05 \text{ Wt. }\%)Bi_2O_3 - Nb_2O_5$ (BTBN) have been synthesized using the conventional solid-state reaction method. The microstructure, electrical properties, and energy-storage performance of the obtained ceramics were examined in detail. The maximum recoverable energy density of 28.21 mJ cm⁻³ with a relatively high efficiency of 46 % was achieved.

Introduction

With the rapid advancement of power electronics towards miniaturization, dielectric materials with high dielectric constant, low loss, high energy storage density, and good temperature stability are highly desired for energy storage applications[1]. In the past few decades, lead-containing perovskite materials were dominating modern electronics. But, the toxicity of lead is harming the environment. Therefore, leadfree ceramics with high energy storage densities are needed in comparison to their lead-based equivalents[2]. BaTiO₃ has gotten a lot of interest among the numerous lead-free perovskite ceramics because of its high dielectric constant, huge polarisation, and remarkable thermal stability of the dielectric properties[3]. The energy storage capacity of a perovskite material can be measured from the P-E loop. The recoverable energy density (W_{rec}) , stored energy density (W_{store}), and energy efficiency (η) of a material is given by,

$$W_{rec} = \int_{P_r}^{P_{max}} E dP$$
, $W_{store} = \int_{0}^{P_{max}} E dP$

$$\eta = \frac{W_{rec}}{W_{store}} \times 100 \%$$

where E is the applied electric field, P denotes polarization, P_{max} denotes maximum polarization, and P_r denotes residual polarization.

Experimental section

BTBN ceramics were synthesized by the conventional solid-state reaction method. Barium titanate oxide (BaTiO₃), bismuth oxide (Bi₂O₃), and niobium pentoxide (Nb₂O₅) were used as starting raw materials. Barium titanate powder was heated for 2 hours at 1150°C in an alumina crucible. After that, we

grinded the material after adding 0.05 wt. % of niobium pentoxide and 0.05 wt. % of bismuth oxide to make a homogenous mixture. Polyvinyl alcohol (PVA) solution was used as a binder, and pellets of BTBN powder were formed and pressed into a 12 mm diameter circular disc. The pellets were then sintered for 3 hours at 1225°C.

Results and discussion



Fig. 1 XRD of BTBN ceramics.

The XRD pattern of BTBN composition, shown in Fig. 1, confirms the single tetragonal phase with space group P4mm and all peak positions are well-matched with the JCPDS number 00-005-0626. The lattice parameters were found to be a=3.9664Å and c=4.0389Å. FESEM image for BTBN ceramics is shown in Fig. 2. The microstructure of the surface shows irregular grain development having an average grain size of 464 nm. The dielectric constant was found to increase with temperature up to a specific temperature and then decreases, as shown in Fig. 3. All polarization systems respond quickly at low

frequencies, but as frequency rises, different polarizations filter out. As a result, the material's net polarization diminishes, resulting in a fall in



Fig. 2 FESEM image of BTBN ceramics.



Fig. 3 Plot of dielectric constant at different frequencies as a function of temperature.



Fig. 4 Ferroelectric hysteresis P–E loops for BTBN ceramics.

dielectric constant. The reason behind this is, near T_d and T_m temperatures, sintered ceramics show two dielectric anomalies. T_d represents the depolarization temperature, which corresponds to ferroelectric to antiferroelectric phase transition; T_m represents the which Curie temperature. occurs when antiferroelectric becomes paraelectric[4]. Dielectric loss $(\tan \delta)$ with temperature fluctuations has followed the same pattern as earlier reported (Fig. not shown here)[2]. Fig. 4 shows the hysteresis loop of BTBN ceramics. The BTBN ceramics showed energystorage density and recoverable energy density of $W_{store} \sim 60.97$ and W_{rec} ~ 28.21 mJ/ cm^3 respectively with an efficiency of 46.26 %.

Conclusion

BTBN lead-free perovskite sample was prepared by the solid-state method. The prepared BTBN ceramics were single-phase crystals with tetragonal symmetry with a P4mm space group. The BTBN ceramics showed energy-storage density and recoverable energy density of $W_{store} \sim 60.97$ and $W_{rec} \sim 28.21$ mJ/cm³ respectively with an efficiency of 46.26 % which is a significant value. We conclude that our sample is a potential candidate for energy storage applications based on the results.

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Inelastic neutron scattering studies and simulations on doped (Bi_xY_{1-x})₂O₃

Prabhatasree Goel¹, M. K. Gupta¹, Sajan Kumar^{1,4}, R. Mittal^{1,4}, Duc Le², S. N. Achary^{3,4} A. K. Tyagi^{3,4} and S L Chaplot^{1,4}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India ²ISIS Neutron and Muon Source, Rutherford Appleton Laboratory, Didcot, Oxon, OX11 0QX, UK ³Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India ⁴Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India

*Corresponding author: knp@barc.gov.in

Abstract

We report inelastic neutron scattering (INS) measurements from 300 K to 1050 K to understand oxygen-diffusion and dynamics in yttria- doped bismuth trioxide. Ab-initio molecular dynamics studies supplement the experimental observations and show that the diffusion of oxygen gets initiated at a lower temperature in comparison to the undoped δ -Bi₂O₃. Although oxygen conduction starts at lower temperature (by about 400 K) at around 700 K, the diffusion is smaller in magnitude. The activation energy required to overcome the energy barrier for diffusion is smaller for the doped systems in comparison to δ - Bi₂O₃.

Fast Cu diffusion in Cu₂Se: An inelastic neutron scattering and simulation investigation

Sajan Kumar^{1,2*}, M. K. Gupta¹, Prabhatasree Goel¹, R. Mittal^{1,2}, A. Thamizhavel³ and S L Chaplot^{1,2}

¹Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India ²Homi Bhabha National Institute, Anushaktinagar, Mumbai 400094, India ³Tata Institute of Fundamental Research, Homi Bhabha Road, Colaba, Mumbai 400005, India

*Email: sksajjan@barc.gov.in

Abstract

Here we present the neutron inelastic and ab-initio molecular dynamics investigation on Cu diffusion in Cu₂Se. Our inelastic neutron scattering measurements show strong broadening of phonon spectra in superionic regime that infers the strong anharmonic character of phonon vibrations. The estimated diffusion coefficients (*D*) at elevated temperatures from ab-initio molecular dynamics simulations trajectories lies in the range of superionic conduction. The calculated energy barrier for Cu migration ~0.2 eV, estimated from temperature dependence of *D* is in good agreement with previous reported values. Our simulations show that the Cu hoping in Cu₂Se mostly occurs via octahedral sites.

Effect of Growth-Temperature on Morphology and Piezoelectric Characteristics of ZnS Nanostructure

Siju Mishra, P. Supraja, R. Rakesh Kumar, and D. Haranath*

Energy Materials and Devices Laboratory, Department of Physics, National Institute of Technology, Warangal 506 004, India

*Corresponding author: <u>haranath@nitw.ac.in</u>

Abstract

In this work, it has been demonstrated the effect of growth temperatures viz. 140° C and 160° C on the morphology and piezoelectric characteristics of zinc sulfide nanosheets (ZnS-NS) grown on aluminum substrates. An increase in growth temperature has greater influence on the aspect ratio of the ZnS-NS due to the presence of extra thermal energy leading to significant structural deformation which in turn allowed the growth temperature window for the ZnS nanosheets to be determined. The open circuit voltage for the as-fabricated devices were ~400 mV and ~600 mV, respectively. For the first time, a methodical study was carried out in ZnS-NS system for designing novel piezoelectric nanogenerators.

Explaining The Improvement In Specific Capacitance Of α-Fe₂O₃ Hollow Sphere Under External Magnetic Field Jovanti Halder, Sudipta Biswas, Ananya Chowdhury, and Amreesh Chandra^{*}

Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur-721302, West Bengal, India.

*E-mail: achandra@phy.iitkgp.ac.in

Abstract

Magnetic supercapacitors have been seen rapid development over the last few years. It has been shown by our team that electrodes having at least one ferromagnetic element can show a significant change in electrochemical performance determined under varying magnetic field environment. This has been mostly attributed to the appearance of Lorentz force and magnetohydrodynamics. Hollow sphere is an effective morphology for supercapacitor electrodes, and the effect of magnetic field on hollow sphere electrode has never been reported. Using α -Fe₂O₃ as a test sample, it is shown that change of supercapacitor performance can also happen, and changes can be quite appreciable. The specific capacitance increases from 73 F g⁻¹ to 97 F g⁻¹ (at 50 mV s⁻¹ scan rate) under the application of a 100 Gauss magnetic field. Also, for 1 A g⁻¹ current density, specific capacitance has shown a rise from 73 F g⁻¹ to 79 F g⁻¹ at 100 Gauss. Modified diffusion behaviour of electrolyte ions near the electrode-electrolyte interface has been considered as one of the main reasons behind performance enhancement.

Introduction

Nowadays, the ever-growing population and economy led towards a need for rising energy consumption. Hence, the need for efficient energy storage devices has also become a big issue.1 Supercapacitors are considered as one of the efficient energy storage devices for its higher power density, its easy fabrication and faster charging-discharging cycles. Among different supercapacitor electrodes, metal oxides (like NiO, MnO₂, Co₃O₄, CuO) are investigated due to their redox activity, enhanced charge storage capability and easy synthesis procedure. But, very few has been reported on the negative electrode material like α -Fe₂O₃. Here, in this report, we have synthesized hollow sphere of α -Fe₂O₃ using a simple hydrothermal method.² Not only that, the synthesized hollow sphere was subjected to cyclic voltammetry and chargedischarge measurements. Here, we have studied electrode performance under non-ambient conditions,³ i.e., under the action of magnetic fields from 0 to 100 Gauss. Specific capacity increment under magnetic field has been explained with the help of Lorentz field effect and magnetic stimulated convection of the electrolyte ions.

Results and Discussion

 α -Fe₂O₃ hollow spheres were synthesized using a simple hydrothermal synthesis procedure. The phase formation of the material was confirmed using XRD (Fig.1 (a)). Fig. 1(b) shows the SEM and TEM image of the α -Fe₂O₃ hollow sphere. The images confirmed the formation of hollow spheres.

The electrochemical analysis for the materials was initially performed using a three-electrode

configuration with Ag/AgCl and Pt rod as the reference and counter electrode, respectively, in 1 M KOH electrolyte. α -Fe₂O₃ delivered a stable potential window of -0.35 to 0.4 V. as shown in Fig.2(a) in CD curves. Following electrochemical analysis at ambient



Fig. 1 (a)XRD of α -Fe₂O₃ (b) SEM micrographs (TEM inset) of α -Fe₂O₃ hollow sphere

conditions, the material was subjected to external magnetic fields varying from 0 to 100 Gauss. Three electrode measurements were performed in 0 to 100 G magnetic fields. The material shows pseudocapacitive nature. The possible redox reaction occurring at the electrode-electrolyte interface is given below:

 $\begin{array}{l} Fe_2O_3 + 2e^- + 3H_2O \leftrightarrow 2Fe(OH)_2 + 2OH^- \\ Fe(OH)_2 + 2OH^- \leftrightarrow FeOOH + H_2O + e^- \end{array}$



Fig. 2(a) CD in three electrode, (b) CV profiles under different magnetic fields, (c) variation of specific capacitance under different magnetic fields (at 50 mV s⁻¹ scan rate)

 α -Fe₂O₃ delivered the maximum specific capacitance of 82 F g⁻¹ at 10 mV s⁻¹ scan rate, and at 200 mV s⁻¹, it decreased to 48 F g⁻¹. The decreasing trend of the specific capacitance was also seen for constant current density. The stability of α -Fe₂O₃ hollow sphere was also evaluated as 99% at 1 A g⁻¹ current density after 1000 cycles.

Both CV and CD measurements were performed under magnetic fields, 0, 10, 20, 50, and 100 Gauss. Fig. 2(b) shows the CV profiles under different magnetic fields

and at 50 mV s⁻¹ scan rate.Fig.2 (c) shows the variation of specific capacitance under different magnetic fields at 50 mV s⁻¹ scan rate. At 0 Gauss, specific capacitance had a value of 73 F g⁻¹, and for 100 Gauss, it was 96 F g⁻¹. Also, CD measurements under magnetic fields were calculated at 1 A g⁻¹ current density; the specific capacitance was 73 F g⁻¹, and under 100 Gauss, it was 79 F g⁻¹. The increase of specific capacitance values under the magnetic field can be explained with the help of magnetohydrodynamic effects (MHD) and Lorentz force. When the magnetic field is applied externally due to the force $\mathbf{F}_{\mathbf{L}} = \mathbf{q} (\mathbf{v} \times \mathbf{B})$, the charged particles making an angle with the magnetic field experience an extra additive force. As a result of this force, the charged particles start moving along the channels (inside the electrode material); therefore, more number of charged particles get accumulated at the electrodeelectrolyte interface. α - Fe₂O₃ contains the ferromagnetic material Fe. and moreover, the metal oxide itself possesses canted antiferromagnetic behaviour. So, under the action of magnetic fields, it shows a tendency to make a magnetically ordered structure. With the enhancement of magnetic field intensity, more number of ions would move through a certain channel in a specified direction, increasing the ion transfer behaviour further. More no of ions get accumulated near the surface electrolyte interface (SEI) and increases the charge storage capability (EDLC). Thus, the magnetic field affects the specific capacitance.

Conclusions

The α -Fe₂O₃ hollow sphere was synthesized using a simple hydrothermal route. The electrochemical performance of the hollow sphere with and without magnetic fields is reported. Under 100 Gauss magnetic field, specific capacitance increases from 73 to 96 F g⁻¹ at 50 mV s⁻¹ scan rate. It is clear that α -Fe₂O₃ can become extremely useful for magnetic supercapacitors.

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The Structural, Dielectric, And Ferroelectric Studies Of Sr Substituted BaTiO₃ Ceramics For Energy Storage Applications

Shashi Priya Balmuchu, Pamu Dobbidi*

Indian Institute of Technology, Guwahati Guwahati-781039

*Corresponding author: pamu@iitg.ac.in

Abstract

In this study, BTO and 30% Sr substituted $BaTiO_3$ ($Ba_0.7Sr_{0.3}TiO_3$) (abbreviated as BTO and BST) have been synthesized via a cost-effective solid-state reaction method. The crystal structure transformed from tetragonal to pseudo-cubic, reducing unit cell volume for Sr substituted BTO ceramic. The Curie temperature (T_c) moved to lower values, from 125°C down to 40°C for BST with enhancement in dielectric constant from 4455 to 4785. The energy density for BTO and BST have the same value at 15kV/cm, i.e. 29 mJ/cm³. However, the enhancement in energy efficiency from 38% to 56.1% can be observed for BST ceramic. The polarization versus electric field loops with low remnant polarization gives minimum hysteresis loss and high energy efficiency for BST compared to BTO ceramic, indicating the suitability for energy storage capacitor usage.

Introduction

In an era of power electronics, electric energy storage and conversion becomes a crucial part of our daily life. Dielectric capacitors are known to have an inherent high power density, i.e. their charging and the discharging rate is quite fast (within μ s to ms range). Therefore, for high power electronic applications, the development of dielectric ceramics capacitor with enhanced energy storage density and efficiency is required [1].

BST (Ba_{1-x}Sr_xTiO₃) ceramics are the solid solution of BTO and STO widely studied ferroelectric material with tunable ferroelectric to paraelectric phase transition temperature by varying the Ba/Sr ratios [2] [3]. The high tunability and high dielectric constant make BST a potential candidate for dielectric capacitors, microwave phase shifters, dynamic random access memories, etc [1].

In this present study, we have studied the influence of structural, dielectric, and ferroelectric properties of 30% Sr doped BTO ceramic. We have studied the effect of Sr substitution systematically but in this study, we only presented the pure BTO and 30% Sr doped BTO samples for comparison. The dielectric and ferroelectric studies were conducted to study their energy storage properties.

Experiment Details

 $Ba_{1-x}Sr_xTiO_3$ with composition (x = 0.0 and 0.3) were fabricated via conventional solid-state technique. The starting chemicals (BaCO₃, SrCO₃, and TiO₂) of high purity (>99%) from Sigma Aldrich were used as a precursor. The raw materials were weighed according to the stoichiometric composition of BTO and BST (x = 0.3) and were separately ball milled for 5 hrs at 150rpm. The mixed slurry was dried at 120°C and was calcined at 1000°C for 6 hrs. The calcined powders were again ball milled for 10 hrs at 300rpm and dried at 120°C. Then, 10-20% polyvinyl alcohol (PVA) was added to granulate the obtained powders and were pressed into a cylindrical disc of 10mm diameter and 1 mm thickness under 3MPa pressure. The green bodies were sintered at 1300°C for 2h to obtain 92-96% maximum relative density. The phase structure of the sintered ceramics was identified by room temperature XRD using X-ray CuKα (1.5406 Å) diffractometer (M/s Rigaku TTRAX-III,18kW). The dielectric measurements were carried out from RT to 250°C using an LCR meter (Wavne Kerr Electronics Pvt. Ltd. 1J43100). Ferroelectric properties were examined at room temperature with a Precision LCII Ferroelectric test system (RADIANT TECHNOLOGIES. INC.).

Results and Discussions

The room temperature XRD pattern of BTO and BST ceramic are shown in Figure 1(a). All detectable peaks attributed to perovskite structure without any presence of other secondary phases. The obtained peaks for pure BTO were matched using the JCPDS card (card No. #01-074-9807) for tetragonal symmetry. The splitting of 002/200 (Bragg) reflection around 2θ =45° implies higher tetragonal symmetry with the P4mm space group for pure BTO [4]. With the addition of 30% Sr to BTO ceramic, the splitting diminishes, and peaks merge into a single peak (200) points towards the mixed phase of tetragonal and pseudo-cubic symmetry. The zoomed portion represents the shifting of the primary reflection towards the higher angle of 2θ around 45-46°, shown in Figure 1(b). The shifting of the primary reflection to a higher angle is due to the incorporation of smaller (Sr²⁺ = 1.44Å) ions into larger (Ba²⁺ = 1.61Å) [3] ions which create lattice distortion. The average crystallite size was calculated from XRD peak broadening, using the Debye Scherrer equation:

$$=K\lambda/\beta\cos\theta \qquad (1)$$

Where D is crystallite size K (Scherrer constant) = 0.89, λ is 0.15406 nm (wavelength of the x-ray sources), β is the full width at half maxima (in radian), and θ is the Bragg's angle. Table 1 shows the estimated crystallite size and unit cell volume of BTO and BST ceramic.

D



Fig. 1. (a) XRD patterns of pure BTO and BST ceramic, (b) Zoomed portion around 2θ =31.5-32.5° and 2θ =45-46° showing shifting of peak and merging of peaks.

Table 1. Structural parameters of BT and BST ceramic calculated using Scherrer equation.

Composition	Volume (Å)	crystallite size (nm)
BTO	64.3903	20
BST	62.8674	41

The dielectric properties as a function of temperature measured at different frequencies for BTO and BST ceramic are shown in Figure 2 (a-b). The dielectric constant slowly rises with increasing temperature and suddenly shows sharp transitions around 125°C and 40°C for pure BTO and BST with increased dielectric constant from 4455 to 4785, respectively. These sharp peaks indicate the Curie temperature (T_C) of the respective ceramics. The inset of Figure 2(a-b) shows the individual dielectric loss.

Well-shaped hysteresis loops for BTO and BST ceramics were obtained for different applied voltages from 500V to 1300V, shown in Figure 3 (a-b). It is observed that the value of maximum polarization increases with the application of an applied electric field for both samples. Pure BTO shows broad P-E hysteresis loops whereas, the loops become slim and slanted for BST. The narrow hysteresis loops with a low remnant polarization value for BST ceramic give better energy storage properties than pure BTO. Therefore, the BST ceramics can be tuned for energy storage applications. The calculated energy storage density and efficiency for BTO and BST at 500V and 1300V are given in Table 2.



Fig. 2. Temperature variation dielectric constant for (a) BTO and (b) BST from RT to 250°C and Inset shows the respective dielectric loss.



Fig. 3. Ferroelectric hysteresis loops at the different applied voltages for (a) BTO and (b) BST.

 Table 2. Energy storage parameters for BT and BST ceramic

Composition	Energy density (mJ/cm ³)	Efficiency (η%)
BTO (500V)	7.77	44.04
BTO (1300V)	29.74	36.93
BST (500V)	10.06	76.35
BST (1300)	29.39	55.14

Conclusion

BST is successfully fabricated by the conventional solid-state method. The Curie temperature (Tc) decreased to 40°C for BST from 125°C (BTO). An enhanced dielectric constant with slim hysteresis loops can be obtained for BST ceramic. P-E hysteresis loop with low remnant polarization suggests the suitability of BST ceramic for energy storage purposes.

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Cyclic voltammetric study of Organo-metallic electrode sustaining high potential scan rates

A. V. Thakur¹, S.D. Sonawane², P. Suryawanshi³, G.M. Vidyasagar³, R.C. Ambare¹, B.J. Lokhande^{1*}

¹ Lab of Electrochemical Studies, School of Physical Sciences, Solapur University, India.

² Dattakala College of Pharmacy, Bhigwan, India.

³Medicinal Plants and Microbiology Laboratory, Department of Botany, Gulbarga University, India.

Corresponding author : bjlokhande@yahoo.com

Abstract

Present work describe the electrochemical performance of the organo-metallic electrodes (OEs) prepared using activated carbon and Ag:C₂₀H₉ClO₅Ag gel obtained from *opuntia cochenillifera* fruit. XRD, FTIR and UV-Vis analyses were used to confirm the formation of material. TEM depicts the formation of spherical and rod like structures with variable sizes ranging from 21.40 nm to 47.21 nm. Cyclic voltammetric analyses in 0.5 M 20 ml H₂SO₄ showed that the electrodes exhibit the structural stability and good performance at scan rate as high as high as $5Vs^{-1}$ within the potential limits – 0.6V and 1.1 V which is higher than any other electrode surviving at that much high scan rate. Prepared electrode exhibits maximum specific capacitance 2.126 F/g at 50 mVs⁻¹. **Keywords :** Biosynthesis, Electrochemical study, Silver dichlorofluresceinate, high scan rate, Organometallic electrodes

Biomaterial Nelumbo Nucifera (Lotus) Leaf - PVA as Solid Electrolyte for Electrochemical Device

Meera Naachiyar R^{1,2}*, Ragam M¹, Selvasekarapandian S², Jenifer K^{1,2}, Jenita rani G¹, Aafrin Hazaana S^{1,2}, Muniraj@Vignesh N²

¹Research Department of Physics, Fatima College, Madurai-625018, ²Materials Research Centre, Madurai-625001

*Corresponding author: meeranaachiyarr.physics@gmail.com

Abstract

Novel bio-based SPE based on Nelumba Nucifera (Lotus) Leaf–PVA with various compositions of NH₄SCN have been prepared under solution casting technique. XRD analysis has been done to reveal the crystalline/amorphous nature of the membranes. The ionic conductivity has been measured using AC Impedance technique. The conductivity observed for Pure PVA in the order of 10^{-10} S/cm and for the optimized (on the basis of conductivity) 1g PVA+300mg NNL (PN) it is 10^{-6} S/cm. For PN+0.9 M.wt% of NH₄SCN (highest conducting) it is 10^{-3} S/cm, and the OCV obtained by using the corresponding electrolyte for the construction of proton battery is 1.57 V.

INTRODUCTION

Since 18th century, the Solid Polymer Electrolytes (SPEs) (emerging from synthetic polymers to biopolymers), have been used as the substitute for Aqueous Electrolytes (AEs) in various electrochemical devices such as batteries. electrochromic displays, etc. SPEs overcome the drawbacks of AEs in safety, flexibility, cost and high performance in terms of specific power and specific energy. In this (SPEs) area of research, the biomaterials have not been used much. Instead, they are mainly used in the textile industry, food industry and pharmaceutical industry due to its fibrous, edible and medicinal nature.

Nelumbo Nucifera (NN) is a perennial herb, where all parts of it are edible. They have more medicinal property and have been used as an antifebrile, antibacterial, anti-diarrheal, sedative etc. Especially, NN leaves (NNLs) have pharmacological effects such as anti-HIV, anti-obesity and antidiabetic [1]. Though it has such heavenly medicinal application, it has not been used as an electrolyte so far. The flavonoids and alkaloids in NNL show the presence of good number of polar groups. Though it has major property of charge transport, it lacks the ability of film formation. Hence the PVA is used as the binder for NNL molecules. To increase the ion transportation, ionic salts have been added. In which, the ammonium salts are preferred for its very good proton donor property.

Polyvinyl alcohol (PVA) is a biodegradable polymer with semi-crystalline nature. It has an excellent film forming ability, flexibility, high tensile strength and a good source of hydrogen bonding [2]. In this work, the NNL is blended with PVA, to which NH₄SCN salt has been added. The polymer electrolytes have been prepared and various characterizations were done.

EXPERIMENTAL TECHNIQUE

The SE has been prepared using the Solution Casting Technique. Using double distilled water as solvent, 1g PVA and 300mg NNL have been blended thoroughly for 24 hrs and various compositions (0.8, 0.9, and 1.0 M.wt%) of NH₄SCN were added separately to that combined solutions and allowed to stir for 24 hrs. The prepared solutions are then poured in polypropylene petri dish and kept in hot air oven under 45°C for 12 hrs. Then, the SE membranes of 0.03cm thickness have been obtained.

RESULTS AND DISCUSSION



Fig. 1. XRD patterns of (a) Pure PVA, (b) NNL powder (c) 1g PVA+300mg NML (PN) (d) PN+0.8 M.wt% of NH₄SCN (e) PN+0.9 M.wt% of NH₄SCN (f) PN+1.0 M.wt% of NH₄SCN

XRD ANALYSIS has been carried out using the X'Pert PRO diffractometer using Cu-Ka radiation operated with 40 kV/30 mA at the rate of 2°/min in the angle range (2 θ) of 10°-80°, which shows the crystalline/amorphous nature of the electrolyte membranes. Fig 1 represents the XRD peaks of Pure PVA membrane, NNL powder, 1g PVA+300mg NNL (PN) membrane and various compositions (0.8, 0.9, and 1.0 M.wt%) of NH₄SCN added with PN. Pure PVA membrane and powder NNL shows intense peak at 19.8° and 21.8° respectively. For PN membrane the peak shows a shift at 20.6°. On the addition of 0.8, 0.9, and 1.0 M.wt% NH₄SCN with PN the peak shift is observed at 22.1°. For 0.8 M.wt% NH₄SCN with PN the intensity of the peak decreases and the broadness increases. For 0.9 M.wt% NH₄SCN with PN there is a complete drop in intensity and observed to have a wide broadness. This shows the high amorphous nature of the electrolyte membrane. On further increase in NH₄SCN (1.0 M.wt%), the intensity slightly increases and the broadness slightly decreases indicating slight decrease in amorphous nature. The results of intensity and broadness are well in accordance with Hodge et al [3] criteria.

Ac IMPEDANCE STUDY has been carried out using the HIOKI-3532 HiTester in the frequency range of 42 Hz to 5 MHz. The Nyquist plot is drawn between the real and imaginary part of the impedance which provides the combination of semicircle (high frequency) and spike (low frequency). Fig 2 shows the Nyquist plot of Pure PVA, PN, and various compositions of (0.8, 0.9, and 1.0 M.wt%) NH₄SCN added with PN and their equivalent circuits. Table 1 represents the ionic conductivity of prepared SPEs. From the table 1 we could infer that, 300mg NNL (optimised) added with 1g PVA shows an increase in conductivity compared with Pure PVA, (which may be due to the chemical constituents like flavonoids and alkaloids) and on further addition of NH₄SCN (0.8 and 0.9 M.wt%) the conductivity increases. The composition PN+0.9 M.wt% of NH₄SCN shows the high ionic conductivity of 8.69×10⁻³ S/cm. This membrane is confirmed to have high amorphous nature, from XRD. On further addition of 1.0 M.wt% of NH₄SCN with PN, the conductivity decreases. This indicates the aggregate formation in the polymer matrix. The conductivity has been calculated using the formula.

$$\sigma = \frac{l}{AR_h} S/cm \qquad (a)$$

Using the highest conducting polymer electrolyte, primary proton battery has been constructed with the skeleton $Zn+ZnSO_4.7H_2O+C(anode)||PN+0.9 M.wt\%$

of $NH_4SCN(electrolyte) ||PbO_2+V_2O_5+C$ and the open circuit voltage obtained is **1.57** V(Fig 2).



Fig. 2. Nyquist plot of (A) Pure PVA (B) 1g PVA+300mg NNL (PN) (C) Various compositions of [(x) 0.8 M.wt%, (y) 0.9 M.wt%, and (z) 1.0 M.wt%) NH₄SCN with PN] (D) OCV value of Primary Proton Battery.

Table	1. Co	onducti	ivity	values.
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Compositions	Conductivity (S/cm)
1g PVA	7.04×10 ⁻¹⁰
1g PVA + 300mg NNL [PN]	3.85×10 ⁻⁶
$PN + 0.8\% NH_4SCN$	6.18×10^{-3}
PN + 0.9% NH ₄ SCN	8.69×10 ⁻³
PN+ 1.0% NH ₄ SCN	4.51×10 ⁻³

CONCLUSION

The proton conducting SPEs prepared using PN+0.9 M.wt% of NH₄SCN shows highest conductivity of 8.69×10^{-3} S/cm at room temperature and it is highly amorphous (XRD). The primary proton battery constructed using this SPE has given the OCV of 1.57 V. Also this membrane can be used in various electrochemical devices as SPE.

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High-Performing Asymmetric Supercapacitor Device using Nanostructured Co₃O₄ and Fe₂O₃Based Electrodes

Ananya Chowdhury, Sudipta Biswas, Swagata Dutta and Amreesh Chandra^{*}

Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur, West Bengal India-721302

*Corresponding author:achandra@phy.iitkgp.ac.in

Abstract

The importance of transition metal-based oxides in the field of energy storage is well accepted. Using novel cost-effective synthesis protocols, nanostructured Co_3O_4 and Fe_2O_3 were synthesized. These nanostructures showed impressive electrochemical activity in 1 M KOH electrolyte owing to their redox activity. Further, asymmetric device was fabricated using these two metal oxides as positive and negative electrode, in order to achieve high specific capacitance and excellent energy density. Such supercapacitor devices can be considered as efficient candidate for future energy storage applications.

Introduction

The need for energy security and sustainability is driving large scale focus on the development of novel generation, storage and transmission energy strategies. Supercapacitors have emerged as a promising energy storage device owing to their highpower density, long cycle life and cost-effectiveness¹. Moreover, metal oxide-based nanostructures are now being widely investigated in supercapacitors due to their exceptional physical and chemical properties. The electrochemical performance of these materials can be tuned by changing size, shape, composition, structure, etc.In this work, we report a high performance supercapacitor based on two transition metal oxides viz., Co₃O₄ and Fe₂O₃. Each of them have good redox property, high theoretical specific capacitance, abundant nature, low cost and wide operating potential, which enhances their electrochemical activity^{2,3}. Further, utilizing their respective positive and negative potential window, the asymmetric device can achieve high energy and power density, useful for practical applications.

Results and Discussion

 Co_3O_4 and Fe_2O_3 were synthesized using simple co-precipitation and mini-emulsion protocols, respectively. The phase formation of both the materials was confirmed by XRD analysis. **Fig. 1** depicts the SEM micrograph of the synthesized materials. The disc like structure for Co_3O_4 and formation of porous nanorods in Fe_2O_3 is clearly visible in **Fig. 1(a, b)**, respectively.

The electrochemical analysis for both the materials were initially performed using a three electrode configuration, with Ag/AgCl and Pt rod as the reference and counter electrode, respectively, in 1 M KOH electrolyte. Co_3O_4 and Fe_2O_3 delivered a

stable potential window of -0.1 to 0.8 V and -0.6 to 0.4 V, respectively, as shown in **Fig. 2(a)**. Both the material showed pseudocapacitive nature, with prominent redox peaks, especially at the lower scan rates. The charge-discharge measurements corroborated the CV findings. The possible redox reaction occurring at the electrode-electrolyte interface are given below:

(a) $Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^ CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^{-ss}$



Fig. 1 SEM micrographs of (a) Co₃O₄ and (b) Fe₂O₃

(b) $Fe_2O_3 + 2e^- + 3H_2O \leftrightarrow 2Fe(OH)_2 + 2OH^ Fe(OH)_2 + 2OH^- \leftrightarrow FeOOH + H_2O + e^-$

 Co_3O_4 delivered a maximum specific capacitance of 129 and 124 F g⁻¹ at 5 mV s⁻¹ scan rate and 1 A g⁻¹current density, respectively, whereas, in Fe₂O₃, it was 96 and 98 F g⁻¹, respectively. The specific capacitance value showed a decreasing trend, with both scan rate and current density. The Fe₂O₃-based



Fig. 2(a) CV in three electrode, (b) CD profiles and (c) specific capacitance of the device

electrode showed better rate capability compared to Co_3O_4 .

After finalizing the working potential window, asymmetric device was fabricated using Co₃O₄ and Fe_2O_3 as the positive and negative electrode, respectively. Coin cell CR2032 was fabricated using proper mass balance formula in 1 M KOH electrolyte. The device successfully achieved a stable potential window of 1.2 V. The charge-discharge profiles, within this window is depicted in Fig. 2(b). Nearly symmetric CD profiles were observed, revealing high Coulombic efficiency of >85%, which suggested the usefulness of the device. From CV and CD profiles, the specific capacitance of the device was estimated to be 30 and 34 F g^{-1} at 5 mV s^{-1} scan rate and 1 A g^{-1} current density, respectively. Further, the device was found to retain 60% of the initial capacitance value at higher current densities, as shown in Fig. 2(c). The impedance spectroscopy of the device was also analyzed and the ESR and R_{ct} value of the device was estimated to be ~ 3.2 and 6.8Ω , respectively. The energy and power density of the device was also calculated. At 1 A g-1 current density, the device showed a maximum specific energy of 16.48 Wh kg⁻¹ with 1.23 kW kg⁻¹ power density. Finally, the cycle stability of the device was investigated, as it is an important factor in order to investigate the utility of the device for practical applications. More than 92% cycling stability of the device after 1000 chargedischarge cycles proved the usefulness of the device for large scale use.

Conclusions

Two different transition metal oxides were successfully synthesized using cost effective synthesis protocol and investigated electrochemically. Co_3O_4 and Fe_2O_3 delivered maximum specific capacitance of 129 and 96 F g⁻¹ at 5 mV s⁻¹. A high performance asymmetric supercapacitor device was fabricated, which delivered high specific capacitance along with specific energy of 16.48 W h kg⁻¹.

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Polyvinyl Alcohol (PVA) And Nelumba Nucifera (Lotus leaf powder) based Li-Ion Conducting Electrolytes for Electrochemical Device Applications

Aafrin Hazaana S^{1,2*}, Ancemma Joseph², Selvasekarapandian S¹, Premiga P^{1,2}, Muniraj@Vignesh N¹, Meera Naachiyar R^{1,2}

¹Department of physics, Fatima College, Madurai-625018, ²Materials Research Center, Madurai-625001

*Corresponding Author: <u>aafrinhazaanas.physics@gmail.com</u>

Abstract

Solid polymer electrolytes (SPE) utilized in the application of electrochemical devices have been prepared based on Polyvinyl alcohol (PVA) and Nelumba Nucifera (Lotus leaf – LL) with the addition of LiClO₄ in different weight percentage using solution casting technique. The amorphous/crystalline nature of the prepared electrolytes has been studied using XRD. Ac Impedance analysis is done to identify and measure the ionic conductivity of the membranes where Pure PVA is showing conductivity in the order of 10^{-10} S/cm. In order to increase the ionic conductivity, different compositions of Lotus Leaf powder is added to 1g of PVA and optimized on the basis of ionic conductivity which shows the value of 3.62×10^{-6} S/cm for the composition 1g PVA+300 mg LL. And on further addition of salt, the high ionic conductivity is observed as 3.03×10^{-3} Scm⁻¹ for 1g PVA+300 mg LL+0.7 M.wt% of LiClO₄ composition of electrolyte and Li-ion conducting primary battery was fabricated with the highest ion conducting membrane resulting with an OCV of 1.65 V.

INTRODUCTION

In current decade, Lithium-ion battery is one of the best applications of electrochemical device fabrication. The synthesis and characterization of solid polymer electrolytes (SPE) has become an active area of research owing to few disadvantages of liquid polymer electrolytes. Synthetic polymers such as PVA, PVP, PAN, PEO etc., used as an electrolyte for long time in battery constructions are still facing few drawbacks such as toxicity, high-cost, lack of availability, nonbiodegradability etc., Thus, to overcome these issues, an attempt of combining the synthetic polymer along with the natural bio-based material is done which may improve the properties of an electrolyte to be prepared. Polyvinyl alcohol (PVA) is a semi-crystalline polymer with excellent film forming ability, high tensile strength and better mechanical stability [1]. Nelumba Nucifera, also known as Lotus, have many medicinal properties and all parts of them like flower, leaf and seed are edible. Subsequently, lotus leaf (LL) contains chemical constituents like flavanoids and alkaloids which help in improvising the ionic conductivity. Hence, PVA and Lotus leaf blend along with an addition of various concentrations of lithium salt (LiClO₄) has been developed using solution casting technique. As per literature survey, solid polymer electrolyte based on PVA/LL with LiClO₄ is not yet done.

EXPERIMENTAL TECHNIQUE

The polymer electrolytes based on PVA and LL with different weight percentage of $LiClO_4$ was prepared using solution casting technique. PVA and LL were magnetically stirred for an hour at room temperature using distilled water as a solvent. Then, PVA and LL is combined together and was allowed to be stirred for 24 hours. Followed by the addition of different weight percentage of $LiClO_4$, the solutions were again stirred for 24 hours in order to obtain the homogeneous mixture. The obtained solution was poured in poly-propylene petridish placed in hot plate and was evaporated in 45°C for 12 hours. The resulting electrolytes were analyzed using different characterization techniques for further applications.

RESULTS AND DISCUSSION

X-RAY DIFFRACTION ANALYSIS

The amorphous/crystalline nature of the membranes has been identified using X-ray diffraction technique. Fig.1 shows the patterns of XRD peaks for Pure PVA, PVA/LL and PVA/LL with different concentrations of LiClO₄. From the figure, the diffraction peak observed for Pure PVA is at $\theta = 19.89^{\circ}$. On further addition of Lotus leaf powder and various concentrations of LiClO₄, the intensity of the peak decreases along with increase in its broadness which reveals the amorphous nature of the sample. The analyzed result can be explained in terms of Hodge et al [3] criterion which determines

the correlation between intensity and broadness of the peak. The high amorphous nature is observed in the membrane with 1g PVA+300 mg LL+ 0.7 M.wt% of LiClO₄. The peaks due to LiClO₄ was absent in the above mentioned polymer matrix describing the complete dissociation of the salt. On further addition of LiClO₄, the crystalline nature of the membrane is increased which is confirmed by the increase in intensity and decrease in broadness of the peak.



Fig.1 (a) Pure PVA (b) Lotus leaf powder (c) 1g PVA+300 mg LL (d) 1g PVA+300 mg LL+0.6 M.wt% of LiClO₄ (e) 1g PVA+300 mg LL+0.7 M.wt% of LiClO₄ (f) 1g PVA+300 mg LL+0.8 M.wt% of LiClO₄

Ac IMPEDANCE TECHNIQUE

Ac Impedance analysis has been done to measure the ionic conductivity of the prepared PVA/LL blend polymer electrolytes with different weight percentage (0.6 wt%, 0.7 wt% and 0.8 wt%) of LiClO₄. The complex impedance plot of Pure PVA and 1g PVA+300 mg LL (Optimized with ionic conductivity of 3.62×10^{-6} S/cm) is ascribed in Fig 6(a) and (b). When compared to Pure PVA, the composition of electrolyte with 1g PVA+300 mg LL shows increase in ionic conductivity which may be due to the presence of flavanoids and alkaloids. Then, Fig 6 (c) depicts the cole-cole plot of 1g PVA+300 mg LL+ (X) M.wt% of LiClO₄ [X = 0.5, 0.6, 0.7, 0.8]. From Fig 6 (c), it is understood that the semicircle region vanishes with increase in concentration of lithium salt confirming that the conduction is due to the charge carriers of ions.



Fig.6 (a) Cole-Cole plot of Pure PVA, (b) Inset graph: 1g PVA+300 mg LL, (c) 1g PVA+300 mg LL+various concentrations of LiClO₄

The ionic conductivity of the membranes prepared has been calculated using the formula,

$\sigma = l/AR_b Scm^{-1}$

Table 1 gives the ionic conductivity of the electrolytes prepared. The highest ionic conductivity measured for 1g PVA+300 mg LL+0.7 M.wt% of $LiClO_4$ is **3.03 x 10⁻³ S/cm.** As the salt concentration increases above 0.8 M.wt% of $LiClO_4$, the ionic conductivity decreases indicating the aggregation of ions.

Table 1	Ionic	conductivity	of prepared	electrolyte	2S
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Polymer compositions	Ionic conductivity
1g PVA (Pure PVA)	$7.00 \ge 10^{-10}$
1g PVA+300 mg LL (X)	3.62 x 10 ⁻⁶
X+0.6 M.wt% of LiClO ₄	2.17 x 10 ⁻³
X+0.7 M.wt% of LiClO ₄	3.03 x 10 ⁻³
X+0.8 M.wt% of LiClO ₄	1.17 x 10 ⁻³

FABRICATION OF PRIMARY BATTERY

The construction of Liion conducting battery is done by sandwiching the highest ion conducting membrane between the pellet form of cathode [PbO₂ (8):V₂O₅ (2): Graphite (1): Electrolyte (0.5)] and anode [Zn powder (3):Zn₂SO₄ (1): Graphite



(1)] and placing them in the battery holder. The Open circuit voltage (OCV) of the cell was measured as **1.65 V** and was retained for 48 hrs.

CONCLUSION

Polyvinyl alcohol (PVA)/Nelumba Nucifera (LL) based SPE's with various composition of LiClO₄ was prepared and optimized with high ionic conductivity of **3.03 x 10^{-3} S/cm** at ambient temperature. Subsequently, Li-ion conducting battery was also fabricated resulting with OCV of **1.65 V**.

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Indoor light harvesting using Bael dye sensitized solar cell

Samah Alhorani^{1,*)}, Sarvesh Kumar¹⁾, Mahaveer Genwa² and P. L. Meena³⁾

¹Department of Applied Sciences (Physics), Faculty of Engineering and Technology, Manav Rachna International Institute of Research and Studies, Sector-43, Faridabad – 121001, India.

²Department of Chemistry, Deen Dayal Upadhyaya College (University of Delhi), Sector-3, Dwarka, New Delhi-110078, India.

³Department of Physics, Deen Dayal Upadhyaya College (University of Delhi), Sector-3, Dwarka, New Delhi-110078, India.

*Corresponding author: samah alhorani@yahoo.com

Abstract

Dye-sensitized solar cells (DSSCs) are well known as the next-generation solar cells with better solar to power conversion efficiency under low lighting environments (e.g., indirect sunlight). This study aims to determine the performance of Bael leaves extract-based DSSC under indirect sunlight. The photovoltaic properties of the Bael extract sensitized solar cell was evaluated by measuring the open-circuit voltage (Voc), the short-circuit current (Isc), the fill factor (FF), and the maximum power density (P_{MAX}). The parasitic resistance: characteristic (R_{CH}), series (R_s), and shunt (R_{sH}) resistance were measured from the I-V curve. Under a light intensity of (334 Lux), the Bael dye was generated I_{SC} = 0.62μ A and P_{MAX} = 491 nW/m^2 .

Introduction

The low photovoltaic performance of the conventional silicon solar cells in the low light intensity has limited their widespread in portable electronic and indoor applications. On the other hand, natural photosensitizer-based dye-sensitized solar cells (DSSCs) are attracting significant attention from researchers for exploiting indoor energy harvesting technology (e.g., wireless sensor nodes) due to their ability to work effectually in low lighting conditions [1,2]. Currently, there is no international standard norm for solar cells characterizing for indoor applications [3]. Pomegranate juice-based DSSC was characterized by measuring the generated opencircuit voltage (Voc) under various types of low light intensity (halogen lamp, LED, and mobile phone) and lighting conditions (e.g., the distance between the cell and light sources). Also, it is found that series and parallel combinations of DSSCs can generate sufficient current and voltage for operating the sensors working in the range mW- μ W [1].

In this paper, we describe the photovoltaic performance of a DSSC based on Bael leaves extract under indoor lighting conditions.

DSSC preparation

Natural dye was extracted from fresh powdered Bael leaves using ethanol at (0.2 g/mL). The working electrode was prepared by depositing the TiO₂ paste on FTO conductive glass using the doctor blade method. After that, the film heated at 440-450 °C for 10-15 minutes in the muffle furnace. The backed TiO₂ was then immersed in the extracted ethanol Bael

dye solution overnight. The counter electrode was also prepared by using the doctor blade method of graphite paste. A liquid electrolyte solution was prepared from potassium iodide, iodine, and sodium nitrate in water and acetonitrile under continuous stirring for 2 hours. Then, one drop from this solution was spotted on electrodes using a capillary. Both electrodes were put together into a cell with the help of binder paper. The schematic representation of the assembled DSSC structure is shown in figure 1.



Fig. 1. Schematic of Bael dye-sensitized DSSC structure.

Characterization techniques

Beal leaves dye extract in ethanol was characterized by UV-1800, a Shimadzu spectrometer in the 400-750 nm wavelength range using transmittance mode. The current-voltage (I-V) characteristics of Beal dye-sensitized DSSC were recorded using the Keithley-2450 Source measure unit.

Results and Discussions

The transmittance spectrum of extracted Bael dye in the wavelength range of 400-750 nm is presented in figure 2. The minimum transmittance wavelength was found at 676 nm and followed by a sharp increase toward a longer wavelength. The maximum transmittance was found at 750 nm. The lowest transmittance was observed in the wavelength range of 484-648 nm. These characteristics indicate that chlorophyll is the main constituent of the Bael leaves extract [4].



Fig. 2. Transmittance spectrum of Bael dye.

The current-voltage (I-V) and power densityvoltage (P-V) characteristics curves performed on the Bael leaves extract sensitized DSSC under indirect sunlight, as shown in figure 3. The values of the short-circuit current (I_{SC}), and the open-circuit voltage (V_{OC}) were calculated from the (I-V) curve. The maximum current (I_{MP}), maximum voltage (V_{MP}), and maximum power density (P_{MAX}) were computed from the (P-V) curve.



Fig. 3. I-V characteristics of assembled DSSC.

The fill factor (FF) was calculated from the following equation [5],

$$FF = \frac{I_{MP} \times V_{MP}}{I_{SC} \times V_{OC}}$$

The key parameters (I_{SC} , V_{OC} , FF, and P_{MAX}) of Bael leaves dye-sensitized DSSC under indirect daylight were presented in table 1.

 Table 1. Photovoltaic performance of Bael dyesensitized DSSC under indirect daylight (334 lux).

Isc	Voc	FF	PMAX
(μΑ)	(mV)		(nW/m^2)
0.62	0.95	0.21	491

The calculated FF value of Bael dye-based DSSC in indirect daylight circumstances was 0.21. The FF value is influenced by series resistance (R_S) and shunt resistance (R_{SH}). The electrical values of (R_S) and (R_{SH}) of DSSC are approximately estimated from the inverse slopes of the I-V curve near V_{OC} and I_{SC}, respectively. The resistance at P_{MAX} is called the characteristic resistance (R_{CH}) and is calculated from the ratio between V_{MP} and I_{MP} [5]. The values of R_{CH}, R_S, and R_{SH} were tabulated in table 2.

Table 2 shows that the R_S value is near twice the R_{SH} value, lowering the FF value and affecting the cell's overall performance. Furthermore, the R_S value is much higher than R_{CH} , showing that the Bael dyebased DSSC is not operating at full power in indirect sunlight. This could be due to low light intensity (<< 100 W/m²) [5,6]. Therefore, different lighting conditions can be investigated for DSSC cell performance improvement.

 Table 2. Parasitic resistances of Bael dye-sensitized

 DSSC under indirect daylight (334 Lux).

RCH	Rs	R _{SH}
(Ω)	(Ω)	(Ω)
1400	2358	1304

Conclusions

Bael leaves dye-sensitized DSSC was successfully fabricated. Even though the observed performance for assembled DSSC under indirect sunlight is poor, it may be considered as potential merit for establishing a cost-effective and environmentally friendly prototype of DSSC as an energy harvester by using a natural dye.

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Influence of Crucible Dimension In the mc-Si Ingot Growth Process G. Aravindan^{1*}, M. Srinivasan¹, and P. Ramasamy¹

¹SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Chennai 603 110.

*Corresponding author: <u>aravindanvpt@gmail.com</u>, <u>aravindang@ssn.edu.in</u>

Abstract

We have numerically simulated two 6.90 Kg mc-Si ingot directional solidification (DS) systems (Different ingot dimension: DSS-1 (200 mm * 200 mm * 100 mm) and DSS-2 (158 mm * 158 mm * 158 mm)) by using Finite Volume Method (FVM). The temperature distribution, melt-crystal (m-c) interface shape, vertical temperature gradient and melt flow velocity have been investigated. DSS-1 has convex m-c interface shape and DSS-2 has concave interface shape. Lower vertical temperature gradient and lower melt flow velocity are obtained for DSS-1 compared to DSS-2.

Introduction

Growth of world population is increasing day by day with energy requirement. Currently energy technology has been turning to the renewable energy side, because of long term requirement. In renewable energy sources solar energy is crucial one. Installed renewable power grids (excluding large hydro) in India (Up to Feb 2016): Wind power is 29,151 MW (59.8 %), Solar power is 9,566 MW (18.6 %), Bio mass power is 8,182 MW (15.9 %), Small hydro power is 4,346 MW (8.5 %) and Waste-to-power is 114 MW (0.2 %). Percentage of wind power in the renewable energy power production is very high but it has drawbacks compared to solar panels such as maintenance cost and lower efficiency after the life time of 20 years (wind energy is 66% and solar panel is 80 %). In the PV market 60 % of solar panels are occupied by the mc-Si solar cells, it is produced by DS process. Efficiency of mc-Si wafer is less than the mono-Si wafers but it has low cast, simple operating process and high mass production compared to mono-Si wafer production. During the mc-Si growth process stress and dislocation reduction is important because it will affect the conversion efficiency of mc-Si wafer solar cells. However melt-crystal (m-c) interface has predominant role, planar or convex interface shape is good for PV application. Y. Y. Teng et al have investigated influence of melt convection and analysed the carbon distribution in the mc-Si ingot [1]. Numerical simulation is best tool to understand and analyse the DS process. In this work two different DS systems have been investigated. Mass of two ingots is same (6.90 Kg). The first ingot is 200 mm * 200 mm * 100 mm and the second ingot is 158 mm * 158 mm * 158 mm. After the simulation we analyze temperature distribution, meltcrystal (m-c) interface, vertical temperature gradient and melt flow velocity.

Model and method

In this simulation starts from the meltfreezing stage of silicon. Numerical simulation was done by CGSim software, based on the FVM method. The mathematical model, model description and material properties are reported already [2]. In this numerical investigation we have used two directional solidification system (DSS). Difference between the two DS systems: The crucible dimension varies and other process parameters are same. In DSS-1 the crucible size is 200 mm * 200 mm * 280 mm and In DSS-2 crucible size is 158 mm * 158 mm * 340 mm. In both cases crucible side wall thickness is 15 mm and bottom thickness is 20 mm. The schematic diagram of DS furnace is shown Figure.1. Figure 1a is DSS-1 and 1b is DSS-2.



Fig. 1. DS Furnace (a) DSS-1 (b) DSS-2. 1 is side insulation, 2 is top insulation, 3 is bottom insulation, 4 is DS block, 5 is quartz crucible, 6 is silicon crystal, 7 is Ar gas inlet, 8 is side heater and 9 is bottom heater.

Results and Discussion

Thermal field has vital role in the DS furnace. Quality of mc-Si depends on the thermal field during the growth process, because thermal stress depends on temperature gradient and also it defines the m-c interface during the solidification process. Planar or convex m-c interface is good for PV application. If the interface shape is planar the impurities are uniformly distributed, if interface shape is convex it will push impurities outside. Concave m-c shape is not good for PV application because if the interface shape is concave the impurities are accumulated in the center region. It will decrease the efficiency of mc-Si ingot, SiC impurities will damage the diamond wire during the cutting process and during the concave m-c interface more multi nucleations are born near to the side position of quartz crucible, it will produce thermal stress on mc-Si ingot. Figure.2 shows the temperature distribution of mc-Si ingot at two stages. Figure.2 a1&b1 correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, a2&b2 correspond to DSS-1 & DSS-2 after 3.30 hr crystallization. DSS-1 has convex m-c interface shape in the two stages. Figure.3 shows vertical temperature gradient of mc-Si ingot at two stages. Figure.3 a1&b1 correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, a2 &b2 correspond to DSS-1 & DSS-2 after 3.30 hr crystallization. Figure.4 shows the velocity field in y direction of mc-Si ingot at two stages. Figure.4 a1&b1 correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, a2&b2 correspond to DSS-1 & DSS-2 after 3.30 hr crystallization. Fluid velocity is lower in the DSS-1 because it has lower vertical temperature gradient. DSS-1 results in good quality ingot grown compared to DSS-2.



Fig. 2. Temperature distribution of mc-Si ingots [Unit: K]. (a1) & (b1) correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, (a2) & (b2) correspond to DSS-1 & DSS-2 after 3.30 hr crystallization



Fig. 3. Vertical temperature gradient of mc-Si ingots [Unit: K/m]. (a1) & (b1) correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, (a2) & (b2) correspond to DSS-1 & DSS-2 after 3.30 hr Crystallization



Fig. 4. Fluid velocity in Y direction [Unit: m/s]. (a1) & (b1) correspond to DSS-1 & DSS-2 after 2.30 hr crystallization, (a2) & (b2) correspond to DSS-1 & DSS-2 after 3.30 hr crystallization.

Conclusion

Numerical analysis has been done in two different dimensions of crucible (DSS-1 and DSS-2) with same silicon mass (6.90 Kg). DSS-1 has convex interface during the crystallization, lower vertical temperature gradient and lower fluid velocity compared to DSS-2. DSS-1 results in good quality ingot grown compared to DSS-2.

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Influence of Cactus-like Morphology on Supercapacitive Performance of Cr₂O₃

Sakshi Kansal¹, Paulomi Singh², Debabrata Mandal², Vikas Sharma², Trilok Singh¹ and Amreesh Chandra^{1,2*}

¹School of Energy Science and Engineering, ²School of Nano Science and Technology, Indian Institute of Technology Kharagpur, Kharagpur-721302

*Corresponding author: achandra@phy.iitkgp.ac.in

Abstract

 Cr_2O_3 is considered to be a promising cathodic material for supercapacitor applications on the account of its fast redox kinetics, mesoporous structure, and better electrochemical stability. Herein, we introduced a one-step synthesis of Cr_2O_3 which depicts a unique cactus-like morphology. Such structure improves the specific surface area and ion diffusion mechanism, which enhances the capacitance value. The prepared Cr_2O_3 displayed a specific capacitance value of 35 F g⁻¹ at 5 mV s⁻¹, with capacitive retention of ~ 60 % at a scan rate as high as 150 mV s⁻¹. This can be attributed to the redox couple of Cr_2O_3 can be used for devising high-performance supercapacitors, with appreciable chemical stability, and rate performance.

Introduction

Increasing global warming direct a way towards the development of advanced energy generation and storage sources that can be renewable and ecological. Supercapacitors are widely preferred for energy storage applications owing to their high power density, greater rate capability, longer lifetime, good thermal and mechanical stability.[1] Recently, Cr₂O₃ has been explored as a promising pseudocapacitive material for the energy-efficient supercapacitors on the account of its appreciable chemical stability, low-cost fabrication, natural abundance, and better rate performance than the traditional transition metal-oxides. Moreover, Cr_2O_3 displays the redox couple of Cr^{4+}/Cr^{3+} , which imparts high specific capacitance and improved electrochemical stability. In this work, we highlight the synthesis of a unique cactus-like morphology of Cr₂O₃ using facile and cost-effective method. The structure significantly proliferates the specific surface area as well as improves the ion diffusion mechanism. Further, as cathodic material, Cr₂O₃ unveils good pseudocapacitive performance with a better rate capability even at higher scan rates and current densities.

Results and Discussion

 Cr_2O_3 was fabricated by utilizing a one-step hydrothermal synthesis protocol. The phase formation and the morphology characterization of the material were confirmed by XRD analysis and SEM micrograph, respectively. Fig. 1(a, b) depicts the unique cactus-like morphology of Cr_2O_3 material at different magnifications. The spikes-containing structure would facilitate electrolyte ion diffusion and ensure high specific surface area.



Fig. 1 SEM micrographs of Cr₂O₃

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The electrochemical analysis for the sample was performed using three electrode-configuration with Ag/AgCl as the reference, and Pt rod as the counter electrode in 1 M KOH electrolyte.



Fig. 2(a) CV in three electrode, (b) CD profiles, and (c) specific capacitance variation with different scan rates, and current densities for Cr_2O_3 material

Fig. 2(a) depicts the cyclic voltammogram of Cr_2O_3 that effectively runs between the potential range of - 0.3 V to 0.4 V without any sign of H₂/O₂ evolution. At the scan rate 5 mV s⁻¹, the material showed a specific capacitance of 35 F g⁻¹ with ~ 60% capacitive retention upto scan rate as high as 150 mV s⁻¹. The pseudocapacitance behaviour in cactus-like Cr_2O_3 can be attributed to the possible faradic reactions that are

occurring at the electrode-electrolyte interface and are given below:[2]

$$\operatorname{CrO}(\mathrm{OH}) + OH^{-} \leftrightarrow \operatorname{CrO}(\mathrm{OH})_{2} + e^{-}$$
(1)

$$\operatorname{CrO}(\operatorname{OH})_2 + OH^- \leftrightarrow \operatorname{CrO}(\operatorname{OH})_3 + e^-$$
 (2)

Further, it becomes imperative to understand the electrochemical performance of a supercapacitive electrode under high current conditions to ensure its practical applications. Hence, charge-discharge profiles of Cr_2O_3 material were performed at various current densities as displayed in **Fig 2(b)**.

S. No.	Current densities (A g ⁻¹)	Specific capacitance (F g ⁻¹)
1.	1	51
2.	2	47
3.	3	40
4.	5	35

Table 1 the specific capacitance values at different	t
current densities for Cr ₂ O ₃ material	

As shown in **Table 1**, when the charge-discharge rate increases from 1 to 5 A g⁻¹, the specific capacitance value remains 35 F g⁻¹. This indicated that the assynthesized Cr_2O_3 material works efficiently at higher current densities with an appreciable rate capability. Moreover, variations of specific capacitance values, with scan rates, and current densities, are displayed in **Fig. 2(c).**

Conclusions

A facile one-step hydrothermal method was used to synthesize a unique cactus-like morphology of Cr_2O_3 , which imparts the material with high surface area and improves the ion diffusion mechanism. As a result, the as-prepared Cr_2O_3 material shows an appreciable value of specific capacitance ~ 51 F g⁻¹ at 1 A g⁻¹ with capacitive retention of 70% even when the current density is raised to a higher value. Hence, hierarchical cactus-like Cr_2O_3 can emerge as a promising cathodic material for used in high-performance supercapacitors.

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High performance Na-ion supercapacitor: Beyond carbon structures

Sudipta Biswas^{1*}, Ananya Chowdhury¹, Shyamal Shegokar², and Amreesh Chandra^{1,2#}

¹Department of Physics, ²School of Energy Science and Engineering, Indian Institute of Technology Kharagpur, Kharagpur, India - 721302

Corresponding author: sbiswas@iitkgp.ac.in, achandra@phy.iitkgp.ac.in*[#]

Abstract

Recent trends in sodium-ion-based energy storage devices have shown a potential use of hollow structures as an electrode material to improve the performance of storage systems. Carbon based material are also the leading material with sodium-based electrode materials. In this paper, V_2O_5 nanorods have been employed as the efficient electrode material for Na-ion batteries. These nanostructures showed impressive electrochemical activity in 2 M NaOH electrolyte owing to their redox activity.

INTRODUCTION

Na-ion, with chemistry similar to Li-ion, was always expected to become useful for energy devices. Limiting factors of the use of the Na-ion based materials was the difficulty in obtaining single-phase material, with desired particle morphology. Over the last few years, there has been a steady development in the field of Na-based systems. Till date, materials with solid morphologies are being used in Na-ion supercapacitors. To bring quantum jump in the performance, newer types of materials will have to be investigated.

Additionally, one should be mindful of the fact that Na+, with a larger ionic radius than Li+, will not combine with any randomly chosen anode. The complementary electrode must be such that it allows space for efficient ion intercalation and deintercalation. Mostly carbon based electrodes are combined with Na-ion based electrodes. But the major limitation of the carbon-based electrodes is the limited redox behavior.

Many recent studies, related to metal oxides, are suggesting the use of hierarchical nanostructures is the way forward for next generation supercapacitors. So, in this study hollow NaFePO₄ structures was employed as positive electrode material.

To boost the device performance nano rods of V_2O_5 was used as the negative electrode material. The combination of the electrode was able to deliver a capacity of 50 F g⁻¹ at 1 A g⁻¹ discharge current. This value is higher than that reported in Na-ion based supercapacitors.

EXPERIMENTAL

Hollow NaFePO₄ and V₂O₅ nanorod were synthesized using hydrothermal process. Various characterization techniques were used for material characterization.

These included: XRD, SEM, TEM, BET, particle size, zeta, etc. Electrodes were prepared using active material, PVDF and carbon in 8:1:1. Mass loading of the electrodes were maintained at 1 mg cm⁻². Both 3 electrode and devices were investigated.

RESULT AND DISCUSSION

Figure 1 depicts SEM and TEM micrographs of NaFePO₄ and V₂O₅, respectively, confirming formation of hollow and rod like structures. XRD analysis for the materials showed good crystallinity for NFP and V₂O₅ powders. Particle size analysis also were in good agreement with the SEM and TEM analysis, where the average particle size of the particles was found to be 1.5 μ m and 20 nm, for NFP and V₂O₅, respectively.

From the three-electrode characterization of both the materials, a stable working potential window was optimized to be 0.8 V (from -0.3 V to 0.5 V) for NFP and 0.9 V (from -1.0 V to -0.1 V) V₂O₅, respectively. Clear redox peaks were observed in both the electrode materials, at low scan rate (5 mV s⁻¹), as shown in the CV profiles. This result of the stable window further confirmed that these materials can be suitably serve the purpose of positive and negative electrodes in aqueous electrolyte to fabricate the asymmetric device. Additionally, the specific capacitance value of both the materials were estimated from CV and CD profiles. NFP and V₂O₅ delivered a maximum specific capacitance of 151 F g⁻¹ and 295 F g⁻¹ at 1 A g⁻¹ current density, respectively.

Finally, asymmetric device was fabricated using properly mass balanced electrode films in 2 M NaOH electrolyte using NFP and V_2O_5 , respectively. Figure 2(a) depicts the CV profiles of NFP, V_2O_5 , and NFP// V_2O_5 device, at 50 mV s⁻¹ scan rate, within a stable potential window of 1.5 V. Figure 2(b) depicts the corresponding CV curves. Nearly symmetric CD



Figure 1. (a) SEM micrographs for NFP structures and (b) TEM micrograph for V₂O₅ nanorods.

profiles, were observed which further suggested good Coulombic efficiency of >90% for the device. The specific capacitance values were estimated at different scan rates and current densities. NFP//V2O5 device showed a maximum specific capacitance of 41 F g⁻¹ at 5 mV s⁻¹ scan rate and 51 F g⁻¹ at 1 A g⁻¹ current density, respectively. The capacity delivered by the device showed low capacity fade, as shown in Figure 2(c). At higher current density, the device showed rate capability of 43%, with a specific capacitance of 22 F g⁻¹. The cycle performance of the device was also investigated, as it is considered to be one of the essential features of a device for industrial as well as small scale application. After 1000 charge-discharge cycles at 3 A g⁻¹, the device showed a capacitance retention of ~92%, proving its usefulness for real world applications. Finally, the energy and power density of the device were calculated as 54.4 W h kg⁻¹ and 701 W kg⁻¹, respectively.

Conclusion

The Na-ion device is able deliver high energy density with stable cycling performance to compete



Figure 2. (a) Stable window, (b) CD and (c) capacity fade for NFP/V_2O_5 device.

the device available in the market. Asymmetric device shows much higher performance that symmetric supercapacitors.

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Role of Minority-spin States and Cu Doping on CO Interaction over Pt₃Cu⁻ Nanocluster

Hemang P. Tanna^{1,*}, Bhumi A. Baraiya¹, and Prafulla K. Jha¹

¹Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara - 390002, Gujarat, India

*Corresponding author: hemang4me@gmail.com

Abstract

First-principles based on dispersion corrected spin-polarized density functional theory (DFT-D3) calculations were performed to investigate the structural properties, relative energetics, and electronic reactivity descriptors (ERDs) of neutral and charged Pt₄, Cu₄, and Pt₃Cu NCs. The interaction mechanism of CO over energetically preferable NCs was examined and our results of ERDs indicate that the doping of Cu atom reduces the strength of CO on Pt atom which can eliminate the poisoning effect of CO.

Evaluation of Xanthan gum with additive salts as an electrolyte for Sodium-ion Batteries

P.Priyanka¹, B.Nalini^{1*}, K.Vichitra¹, G.G.Soundarya¹

¹Department of Physics, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore 641043

*Corresponding author: jyothsnalalin99@gmail.com

Abstract

The skyrocketing demand of Lithium ion batteries (LIBs) leads to the urge to develop potential energy storage devices. Sodiumion batteries (SIBs) could be a good alternative due to its high abundance and cost effectiveness. The replacement of liquid electrolytes with polymer electrolytes is one of the frontiers of enhancing sodium-ion battery competitiveness. An attempt has been made to synthesize a bio polymer electrolyte based on Xanthan gum (XG) with the addition of electrolytic salts such as sodium hydroxide (NaOH) and sodium sulfate (Na₂SO₄) by solution casting method. The complexation between XG and the salt is verified by Fourier transform infrared spectroscopy (FTIR). The ionic conductivity of the prepared electrolytes is measured through AC impedance analysis. The highest conductivity value of 2.9×10^{-5} Scm⁻¹ is observed for 0.05g Na₂SO₄ incorporated XG membrane which qualifies itself as a prospective electrolyte for sodium-ion battery application.

Introduction

In SIBs, traditional organic liquid electrolytes are widely used and there occurs issues such as high flammability, thermal runaway, risk on leakage of electrolyte and safety concerns. Therefore as a replacement, solid polymer electrolytes are under study due to its lower flammability, improved durability, good thermal, chemical and mechanical stability as well as good electrochemical performance [1]. Xanthan gum (XG) is a polysaccharide found in the microbial world that has the capacity to make clear solutions with increased viscosity and stability over a wide temperature range. Pawlicka et.al., reported that XG prepared with addition of acetic acid shows the conductivity value of 7.26x10⁻⁵ Scm⁻¹ [2]. Another report shows the combination of XG with glutaraldehyde plasticized with ethylene glycol which exhibited a maximum conductivity value of 7.39x10⁻⁵ Scm⁻¹ [3]. In the present research work, the XG with different ratios of electrolytic salts (NaOH and Na₂SO₄) are studied and reported..

METHODOLOGY

Xanthan gum based polymer electrolyte is prepared by solution casting method wherein, 0.5 gram of XG is added in 50 ml of distilled water. After complete dissolution, the solution is casted on a petridish, glycerol is coated on the petridish for easy retrieval of the film. The solution casted membrane is air dried for two days. The obtained film is homogeneous in nature. Then the same procedure is repeated by the addition of two different electrolytic salts such as NaOH (0.02, 0.04, 0.06, 0.08 and 0.1g) and Na₂SO₄ (0.025, 0.05, 0.075, 0.1g) with varied salt concentrations. While incorporating XG with NaOH, films are obtained with more moisture content and XG with 0.04g NaOH does not show a good film. Also, the addition of salt makes the film yellow in color. The film forming capacity is well observed for different concentrations of XG with Na₂SO₄ than NaOH. The prepared membranes are characterized by FTIR and AC Impedance analysis in the frequency range of 1 MHz to 100 mHz, with a sinusoidal amplitude of 10mV. The prepared membranes are analyzed by sandwiching them in-between copper foil on both the sides.

RESULTS AND DISCUSSION

FTIR analysis



Fig. 1. (a&b) FTIR spectrum of XG and XG with addition of salt

The FTIR spectrum of pure XG membrane (Fig. 1 (a)) shows a broad band observed at 3360 cm⁻¹ assigned to the axial deformation of hydrogen bonded O-H. The band at 2950 cm⁻¹ shows the absorption of symmetrical and asymmetrical stretching of C-H [4]. The band at 672 cm⁻¹ is attributed to the C-H bending vibration. In addition of salt (Fig. 1(b)), the blue shift in wavenumber from 672 cm⁻¹ to 660 cm⁻¹ is attributed to the CH bending of alkyne group. The peak shift is observed from 3360 to 3324 cm⁻¹ of O-H group and 1648 to 1654 cm⁻¹ indicates that C=O formation from XG in addition of salts. There is no heat treatment involved in the samples, thus the properties of electrolytic salts are preserved in the host matrix which could enhance the electrical properties of the membrane.

AC Impedance analysis

The ionic conductivity is calculated by A.C impedance spectroscopy with the parameters Rb (bulk resistance), L (thickness of the sample) and A (area of the sample). The ionic conductivity is calculated from nyquist plot using fitted R1 and R2 values. R1 is the solution or electrolytic resistance and R2 is the resistance due to the insulating matrix. Table 1 shows the ionic conductivity for different ratios of NaOH and Na₂SO₄. The Nyquist plot of XG added Na₂SO₄ electrolytic salt with four different ratios and equivalent circuit fit is illustrated in the Fig. 2. The pure XG membrane exhibits an ionic conductivity value of 8.539x10⁻⁶ Scm⁻¹.



Fig. 2. Nyquist plot of XG with different ratios of Na₂SO₄

Among all the ratios, XG with 0.05g Na₂SO₄ shows a higher conductivity value of 2.9×10^{-5} Scm⁻¹, comparable values of ionic conductivity is observed in

other literatures [2,3], where the preparation of XG is carried out using complex addition of acids and crosslinking of polymer membranes with plasticizers. In our work, the ionic conductivity is improved by a simple procedure with the addition of electrolytic salts into the XG host matrix.

Table 1. Ionic conductivity of XG with NaOH and Na_2SO_4 membranes

XG: NaOH		XG: Na ₂ SO ₄	
Conc. (g)	Ionic conductivity (Scm ⁻¹)	Conc. (g)	Ionic conductivity (Scm ⁻¹)
0.02	2.320x10 ⁻⁸	0.025	5.412x10 ⁻⁷
0.06	4.147x10 ⁻⁷	0.05	2.984x10 ⁻⁵
0.08	2.090x10 ⁻⁷	0.075	1.889x10 ⁻⁶
0.1	3.196x10 ⁻⁶	0.1	5.940x10 ⁻⁶

CONCLUSION

When appropriate concentration of electrolytic salt is added to the XG membrane, prevailance of dissociated ions of salt in the host matrix results in an increment of the number of charge carriers and hence conductivity value increases. A higher ionic conductivity value is observed for XG with 0.05g of Na₂SO₄ membrane. The evaluation and optimization of XG with different electrolytic salt combinations are studied and found a free standing film with good ionic conduction that is suitable for sodium-ion battery application as an electrolyte.

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Enhanced Thermoelectric Properties of Tellurium Excess Silver Telluride Nanoparticles

Amish Kumar Gautam¹ and Neeraj Khare²

^{1, 2} Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016

*Corresponding author: nkhare@physics.iitd.ernet.in

Abstract

Silver telluride (Ag₂Te), a metal chalcogenide, is probable for thermoelectric applications due to its intrinsic low thermal conductivity and high carrier mobility. In the present study, we have synthesized Ag₂Te and tellurium excess silver telluride (Ag₂Te_{1.1}) nanoparticles using hydrothermal method. XRD and EDX techniques are used for the phase identification and elemental composition of the samples. Temperature-dependent thermoelectric measurements of the samples were measured in the 313-373 K temperature range. Ag₂Te_{1.1} shows ~ 20 % enhancement in the thermoelectric figure of merit (*zT*) as compared to the Ag₂Te at 313 K. This enhancement in *zT* is due to ~ 130 % enhanced Seebeck coefficient and simultaneous ~ 31 % reduction in the thermal conductivity due to the increased phonon scattering at the boundary of the impurity phase present in Ag₂Te_{1.1}.
ZnIn₂S₄ Nanostructure For Photoelectrochemical Water Splitting

Mohit Khosya¹, Dheeraj Kumar¹, and Neeraj Khare^{1*}

¹Department of Physics, Indian Institute of Technology Delhi, Hauz Khas, New Delhi-110016

*Corresponding author: nkhare@physics.iitd.ernet.in

Abstract

In the present work, visible light active zinc indium sulfide (ZnIn₂S₄) nanostructure has been synthesized using the hydrothermal method. XRD pattern confirms the formation of a single cubic phase of ZnIn₂S₄ (ZIS) nanostructure. SEM and EDS measurements confirm the surface structure and elemental composition of the ZIS sample, respectively. The bandgap (E_g) value of ZIS is observed to be ~2.4 eV using UV-Vis absorbance spectra. The potentiality of ZIS photoelectrode for photoelectrochemical (PEC) activity has been demonstrated. The current density of ZIS photoelectrode under dark and light illumination conditions is observed to be 6.67 μ A/cm² and 18.55 μ A/cm² at 1 V vs. Ag/AgCl, respectively.

Defect analysis of In₂S₃ deposited by thermal evaporation by mean of high vacuum treatment

Sumit Kumar*

Department of Physics, Birla Institute of Technology and Science Pilani, Goa Campus, Zuarinagar, Goa, 403726, India

*sumitkr1585@gmail.com

Abstract

Di-indium tri-sulphide (In_2S_3), an n-type semiconductor with a variable bandgap, has recently received considerable interest in the solar sector. Thermal evaporation was used to evaporate In_2S_3 powder in this investigation. The structural characteristics of the film were studied using XRD Photoluminescence spectroscopy was used to investigate the interband defects caused by empty sites in the crystal structure. Instead, surface adsorbed groups appeared on the surface, resulting in the sample being subjected to a high vacuum treatment. This work demonstrates detection of such adsorbed groups by mean of high vacuum treatment.

A Simple Sonochemical Method of Synthesis of rGO/Co₃O₄ Composite With Binder Free Electrode For Supercapacitors

D.R. Madhuri¹, K. Kavyashree¹, Ashok R Lamani¹, H.S. Jayanna¹, G. Nagaraju², Shridhar Mundinamani³

¹Department of PG Studies and Research in Physics, Kuvempu University, Jnana Sahyadri, Shankaraghatta, 577451 ²Department of Chemistry, Siddaganga Institute of Technology, Tumakuru 572103 ³Department of Physics, Siddaganga Institute of Technology, Tumakuru 572103

*Corresponding author: ashok1571972@gmail.com

Abstract

In the present work, we have used Phyllanthus Emblica (amla) as a fuel as well as reducing agent to avoid toxic chemicals. rGO/Co₃O₄ composite was prepared by a simple sonochemical method. The electrodes were prepared by using Whatman filter paper without using any binder. The physico-chemical characterizations were performed by XRD, FT-IR, SEM and Raman spectroscopy. Electrochemical measurements were studied by cyclic voltammetry with two electrode system. The result revealed that the composite material has a very good specific capacitance and excellent cyclic stability.

INTRODUCTION

Supercapacitors have attracted more attention due to its good cycling stability, fast charge-discharge and high power density. Recently graphene has emerged as a promising material for supercapacitor due to its excellent electronic conductivity, extremely high specific area, outstanding mechanical strength, superior thermal conductivity and reasonable chemical stability [1,2]. However, it has been reported that electrodes made of graphene may display decreased surface area due to restacking of the graphene sheets and formation of agglomeration [3]. This drawback can be overcome by the addition of transition metal oxides. Transition metal oxides such as NiO, MnO₂, Fe₂O₃ and Co₃O₄ are being studied as promising materials for pseudocapacitors [4-11].

EXPERIMENTAL

Preparation of graphene oxide: Graphene oxide was prepared by modified Hummer's method.

Preparation of cobalt oxide: Cobalt oxide (Co_3O_4) was prepared by solution combustion method. 1 g of cobalt nitrate was dissolved in 10 mL of DI water. 1.5 mL of amla extract fuel was added and mixed well. The mixture was kept in a pre-heated muffle furnace. Black coloured powder was formed.

Preparation of rGO/Co_3O_4 composite: 300 mg GO was dispersed in 100 mL of DI water, ultrasonicated for 30 mi n. Added 2 mL of reducing agent (amla extract) and again ultrasonicated for 15 min. 300 mg of Co3O4 is added to the above solution, kept under ultrasonicated for 30 min. This was allowed to wash with DI water several times until clear solution was formed.

RESULT AND DISCUSSION

The XRD pattern is shown in figure 1. Diffraction peaks corresponding to GO appears at $2\theta \approx 9.6^{\circ}$ and 42.3° (PDF no. 44-558) is the characteristic peak. The observed planes of Co₃O₄ belong to cubic structure (JCPDS card No. 42-1467). The average crystallite size of the Co₃O₄ is found to be 44nm.



Fig. 1. XRD pattern of GO, Co₃O₄, rGO/Co₃O₄

Figure 2 depicts the FT-IR spectra. The broad peak at 3426 cm⁻¹ is due to the presence of O-H stretching vibration in the hydroxyl group. Small

peak at 2925 cm⁻¹ indicate the C-H stretching of heterocyclic compounds. The presence of peak at 1623 cm⁻¹ indicates the presence of carbonyl group. The peak at 1110 cm⁻¹ attributes the C-O stretching.



Fig. 2. FTIR spectra of GO, rGO/Co₃O₄

The composite material is also having these peaks but with decreased intensity. This indicates that GO is well reduced. It can be clearly seen that there are strong peaks at 659 and 568 cm⁻¹, which suggests that the presence of Co_3O_4 .

Raman spectra of GO and rGO/Co3O4 composite is shown in figure 3. G band at 1595 cm⁻¹ represents the E_{2g} phonons of the C sp² atom and D band at 1350 cm⁻¹ is due to defects like edges and disordered carbon. I_d/I_g ratio for GO is 0.947. Peaks located at 492 and 679 cm⁻¹ are due to E_{2g} and A_{1g} active modes of Co₃O₄ respectively. I_d/I_g ratio of the composite material is 0.97.



Fig. 3. Raman spectra of GO, rGO/Co₃O₄



Fig. 4. SEM image of a) GO, b) rGO/Co₃O₄ composite

Figure 4a shows SEM image of GO. It consists of randomly aggregated crumpled sheets closely associated with each other. The wrinkled GO sheets are loosely connected to each other. Figure 4b shows rGO/Co_3O_4 composite. The spherical shaped cobalt oxide is distributed on graphene sheets.

Electrochemical performances of the prepared samples are studied using cyclic voltammetry (CV) at

different scan rates in two electrode system which is shown in figure 5. The specific capacitance vales are calculated at scan rates 50, 25, 10, 5, 2 mVs⁻¹ and it is given by 28.56, 50.28, 130.68, 289.6 and 360.4 mVs⁻¹ respectively. The cyclic stability of the prepared sample is tested over 1000 cycles at 120 mVs⁻¹ and only 9% loss of specific capacitance is found at the end of 1000 cycles.



Fig. 5. CV curve of rGO/Co₃O₄ composite at different scan rate with 1M NaOH electrolyte

CONCLUSION

 rGO/Co_3O_4 composite was prepared by a simple sonochemical method and green approach was used which is environmentally friendly and non-toxic in nature. Electrochemical performances showed that it has a very good specific capacitance value as well as excellent cycle stability.

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A Triboelectric Nanogenerator Based on PDMS and Parafilm For Biomechanical Energy Harvesting

P. Ravi Sankar¹, K. Prakash^{1, *}, P. Supraja² and R. Rakesh Kumar²

¹ Flexible Electronics Lab, Department of ECE, National Institute of Technology-Warangal, India-506004 ² Energy Materials and Devices Lab, Department of Physics, National Institute of Technology-Warangal, India-506004

000001

*Corresponding author: <u>kprakash@nitw.ac.in</u>

Abstract

In this report, a triboelectric nanogenerator is fabricated using parafilm, polydimethylsiloxane (PDMS) films for the first time. The fabricated TENG has been used for low-frequency mechanical energy harvesting to drive wearable and low-power electronic gadgets. The parafilm and PDMS layers act as triboelectric layers, and packaging aluminium foil acts as conducting electrodes. A flexible TENG with a dimension of 5 x 5 cm² generated an output voltage ~ 8 V and output power of 20.25 μ W at the applied load of 1 M Ω . Further, TENG was explored for switching on several LEDs. The current report presents a simple and cost-effective method for fabricating TENG and can be used for self-powered device applications.

A Numerical Study for Optimizing Performance of Lead-Free Perovskite Solar Cell

Omkar V. Rambadey¹*, Anil Kumar¹, P.R. Sagdeo¹

¹Materials Research Laboratory, Department of Physics, Indian Institute of

Technology Indore, Indore-453552, India

*Corresponding author: phd1901151013@iiti.ac.in

Abstract

In past few decades, the research on solar cell materials and devices has acquired significant attention, which has contributed into enhancing the performances on even commercial scales. Moreover, the optimization of various parameters from the aspect of device fabrication has been an important step in this context, and for this purpose, SCAPS simulation has gained enough popularity in recent years. In this work, device optimization has been attempted for lead-free methylammonium germanium iodide perovskite material with p-Si and TiO₂ as hole and electron transport layers (HTL/ETL), respectively, using SCAPS simulation. Results suggest that p-Si could be used as an affordable HTL with adequate device performance.

Microwave Heat Treatment to Reduced Graphene Oxide (RGO) for Enhanced Electrochemical Supercapacitive Application

Poonam Mahendia¹, Suman Mahendia^{2*}, Tristan D. Clemons³, and O. P. Sinha¹

¹Amity Institute of Nanotechnology, Amity University, UP, Noida, India ²Department of Physics, Kurukshetra University, Kurukshetra, Haryana, India ³Northwestern University, United States of America

*Corresponding author: smahendia@kuk.ac.in

Abstract

The state of art in improving the porosity of reduced graphene oxide (RGO) prepared via chemical reduction of GO synthesized from modified Hummers method through microwave heat treatment (MWHT) is presented. The prepared RGO before and after MWHT were tested for electric double layer capacitor EDLC type supercapacitor (SC) in a symmetric parallel plate type cell device design. The electrochemical performance of the prepared cell device has been checked from Cyclic Voltagrams (CV) measurements and cross confirmed through Electrochemical Impedance spectroscopy (EIS) and Galvanostatic Charge-discharge (GCD) measurements. After MWHT, the RGO based cell shows enhanced electrochemical performance depicting the enhanced porosity after treatment which hence plays a major role in achieving enhanced specific capacitance.

Morphology Driven SnO₂ as Electrode Materials for Applications Ranging from Supercapacitors to Sensors

Surbhi Priya^{1*}, Debabrata Mandal², Ananya Chowdhury³, Trilok Singh¹, Amreesh Chandra^{1, 2, 3#}

¹School of Energy Science & Engineering,²School of Nanoscience and Technology and ³Department of Physics, IIT Kharagpur, Kharagpur, India, 721302

Corresponding author: *surbhipriya2010@gmail.com, #achandra@phy.iitkgp.ac.in

Abstract

Metal-oxide nanoparticles are emerging as promising materials for use in supercapacitors as well as in field of sensors due to their inherent surface properties. It is found that SnO_2 can be excellent electrode material for supercapacitors and sensing because of its suitable physio-chemical properties and possibility to perform good redox reaction. In this paper, we present a novel strategy to tune the morphology of SnO_2 nanoparticles from solid to hollow structures. The electrochemical measurements are done in three-electrode configuration. A high specific capacitance of 109 F g⁻¹ was recorded in case of hollow SnO_2 particle and 28 F g⁻¹ in the case of solid SnO_2 particle-based electrodes. Along with electrochemical characterization, we also report glucose sensing capability. The CV profiles of the hollow and solid SnO_2 , before and after the addition of glucose molecules, were recorded in 1 M PBS solution containing 0.5 mM [K₄Fe(CN)₆].The fabricated glucose sensor is able to deliver high sensitivity and low detection limit. This work can initiate significant activity on various applications of SnO_2 using hollow structures, which has remained ignored till now.

Introduction

Growth in energy consumption promotes the development of diverse forms of energy. Therefore, the storage of these many forms of energy becomes a critical concern. In the realm of energy storage, supercapacitors have received a lot of attention due to their high-power density and ultralong cycle life. Also, biosensors are among few most useful advancements in field of science. Bio-sensor discovery was based upon glucometers that worked based on the strategy of electrochemical detection of oxygen or hydrogen peroxide by employing immobilized glucose oxidase electrodes. Recent synthesis of metal advancement in oxide nanomaterials and the ability to tune their morphology accordingly has resulted into excellent capacitance in case of supercapacitors accompanied with increase in sensitive limit of biosensors. Also different morphologies of solid structures, with varying degrees of confinement, have been reported. Recently, the use of hierarchical hollow structures in next generation sensors, energy storage devices, EMI shielding, catalysis, etc. is being suggested. As the width of cage is tuned, the hollow structures can also compete with highly active 2D structures, with an additional advantage of economical synthesis protocols. Strangely, the use of hollow structures of simple oxides, for detecting VOCs, remains ignored till date. Using SnO₂ as a model system for supercapacitor and glucose sensing, the advantage of hollow morphologies, over the solid counterpart is established.

Synthesis of Material

Synthesis of solid nanospheres has been done through co-precipitation method. In this process, CTAB was mixed with DI water by stirring until a homogeneous solution (0.08 M) was obtained. The solution of diluted $NH_3 \cdot H_2O$ was then added to the CTAB solution under continuous stirring. Subsequently, $SnCl_4$ solution was added and the product was aged at ambient temperature for 96 h. The resulting product was then filtered, washed with distilled water and annealed.

Hollow nanoparticles were synthesized through mini-emulsion method. A solution of SnCl₄ with PGPR was made. The whole mixture was then placed in ultrasonic gun at 50 Hz for 3 min. This resulted in a milky white solution. TEA was added to the mixture, which was subjected to reflux at 200 °C for 3 h. Finally, the obtained product was centrifuged at 1000 rpm and was washed to get the desired morphology.

Results and Discussion

Two different morphologies of SnO_2 i.e. solid nanospheres and hollow nanoparticles were synthesized. The phase formation of both the material was confirmed by XRD analysis. The solid structure of SnO_2 as well as the formation of hollow nanoparticles are clearly visible in TEM micrographs shown in Fig.1(a, b), respectively. Further, N_2 adsorption-desorption measurements were performed to estimate the surface area and pore sizes of the synthesized nanomaterials. All the BET isotherms depicted type IV hysteresis loops, which indicated the formation of mesoporous structures. The surface area of solid and hollow nanostructures was recorded as 10 and 30 m² g⁻¹ respectively.



Fig. 1 TEM micrographs of SnO₂ (a) solid and (b) hollow nanostructures.

The electrochemical analysis for both the morphologies were initially performed using three electrode configurations with Ag/AgCl and Pt rod as the reference and counter electrode, respectively, in 1 M KOH electrolyte. The obtained CV profiles were almost rectangular in shape for both the morphologies, as shown in Fig. $2(a_1, b_1)$. Both of them showed pseudocapacitive nature with some prominent redox peaks, especially at the lower scan rates. The charge-discharge measurements further supported the CV findings.

Hollow SnO₂ delivered a maximum specific capacitance of 109 F g⁻¹ at 1 A g⁻¹ current density, whereas, that for solid SnO₂ was found to be 28 F g⁻¹. The appreciable increment in the specific capacitance value in the hollow nanoparticles compared to the solid counterpart could be attributed to the high surface area, inside cavity and a greater number of ion-transport channels. Nearly symmetric CD profiles were observed revealing high Columbic efficiency of >80%, which suggested the usefulness of the device. Finally, the cycle stability of the device was investigated as it is an important factor in order to device the utility of the device for practical applications.

The second application of synthesized nanomaterials included glucose sensing. The CV profiles were recorded for both the morphologies twice, first observation is taken before adding glucose molecules in 1 M PBS solution containing 0.5 mM $[K_4Fe(CN)_6]$ and second observation is recorded after adding up the glucose molecules in above mentioned electrolyte. The potential windows for solid and hollow SnO₂ with and without glucose were

optimized between 0 and 0.5 V against Ag/AgCl, at a scan rate of 50 mV s⁻¹. In case of hollow SnO₂ nanoparticles, the peak current was higher than its solid counterpart. Further limit of detection was calculated for both the morphologies using standard deviation [Fig. $2(a_2, b_2)$]. The calculated LOD for hollow and solid nanoparticles are 5.5 and 8.2 nM respectively. Results conclude that hollow SnO₂ electrode has the ability of detecting glucose over a wide linear range and even at low concentrations, with high sensitivity. This hike in peak current and better LOD can be attributed to the fact that increased surface area ensured maximum electron transfer between electrolyte medium and electrode.



Fig. 2 CV and LOD profile for SnO₂ (a₁, a₂) solid and (b₁, b₂) hollow nanostructures.

Conclusions

Two different morphologies of SnO_2 were successfully synthesized using cost effective synthesis protocol and their electrochemical and sensing performance were investigated. Hollow nanoparticles clearly superseded its solid counterpart in both applications with specific capacitance as high as 109 F g⁻¹ and LOD 5.5 nM. It further Established the fact that increased surface area was the key for better performance in electrochemical as well as sensing applications.

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Effect of gas flow pattern on impurities distribution in multicrystalline silicon ingot grown by directional solidification process: Numerical Simulation approach

R. Muthukumar, V.Kesavan, S.Ashok, K. Aravinth*, M. Srinivasan, P. Balaji Bhargav, P. Ramasamy

SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai - 603 110, India *Corresponding author: aravinthk@ssn.edu.in

Abstract

In the present study, numerical simulations were carried out for conventional as well as modified gas flow pattern (Inlet gas tube design) in directional solidification (DS) furnace. The effect of modified gas flow pattern on the carbon and oxygen impurity concentrations was studied in detail. The obtained results were compared with conventional and modified grown mc-Si ingots by numerical modelling understanding the impurities segregation during mc-Si growth process by DS model.

Enhancement of the charge carrier extraction in carbon based perovskite solar cells using MAPbI₃:NiO composites

R. Isaac Daniel, R. Govindaraj ,N. Santhosh, K. R. Acchutharaman, B. Vasanth, M. Senthil Pandian, P. Ramasamy

Department of physics, SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam-603110, Tamil Nadu, India

*Corresponding author: isaacdaniel1208@gmail.com

Abstract

A variety of approaches utilizing perovskite composites with organic and inorganic materials have been developed to improve the power conversion efficiency (PCE) of PSCs. In this study, we investigated the performance of carbon-based Perovskite Solar Cells (C-PSC) using perovskite composites with p-type nickel oxide (NiO) semiconductor material of varying weight, and the results were compared with C-PSC made with pristine methylammonium lead iodide (MAPbI₃) as a perovskite precursor. The single-step method was used to coat the perovskite layers.

Synthesis, Characterization And Electrochemical Supercapacitor Study Of Mesoporous Cobalt Oxide

O. C. Pore^{1,2}, D. B. Mane¹, V. J. Fulari², G. M. Lohar^{*1}

¹Department of Physics, Lal Bahadur Shastri College of Arts, Science and Commerce, Satara 415002, ²Holography and Materials Research Laboratory, Department of Physics, Shivaji University, Kolhapur, 416004 (M.S.) India,

*Corresponding author: gauravlohar24@gmail.com

Abstract

In the present study, mesoporous cobalt oxide (Co₃O₄) nanostructure was synthesized by hydrothermal method followed by annealing treatment. The formation of Co₃O₄ was confirmed by XRD and FT-IR study. The FE-SEM image shows the mesoporous structure. The prepared Co₃O₄ electrode on carbon cloth as a current collector exhibited maximum specific capacitance of 112 F g⁻¹ at a current density of 1 mA cm⁻². It shows a maximum energy density of 3.15 Wh kg⁻¹ and a maximum power density of 630 W kg⁻¹. The Co₃O₄ electrode exhibited excellent cyclic stability of 88.1% over 2000 CV cycles.

Introduction

Nowadays, with increasing environmental pollution issues and the depletion of fossil fuels, renewable energy storage devices have been attracting more interest for researchers [1]. The supercapacitor, as an emerging and promising energy storage device, has attracted more attention from researchers because of its promising properties such as high energy and power density, long cyclic stability, fast charging and discharging rate and operating safety [2,3]. In recent years transition metal oxide-based nanostructures have been widely used as electrode material for pseudocapacitors [4].

Out of many transition metal oxides, Co₃O₄ have been considered a promising candidate for supercapacitor application because of its high theoretical capacitance value (3560 g⁻¹), F environmentally friendliness and better electrochemical capability [5]. Pang et al. [6] synthesized Dendrite-like Co₃O₄ nanostructures by a hydrothermal method which exhibited maximum specific capacitance of 207.8 F g⁻¹ at a current density of 0.5 A g⁻¹ and shows better cyclic stability 97.5% over 1000 cycles. Jang et al. [7] synthesized porous Co₃O₄ nanorods by a hydrothermal method which shows specific capacitance of 226.3 F g⁻¹ at a scan rate of 10 mV s⁻¹ and cyclic stability of 76% over 5000 cycles.

In the present investigation, the mesoporous Co_3O_4 was synthesized by hydrothermal method followed by annealing treatment. The working electrode was prepared on carbon cloth (CC) as a current collector. The prepared Co_3O_4 electrode exhibited a maximum specific capacitance of 112 F g⁻

¹ at a current density of 1 mA cm⁻². Also, it shows good cyclic stability of 88.1% over 2000 CV cycles.

Experimental

SYNTHESIS OF CO₃O₄ POWDER AND WORKING ELECTRODE

In the actual experiment, 0.1 M Co(NO₃)₂6H₂O as well as 0.2 M CO(NH₂)₂ were dissolved in 80 mL double distilled water (DDW). Then pH of the solution was adjusted \approx 11 by dropwise addition of NH₃ (30%) with constant stirring for 30 min. The obtained solution was transferred into 100 mL of Teflon lined stainless steel autoclave and kept at 160 °C for 18 h. After completion of the reaction, the reaction product was washed with DDW, ethanol several times and dried in a hot air oven at 80 °C overnight. Afterwards, the obtained powder was annealed at 400 °C for 2 h.

In preparation of the working electrode, the assynthesized Co_3O_4 powder was used as active material and Polyvinylidene fluoride (PVDF) as a binder in the ratio of 90:10. The slurry was prepared by adding N-methyl-2-pyrrolidinone (NMP) as a solvent and coated uniformly on precleaned CC. Afterwards, the electrode was dried at 80 °C overnight and used as a working electrode for supercapacitor study.

Result and discussion

Fig. 1 shows structural and morphological characterizations of hydrothermally synthesized Co_3O_4 . Fig. 1 (a) presents the XRD pattern of assynthesized powder. The position and relative intensities of the XRD pattern are well-matched with JCPDS card number 01-074-2120 which is

corresponding to the Co₃O₄. The peaks observed at 19.14, 31.19, 36.87, 38.41, 44.85, 48.53, 59.44, 65.22, and 74.04° are corresponding to the crystal planes (111), (220), (311), (222), (400), (511), (440) and (533) respectively. Fig. 1 (b) shows the FT-IR spectrum of Co₃O₄. The characteristic peaks observed at 563 and 660 cm⁻¹ are assigned to the Co-O stretching vibrations, which confirms the formation of Co₃O₄ [8]. The peaks observed at 3432 and 1632 cm⁻¹ are assigned to the O-H stretching and bending vibration of absorbed water molecules [9]. Fig. 1 (c) shows the FE-SEM image of Co₃O₄ which indicates the mesoporous structure. Fig. 1 (d) shows the EDS spectrum, shows the presence of Co and O elements which also confirms the formation of Co₃O₄.



Fig. 1. (a) XRD spectrum (b) FT-IR spectrum (c) FE-SEM image (d) EDS spectrum of hydrothermally synthesized Co₃O₄.

All the supercapacitor study was done in 1 M KOH electrolyte. Fig. 2 (a) shows the CV curves of the Co₃O₄ electrode at different scan rates (5 to 100 mV s⁻¹). Fig. 2 (b) presents the GCD curves of the Co₃O₄ electrode at different current densities (1 to 7 mA cm⁻²). Fig. 2 (c) presents the specific capacitance calculated from the GCD curve as a function of applied current density. The Co₃O₄ electrode exhibited specific capacitance of 112.0, 106.7, 88.9, and 79.0 F g^{-1} at a current of 1, 2, 5, and 7 mA cm⁻² respectively. Lower charging rate at lower current density provides a maximum contribution of electroactive material during redox reactions, resulting in a high specific capacitance value. But as current density increases, the utilization ratio of electroactive material gets lowered hence specific capacitance decreases.

Fig. 2 (d) shows the Regone plot of the Co_3O_4 electrode which exhibited a maximum energy density of 3.15 Wh kg⁻¹ and maximum power density of 630 W kg⁻¹. Fig. 2 (e) presents the Nyquist plot of the Co_3O_4 electrode and the inset of Fig. 2 (e) shows its equivalent circuit diagram. The values of solution

resistance (R_s) and charge transfer resistance (R_{ct}) are 1.098 and 1.326 Ω respectively. The lower R_s and R_{ct} values indicated the good attachment of material with the CC current collector as well as good electrical conductivity. Fig. 2 (f) depicts the capacity retention vs cycle number of Co₃O₄ electrode. It shows excellent cyclic stability of 88.1% over 2000 CV cycles.



Fig. 2. Supercapacitor study of Co₃O₄ electrode with CC as a current collector (a) CVs at different scan rates (b) GCD at different current densities (c) specific capacitance vs current density (d) Regone plot (e) Nyquist plot (Inset: equivalent circuit diagram) (f) Capacity retention vs cycle number (Inset: CVs at different cycle number)

Conclusion

In summary, mesoporous Co_3O_4 were synthesized by hydrothermal method followed by annealing treatment. The working electrode was prepared by using carbon cloth as a current collector. The prepared electrode shows a specific capacitance of 112 F g⁻¹ at a current density of 1 mA cm⁻² and capacity retention of 88.1% over 2000 CV cycles.

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Supercapacitor Performance of the Nickel Oxide Decorated Vertical Graphene Nanosheets Electrode

V. Madhav Kumar^{1, 2} S. R. Polaki^{*, 1}, R. Krishnan¹, Tom Mathews^{1, 2} and M. Kamruddin^{1, 2}

¹Materials Science Group, IGCAR-Kalpakkam, ²Homi Bhabha National Institute, Tamil Nadu, India, 603102.

 $* Corresponding \ author: \ polaki@igcar.gov.in$

Abstract

The hybrid structures with the combination of carbon nanostructure (EDLC type) and metal oxides (Pseudo type) are gaining attention, due to their high capacitance and superior cycle life compared to conventional storage devices. In the present study vertical graphene nanosheets (VGN) are decorated with NiO nano-particles using Pulsed Laser deposition Technique. Herein, we report the enhanced electrochemical capacitance of NiOx/VGN hybrid electrodes. As grown VGN exhibited areal capacitance value 0.14mF/cm² and it is increased upto 104 mF/cm² with NiOx decoration.

Low temperature processable carbon electrode perovskite solar cell (CPSC) based on SnO₂ ETL

K.R. Acchutharaman, N. Santhosh, R. Isaac Daniel, R. Joel Kingston, Muthu Senthil Pandian and P. Ramasamy

Department of Physics, SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Chennai -

603110, Tamil Nadu.

*Corresponding author: acchuthan2017@gmail.com

Abstract

The emergence of perovskite solar cells (PSCs) brings a new era in solar cell research due to their incredible improvement of power conversion efficiency (PCE) within a short span of time. Although PSC has a higher PCE, commercialization remains a big issue. In order to extend the application of PSCs for flexible devices, here we fabricated PSC with low temperature processable SnO_2 based electron transport layer (ETL) with a PCE of 7.9%. Additionally, we fabricated a hydrophobic low temperature processable carbon electrode on top of the PSC to address the perovskite layer's moisture instability.

Introduction

People use more energy today, and the environment is polluted to a greater extent than ever before. They are searching for renewable energy sources to solve this issue. The conversion of solar energy (renewable resource) to electricity through solar cells is one way to solve this issue. The first generation of solar cells has greater efficiency and stability, but the expense and demand for a thick silicon wafer have made silicon an increasingly difficult commodity to obtain. Fortunately. researchers have found a solution in PSCs which have the same performance as commercial siliconbased solar cells while being less expensive and easier to manufacture. Despite the fact that PSCs compete with Si-based solar cells, commercialization of PSC is hampered by the following two issues. (i) Degradation of the perovskite layer due to UV and moisture exposure. (ii) Inability to lengthen the fabrication process for flexible solar cells due to the requirement of high temperatures for the TiO₂ based ETLs.

We attempted to address the aforementioned difficulties in this study by manufacturing a PSC with a carbon-based top electrode and using SnO₂ as an ETL to replace the high-temperature processable TiO₂ ETL. The fabricated hole transport free carbon electrode-based perovskite solar cell (CPSC) architecture glass/FTO/c-SnO₂/mis SnO₂/MAPbI₃/carbon. At temperatures of 180 °C and 120°C, respectively, the compact (c-SnO₂) and mesoscopic SnO₂ (m-SnO₂) ETLs are prepared. The hydrophobic property of the carbon layer on top of the PSC shields the device from moisture. The constructed PSC with low temperature processed SnO₂ and hydrophobic carbon top electrode achieves a PCE of 7.9%.

Fabrication of CPSC PXRD

synthesized SnO₂ nanoparticles were hydrothermally using SnCl4.5H2O and NaOH. The c-SnO₂ layer was applied to the FTO substrates by spin coating a precursor solution of 4ml DI water and 1ml SnO₂ colloidal dispersion (15%) in DI water. The prepared layer was annealed for one hour at 180 °C. The m-SnO₂ layer was applied over the $c-SnO_2$ layer by spin coating a dispersion solution of 50mg of synthesized SnO₂ nanoparticles in 1 ml of ethanol and annealed it for 30 minutes at 120 °C. The remaining fabrication steps, such as deposition of the perovskite layer over the SnO₂ layer and carbon electrode, were carried out in the same manner as described in our previous report [1].

Characterization of SnO₂ nanoparticles

Fig. 1 shows the PXRD pattern of a synthesized sample. All of the synthesized sample's diffraction peaks and diffraction planes match the standard JCPDS file number of 21-1250, indicating that the SnO_2 nanoparticles are in the tetragonal rutile phase. Scherrer formula was used to calculate the average crystalline size of the sample, and the peak with the highest intensity was found to be 24.5 nm.



Fig. 1. PXRD pattern of SnO₂ nanoparticles





Fig. 2. PL emission spectra of bare MAPbI₃ and MAPbI₃ on SnO₂ ETL

A photoluminescence investigation was carried out for glass/MAPbI3 film and glass/c-SnO₂/m-SnO₂/MAPbI₃ film at an excitation wavelength of 516 nm to evaluate the electron extraction behavior of the low temperature processed SnO₂ ETL. Fig. 2 displays the results of the measured Pl emission spectra. The intensity of the emission peak of the perovskite film on SnO₂ ETL is slightly lower than the intensity of the MAPbI₃ film alone, as shown in this figure. As a result, the SnO₂ based ETL significantly suppresses non-radiative recombination by efficiently extracting photo-generated electrons from the perovskite layer.

Photovoltaic Characterization of CPSC



Fig. 3. J-V curve of the fabricated devices

The low temperature processed SnO_2 ETL based CPSC was tested for current density – voltage (J-V). The fabricated devices' J-V responses are illustrated in Fig. 3 and the corresponding J-V parameters are listed in the table 1. All the devices show PCE of roughly 8% with an average short circuit density of 21.31 mA/cm² when the J-V parameters of the constructed ones are examined. Device S3 has the highest PCE of 7.9 %, a short circuit density of 21.46 mA/cm², an open circuit voltage of 0.862 V, and a fill-factor of 43.3% among the three constructed

devices. The manually doctor-bladed carbon electrode on top of the perovskite layer results in a higher series resistance and a slightly lower shunt resistance. The fill-factor of the device is limited to 50% by such dynamics in the series and shunt resistance. The lower temperature processed SnO_2 ETL, on the other hand, confirms that it is a better replacement for the high temperature processable TiO₂ ETL due to its higher short circuit current density.

Device	J_{sc} (mA/cm ²)	V _{oc} (V)	FF (%)	Rs (Ω)	R _{sh} (ΚΩ)	η (%)
S 1	21.22	0.860	42.4	64.00	1.053	7.7
S2	21.24	0.866	43.4	62.02	1.008	7.9
S 3	21.46	0.862	43.3	60.74	0.798	7.9
Mean	21.31	0.863	43.0	62.26	0.953	7.8

Table 1. J-V parameters of the fabricated device

Conclusion

In conclusion, SnO₂ nanoparticles in the mesoscopic layer were used to build totally low-temperature processable CPSC. The hydrothermal process was used to make SnO₂ nanoparticles. The PXRD pattern confirmed the strong crystallinity and tetragonal rutile phase of the synthesized SnO₂ nanoparticles. The compact and mesoscopic SnO₂ ETLs were made at 180°C and 120°C, respectively, at low temperatures. Over the SnO₂ layer, a two-step spin coating method was used to create a perovskite (MAPbI₃) layer. A carbon electrode that can be processed at low temperatures was also created. The champion device has a better short circuit current density of 21.46 mA/cm² and a PCE of 7.9 % than the other two fabricated devices. We expect that our research will pave the way for perovskite solar cells to become commercially viable.

Acknowledgement

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SmFe_{0.9}Ni_{0.1}O₃-Polyanaline Nanocomposite for Supercapacitor Applications

Mudasir H. Rather^{*}, Feroz A. Mir, Ashiq H. Shah, and Peerzada Ajaz Ahmad Department of Physics, Baba Ghulam Shah Badshah University, Rajouri, 185234

*mudasirh437@gmail.com

Abstract

 $SmFe_{0.9}Ni_{0.1}O_3$ -Polyanaline (SFO-PANI) composite are prepared by chemical oxidative polymerization method. This prepared nanocomposite was characterized by X- ray diffraction (XRD), and electrical measurements for structural, and dielectric properties respectively. XRD data analysis confirms the orthorhombic crystal structure with Pbnm space group. The dielectric constant show well dispersion with applied frequency. A simple supercapacitor of this material was designed, and was further studied by charging and discharging using KMnO₄ (with 0.1M) as an electrolyte. The preliminary designed capacitor show good charge retention capacity and could be a good candidate for future energy storage applications.

Introduction

Inorganic and organic crossover materials can bind the eminence of both (inorganic-organic) components and offer outstanding properties through arrangement of one over other.Conducting polymers show different kinds of properties such as electrical, magnetic and optical.These conducting polymers are widely used in electrochemicalcapacitors, electronic devices, rechargeable batteries, electrodes, sensors, fuel cells, light emitting diodes. Consideration it with other polymers, polyaniline attracted much attention. Pani is widely used because due to its easy preparation [1].

Pani has a poor processability, infusibility and some other properties, to reduce these limitations Pani/metal oxides composites have attracted large attention [2].Number of metal oxides used to improve thermal stability of Pani in composite. From the literature survey, we have seen lot of work on PANI/MnO₂, PANI/NiO, and PANI/Co₃O₄.

Currently various studies has been carried on PANI metal oxide based nano-composites [2]. Further, It has been observed that the incorporated metal oxide properties can drastically impact the features of a supercapacitor [3]. The principle of energy storage of the supercapacitor depends on the material of electrode. The parameters like specific capacity, energy density and power density of the supercapacitor depends on electrode material.

Also SFO has a wide-gap, high-spin Mott insulator with strongly correlated system [4]. Moreover, it also possesses a GdFeO₃-type structure, which crystallizes with distorted orthorhombic structure, four Fe ions and four rare-earth ions per unit cell, and conforms towards the space group D^{2H}_{16} -Pbnm [3] .The crystallographic unit cell of SFO are visualized like a corner having FeO₆ octahedron generating a threedimensional deformed perovskite structure when iron is in the high spin state. SFO has actually has T_N at around 670 K. Furthermore, at room temperature, the SFO system is insulator and becomes semi conductive at high temperatures [4].

Keeping the properties of SFO in to consideration, we carried out studies on preparation and characterization of PANI-SFO nanocomposites. Further this prepared nano-composites was exploited for supercapacitor applications.

Experiment

Polycrystalline powders of SFO were synthesized by the citric acid method, and details are given already given in elsewhere [3]. To prepare nano-composite of Pani-SFO, an in situ-polymerization method was adopted. For more details, readers are referred to this publication [4]. This prepared nano-composite was characterized by XRD with D8 Advance Bruker Xray diffractometer having Cu K α with λ =1.5418 Å radiation.For the design of supercapacitor (electrodes), an approximately 9 grams of activated carbon powder was mixed with 10ml of ethanol. This prepared composite was then deposited on aluminum thin foil (4cmx0.8cm) by manual brushing. The (0.2 prepared Pani-SFO composite grams) werecoated on two electrodes with the help of coating brush. Supercapacitor was prepared sandwich fashion, the separator we use was a tissue paper and the electrolyte used was potassium permanganate (KMnO₄) with 0.1M.The charging- discharging cycling of this designed Supercapacitor was carried out by using Kithley SM 2450 source meter. For the charging- discharging cycles, a constant voltage of 2V, and a constant current of 300 mA was used. This charging- discharging study was done for 20 cycles. Further to this designed supercapacitor, the frequency

dependent dielectric study was done in the frequency range 20 Hz–200kHz by using High Precision LCR meter(Scientific,SM6023).



Fig.1.XRD pattern of PANI-SFO nano-composite.

XRD analysis

The XRD patterns of SFO-PANI composite is shown in Fig.1. To confirm it further, this XRD pattern was indexed by using Powder X software. The analysis of diffraction peaks has shows that SFO-PANI is having an orthorhombic structure (space group = Pbnm).



Fig.2. shows frequency Vs capacitance and frequency Vs loss graph.

Dielectrics studies

Fig.(2) shows the variation of capacitance and loss with frequency for Pani-SFO composites, therein decrease capacitance and loss with increase in frequency are observed. The observed large capacitance and less loss could be a good reason for its charge retention of the charges. This property could be exploited for the super-capacitance and hence energy storage applications.



Fig.3.Charging discharging cycling of a designed Supercapacitor.

Charge and discharge studies

Charging discharging for 20 cycles show that this capacitor remain very stable and could retain the accumulated charge for the required time. However, long-term cycling stability of these electrodes needs to be studied.

Conclusion

Pani-SFO composite are prepared by chemical oxidative polymerization reaction technique. These samples are characterized by XRD, dielectric measurements and charging-discharging. Due to the presence of SFO particles in polyaniline matrix, present composite show orthorhombic crystal structure. An increase in grain size and decrease in crystallinity with composite formation can be observed. From the ac conductivity investigations, charge carrier follows the correlated barrier hopping transport mechanism. Pani-SFO composite were rarely used for the electrode material. In future supercapacitorswill be widely used in automobiles, buses, trains, cranes, elevators, electronic devices.

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NiMoO₄-MoO₃ composite as anode material for Li-ion battery application

Mathew K Francis^{1,2}, P. Balaji Bhargav^{1,2}, K Ganesh Kumar^{1,2}, Nafis Ahmed^{1,2} and Balaji C^{1,2}

¹Department of Physics, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Tamilnadu 603110, India ²SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Tamilnadu 603110, India

*Corresponding author: balajibhargavp@ssn.ed.in

Abstract

NiMoO₄/MoO₃ was synthesized by the sol-gel method. The structural properties were studied using XRD and Raman analysis. The prepared sample was used as an anode material for Li-ion battery. The cycle stability and charge discharge performance of NMO and mesoporous MoO₃ anode were systematically analyzed. The NiMoO₄/MoO₃ anode, exhibited a first discharge capacity of 1031 mAh/g and a reversible capacity of 324 mAh/g after 50 cycles. This material is an encouraging candidate for high performance LIBs anode.

EFFECT OF YTTRIUM SUBSTITUTION AT B-SITE IN LiCoO₂ CATHODE

P. Sarumathi¹, D. Lakshmi¹, M. Infanta Diana¹, P. Christopher Selvin^{1*}

¹Luminescence and Solid State Ionics Lab, Department of Physics, Bharathiar University, Coimbatore-46, India.

*Corresponding author: *csphysics@buc.edu.in

Abstract

Among various cathode materials used in Lithium ion batteries (LIB), Lithium Cobalt Oxide, LiCoO₂ (LCO) is more conventional but suffers with low capacity. In this research work, an attempt has been made to replace the Co^{3+} by Y^{3+} element which is expected to puff up the volume of the unit cell and electrical conductivity. The samples were prepared by sol-gel method and analyzed for structural, morphological and electrical properties. The mixed phase of LiYO₂ (LYO) and single-phase trigonal crystal system of LCO was found by X-ray diffraction (XRD) studies and confirmed with TEM-SAED pattern. AC impedance analysis showed a greater electrical conductivity of LYO sample (10^{-4} Scm⁻¹) when compared to the LCO (10^{-5} Scm⁻¹), suggesting a viable option for cathode material for LIBs.

Introduction

Lithium ion batteries (LIBs) have wide range of applications and research on this technology is never ending. Electrode materials for LIBs are performance determining contributors, especially, voltage window and capacitance of the device is relied on cathodes of it. In this view, layered LiCoO₂ (LCO) cathode is a significant candidate possessing a great amount of stability with theoretical capacity ~ 274 mAhg⁻¹ [1].

In LCO, Co and Li are located in octahedral sites in alternating layers and form a hexagonal symmetry. When a bigger element such as Y^{3+} is placed at the site of Co³⁺, the available space of ion migration during redox process is improved and hence total electrical conductivity and specific capacitance of the device improve as well. There are wide ranges of reports available on partial doping/ replacement of Co³⁺, yet yttrium is attempted for the first time for cathodic purpose (LiYO₂ (LYO)). Further, to avoid the sample becoming hard due to the high temperature heat treatment of metal oxide cathodes, LYO is calcined at the same temperature of LCO and the results are systematically compared and discussed.

Experimental

LCO powder was prepared by sol-gel method with stoichiometric amounts of $Co(NO_3)_2.6H_2O$, LiNO₃ and dissolved in 50 ml of distilled water to form a solution. Then citric acid as complexing agent was dissolved in 5 ml of distilled water and added drop wise to the solution while they were bath heated at 70 °C - 80 °C until gel formation was achieved. Later, the gel was heated to 200 °C in the furnace for 1 hr and

obtained powders were collected and calcined at 700 °C for 24 hrs. In a similar way, LYO was prepared by replacing Co salt with yttrium nitrate.

Results and Discussions

The powders were subjected to structural, morphological and electrical analyses. The Fig. 1 shows the XRD pattern of LCO and LYO.



Fig. 1. XRD pattern of LiCoO2and LiYO2

In a simple LCO crystal structure, Li ions migrate through the lattice by hopping mechanism. When an atom with higher ionic radii (Y^{3+}) is included in the unit cell a larger space for Li⁺ ions to hop and better charge migration is possible. Phase pure LCO and LYO materials are possible when annealing the samples at higher temperature. However, to avoid the evaporation of Li at high temperature, here both the samples were annealed at 700° C for 24 h [2]. The resultant XRD pattern is shown in Fig. 1. Still, LYO sample contains redox inactive secondary phase Y₂O₃ whereas LCO is phase pure. Even longer duration of thermal processing did not benefit in achieving phase pure LYO sample. The LCO system falls into the trigonal system whereas LYO falls into the mixed symmetry, monoclinic LiYO₂ and shifted rhombohedral LiYO₂. The structural parameters obtained for LCO and LYO samples are given in Table 1. The crystallite size (D) was calculated by Debye-Scherrer formula. Due to the doping, structural aspects become perplexed by means of dislocation density (δ) and strain values (ϵ).

Table 1. Comparison of Crystallite size, Dislocation density and Strain value of LiCoO2and LiYO2

Parameter/ Sample	D(nm)	δx10 ¹⁵ lines/m ²	3
LiCoO ₂	66.93	1.537	0.037
LiYO ₂	23.85	4.536	0.010

The TEM and SAED images in Fig.2 reveal the agglomeration of the samples as it was proven from the large crystallite size. The bright spots in the LCO samples indicate the high crystallinity of this sample [3]. On the other hand, indeed bright spots are seen in the SAED pattern of LYO sample but the rings are not properly formed which indicates the immature crystal structure/mixed symmetry.



Fig. 2. TEM and SAED images of (a) LiCoO₂and (b) LiYO₂

The Fig. 3 shows the fitted Nyquist plots of LiCoO₂ and LiYO₂ with their corresponding equivalent circuits as inset. The LYO sample shows a better total conductivity of ~ 10^{-4} Scm⁻¹ where LCO sample was of ~ 10^{-5} Scm⁻¹. The higher electrical conductivity of LiYO₂ sample may be accounted due to the better electrical properties of Y³⁺ ions. Although, multiple phases of LYO were observed in XRD, phase dependent electrical conductivity was not analysed.



Fig.3. Nyquists plots of (a) LiCoO2and (b) LiYO2

Conclusion

LCO and LYO samples prepared by sol-gel technique and the samples were analyzed for different properties. XRD analysis revealed the mixed phase in LYO sample which indicated the immature crystal symmetry of this sample due to insufficient annealing temperature. However, LYO sample fell with higher electrical conductivity due to the better electrical aspects of the Y^{3+} than Co^{3+} . Optimizing higher annealing temperature and the structure/ phase-related ambiguities, LiYO₂ will serve great for cathodic applications in Li-ion battery technology.

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Preparation of CdS/TiO₂ Heterojunction on Ti Foil for Photoelectrochemical Solar Cell Application

S. V. Waghmare¹, P. K. Pagare¹, A. P. Torane¹, C. H. Jadhav², S. H. Mujawar^{1*}

¹ Department of Physics, Yashavantrao Chavan Institute of Science, Satara- 415001 (Maharashtra) ²Department of Physics, University of Aberdeen, United Kingdom

*Corresponding author: sarfrajmujawar695@gmail.com

Abstract

The CdS/TiO₂ heterojunction have been successfully prepared via electrochemical anodization and chemical bath deposition method on titanium metal foil (Ti). The prepared heterojunction was characterized using X- ray diffraction (XRD), scanning electron microscopy and diffusion reflectance spectroscopy (DRS) techniques. The XRD patterns clearly show the peaks of CdS, TiO₂ and Ti foil. The SEM images of anodized TiO₂ material show nanotubular morphology while CdS exhibits nanopellets like morphology. The DRS is useful to calculate the band gap of TiO₂ and CdS material. The I-V characteristics of heterojunction under dark and illumination is measured.

Compatible Iron Disilicides Synthesis Employing Reaction Spark Plasma Sintering

Priyanka^{1,2}, M. Saravanan^{1,2}, N.K. Upadhyay¹, Radhey Shyam¹, S. R. Dhakate^{1,2}

¹CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi-110012, India ²Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, India

*E-mail: sangwanpk23@gmail.com

Abstract

Green power generation and its realisation employing thermoelectric technology mainly depend on non-toxic, environmentfriendly thermoelectric constituent materials. Currently, the main focus of thermoelectric research emphasis on earth crust abundance silicide-based materials. Iron disilicides (FeSi₂) are one of the silicide family thermoelectric materials; are suitable for mass production and also stable at mid and high operating temperatures. However, the compatibility issues like both ntype and p-type, impede their device applications. In the present study, we report both n-type and p-type FeSi₂ synthesis via suitable doping, employing the combination of spark plasma sintering and vacuum sealing techniques. The synthesized n-type and p-type FeSi₂ materials were characterized using the X-ray diffraction (XRD) technique for their phase purity. The significant power factor enhancement was achieved by aluminium and cobalt doping in FeSi₂ material.

Introduction:

Thermoelectricity is based on two discovered effects, one is the Seebeck effect and another is the Peltier effect. Thermoelectric materials are classified into three different categories according the application, low-temperature, to midtemperature and high-temperature applications. Further, the efficiency of thermoelectric material is defined by the dimensionless parameter figure of merit (ZT). The ZT of a material mathematically defined as $ZT = \alpha^2 \sigma / \kappa$, where α is Seebeck coefficient, σ is electrical conductivity, and κ is the sum of κ_e (thermal conductivity due to charge carriers) and κ_L (thermal conductivity due to lattice vibration). The commercial application of thermoelectric material should be eco-friendly, nontoxic and earth-abundant along with a high ZT value¹⁻⁵. However, the reported high ZT thermoelectric materials contain either toxic or expensive elements. For achieving the highest ZT, optimize the three one could mutually interdependent parameters. One can increase ZT, by using the different strategies, either reducing the thermal conductivity or increasing the power factor. Iron disilicides (FeSi₂) based thermoelectric materials possess robust mechanical strength, high thermal and chemical stability. Their abundance in earth crust makes them inexpensive for commercial application. However, their low figure-of-merit limit its widespread application of thermoelectric power generation.

FeSi₂ have several similar phases, such as α -Fe₂Si₅ (tetragonal), ϵ -FeSi (cubic) and β -FeSi₂ (orthorhombic). All these phases are very hard to differentiate and variations in these phases fallouts in metallic and semiconducting behaviour³⁻⁵. The desired β -FeSi₂ phase have orthogonal crystal

structure space group Cmca with the lattice parameters a (9.863Å), b (7.884Å) and c (7.791Å)⁵. In order to get β -FeSi₂, several studies were reported on Iron disilicides such as ball milling, hot pressing, long-duration annealing, arc melting etc. In addition, several doping elements were added in FeSi₂, to improve its thermoelectric properties. However, it is very difficult to identify the single and straightforward processing technique, to obtain compatible p & n-type thermoelectric elements.

In the present study, a combination of spark plasma sintering and vacuum sealing techniques were used to synthesise single-phase β -FeSi₂. The possibility of realizing compatible n & p-type β -FeSi₂ thermoelectric elements was explored by suitable doping elements and reactive sintering process. The significant power factor values in both n & p-type β -FeSi₂ were achieved employing this combination of two techniques. The good power factor values arise from the increased Seebeck coefficient of the synthesized material. The synthesized n & p-type β -FeSi₂ were characterized for phase purity, using X-ray diffraction (XRD) and for transport properties, using ZEM 3 Seebeck & electrical resistivity measurement system.

Experimental Work:

Iron powder (purity 99.5%), Silicon powder (purity 99.9%), Aluminium (purity 99.5%) and Cobalt (purity 99.5%) were taken in the stoichiometric proportion of FeSi₂, Fe_(1-x)Co_xSi₂ and FeSi_(2-x)Al_x, at a suitable doping level (x = 5 at%). The powders were carefully mixed in ball milling for ~30 min. The mixed powders were subjected to spark plasma sintering (SPS 725, Fuji electric co., Japan) using a cylindrical graphite die and punch set up, having a diameter ~12.7 mm, under vacuum conditions. The

consolidation was performed at a temperature ~1173 K and a heating rate of 50 K/min with 5 min holding time, and 60 MPa uniaxial pressure. To get the desired semiconducting β -FeSi₂ phase, which is transformed from α -Fe₂Si₅ and ϵ -FeSi, all sintered specimens were heat-treated at 1173 K for 48 hrs. in a vacuum-sealed quartz tube. The structural and phase analysis were characterised by X-ray diffraction (XRD) with CuK_{α} radiation using a RigaKu (Mini-Plex) diffractometer at a scan speed of 5° per minute. The value of the Seebeck coefficient and electric conductivity of the specimens were characterized using Ulvac-ZEM-3 apparatus, under helium atmosphere.

Result and Discussion:

The X-ray diffraction analysis was performed for all the synthesized samples, shown in Fig.1. The XRD patterns reveal the peaks of α -Fe₂Si₅ and ϵ -FeSi before annealing confirming no formation β - FeSi₂ phase during SPS sintering. On subsequent annealing of the SPS synthesized material, β phase conversion is confirmed (Fig.1). Also, the XRD pattern confirms all the synthesized samples are impurity-free in nature. The trace doping element addition does not make any significant change in the XRD patterns, after annealing at 1173 K for 48 hrs.



Fig.1 XRD patterns of FeSi₂ (Before and After annealing) and with 5 at.% Al-doped & Co-doped FeSi₂

The temperature dependence of the Seebeck coefficient and electrical conductivity values, of the synthesized samples, is shown in Fig.2. It is interesting to note that, the FeSi₂ compound shows the semiconducting nature after annealing; the doping of aluminium alters it into a p-type semiconductor on the other hand doping of cobalt, alters it into the n-type semiconductor. The maximum Seebeck coefficient value of ~ 376 μ V/K was achieved in aluminium doped p-type FeSi₂ and the maximum Seebeck coefficient value of

~-201 μ V/K was achieved in cobalt doped n-type FeSi₂. In Al-doped FeSi₂, the Seebeck coefficient increasing with the temperature initially (up to 473 K) and decreases with the temperature. The electrical conductivity of all the samples, as shown in Fig.2, exhibits a continuous increase with increasing temperature. The highest power factor values of ~ 0.075 mW/mK² for Al-doped FeSi₂ and 0.71mW/mK² for Co-doped FeSi₂ were obtained and are primarily due to its very high Seebeck coefficient values.



Fig. 2 Temperature dependence of the Seebeck coefficient and electrical conductivity of synthesized FeSi2

Conclusion:

The β - Fesi₂ was synthesized successfully by the combination of spark plasma sintering vacuum sealing technique. Further, both p-type and n-type Fesi₂ were realized by the addition of suitable doping elements. A significant enhancement in power factor values was achieved in Fesi₂ material using these simple processing techniques.

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Polymer Based Flexible Piezoelectric Nanogenerator For Energy Harvesting Applications

Neha Thakur, Qaiser Yousuf, and Jayant Kolte*

School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala, 147001

*Corresponding author: jayantkolte@thapar.edu

Abstract

Barium calcium zirconate titanate (Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O₃, BCZT) ceramic have been successfully synthesised by sol-gel method. The BCZT powder is calcined at 900 °C, to obtain the single-phase perovskite structure. The flexible BCZT/ Polyvinylidene fluoride (PVDF) films have been fabricated by solution casting method. The particles are homogenously dispersed in the PVDF matrix. β -phase is confirmed by the X-ray diffraction and Fourier transform infrared (FTIR) spectroscopy studies. The dielectric constant increases with increase in weight percentage (wt%) of BCZT in PVDF. The highest dielectric constant is 91.35 and tan δ is 0.05 at 1 KHz.

Investigation of Reciprocity Between Photovoltaic Quantum Efficiency & Electroluminescence Emission of CH₃NH₃PbI_{3-x}Cl_x Perovskite Solar cell

Deeksha Gupta^{1,2}, A. K. Chauhan^{*1,2}, P. Veerender¹, S.P. Koiry^{1,2}, P. Jha^{1,2}, C. Sridevi¹

¹Technical Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai, 400085 India ²Homi Bhabha National institute, Anushaktingar, Mumbai, 400094 India **Corresponding author: akchau@barc.gov.in*

Abstract

The detailed balanced theory and optoelectronic reciprocity relations between light absorption and light emission is well studied for state-of-the art commercialized silicon solar cell. In this work, reciprocity principle is verified for solution-processed CH₃NH₃PbI_{3-x}Cl_x based planar perovskite solar cells. For this purpose, we utilized the external quantum efficiency (EQE) and electroluminescence (EL) measurements and found a good agreement between calculated and experimental values of EQE and EL. The findings indicates that mixed halide perovskite material has a very small energetic loss to absorption edge broadening ~ 23 meV.

Simulation of FTO/TiO₂/CH₃NH₃PbI₃/CuSCN/C Solar Cell

Ritu¹, Gagandeep², Ramesh Kumar², Fakir Chand^{1*}

¹Department of Physics, Kurukshetra University Kurukshetra-136119, India ²Department of Physics, Guru Jambheshwar University of Science & Technology, Hisar-125001, India

*Corresponding author: fchand@kuk.ac.in

Abstract

The enhanced optoelectronic properties of organo-halide perovskite solar cells have sparked our interest. The cell structure FTO/TiO₂/ CH₃NH₃PbI₃ /CuSCN /C is modelled employing SCAPS-1D numerical simulator. The performance parameters of the suggested structure (PCE=13.85%, FF=60.98%, J_{sc} =27.57 mA/cm², V_{oc} =0.82 V) match the experimental results well. The influence of absorber thickness and temperature on cell performance is also investigated.

Key words: Perovskite solar cell, SCAPS-1D, PCE. Temperature

Introduction

Because of their low cost, ease of manufacture, and high efficiency, perovskite solar cells (PSCs) have received a lot of attention. PSC PCE rises exponentially from 3.8% to 25.2% [1].



Fig.1. (a) Perovskite Solar Cell, (b) Band alignments.

The structure: FTO/TiO2/Perovskite/CuSCN/C is simulated in this study using the one-dimensional Solar cell capacitance simulator (SCAPS-1D) software [2] and shown in Fig. 1 along with band alignment. The effect of absorber layer thickness and temperature on power conversion efficiency (PCE), fill factor (FF), short-circuit current (J_{sc}) and opencircuit voltage (V_{oc}) of PSC was also explored. The simulation parameters were based upon a number of studies [3,4].

Results and discussion:

V_{oc} and FF fell from 0.85 V, 68.49% to 0.82 V, 58.57% as absorber thickness increased from 100 nm to 1500 nm, as seen in Fig.2. (a and c), whereas J_{sc} increased from 12.26 mA/cm² to 28.31 mA/cm² as shown in fig.2 (b). With the increase in absorber thickness from 100 nm to 900 nm, the PCE went from 7.19% to 13.85%, but with a further increase in absorber thickness (i.e., from 900 nm to 1500 nm), the PCE was reduced from 13.85% to 13.64%. Hence, as the thickness of the solar cell increases, the absorption of photons increases, boosting the generation rate. However, if the thickness is enhanced beyond a certain limit, the recombination rate increases as well, resulting in a decrease in PSC performance. The thickness at which the generation rate is highest and the recombination rate is lowest is 900 nm. As a result, the optimum solar cell thickness is 900 nm, with the following performance parameters: PCE=13.85%, FF=60.98%, $J_{sc} = 27.57 \text{ mA/cm}^2$ and $V_{oc}=0.82 \text{ V}$.





Fig.2. Impact of absorber thickness (nm) on cell parameters (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE

With increasing temperature, the performance parameter J_{sc} remained nearly constant at 27.57 mA/cm², as shown in Fig.3. (b), but other performance parameters V_{oc} , FF, and PCE fell from 0.82 V, 60.98%, 13.85% to 0.79 V, 56.43%, 12.40%, as mentioned in Fig.3 (a, c and d). The decline in solar cell performance at higher temperatures is due to increased carrier dispersion, which increases the recombination rate. As a result, after optimization, the temperature is set at 300 K with the following performance parameters: V_{oc} =0.82 V, J_{sc} =27.57 mA/cm², FF=60.98% and PCE=13.85%. The obtained results are in close matching with the experimental study [5].





Fig.3. Effect of Temperature (K) on performance parameters (a) V_{oc} , (b) J_{sc} , (c) FF and (d) PCE.

Conclusions

The highest performance was achieved with a 900 nm optimised absorber thickness and the following performance parameters: PCE=13.85%, FF=60.98%, $J_{sc} = 27.57 \text{ mA/cm}^2$ and $V_{oc}=0.82 \text{ V}$. The obtained results are quite close to the experimental findings (PCE=11.84%, FF=73.59%, $J_{sc}=17.24 \text{ mA/cm}^2$, $V_{oc}=0.933 \text{ V}$).

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Corn Husk Derived Micro Porous Carbon: A Promising Electrode Material for Supercapacitor

Nagaraju Macherla¹, Manjula Nerella¹, Ram Gopal Reddy Lekkala¹, and Kusum Kumari^{1*}

¹Department of Physics, National Institute of Technology, Warangal, Telangana, India 506004

*Corresponding author: kusum@nitw.ac.in

Abstract

Extensive research has been carried out on porous carbon electrode materials for supercapacitor owing to their excellent microstructural properties. In the present study, a renewable resource, abundantly available corn husk is utilized as a raw material for synthesizing the micro porous carbon (MPC) using carbonization followed by chemical activation method. The resultant porous carbon possesses a high specific surface area of 1458 m² g⁻¹ with dominant micro porosity. A symmetric supercapacitor is fabricated by employing MPC electrodes and maximum specific capacitance of 95 F/g is achieved at a current density of 1 A/g in 6 M KOH electrolyte. Besides, it illustrates excellent rate capability of 92% at high current density of 10 A/g. Hence, this work highlights that the fissile synthesized MPC is believed to be a promising electrode for supercapacitors.

The structural, optical and dielectric properties of La, Se co-doped BFO

Joana Preethi A¹, Ragam M²

¹Research scholar, Research Centre of Physics, Fatima College, Madurai, India, ²Assistant Professor, Research Centre of Physics, Fatima College, Madurai, India.

-¹Corresponding author e-mail id: jonapreethi08@gmail.com

Abstract

Pure and Selenium (Se), Lanthanum (La) co-doped BiFeO3, $Bi_{0.92}La_{.08}Fe_{1-x}Se_xO_3$ (L₈Se_x), (where, x=0.1, 0.25, 0.5, 1) nanocomposites were synthesised using sol-gel technique. The structural properties and optical properties of synthesised samples were analysed. Effect of doping in dielectric characteristics of the synthesised samples were studied. Besides, dielectric loss of the samples were investigated.

Introduction

Bismuth Ferrite (BFO) has recently been one of the most researched topics owing to its room temperature multiferroic properties which makes it a potential candidate for applications in numerous fields including smart devices, memory devices, sensors and energy applications. It is known to exhibit both ferroelectricity and anti-ferromagentism with high curie and Neel temperature respectively [1]. Recently, Dielectric materials with high energy storage density, good temperature stability, and low dielectric loss have gained the potential applications in capacitor technology. Developing capacitors with improved energy density, storage efficiency and operation sustainability in severe environments are one of the main aim of the ceramic industries. The ferroelectric and ferromagnetic properties can be increased by substitution of A-site cation with rare earth elements or by replacing the B-site cation with transition metals and rare earth elements [2]. To enhance the features of present electrochemical energy storage devices, the dielectric properties of capacitors need to be optimized and finding a suitable dielectric material is vital for industrial applications. In this context, various attempts have been made by doping the A and B sites of BFO nanostructure with Rare earth elements such as lanthanum (La) and selenium (Se) to enhance the optical and dielectric properties thus modifies the conductivity properties towards energy production and energy storage applications.

Experimental Technique

Pure BFO nanomaterials were synthesized by the standard sol-gel technique. Bismuth nitrate and Iron nitrate were dissolved separately in 2-Methoxy ethanol (2MEO) in 1:1 molar ratio and stirred for 1 hour. 1ml Acetylacetone was added as the chelating agent in the

second solution. Both the solutions were mixed together and stirred for 2 hours. The mixed solution was then heated at 100°C for 24 hours. The gel formed was grounded and then calcined at 500°C for 1 hr.

Various samples of (La, Se) co-doped BFO nanoparticles with empirical formula $Bi_{0.92}La_{0.08}Fe_{1-x}Se_xO_3, x = 0\%, 10\%, 25\%, 50\%,$ 100%, labelled as BLFO, BLFSO (Se=0%, 10%, 25%, 50%) and BLSO (Fe=0% & Se=100%) were synthesized by sol-gel method. Nitrate salts of Bismuth and Lanthanum were stoichiometrically dissolved in acetic acid and ethylene glycol for 2 hours. Iron nitrate and selenium powder (Se= 0%, 10%, 25%, 50%, 100%) were dissolved in acetic acid at 40°C for 2 hours. Then, both the solutions were mixed for 3 hours under constant magnetic stirring. The mixed solution was dried in oven at 90°C for 12 hours. The obtained gel was then calcined in the furnace at 600°C for 3 h. After cooling, the calcined powder was ground to get the nanoparticles.

Results and discussion



Fig. 1. XRD patterns of Pure BFO, BLFSO and BLSO samples

The XRD analysis was used to investigate the crystalline structure of BFO and the derived (La-Se doped) nanomaterials and the results are presented in Fig. 1. The XRD patterns of pure BFO (JCPDS card no. 20-0169) corresponds to rhombohedral structure with distorted perovskite structure corresponding to R3c space group [3]. In addition to this, a slight shift in peak position is observed which can be attributed to the doping of the Se powder. The doping to Se to BLFO nanomaterials play a vital role in the phase transformation of BFO from rhombohedral to orthorhombic phase. The samples with lower concentrations showed mixed rhombohedral and orthorhombic phases while the higher concentrations show pure orthorhombic phase.



Fig. 2. Uv-Vis spectra of BLFSO samples



Fig.3. PL spectra of BLFSO samples

The UV-Vis absorption spectra was used to investigate the effect of La,Se doped BFO at room temperature in the wavelength range of 200nm - 800 nm. The absorption is found to be increased for the La,Se doped samples when compared to the pure BFO samples but on comparing the BLFSO samples the intensities were found to decrease with increase in Se concentration. The absorption peaks were observed at 485nm (BFO), 456nm (BFLO), 462nm (Se=10%), 483nm (Se=25%), 464nm (Se=50%),304nm (BLSO). The room temperature PL emission spectra was investigated. The PL spectra shows clear peaks at 301 nm, 365 nm, 463nm and 560 nm.



Fig.4 & Fig.5. Dilectric studies

The room temperature dielectric studies of the synthesised samples were used to investigate the effect of La and Se doping of BFO. It was found that the dielectric constant increased with increase in Se concentration while the dielectric loss was decreased with increase in doping concentration. Such materials are potential candidates for energy harvesting and energy storage applications. Further research in these nanostructures may result in novel integrated device to harvest and store solar energy.

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Fabrication of an efficient CsPbIBr₂ based carbon electrode perovskite solar cell via organic cation passivation

Akanksha Choubey, P. Nagapandiselvi, N. Santhosh, M. Senthil Pandian and P. Ramasamy

Department of Physics, SSN Research Centre, Sri Sivasubramaniya Nadar College of Engineering, Kalavakkam, Tamilnadu, 603110

*Corresponding author: choubeyakanksha15@gmail.com

Abstract

Perovskite solar cells (PSCs) have emerged as an efficient and advanced solar cell in the realm of solar cells. In which Organicinorganic and all inorganic PSCs are comparable to silicon solar cells due to their high efficiency. Wherein, cesium lead halide based inorganic PSCs have gained attention of solar cell researchers due to their superior stability compared to organic-inorganic PSCs. Carbon based electrodes have been widely applied in PSCs, as it offers excellent hydrophobicity for all inorganic PSCs and makes the device more stable without the use of any expensive noble metal electrodes. Herein, we have worked on synthesis of good quality CsPbIBr₂ layer and fabrication of an efficient CPSC by doping the perovskite with different ratios of Methyl ammonium (MA). Fabricated devices delivered the highest efficiency of 5.1 % and displayed good moisture and thermal stability.

The CsPbI₃ Mediated Electroactive β-phase in PVDF Composite Film for Piezo-phototronic Applications

Bidya Mondal, Hari Krishna Mishra, Dipanjan Sengupta, and Dipankar Mandal^{*}

Quantum Materials and Devices Unit, Institute of Nano Science and Technology, Knowledge City, Sector 81, Mohali 140306, India

*Corresponding author: dmandal@inst.ac.in

Abstract

In this work, the nucleation of electroactive β -phase in polyvinylidene fluoride (PVDF) film by incorporation of a very low amount of cesium lead iodide (CsPbI₃) perovskite is achieved. CsPbI₃ is an emerging material with the typical band gap energy ~1.73 eV. Here CsPbI₃ interacts with PVDF interfacially and enables to induce electroactive β -phase in PVDF and it also retains the long term stability. Thus CsPbI₃ incorporated PVDF composite film turns to be a self-poled film where traditional stretching and poling can be avoided. In the context of green mechanical energy harvesting application, it is expected to exhibit the piezo-phototronic effect that may widen its optoelectronic applications.

Introduction

Recently, lead halide perovskite have gained lots of interest in photovoltaic technology because of their high power conversion efficiency. But the main drawback of this material is its stability issues under ambient environment. To address the stability issues, it is speculated to blend with hydrophobic material so that consecutively the resulting materials become flexible and also shows mechanical energy harvesting abilities. Thus to harvest both solar energy and mechanical energy, a hybrid device is fabricated. In this context, PVDF is a well-known potential piezoelectric polymer due to its soft, flexible, lightweight, and outstanding piezo-, pyro-, and ferroelectric properties. It is a semi-crystalline polymer that exhibits mainly three crystalline phases (α -, γ - and β -phase) where non-polar α -phase is not piezoelectric while semi-polar γ - and polar β -phase are piezoelectric in nature $.^{1}$ The β -phase is most emergent in mechanical energy harvesting due to high degree of piezoelectric coefficient (d_{33}) , voltage coefficient (g), and electromechanical coupling constant (k). There are several approaches has been adopted to convert α to β -phase in PVDF, e.g., mechanical stretching, high electric field poling, LB film formation, spin coating, electrospinning to mention a few. Each techniques have merits and demerits, and in this regards, our approach is much beneficial since mechanical stretching, high electric field is possible to avoid. In this context, $CsPbI_3$ was incorporated into PVDF matrix to nucleate β -phase. It has been also observed that $CsPbI_3$ and PVDF composite film exhibits photoemission in the visible region even upon prolong ambient environment exposer that indicates it has tremendous potential in the piezo-phototronic applications.²

Experimental Methods

CsPbI₃ was synthesized by hot injection method as reported previously.³ A 6 wt% (w/v) PVDF solution was prepared by dissolving PVDF powder into DMF. Then 0.25 wt% (w/v) CsPbI₃ was added to the solution and stirred to ensure homogeneous dispersion. Afterwards, film was casted on clean glass slide at 60°C for 3 h and named as PVDF/CPI. A neat PVDF film was also made as reference in similar conditions.

Results and Discussions

UV-visible absorption spectra of CsPbI₃ confirms the perovskite phase formation as shown in Fig. 1a.³ This plot shows the absorption onset at 712 nm. The band gap energy was calculated from Tauc plot using the following $(\alpha h \upsilon)^2$ vs. energy (h υ) relation

$$(\alpha h \upsilon)^{1/n} = A(h \upsilon - E_a) \tag{1}$$

Where A is constant, α is absorption coefficient, E_g is band gap energy, and the value of n for direct allowed transition is 1/2. The calculated bang gap was ~1.75 eV as shown in Fig. 1b.



Fig. 1. a) UV-visible absorption spectra of CsPbI₃. (b) Tauc plot for energy band gap calculation. (c, d) FTIR spectra of neat PVDF and PVDF/CPI film in different regions.

Fourier transform infrared (FTIR) spectra of neat PVDF and PVDF/CPI film is shown in Fig. 1c. The characteristics vibrational bands of neat PVDF at 762, 795, 976 cm⁻¹ correspond to the predominantly α -phase while bands at 836 and 1231 cm⁻¹ correspond to γ -phase.¹ It is evident that there is no signature of vibrational band of β - phase in neat PVDF film. In contrast, PVDF/CPI film shows a new prominent band at 1273 cm⁻¹ which indicates that β - phase has been induced.⁴.



Fig. 2. I-V characteristics of PVDF/CPI film in different conditions.

The resultant electroactive phase content and relative proportions of γ -phase and β -phase were calculated and tabulated in table 1.⁴

Table 1. The electroactive β , γ -phase contents in neat PVDF and PVDF/CPI composite film.

Film	Electroactive Phase (F_{EA} %)	β- phase (F_β %)	γ -phase $(F_{\gamma}\%)$
Neat PVDF	64	0	64
PVDF/CPI	81	37	44

Furthermore, interfacial interactions between PVDF and CsPbI₃ were confirmed by observing the shift of the –CH₂ vibrational modes as shown in Fig. 1d.⁴

As an application of PVDF/CPI film, the current (I)voltage (V) characteristics was measured in dark, UV light exposure, and a fixed compressive strain without light exposure as illustrated in the Fig 2. This I-V curve shows semiconducting behaviour and detects the different external stimulus.²

Conclusions

In summary, very low amount of CsPbI₃ incorporation into PVDF nucleates the stable electroactive β -phase in PVDF/CPI composite film. Furthermore, due to hydrophobic nature of PVDF, the phase degradation of CsPbI₃ was prevented. Thus it is noteworthy that the PVDF/CPI film can be a potential candidate for ferro-, pyro-, piezo-electric, optoelectronic, and piezophototronic applications.

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Moving from solid to porous nanostructures for enhancing the magnetic field dependent electrochemical performance of Mn₃O₄ nanoparticles

Chinmayee Chowde Gowda¹, Sudipta Biswas² and Amreesh Chandra^{1,2*}

¹School of Nano Science and Technology, ²Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur-721302 *Corresponding author: achandra@phy.iitkgp.ac.in

Abstract

Transition metal oxides have been used as electrode material because of their high pseudo capacitance, chemical stability, and low resistance. Mn-based oxides have been extensively used as efficient electrode material for supercapacitors. Large number of particle morphologies have been investigated to tailor the electrochemical performance of Mn based oxides. The change in specific capacitance, has been directly attributed to the change in specific area. Recently, Mn-oxides have also shown varying electrochemical performance near changing magnetic field environment. But there are no studies, which deals with the possibility of magnetic field dependent variation in these oxides as function of changing morphologies. This should happen because the surface states are known to vary as we move from one morphology to another. In addition, interaction of surface states with magnetic field decides the response of the particles. We report magnetic field dependent electrochemical performance of solid, hollow and porous Mn₃O₄ nanoparticles. It is noted that the hollow and porous structure exhibits the highest specific capacitance of 87 F g⁻¹ and 70 F g⁻¹, respectively when 30 Gauss magnetic field is applied.

Comparative study on the Hole Selective Nature of MoO₃ and V₂O₅ in Carrier Selective Solar Cells

Rameeja T. Abdul Rasheed¹, Sneha Babu¹, Sreena S.¹, Antony Sharon² and

Aldrin Antony^{1,2*}

¹Department of Physics, ²Centre of Excellence in Advanced Materials, Cochin University of Science and Technology, Kochi 682022

*aldrin@cusat.ac.in

Abstract

TMOs with higher work functions like MoO_3 and V_2O_5 are being used as hole selective layer for c-Si solar cells. The dark diode characteristics and capacitance-voltage characteristics of these transition metal oxides with Si are studied with structures fabricated in a diode configuration and illumination characteristics are studied with the TMOs in a solar cell configuration with n⁺ BSF on textured Si wafer. The results of the study are compared with previously reported values in literature. Vanadium pentoxide has exhibited a superior hole- selective nature which is evident from the values of the Built-in Potential (V_{bi}) extracted from Mott-Schottky plot and Open Circuit Voltage (V_{oc}) extracted from the illuminated current- voltage characteristics.

Introduction

Transition Metal Oxides are gaining popularity due to its potential to replace doped hydrogenated amorphous Silicon (a-Si:H) as electron and hole selective contacts using Dopant – Free Asymmetric Heterocontact (DASH) architecture. High Work function (>5 eV) TMOs such as MoO₃, V₂O₅ and WO₃ are explored as hole selective contacts whereas low work function TiO₂ and MgO are frequently used as electron selective contact in Carrier Selective Solar Cells (CSCs). TMOs offer relative ease of deposition through industrially feasible low temperature techniques such as Thermal Evaporation and Atomic Layer Deposition (ALD).

MoO₃-HSL solar cells have already demonstrated efficiencies exceeding 20% [1]. In this work, we compare the hole selective nature of MoO₃ and V₂O₅, their dark and illumination characteristics to effectively employ them in suitable hetero contact architecture. The Dark J-V characteristics of diodes fabricated on silicon wafers (n-Si) were used to identify the diode ideality factor and Dark saturation current density (Jo), and capacitance voltage measurements were performed to measure the Built-in Voltage (Vbi). Identical solar cells using MoO3 and V₂O₅ as HSL were fabricated and their illumination characteristics obtained using solar simulator at standard conditions of AM 1.5G spectrum at a temperature of 25 degree Celsius. The illuminated J-V characteristics sheds light on the loss mechanisms and recombination centers present in the fabricated cell. A comparison of the open circuit voltages (Voc) and Short circuit current densities (Jsc) elucidates the charge transport mechanism in the two oxides.

Comparison of Dark Characteristics of MoO₃ and V₂O₅ Diodes

Thermally evaporated MoO₃ and V₂O₅ films of thickness 20nm were deposited on 500 μ m n type silicon CZ wafer (1-5 Ω cm), rear contacted with ~240 nm of Silver and front contacted with ~60 nm of circular gold electrodes (500 μ m diameter) were studied using Keithley 4200- SCS semiconductor parameter analyzer equipped with Suss Micro-Tec microprobe station. The Dark J-V yielded a reverse saturation current density of 6 × 10⁻⁷ A/cm² for MoO₃ and 4.1x10⁻⁶ A/cm² for V₂O₅ diodes. The ideality factor extracted from the semi-log plot were 1.45 and 2.8 for MoO₃ and V₂O₅ respectively.



Fig.1Dark -diode characteristics and corresponding Mott-Schottky as inset for (a) MoO_3 and (b) V_2O_5 as the hole selective layer for Si.

Analysis of the Mott-Schottky plot from the C-V measurements of the TMO-Si junction gave a built-inpotential for MoO₃ in the range of 589mV whereas for V₂O₅, it revealed a much higher value in the range of 710mV to 750 mV. The high value of the ideality factor in the fabricated V₂O₅ diodes suggests a high
recombination at the interface. Built- in- potential is an indicative of the extent of band bending and consequently, the maximum open- circuit voltage (V_{oc}) the junction can achieve in a solar cell configuration. The exceptional values of V_{bi} achieved in V_2O_5 diodes demonstrates its potential to achieve excellent open circuit voltages (V_{oc}), provided the passivation is intact.

The illuminated J-V Characteristics of solar cells fabricated in the configuration (Ag/ITO/TMO/n-Si/n⁺/Al) with MoO₃ and V₂O₅ as the TMO were studied and compared. Device with MoO₃ as HSL attained a V_{oc} of 410mV, J_{sc} of 23.3 mA/cm², Fill factor of 36.8% and an efficiency of 3.5 %, whereas the device with V₂O₅ as HSL attained a V_{oc} of 460 mV, J_{sc} of 24.9 mA/ cm², Fill Factor of 30.5% and efficiency of 3.49% .Both the cells showed comparable performance. The S shaped curve indicates that the ITO layer is little resistive and not optimized, causing a high series resistance. Sputtering of The ITO layer is also affecting the passivation quality at the interface due to the high ion bombardments during the sputtering process.



Fig. 2. Illuminated J-V characteristics of device with $(a)MoO_3 as HSL (b) V_2O_5 as HSL$

Our solar cells showed higher Voc value for the V2O5 HSL layer. The Built in potential measured from C-V studies were also indicating a similar trend. The findings are in line with the studies conducted by Gerling et al.[2][4] and Osbel Almora et al.[3]. The solar cells in the DASH configuration (ITO/TMO/ncSi/n+/TiAl) attained a Voc of 593mV for V2O5 as TMO when compared to 581mV for MoO3 as the TMO layer [2]. Similar results were obtained for (ITO/TMO/n-cSi/(i/n)a-SiCx:H/TiAl) structures with textured c-Si. The device with V₂O₅ as HSL exhibited a higher Voc of 605 mV in comparison to MoOx HSL of 563 mV[3].Device fabricated with rear structure of a-Si:H(n) and a-SiCx:H have also followed this trend, yielding 606 mV for V2O5 based device and 581 mV for MoO₃ based device[4]. Back contacted dopant free configuration reported by García et al. exhibits similar trend with $610 \text{ mV} V_{oc}$ attained for V_2O_5 and 561 mVattained for MoO₃ [5].

The device fabricated in the present work with V_2O_5 as HSL has not attained the high V_{oc} values reported in literature[2][3][4][5]. This may be due to the insufficient oxide layer (SiO_x) formation at the TMO-nSi junction. The low V_{oc} values is an indicative of a weak inversion region. Further optimisation of ITO may lead to better results by minimizing the sputter damage.

The studies indicate a considerable improvement in the open circuit voltage (V_{oc}) demonstrated by the device with V_2O_5 as the HSL in comparison with the device employing MoO₃ as the HSL by 50mV.This is coherent with the built-in potential(V_{bi}) values obtained in the diode configuration. The evidence from this study suggests that V_2O_5 is a promising candidate for Dopant Free Carrier Selective Solar Cells. Proper optimization of the TCO layer could eventually lead to good illumination characteristics and higher open circuit voltage.

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Ascendancy of Supercapacitive Demeanour of Nickel Doped Cobalt Oxide Thin Film Electrode

Shubhangi Gavande^{1,4}, Shivani Gavande², Arati Diwate³, Bhanudas Karche⁴

¹Department of Physics, Sangameshwar (Autonomous) College, Solapur - 413001, (M.S.), India., ²Research Scholar, Functional Materials Research Laboratory, School of Physical Sciences, P.A.H. Solapur University, Solapur- 413255, (M.S.), India., ³Department of Chemistry, Sangameshwar (Autonomous) College, Solapur -413001, (M.S.), India., ⁴Department of Physics, Shankarrao Mohite Mahavidyalaya, Akluj, Dist. Solapur (M.S.),

India.

*Corresponding author: *1,3e-mail: shubhangi.gavande15@gmail.com

Abstract

Cobalt oxide was potentiostatically electrodeposited on stainless steel substrates and 2% Nickel was consolidated in the pure Cobalt oxide in the form of thin, uniform films. Both the deposited films were annealed at 500°C annealing temperature. The X-ray diffraction analysis showed simple cubic crystal structure and Contact angle measurement showed hydrophilic nature of both Ni-doped Co₃O₄ and pure Co₃O₄. The cyclic voltammetry study showed a heave in Specific capacitance from 284 Fg⁻¹ of pure Cobalt oxide film to 727 Fg⁻¹ of Ni-doped Co₃O₄ at 5mVs⁻¹ scan rate in 1M aqueous Na₂SO₄. The charge-discharge scrutiny exhibited accretion in Specific energy from 4.33 Whkg⁻¹ to 10.5 Whkg⁻¹, Specific Power from 3 kWkg⁻¹ to 13.22 kWkg⁻¹ on 2% doping of Nickel in Cobalt oxide. Significant supercapacitive behaviour of Ni-doped Co₃O₄ electrode was remarkably observed.

Keywords: Cobalt oxide, Nickel, doping, cyclic voltammetry, charge-discharge.

Bismuth Telluride Based High Performance Thermoelectric Generators

Rishikesh Kumar^{1,2}, Ranu Bhatt^{1,*}, Shovit Bhattacharya¹, Manbendra Pathak², M.K. Khan², Ajay Singh¹, K.P. Muthe¹

¹Technical Physics Division, Bhabha Atomic Research Centre, Mumbai-400084 ²Department of Mechanical Engineering, Indian Institute of Technology, Patna

*Corresponding author: rbhatt@barc.gov.in

Abstract

In Bi-Te based thermoelectric generators (TEG) conversion efficiency (η) has been hindered due to poor performance of n-type thermoelectric material as compared to counter p-type material. In present work, we have synthesized polycrystalline n-type thermoelectric material with composition Bi₂Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01} using high energy ball-mill. We achieved power factor ($\alpha^2\sigma$) value of 1.4 W/m-K² in this material which is 50 % higher than the value obtained in commercial n-type Bi_{2.5}Se_{1.5}Te₃ material. Unicouple TEG developed using synthesized n-type material in combination to commercially available p-type Bi_{0.5}Sb_{1.5}Te₃ material, exhibits device resistance of 7.5 m Ω . We achieved open circuit voltage (V_{oc}) of 70 mV and load voltage (V_L) of ~35 mV at matching load. With this maximum power output (P_{out}) of ~160 mW is achieved at temperature gradient Δ T of 238 K.

Introduction

In present scenario of rapidly exhausting renewable energy resources and conventional power generation method, nearly 60 % of energy get dissipated in the environment unused. This dissipated energy cover broad spectrum of energy varying in temperature range from room temperature to 1000°C, and thus requires promising technology for their reutilization. TEGs effectively gathers the waste heat and convert them into useful electrical voltage, which can be further utilized in various application as medical equipment, environmental monitoring, electronic component, space applications, automobiles etc¹. The n of these devices depends upon their figureof-merit, $zT = \alpha^2 \sigma T / \kappa$, where α , σ , κ and T are Seebeck electrical conductivity, coefficient. thermal conductivity, and absolute temperature, respectively. Some of the established thermoelectric material in various temperature range are SiGe (1000°C), PbTe (500°C), Half Heusler (500-700°C), Bi₂Te₃ (30-300°C)²⁻³.

Until now low-grade waste heat covers the 50% of the total waste heat, which can be harvested using Bi-Te based thermoelectric material. It is established that the n-type composition of this family is underperformed as compared to p-type composition which restricts the η of these TEG. Several reports are available where different sophisticated techniques as nanostructuring, spark plasma sintering, liquid state sintering and doping have been reported for zT improvement⁴. In this work, we have synthesized n-type $Bi_2Te_{2.7}Se_{0.3}$ material with Cu (1 at. %) and Se (1 at. %) as invisible dopant. Synthesized material shows improved thermoelectric properties as compared to commercially available n-type Bi_2Te_3 material. Unicouple thermoelectric generator was fabricated using synthesized n-type material in combination to commercially available p-type $Bi_{0.5}Sb_{1.5}Te_3$ material, and tested in temperature range of 300 K -573 K.

Experimental

Polycrystalline n-type Bi₂Te_{2.7}Se_{0.3} (doped with 1 at. % Cu and Se) was synthesized in high energy ball mill at 500 RPM. The milling was performed in WC jar for the duration of 30 hours. Structural analysis was carried out by recording x-ray diffraction (XRD) pattern in PROTO make powder x-ray diffractometer using Cu-K_a x-ray source. For thermoelectric measurements powdered n-type and p-type samples were sintered in vacuum hot-press at 673 K in the vacuum of the order of 10⁻⁵ torr. Temperature dependence of α and σ was measured in Linseis make LSR-3 set up, whereas the κ was recorded in Laser Flash Analysis (LFA-1000) set-up. For device fabrication n-type and p-type (commercial $Bi_{0.5}Sb_{1.5}Te_{3}$) thermoelement were sintered using Ni as diffusion barrier layer. The elements were interconnected with silver electrode using CuAg based brazing alloy. The output of the device was measured in indigenously designed testing unit set-up in vacuum.

Results and Discussion

Figure 1(a) shows the XRD graph for $Bi_2Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01}$ and $Bi_{0.5}Sb_{1.5}Te_3$ sintered pellet. The XRD of $Bi_2Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01}$ shows diffraction peak similar to $Bi_2Te_{2.7}Se_{0.3}$ and are indexed to the rhombohedral structure (JCPDF 15-0863), with some shifting towards higher angle side indicating strain in the sample due to addition of Cu/S atom.



Fig. 1. (a) XRD pattern, temperature dependence (b) electrical conductivity, (c) Seebeck coefficient and (d) power factor.

The particle size of both the material is calculated using Scherer formula given below;

$$d = \frac{0.9\lambda}{\beta\cos\theta}.$$
 a)

Where λ is wavelength (0.154 nm) and β is full-widthhalf-maximum (FWHM) of the XRD peaks. Using this relation the particle size of the sample came out to be 80 nm and 100 nm for p-type and n-type material respectively. Figure 1(b-d) shows the temperature dependent thermoelectric parameters of Bi₂Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01} material and commercial ntype (Bi₂Te₃) and p-type (Bi_{0.5}Sb_{1.5}Te₃) materials. It is observed that Bi2Te2.7Se0.3Cu0.01S0.01 shows increasing trend in σ with temperature rise, however both the commercial material show metal type behavior in σ indicating strong electron-phonon scattering at higher temperature. The σ of Bi₂Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01} increase from 450 O-cm⁻¹ to 680 O-cm⁻¹(at 573 K) which is much higher than the commercial n-type material. The improved σ shows the donor type behaviour of Cu atoms giving rise to increased carrier concentration. Additionally, substitution of Se at Te site also enhances Te vacancies resulting in higher electronic contribution. As compare to commercial n-type material, along with higher σ significantly higher α (-

180 μ V/K) is observed in Bi₂Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01} material, which remain stable till 400 K. The negative α value confirms the electron as majority charge carrier, however beyond 400 K a value decreases suggesting the onset of bipolar conduction due to lower band gap (E_g). The value of E_g estimated using Goldsmid-Sharp relation⁵, ($E_g = 2e\alpha_{max}T_{max}$) comes out to be 0.14 eV and 0.15 eV for $Bi_{2}Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01}$ and $Bi_{0.5}Sb_{1.5}Te_{3}$, respectively. With the measured thermoelectric parameters we achieved maximum power factor value of 2.3 W/m-K² $(Bi_{0.5}Sb_{1.5}Te_3)$ and 1.4 $W/m-K^2$ $(Bi_2Te_{2,7}Se_{0,3}Cu_{0,01}S_{0,01})$. With measured κ value of 1.3 W/m-K we achieved $zT_{max} \sim 0.3$ which remain stable in the measured temperature range.

Fabricated unicouple TEG exhibits device resistance of 7.5 m Ω measured using four probe method. Fig. 2(a-b) shows the thermoelectric performance of TEG as a function of ΔT . We achieved maximum V_{oc} of 70 mV and V_L of 35 mV at matching load resistance. With measured load resistance maximum P_{out} of 160 mW is achieved at ΔT of 238 K.



Fig. 2. (a) V_{oc} , V_L and load current (IL) of unicouple TEG, (b) P_{out} of TEG, inset in fig. 2 (b) shows schematic of TEG.

Conclusions

N-type Bi₂Te_{2.7}Se_{0.3}Cu_{0.01}S_{0.01} material synthesized using high energy ball-mill shows better thermoelectric performance as compared to commercial n-type Bi2Te3 material. We achieved $(\alpha^2 \sigma)_{max}$ of 1.4 mW/m-K² which is double the value of commercial n-type material. Unicouple TEG shows maximum V_{oc} of 70 mV and $(P_{out})_{max}$ 160 mW at ΔT 238 K.

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Crystal Structure and Broadband Dielectric Response of LiPb₂Mg₂V₃O₁₂ Ceramics

Rakhi. M¹ and Subodh G*

Department of Physics, University of Kerala, Thiruvananthapuram-695581 Kerala India *Corresponding author: gsubodh@gmail.com

Abstract

A low temperature dielectric ceramics $LiPb_2Mg_2V_3O_{12}$ having garnet structure was prepared through conventional solid state reaction route. Its phase purity, crystal structure and broadband dielectric responses were investigated. Rietveld refinement analysis of the compound confirms cubic structure with space group Ia/3d. The observed Raman vibrational modes and group theoretical calculations also confirm the *Ia/3d* space group. At the optimum sintering temperature of 675°C, LiPb_2Mg_2V_3O_{12} possesses a density of 93% and shows a relative permittivity of 8 and dielectric loss of 0.002 at 1GHz.

Introduction

Recently the Microwave dielectric ceramics have become an indispensable component in wireless communication products, such as mobile phones and base stations, GPS, WLAN, Wi-Fi etc., due to the advances in 5G communication technology. These materials has been widely used as dielectric resonators, dielectric filters, dielectric oscillators, phase shifters, microwave capacitors, duplexer, dielectric wave guide substrate etc [1-4]. In comparison to the Al- and Si-based traditional ceramic that have high sintering temperatures (> 1300 °C), it is reasonable to study the low sintering temperature garnet based vanadate system for the microwave applications. Thus, it is of great interest to search for novel low-firing microwave dielectric materials from garnet vanadates. For the microwave applications, ceramics should possess low dielectric loss for selectivity, high relative permittivity (ε_r) for miniaturization and zero temperature coefficient of resonant frequency (τ_f) for temperature stability.

EXPERIMENTAL METHODS

The high purity raw materials such as Li_2CO_3 , MgO, PbO and NH_4VO_3 are weighted according to its stoichiometry and are ball milled using cerium balls in acetone medium for 24 hours. Then the obtained powder was calcined at temperature around 650°C. The phase purity and crystal structure of the calcined samples were analysed by X-Ray diffraction (XRD).TOPAS 4.2software was used for the Rietveld refinement. The Raman spectra were recorded using LABRAM-HR 800 Raman spectrometer. For dielectric measurements the calcined powders were grounded and mixed with 5 wt% PVA solution. The slurries were dried and pressed into cylindrical pellets

of diameter 15 mm and 1-2 mm thickness for broadband dielectric responses. Densities of the samples were measured using Archimedes principle. The surface morphology of the sample was analysed using a scanning electron microscope (ZEISS EVO 18). The broadband dielectric response of the material from 1 MHz to 1 GHz was performed using a Keysight E4991B impedance analyzer.

RESULTS AND DISCUSSIONS

The absence of any additional reflections in the XRD pattern confirmed the single-phase nature of the compound and its crystalline nature is also very clear from its sharp diffraction peaks. In order to understand the crystal structure in detail, Rietveld refinements of the XRD patterns of the compounds were carried out, which are shown in Figure (1). The obtained refinement parameters are R_p =8.65%, R_{wp} =11.65% and χ^2 =4.39. The refined lattice parameters obtained are *a*= 12.81 Å. The inset of Fig (1) indicates the garnet structure of the compound. In which the three crystallographic sites 24*c*, 16*a* and 24*d* are occupied by Li/Pb, Mg²⁺ and V⁵⁺ respectively.



Fig.1. Rietveld refinement of X-Ray diffraction pattern of LPMVO ceramics



Fig.2. De-convoluted Raman spectrum of LPMVO

The vanadate garnets have a general composition $A_3B_2C_3O_{12}$. The cations in the A site, B and C site have 8,6 and 4 nearest oxygen neighbours and this anions are occupied in the 96h site. According to the group theory calculations, the garnet system possesses 98 vibrational modes, out of which 55 of them are silent in nature and one is acoustic. The remaining are IR and Raman active active bands are 17 and 25 respectively.

 Γ acoustic = F_{1u}

The Raman active modes represent $3A_{1g}+8E_g+14F_{2g}$. In which A_{1g} , E_g and F_{2g} corresponding to internal modes, translational and rotatory modes respectively. The modes under 300 cm⁻¹ are related to the translation motion of A site cations/CO₄ and or BO₆ cation group. The peaks above 600 cm⁻¹ are related to the symmetric stretching of tetrahedral (VO₄) group [5]. Fig. (2) shows 12 deconvoluted Raman active peaks corresponds to LPMVO out of 25 predicted by factor group analysis. The polycrystalline nature of samples, low resolving power of instrument, the overlapping of bands etc., may be the reason for the lesser number of Raman active peaks in ceramic. The sharp and intense lines at 812.5 cm⁻¹ for LPMVO may correspond to the stretching modes of VO₄ groups.

Figure (3) shows the SEM micrographs for LPMVO sintered at the optimum sintering temperature. It shows a relatively dense microstructure with an average grain size of $\sim 2 \mu m$ for LMPVO ceramics.



Fig.3. The microstructure of thermally etched LPMVO



Fig.4.The broadband dielectric properties of LPMVO

The figure (4) shows the Broad band dielectric measurement LPMVO at the optimum sintering temperature of 675°C. It shows dielectric constant and dielectric loss of around (8, 0.002) for LPMVO at 1GHz frequency. As frequency increases the dielectric constant and dielectric loss shows a decrease due to the decrease in polarization.

CONCLUSIONS

 $LiPb_2Mg_2V_3O_{12}$ ceramic with garnet structure were prepared through conventional solid state reaction route. The phase purity, crystal structure and microstructure were analysed through XRD, Raman and SEM. The low relative permittivity and low dielectric loss makes them a promising candidate for microwave applications.

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Photocatalytic Degradation of Methyl red using Hydrothermally Prepared Cu₂SnS₃ (CTS) Nanoparticles

Archana R. Machale¹, Harshad D. Shelke², Sarfraj H. Mujawar¹ and Laxman D. Kadam³

¹Solid State Physics Laboratory, Yashwantrao Chavan Institute of Science Satara-415001, ²Department of Physics, Shivaji University Kolhapur-416004,

³Department of Physics, Arts, Commerce and Science College Ramanand Nagar, Sangli-416308.

*Corresponding author: kdlaxman 222@yahoo.co.in

Abstract

Ternary copper tin sulfide, Cu₂SnS₃ nanoparticles were synthesized by hydrothermal method. The structural, morphological and optical properties were studied by using X-ray diffraction, SEM, UV-visible, and FT-IR spectroscopy. The photocatalytic activity of CTS was investigated by for the degradation of methyl red under the visible light irradiation.

Mechano-chemical synthesis of Pure CsPbBr₃ and Na-doped Cesium Lead Bromide (CsPb_{1-x}Na_xBr₃, x=0.05, 0.1 and 0.15), and their Optoelectronic properties

T. Kayalvizhi¹, Ayyappan Sathya², and K.R.S. Preethi Meher^{*3}

¹Department of Materials Science, School of Technology, Central University of Tamil Nadu, Neelakudi Campus, Thiruvarur – 610005, ²Department of Physics, School of Electrical & Electronic Engineering, SASTRA Deemed to be University, Thirumalaisamudram, Thanjavur – 613401

*Email: preethimeher@cutn.ac.in

Abstract

In this paper, we have synthesized the CsPb_{1-x}Na_xBr₃ (x=0, 0.5, 0.1, and 0.15) by mechano-chemical synthesis method at room temperature. X-ray diffraction studies confirmed the orthorhombic phase formation for all the compositions synthesized. Diffuse reflectance spectra obtained for the powdered samples confirmed the absorbance wavelength of around 560 nm for CsPbBr₃ and a slight decrease in absorbance wavelength to 515 nm for 5 mol% Na doped sample. Photoluminescence spectra recorded for all the compositions exhibited strong luminescence around 530 nm which is close to that of absorbance wavelength. Direct observation of compositions illuminated under UV short wavelength radiation gave bright green emission. The Na-doped compositions thus developed in this work are being tested further for their stability to heat and moisture in comparison to the parent phase.

Study of Isotope Effect in Ti₂CrV-H/D System

Priyanka Ruz*, Asheesh Kumar, Seemita Banerjee, Dheeraj Jain, V. Sudarsan*

Chemistry Division, Bhabha Atomic Research Centre, Mumbai-400085 *Corresponding author: <u>pdas@barc.gov.in</u>, <u>vsudar@barc.gov.in</u>

Abstract

 Ti_2CrV alloy has been prepared using arc melting method. Room temperature deuterium uptake (D/M ~ 9) of this alloy is exceptionally higher compared to other Ti based alloys. The body centered cubic (BCC) phase of the alloy has undergone phase transformation to face centered cubic phase (FCC) upon deuterium absorption. Desorption peak temperature of the saturated deuteride of this alloy is 374 °C which is nearly same to its hydride desorption peak temperature (377 °C). Further DSC studies reveal normal isotope effect in this alloy system.

Realizing Half Metallic Gold Nanorods via Platinum Decoration: A First Principles Study

Sushil Kumar and R. K. Moudgil^{*}

Department of Physics, Kurukshetra University, Kurukshetra, India - 136 119

*Corresponding author: rkmoudgil@kuk.ac.in

Abstract

We have studied the effect of adding a Pt shell on the electronic structure of a freestanding Au nanorod, using first principles based quantum simulation approach. The nanorods are modeled to have a hexagonal cross-section and the simulations are performed using the density functional theory implemented in the SIESTA code. The formation of Pt shell around Au nanorod results in an increase in both the number of nearest neighbours of an Au atom and the lattice constant. Interestingly, we find that the Pt shelling introduces magnetism and half-metallic character in the otherwise non-magnetic and metallic Au nanorods. Tailoring of the electronic band structure in this way can facilitate the realization of future spintronic devices based on noble metals.

INTRODUCTION

Noble metals nanostructures have fascinated materials researchers due to their inert and highly metallic character. Besides the usual nanostructures (such as atomic clusters, chains, monolayers, etc.), it has been found that the core-shell nanostructures [1-2] show an improvement in physical properties of the core material. Here, one nanostructure (core) is surrounded by another nanostructure (shell). This has opened up an alternate window to fabricate new nanostructures with desired properties. Moreover, in this way a less noble core can be protected by a highly noble shell around it. Controlled chemical process has led to the synthesis of core-shell nanowires (NWs) of Cu, with Ag, Au and Pt shells [1], preventing the galvanic replacement of core. This has improved the performance of Cu@Ag (Cu core with Ag shell) NW on a level with the pristine Ag NWs, for making transparent and conducting films for organic light emitting diodes (OLEDs) and perovskite solar cells. Au@Pt core-shell NWs [2] are found to be a better electrocatalyst than Pt for ethanol based fuel cell applications.

Inspired from the above, we study here the electronic structure of a freestanding Au nanorod (NR) and its core-shell structure with Pt using the density functional theory (DFT). As an important result we find that the Au@Pt NR, unlike the Au NR, develops magnetism and half-metallic character.

MODEL AND SIMULATION DETAILS

We have cut out the unit cell of Au NR from the Au(111) surface, such that its cross section looks like a hexagonal. Accordingly, the [111] direction is the periodic direction for the Au NR. The core-shell structure Au@Pt is formed by attaching the Pt atoms

to the Au NR in a manner such that the hexagonal shape of the cross-section is retained. The cross-sectional and side views of both the structures are shown in Fig. 1.

We calculate the structure and electronic structure of these NRs using the DFT as implemented in the SIESTA [3] code- a pseudopotential and numerical atomic orbitals (NAOs) based O(N) method. We use the norm-conserving pseudopotential with the Troullier-Martins [4] parametrization. Efficient NAOs with double zeta polarization (DZP) are employed as the basis sets to solve the Kohn-Sham equations. Exchange and correlations are included using the generalized gradient approximation with PBEsol [5] flavor.



Fig. 1. Ball stick sketch of (a) cross-sectional, and (b) side views of optimized Au and Au@Pt NRs. Rectangular cut outs in (b) represent the unit cell for the two NRs.

For grid integration, a mesh cutoff of 450 Ry is selected by total energy convergence. For Brillouin zone integration, k-sampling of $1 \times 1 \times 30$ and $1 \times 1 \times 15$ for Au and Au@Pt NRs, respectively, is used. Structural optimization is carried out using the conjugate-gradient technique with a force tolerance of 0.01 eV/Å.

RESULTS AND DISCUSSION

The optimized structures of both Au and Au@Pt NRs are shown in Fig.1. The lattice constants for the relaxed structures are found to be 6.369 Å for Au and 6.783 Å for Au@Pt NRs. In this way, the shelling results in an increase of the width of the NR from 3.408 Å to 6.421 Å. It can be seen from Fig. 1(a) that the bond of Au5 with other Au atoms is broken in the Au@Pt. Now this Au5 atom is bonded by 6 Pt atoms which forms a hexagonal (see the highlighted atoms in Fig. 1(b)). Also, the other Au atoms which were earlier bonded to 3 Au atoms, are now bonded with 5 Pt and 2 Au atoms. Thus, the Pt shell results in a modification of the structure of Au NR, with an increase in the co-ordination number. Turning to the stability, the Au@Pt NR is found to be more stable with a binding energy of 4.427 eV/ atom as compared to 2.692 eV/atom that for the Au NR. As a result of



Fig. 2. The simulated electronic band structure and the density of states (DOS) of (a-b) Au, and (c-d) Au@Pt NRs. Here, the Fermi level is shifted at 0 eV.

modification in structure due to shelling, the electronic band structure of the Au NR undergoes a dramatic change. More precisely, the Pt shelling makes the Au NR magnetic and half-metallic, as can be noticed from the electronic band structure and density of states (DOS) for the considered NRs in Fig. 2. The predicted spin magnetic moment per atom for Au@Pt is 0.131 μ_B , where μ_B is Bohr magneton. In Au@Pt NR, the down-spin channel has a band gap of 88.8 meV at the Fermi energy E_F, while no gap for the up-spin channel. This makes the shelled NR a half-metallic material, as is clearly visible from the magnified DOS depicted in the inset of Fig. 2(d). Moreover, a gap present in the DOS of Au NR at around 0.5 eV disappears in Au@Pt (see Figs. 2(b) and 2(d)). Furthermore, we notice that the number of bands crossing the Fermi level E_F decreases from 2 to 1 in going from Au to Au@Pt. Thus, our study predicts a lower ballistic conductance in the Au@Pt NR as compared to Au NR.

CONCLUSIONS

In conclusion, we have calculated the electronic structure of the Au NR and its core-shell Au@Pt counterpart using first principles. We find that the formation of Pt shell on Au NR causes an increase in the lattice constant. This follows by breaking of some Au-Au bonds of the Au NR, and one gets a significantly transformed structure having completely different electronic properties in comparison to the original Au core. Notably, we observe a transition from a conducting non-magnetic structure to a half-metallic magnetic state. This may make the Au@Pt core-shell NR useful for applications in noble metals based spintronic devices.

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Spin-Drag Rate in a Quasi-One-Dimensional Electron Gas

Vishal Verma¹, Devi Puttar¹, Vinayak Garg^{1,*)} and R. K. Moudgil²

¹Department of Physics, Punjabi University, Patiala-147 002, India

²Department of Physics, Kurukshetra University, Kurukshetra-136 119, India

*Corresponding author: vinayak2000@gmail.com

Abstract

Abstract. In this paper, we calculate the spin-drag rate in a quasi-one-dimensional electron gas (Q1DEG) employing the randomphase approximation (RPA) over a wide range of temperature *T*, and some selected values of spin-polarization parameter ζ . We find that spin-drag rate is more for the unpolarized case (ζ =0), and it peaks around *T*~0.25*T*_{*F*↑} for all ζ -values. Further the spin-drag rate increases with decrease in the transverse width of Q1DEG, at fixed ζ and electron number density.

Finite-T Polaronic Effects on the Plasmon-Phonon Modes in a GaAs based Electron Quantum Wire

Devi Puttar¹, Vishal Verma¹, Vinayak Garg^{1,*} and R. K. Moudgil²

¹Department of Physics, Punjabi University, Patiala-147 002, India ²Department of Physics, Kurukshetra University, Kurukshetra-136 119, India

*Corresponding author: vinayak2000@gmail.com

Abstract

In this paper, we study the role of polaronic effects on the plasmon-phonon (pl-ph) coupled modes in an *n*-type *GaAs* based quantum wire structure. The effect of temperature *T* is explored on the *pl-ph* modes using the random-phase approximation (RPA) at fixed wire width and electron number density. We find that *pl-ph* excitation spectrum splits into two branches and each energy branch shows blue shift with rise in *T*. However, the lower branch of the modes get soften in energy as compared to the true plasmon modes of the wire at non-zero *T*.

Effect of Etching Time on Structural and Morphological Properties of MXene

Sahil Gasso, Manreet Kaur Sohal and Aman Mahajan*

Materials Science Laboratory, Department of Physics, Guru Nanak Dev University, Amritsar-143005, India

*Corresponding author: aman.phy@gndu.ac.in

Abstract

In the present work, two-dimensional MXenes were synthesized using chemical etching method with varying etching times, i.e., 24, 48, and 72 h. The samples were structurally and morphologically characterized using X-ray diffractometer and field emission scanning electron microscopy. It is observed that 24-h-etched MXene annealed at 150° C exhibited pure structural phase of MXene in comparison to longer etching times-based MXenes. The development of TiO₂ nanocrystals is attributed to TiO₂-coupled MXene formed at longer etching times (48 and 72 h).

Introduction

Recently, MXenes, a two-dimensional (2D) material with general formula $M_{n+1}X_nT_x$, where M is a transition metal, X is C or N, and T_x are surface functional groups, have made its way in various applications, such as electrochemical energy storage, water purification, gas sensors, and electrochromic devices.^{1, 2} MXene has attracted widespread attraction owing to its exceptional structural and electrical properties, like high electrical conductivity and bandgap tunability occurring due to modifiable surface functional groups.³ These properties have shown strong dependence on the band structure, elemental composition, and synthesis process involving etching conditions, pre-treatment, and post-treatment of MXenes.^{4, 5} Hence, effective tuning of all the abovementioned parameters is of pivotal importance for producing MXenes with desired properties concerning different applications.

Hitherto, the most widely explored synthesis method of $MXene(Ti_3C_2T_X)$ involves the etching of MAX phase (Ti_3AlC_2) using mild etching agents.⁶ By controlling the etching conditions, MXene characteristics can be modulated.

In this context, the present work focused on different etching times of MXene from MAX phase using mild etching agents, namely, LiF and HCl, and annealing at varying temperatures. The synthesized samples are further investigated for their morphological and structural properties.

Experimental Work

All the chemicals, namely titanium aluminum carbide (MAX-Ti₃AlC₂), hydrochloric acid (HCl), and lithium fluoride (LiF), were procured from Sigma-Aldrich and used without further purification.

Chemical etching method was used to synthesize $Ti_3C_2T_x$ MXene using mild acids. Typically, 1 g of LiF was added into 20 mL of 6-M HCl solution and magnetically stirred until the complete dissolution. Then, 0.5 g of 2-g MAX was added to the above solution with an interval of 30 min to avoid the violent reaction. The above solution was placed at 30°C and magnetically stirred continuously for 24, 48, and 72 h. Samples obtained at different etching times, i.e., 24, 48, and 72 h are labeled as 24M, 48M, and 72M. The etched material were washed with deionized water and centrifuged at 6000 rpm for 10 min for 5–6 times. The resultant MXenes were dried overnight and subsequently annealed at 150°C.

Structural and morphological investigations of the etched MXenes were performed using X-ray powder diffraction (XRD) employing Rigaku diffractometer with Cu K_{a1} radiation ($\lambda = 1.54056$ Å) in the range 7°-70° and field emission scanning electron microscope (FESEM; Supra-55).

Results and Discussion

The phase and purity composition of the prepared 24M, 48M, and 72M samples were revealed from their XRD patterns (Fig. 1). All three samples exhibited major diffraction peaks at 9.1°, 18.3°, 27.5°, and 60.7° corresponding to the (002), (004), (006), and (110) lattice planes of MXene. Moreover, the Al peak, which appears at 39° in MAX sample, did not appear in all the etched MXene samples, indicating successful formation of MXene. The peak belonging to (002) plane in MAX phase shifted to low Bragg's angle and broadened after etching, resulting in large d spacing. Alongside, TiC diffraction peaks at 36.2°, 41.7°, 72.6°, and 74.1° assigned to (103), (105), (311), and (118) diffraction planes were present in both MAX and MXene samples (Fig. 1). Further, with increasing etching times, the intensity of (002), (004), and (006) planes of MXene decreased. Notably, the diffraction pattern of 72M sample exhibited a minor peak corresponding to TiO₂.



Fig. 1. Diffraction patterns of MAX and MXenes (24M, 48M, and 72M).

FESEM images of parent MAX and MXenes with different etching times, i.e., 24 h, 48 h, and 72 h, annealed at 150°C are shown in Fig. 2. It has been observed that the successful etching of MAX results in stacked and exfoliated morphology of delaminated MXene sheets ($Ti_3C_2T_x$) due to the removal of Al from MAX (Ti_3AlC_2) phase. The average width between the consecutive delaminated sheets in all the MXene samples are found to be in the range 40–50 nm.

Interestingly, small blisters were discovered on the surface and edges of delaminated MXene sheets that could be due to the bubble liberation caused by H₂ gas emission during the etching process. When annealed at 150°C, the amount of growth of these blisters increased with increasing etching duration (24M < 48M < 72M). These blisters may be formed by oxides bonding with Ti atoms to generate TiO₂. These TiO₂ formations obliterate the purity of the MXene phase and result in sheets containing TiO₂ nanocrystals; thus, limiting MXene use in various applications.⁷

Conclusion

In conclusion, MXene was successfully synthesized using moderate etchants with different etching times (24M, 48M, and 72M). Using structural and morphological studies, the effect of varying etching times on MXene properties were investigated, and it has been observed that with etching time above 24 h results in the formation of TiO₂ nanocrystals in

MXene. Thus, increasing etching time is not favorable, since it reduces the purity of the MXene phase; hence, limiting their applications in various fields, such as gas sensors and electrochemical energy storage devices.



Fig. 2. FESEM images of (a) MAX, (b) 24M, (c) 48M, and (d) 72M samples.

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Effect of interaction strength on magnetic properties of transition metal doped hexagonal Aluminum Nitride monolayer

Parvathy Harikumar¹, Sharat Chandra¹

¹Materials Physics Division, Materials Science group, Indira Gandhi Centre for Atomic Research, Kalpakkam, India

*Corresponding author: parvathy@igcar.gov.in

Abstract

The electronic and magnetic properties of transition metal viz. Mn and Cr doped hexagonal monolayer of Aluminum Nitride is studied using the Green's function based single impurity Anderson model extended to semiconductors by F.D.M. Haldane. The effect of interaction strength was found to be profound in the case of Cr doped AlN and was seen to exhibit good half metallic properties suitable for spintronic applications. Cr was also found to induce a small moment on the neighboring N atoms.

Anomalous phonons in vertically and horizontally aligned MoS₂

Deepu Kumar^{1*}, Rahul Kumar², Mahesh Kumar² and Pradeep Kumar¹

¹School of Basic Sciences, Indian Institute of Technology Mandi, 175005, India ²Department of Electrical Engineering, Indian Institute of Technology Jodhpur, 342037, India

*Corresponding author: <u>deepu7727@gmail.com</u>

Abstract

Recently, vertically aligned (VA) MoS_2 has gained popularity due to a potential candidate in gas sensor device applications to detect hazardous and toxic gases such as NO_2 as compared to the horizontally aligned (HA) MoS_2 . Here, we performed a comparative temperature-dependent Raman study on VA and HA MoS_2 . We observed an anomalous softening, below ~ 50 K, in both systems attributed to the induced strain due to the thermal expansion coefficient mismatch between substrate and MoS_2 in a low-temperature regime. Above 50 K, the softening of mode with an increase in temperature is understood by considering the three-and four-phonon anharmonic model. Intensities of the modes as a function of temperature are observed to be strongly dependent on the Bose-Einstein thermal factor.

Electric Relaxation Effect Along with Electric Modulus Analysis in Various Reduced Graphene Oxide–Poly (vinyl alcohol) Nanocomposite

A.K. Bhunia^{1*}, T.N. Ghosh², S.S. Pradhan³

¹Department of Physics, Government General Degree College at Gopiballavpur-II, Jhargram 721517, West Bengal, India

² Department of Electronics, Midnapore College (Autonomous), Midnapore 721101, West Bengal, India ³ Department of Physics, Midnapore College (Autonomous), Midnapore 721101, West Bengal, India

*Corresponding author: amitphysics87@gmail.com

Abstract

In this report, we mainly focused the analysis of electric modulus of the four reduced graphene oxide (rGO)–Poly (vinyl alcohol) (PVA) nanocomposite to study the relaxation time (τ_0) and activation energy (E_A). Maximum peak of the frequency dependence imaginary component of the electric modulus has been changed with the change in temperature (30 to120 °C) and rGO contents (wt 5% , 8%,10%. and 12%) in the nanocomposites. The observation showed that E_A increases whereas τ_0 decreases with the increase of the rGO content from 5 wt% to 12 wt% within the nanocomposites. The E_A value increases form 0.125 eV to 0.251eV with the increase of the rGO content. The characteristic relaxation time in the nanocomposites varies from a minimum 5.25*10⁻⁸ sec to a maximum 3.25*10⁻⁷ sec.

Introduction

Graphene is a two-dimensional atomic crystal with a honeycomb structure of sp²-bonded carbon atoms that exhibits outstanding electrical, thermal, and mechanical capabilities [1]. Two important graphenebased compounds are graphene oxide (GO) and reduced graphene oxide (rGO). Electrically, rGO is a conductor with a significantly better responsible candidate than GO [2]. PVA (poly (vinyl alcohol)) is a semi-translucent, non-conducting polymer with a high dielectric strength [3]. By adding a small amount of dopant, such as nanoparticles or carbon-based 2D materials, it can quickly increase its optical, electrical, and relaxation properties. Conductive fillers, such as rGO, have been used with different polymers for a variety of purposes [2,4,6]. In this work, we report about the electric modulus analysis of the four reduced graphene oxide (rGO)–Poly (vinyl alcohol) (PVA) nanocomposite with rGO weight percent 5.8,10,12% and the relaxation mechanism from the concept of relaxation time and activation energy.

Experimental

Reduced graphene oxide (rGO) was fabricated with the help of modified Hummer and Offeman method

[5]. The rGO-PVA composites were prepared by chemical solution casting method as reported in our previous article [4, 6]. Briefly, PVA was dissolved in 90° C heated water. Then the solution was cooled into room temperature. Under constant magnetic stirring,

required amount of GO solution was mixed PVA solution at room temperature. After 1.5 h, required amount of pure hydrazine monohydrate was added with the mixed solution. The reaction was kept overnight under constant stirring. After complete reaction, the mixture solution was kept in a petri dish for the formation of thin film shape rGO-PVA nanocomposites. With the adjustment of the amount of GO, PVA and hydrazine monohydrate, separate nanocomposites rGO concentration 5 wt%, 8 wt%, 10 wt%, 12 wt% were fabricated for different characterization [6]. The electric modulus of the thin films was investigated with the help of LCR meter (HIOKI 3536 LCR METER), frequency range 1 Hz–1 MHz, and temperature range 30 to 120^oC.

Results and discussion

The real (M') and imaginary part (M") of the modulus can be expressed by the following relations [4]:

$$M'(\omega) = \frac{\varepsilon'(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2} , M''(\omega) = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)^2 + \varepsilon''(\omega)^2}$$

The variation of M" with frequency from 1Hz to 1MHz under different temperatures varies from 30°C to 120°C for the different rGO-PVA nanocompites are shown in Fig.1. The peak value gradually shifted toward higher frequency with the increment of the temperature in all of the nanocomposites. The peak values arise at different frequencies at a particular temperature for different wt% rGO content PVA nanocomposites. PVA-rGO with rGO content 5 wt% sample shows peak values from the frequency (f_{max}) range 7933.5Hz to 23359Hz with the temperature changes from 30 to 120°C. PVA-rGO with rGO content 8, 10, and 12 wt% shows peak values from the frequency range 6586.5Hz to 19152Hz, 4830.5 to 12900Hz,and 9555.5 to 42162.7 Hz, respectively with the same temperature range (30°C to 120°C). Thus, peak shifting depends on temperature as well as rGO contents. This temperature and rGO content dependent peak shift arise may be due to variation of carrier relaxation and charge transport process.



Fig. 1. Frequency dependence of the imaginary component of the electric modulus at temperatures from 30 to120 °C for (a) PVA-rGO wt 5%, (b) PVA-rGO wt 8%, (c) PVA-rGO wt 10%, (d) PVA-rGO wt 12%

The carrier relaxation life time (τ_M) is related with the angular frequency ω_{max} by the relation:

 $\omega_{\text{max}}\tau_{\text{M}}=1 \text{ or } \tau_{\text{M}}=1/(2\pi f_{\text{max}}).$

The τ_M value for PVA-rGO with rGO 5 wt% varies from 2*10⁻⁵ to 6.81*10⁻⁶ sec with the temperature changes from 30 to 120^oC. The same value for PVArGO with rGO content 8, 10, and 12 wt% varies from 2.45*10⁻⁵ to 8.32*10⁻⁶ sec, 3.29*10⁻⁵ to 1.25*10⁻⁵ sec, 1.66*10⁻⁵ to 5.72*10⁻⁶sec, respectively with the said temperature range. The temperature (T) dependent relaxation process can be expressed by the following Arrhenius law [7]:

 $\tau_{\rm M} = \tau_0 \exp \left(E_{\rm A} / kT \right)$

where E_A = activation energy, τ_0 = pre-exponential factor/characteristic life time. The variation of $ln(\tau_M)$ with 1/T and its corresponding straight-line fittings are shown in Fig. 2. The straight line gives E_A and τ_0 . Their values are tabulated if Table-1. The activation energy gradually increases from 0.125eV to 0.251eV whereas characteristic life time decreases from 3.25* 10^{-7} sec to 5.25 * 10^{-8} sec with the increment of rGO content from 5 wt% to 12 wt% within the rGO-PVA nanocomposites.



Fig. 2. Plot of $\ln (\tau_M) vs. 1/T$ for (a) PVA-rGO wt 5%, (b) PVA-rGO wt 8%, (c) PVA-rGO wt 10%, (d) PVA-rGO wt 12% nanocomposite .

Fable 1. Activation energy a	nd Relaxation Life time
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Sample	Activation	Characteristic	
	energy (E _A)	life time (τ ₀)	
PVA-rGO	0.125eV	3.25*10 ⁻⁷ sec	
wt 5%			
PVA-rGO	0.136 eV	2.85*10 ⁻⁷ sec	
wt 8%			
PVA-rGO	0.175 eV	1.5*10 ⁻⁷ sec	
wt 10%			
PVA-rGO	0.251 eV	5.25*10 ⁻⁸ sec	
wt 12%			

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Effect of M and S₂ Vacancies at Different Sites on MS₂MLs (M = Mo, W): An *Ab initio* Study

Arun Kumar^{1*}, Anjna Devi¹², Rekha Devi¹, Kritika Thakur¹, Neha¹, Alisha Guleria¹, Rajendra Adhikari³, Hansa Devi¹,

¹Department of Physics, Swami Vivekanand Government College Ghumarwin, District Bilaspur, Himachal Pradesh, India, 174021

²Department of Physics, Himachal Pradesh University Shimla, Himachal Pradesh, India, 171005 ³Department of Physics, Kathmandu University, Dhulikhel, Nepal, 45200

*Corresponding author: arun242493@yahoo.com

Abstract

The effect of vacancies (M (= Mo, W) and S_2) on structural and electronic properties of MS₂MLs (at different vacancy concentrations) have been studied. With the decrease in percentage of vacancy concentrations the magnitude of binding energy increases. These vacancies help to tune the electronic band structure by creating additional acceptor and donor levels near Fermi and hence suggest their applications in electronics.

Introduction

Various studies on the vacancies in the transition metal dichalcogenide monolayers (TMDMLs) revealed that their electronic band structures can be tuned significantly. These materials show potential applications in the field of electronics, optoelectronics and spintronics [1-3]. Till now TMDMLs (MX₂MLs, M = Mo, W, Cr and X = S, Se) with either M or X and X₂ vacancies have been studies and observed that vacancy of M-atom leads to formation of acceptor energy level, whereas X or X₂ vacancies leads to the formation of donor energy level in the electronic band structure [4-5].

In the present paper we have created both M (= Mo, W) and S₂ vacancies at different sites in the corresponding pristine monolayers (with different concentrations of vacancies (3.125% and 2.083%)) and observed their effect on electronic band structure.

Computational Detail

All the calculations have been performed using SIESTA (Spanish Initiative for Electronic Simulation with Thousands of atoms) code [6]. We have used PBE functional [7] (GGA functional) and double zeta polarization (DZP) basis set with confinement energy of 20meV. All the structures have been relaxed using conjugate gradient (CG) method with force tolerance 0.01 eV/Å. Brillouin zone integration was performed by taking 7x7x1 k-point mesh. About 15 Å vacuum used along z-axis to separate two dimensional single layers of MS₂.

Result and Discussion

In fig. 1 we have shown MS_2MLs with M and S_2 vacancies with 3.125% (figure 1(a)) and 2.083% (figure 1(b)) concentrations of vacancies. MS_2ML(93) and MS_2ML(141) represent the MS_2MLs with 93 and 141 atoms per supercell respectively with M and S₂ vacancies. The percentage of vacancies calculated using formula

$$vacancy \% = \frac{N - (N - 3)}{N} \times 100$$
(1)

here N (96 and 144) represents no of atoms in the supercell without vacancy and N-3 (93 and 141) represents the no of atoms in the supercell with M and S_2 vacancies.



Fig. 1. Structures of MS_2MLs with M (M=Mo, W) and S_2 vacancies at different concentration of vacancies (a) 3.125% and (b) 2.083%. 93 and 141 represents the total number of atoms taken for simulation in the supercell.

In table 1 we have listed the average M-S bond (b_{M-S}) length in the pristine MS₂MLs without vacancies and average M-S bond lengths in the vicinity of vacancies ($b_{M-S(M)}$ and ($b_{M-S(S2)}$)). All the M-S bond lengths in the vicinity of vacancies are found to be smaller than the corresponding M-S bond length of pristine monolayers. This decrease in bond length is due to decrease in coordination number in the vicinity of vacancies [8].

We have also calculated the binding energy (in table 1 magnitude of binding energy listed) of the studied systems using formula

(2)

$$E_b = \frac{E_{total} - (nE_M + mE_S)}{n + m}$$

where E_{total} is the total energy of the studied system and E_M (M=Mo, W) and E_S represents the energy of the isolated atoms constituting the system and n and m are number of M and S atoms of the respective studied system. The binding energy is less for the systems having vacancies than the pristine monolayers. Also with the decrease in the percentage of vacancies, the binding energy increases (clear from table 1).

Table 1. Structural and electronic parameters of all the studied MS_2MLs , including average M-S bond length (b_{M-S}), average M-S bond length near M vacancy ($b_{M-S}(M)$), average M-S bond length near S₂ vacancy ($b_{M-S}(s_2)$), magnitude of binding energy (E_b) and energy band gap (E_a).

System	b _{M-S}	b _M .	b _M .	E _b	$\mathbf{E}_{\mathbf{g}}$
	(Å)	S(M)	S(S2)	(eV/atom)	(eV)
		(A)	(A)		
MoS ₂ ML	2.437 ^[9]			4.886	1.626 ^[9]
WS_2ML	2.447 ^[9]			5.447	1.83[9]
MoS ₂ ML(93)	2.437	2.399	2.422	4.758	0.16
MoS ₂ ML(141)	2.437	2.406	2.424	4.792	0.35
WS2ML(93)	2.447	2.407	2.434	5.367	0.37
WS2ML(141)	2.447	2.409	2.439	5.401	0.38

The electronic band structure and corresponding density of states (DOS) of the studied systems shown in figure 2. From electronic band structures it is clear



Fig. 2. Electronic band structure and density of states (DOS) of MS2MLs with vacancies. Dotted red horizontal line indicate the Fermi energy level (E_F). Bold magenta coloured horizontal lines above and below the Fermi level represents the conduction band minimum (CBM) and valence band maximum (VBM) corresponding to pristine monolayers without vacancies. In DOS blue and red coloured plots represent the contribution for DOS due to first nearest neighbors (FNNs) of M and S₂ vacancies respectively.

that with the creation of M and S_2 vacancies, the valence band maximum (VBM) and conduction band

minimum (CBM) shifts upwards in comparison to corresponding pristine monolayers (VBM and CBM corresponding to pristine monolayers are represented by magenta coloured bold horizontal lines). Also some additional bands are created near the Fermi level. Both Mo and W vacancies create bands below Fermi level. known as acceptor level and S2 vacancies create additional bands above the Fermi level known as donor level. This is clear from the DOS plots for the atoms near the vacancies (blue coloured DOS for FNN atoms near M vacancy and red coloured DOS for FNN atoms near S_2 vacancy). This leads to decrease in the energy band gap as listed in table 1. Also with decrease in the vacancy concentration electronic energy band gap increases, but smaller that the corresponding pristine monolayers.

Conclusion

The M-S bond lengths near the vacancies decreases due to decrease in coordination number. Also with the decrease in percentage of vacancies the magnitude of biding energy increases, but smaller that the corresponding pristine monolayers. These vacancies create additional acceptor and donor levels near Fermi level in the electronic band structure and hence decreases the energy band gap. This suggest their applications in electronics.

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Layer dependent anomalous Raman scattering in T_d-WTe₂

Arnab Bera¹, Satyabrata Bera,¹ Sk Kalimuddin,¹ Mainak Palit¹, Raktim Datta,² Biswajit Das,¹ Mohan Kundu,³ Subodh Kumar De,² Mintu Mondal^{1*}

¹School of Physical Sciences, Indian Association for the Cultivation of Science, <u>Kolkata</u>-700032, India ²School of Material Sciences, Indian Association for the Cultivation of Sciences, <u>Kolkata</u>-700032, India ³Department of Physics, Acharya Prafulla Chandra College, New Barrackpore, Kolkata, 700131, India

*Corresponding author: Mintu.Mondal@iacs.res.in

Abstract

Tungsten ditelluride (WTe₂) is a Weyl semimetal belonging to the class of layered transition metal di-chalcogenides (TMD). It shows exotic properties like high magnetoresistance, large thermo-emf, anomalous Hall effect *etc*. The electronic properties are strongly related to its crystal structure and change drastically on the reduction of thickness of the crystal from bulk to a few layers. Through systematic layer-dependent Raman spectroscopy studies, we show how the point group symmetry of the crystal changes from bulk (C_{2v}) to monolayer (C_{2h}). Redshift and evolution of few characteristic Raman modes (for example, A_1^3 mode, centered at ~115.7 cm⁻¹) are analyzed to investigate the anomalous behavior.

Asymmetric Negative Differential Resistance Behavior in Ag/TiO₂/FTO based Resistive Switching Memory Device

Nabamita Chakraborty¹, Ankita Chandra², Biswajit Das¹, Abhijit Mallik³, and Kalyan K. Chattopadhyay^{*1,2}

¹Thin Film and Nano Science Laboratory, Department of Physics, Jadavpur University, Kolkata 700 032, India, ²School of Material Science & Nanotechnology, Jadavpur University, Kolkata 700 032, India ³Department of Electronic Science, University of Calcutta, Kolkata 700 071, India

*Corresponding author: kalyan_chattopadhyay@yahoo.com

Abstract

In this work, we performed an investigation on the memristive effects on TiO_2 nanorod arrays (TNAs) based RRAM devices, grown on FTO coated glass substrate via hydrothermal technique. According to our experimental results, the device exhibited a hysteretic current-voltage behavior which shows the memory effect along with the negative differential resistance (NDR) state in both the positive and the negative biases.

Energy-loss in Graphene superlattice

Kavita N. Mishra

Physics department, Faculty of Science, The M S University of Baroda, Sayajigunj-390002, Vadodara, Gujarat,

India.

Email:kavita.physics@hotmail.com

Abstract

An interest has been sparked off in graphene based multilayer (GBM) and graphene based superlattice (GBS) structures because of their potential applications in technology. This paper consists of theoretical investigation about energy-loss of GBS within Random Phase Approximation (RPA). The energy-loss is dependent on the charge density and separation between layers of GBS. As the charge density is increased the intensity of energy-loss is increased. With increase in distance between the layers the zero energy-loss regions is less compared to more compact GBS. Thus GBS can be considered as better device making material with lesser energy-loss than SLG. This low energy-loss in GBS can have better technological applications as energy storage devices.

Introduction

Superlattice are novel class of materials composed of alternating layers of two or more different constituents. A multi-quantum well structure is called superlattice structure if number of layers are very large (theoretically infinite). Superlattice structures can be experimentally realized with the help of molecular beam epitaxy (MBE), sputtering techniques etc [1]. Our model superlattice consists of repeated layer of single layer graphene (SLG) lying on SiO₂ substrate. Unique properties of graphene, inspired to think that graphene based superlattice (GBS) structures stand a better chance of application in various industries. The interlayer interactions are strong enough to make it a better component that can be utilized in developing efficient electronic devices[2].

When an external particle travels above a system it interacts with the system and loses some amount of energy to the system. This energy may or may not create plasma oscillations. The portion where plasmons are not created is known as single particle excitation regime and the portions where plasmons are created is known as collective excitation regime. These excitations are damped and decay into electron-hole pairs via loss function.

Energy-loss suffered by the moving charged particle above a system has gained importance in past years. This physical phenomenon is of great utility to characterize the probing instrument as well as the given system. The amount of energy-loss can be measured experimentally through electron energy loss spectroscopy (EELS). In this process a beam of electron is incident on the surface of the substance. The electrons undergo inelastic scattering and lose some amount of energy and deflect their original path. The EELS helps in probing the surface properties of the substance. The contribution of Plasmons in energy-loss in graphene have been studied experimentally by scanning tunneling microscopy (STEM) EELS [3]. This paper focuses on theoretical calculations of energy-loss of GBS within random phase approximation (RPA) using dynamic dielectric function.

Methodology

 $\varepsilon(q,\omega)$ is the dynamic dielectric function defined within RPA, as [4] $\varepsilon(q,\omega)=1-V(q)\Pi(q,\omega)$ (1) with real and imaginary parts ε_1 and ε_2 V(q) is coulomb potential, which is given by $V(q) = \frac{2\pi e^2}{q\varepsilon_0} S(q,q_z)$

 ε_0 =2.5 for SLG, where structure factor, $S(q,q_z)$ that depends on q and q_z , components of the wave vector parallel and perpendicular to the layers, is defined as [5],

$$S(q,q_z) = \frac{Sinh(qd)}{Cosh(qd) - Cos(q_zd)}$$
(2)

For computing our results, both, full expressions as well as long wavelength limit expressions of polarization function has been used. The long wavelength limit of $\Pi(q, \omega)$ is given as [4]

$$\Pi(q,\omega) = \begin{cases} \frac{D_0 \gamma^2 q^2}{2\omega^2} \left[1 - \frac{\omega^2}{4E_f^2} \right] & \text{for } \gamma q < \omega < 2E_f \quad (3) \\ D_0 + i \frac{\omega}{\gamma q} & \text{when } 0 < \omega < \gamma q \end{cases}$$

where, $D_0 = 2k_F/\pi\gamma$ with $k_F = \sqrt{\pi n}$ is the Fermi wave vector. γ is band parameter and E_f is the Fermi energy. The energy-loss function for a system is determined by imaginary part of dynamic dielectric function, given as [6]

$$\operatorname{Im}\left(\frac{1}{\varepsilon}\right) = \frac{\varepsilon_{2}(\vec{q},\omega)}{\varepsilon_{1}^{2}(\vec{q},\omega) + \varepsilon_{2}^{2}(\vec{q},\omega)} \tag{4}$$

Results and Discussion

The energy-loss function is obtained for long wavelength limit of polarization in graphene given as eq. 3 in low frequency regime The results have been obtained for two values of *d* i.e. d = 400 Å and 800 Å and two values of charge density $n = 10^{12} cm^{-2}$ and $10^{14} cm^{-2} \cdot S(q,q_z)$ can be expressed as

$$S(q,q_{z}) = \frac{qd}{1 + \frac{(qd)^{2}}{2} - Cos(q_{z}d)}$$
(5)

Since, $-1 < Cos(q_d) < 1$, lower and upper boundaries correspond to $Cos(q_d) = \mp 1$. The intensity plots have been plotted for the loss functions with the vertical bars on the right side of each figure indicates the intensity of energy-loss with white color depicting the maximum loss while the black color is the zero loss function region. For particular values of q the loss intensity is maximum in (ω, q) space. As the value of *n* is increased the intensity of energy-loss is increased depicted in Fig 1 and 2. With increase in distance d between the layers (i.e. almost SLG behavior) the zero energy-loss region is less compared to more compact GBS as seen in Fig 2 and 3. Thus GBS can be considered as better device making material with lesser energy-loss than SLG. This low energy-loss in GBS can have better technological applications as energy storage devices.



Fig. 1. Density Plots of energy-loss function of GBS plotted for $n=10^{12}$ cm⁻² and d=400Å for lower (Cos (q_z d) = -1) and upper boundaries (Cos(q_z d)=1).



Fig. 2. Density Plots of energy-loss function of GBS plotted for $n=10^{14}$ cm⁻² and d=400Å for lower (Cos(q_zd)= -1) and upper boundaries (Cos(q_zd)=1).



Fig. 3. Density Plots of energy-loss function of GBS plotted for $n=10^{14}$ cm⁻² and d=800 Å for lower (Cos(q_zd)= -1) and upper boundaries (Cos(q_zd)=1).

Conclusion

This paper explains energy-loss in graphene based superlattice (GBS), using RPA. The energy-loss is dependent on the charge density and separation between layers of GBS. As the charge density is increased the intensity of energy-loss is increased. With increase in distance between the layers (i.e. almost single layer graphene (SLG) behavior) the zero energy-loss regions is less compared to more compact GBS. Thus GBS can be considered as better device making material with lesser energy-loss than SLG. This low energy-loss in GBS can have better technological applications as energy storage devices.

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Characterizations of a Few Layered MoS₂ Phototransistor Using a Homebuilt Cost Effective Measurement Setup

Shubhrasish Mukherjee^{*1}, Atindra Nath Pal¹ and Samit Kumar Ray²

¹S. N. Bose National Centre for Basic Sciences, Sector III, Block JD, Salt Lake, Kolkata – 700106 ²Indian Institute of Technology Kharagpur, 721302, West Bengal, India *Corresponding author: shubhraphysicsbu@gmail.com Abstract

Having an atomically thin profile, semiconducting transition metal dichalcognides (TMDC) promising 2D materials for electronic and optoelectronic device applications. In this work, a phototransistor based on the mechanically exfoliated few layered MoS_2 nanosheet is fabricated, and its light-induced electric properties are investigated using a low cost homemade setup. This device shows excellent switching behavior (10⁴) and higher photoresponsivity ($4.51 \times 10^6 \text{ A/W}$) at a low bias (V_{ds} =1V), making it promising for technological applications.

Amplification Of Phonons In Undoped Bilayer Graphene In The Presence Of External Temperature Gradient

Subhana Nafees, SSZ Ashraf

Physics Department, Aligarh Muslim University, Aligarh-202002, Uttar Pradesh, India

Email id: subhananafees@gmail.com

Abstract

We present a theoretical investigation on the amplification of acoustic phonons interacting with electrons confined in Bilayer graphene (BLG) due to external temperature gradient (∇T) by using Boltzmann transport equation approach. From our research work, we investigated that for T=77k, the calculated value for ∇T is found to be 3.2063×10^{-23} K/m whereas for Single layer graphene (SLG) it comes out to be 30.478K/cm as reported in Ref[2].

Introduction

Motivation of this work lies in the property of Bilayer graphene to use it in amplification and generation of high frequency acoustic phonon. Amplification of phonons occurs when $v_D > v_s$ (v_D being the drift velocity of electrons and v_s is the speed of sound).

Formalism and Analytical Result

Due to electron phonon interaction transition rate induced in the system is given by Fermi's golden rule

i.e.,
$$W^{\pm}(k, k') = \frac{2\pi}{\mathfrak{h}} \begin{bmatrix} N_q \\ N_{q+1} \end{bmatrix} |M_q|^2 \delta_{k-q,k'} \delta(\varepsilon_{k'} - \varepsilon_k \pm \mathfrak{h}\omega_q)$$

The acoustic wave collides with charge carriers and the kinetic equation for the acoustic phonon population N_q in the medium is governed by the following Equation[1] $\partial Nq/\partial t = 1/\tau_q N_q$ (1) Where τ_q the electron-acoustic phonon relaxation time is related to Γ_q that is the phonon growth rate or the amplification/attenuation coefficient as $\tau_q = (v_s \Gamma_q)^{-1}$. The kinetic equation for the acoustic phonon population $N_q(t)$ in the graphene sheet is given by

$$\frac{\partial N_q(t)}{\partial t} = \frac{2\pi}{\mathfrak{h}} g_s g_{\mathfrak{v}} \sum_{k,k'} |C_q|^2 \delta_{k,k'} \{ [N_q(t) + 1] f_k (1 - f_{k'}) \times \delta(\varepsilon_{k'} - \varepsilon_k + \mathfrak{h}\omega_q) - N_q(t) f_{k'} (1 - f_k) \times \delta(\varepsilon_{k'} - \varepsilon_k + \mathfrak{h}\omega_q) \}$$
(2)

Where $g_s = 2$, $g_v = 2$ account for the spin and valley degeneracies, respectively. For acoustic phonons, the

matrix element (from Ref.2)is given as $|C_q|^2 = \Lambda^2 \hbar q / 2AV_s \rho$, where Λ is the deformation potential, *e* is the electronic charge, ρ is the density of graphene sheet, V_s is the velocity of sound. In equation (1), the summation over k and k' can be transformed into integrals by $\sum_{k,k'} \rightarrow A^2 / (2\pi)^4 \int d^2k d^2k'$ where A is the area of the sample.

$$\begin{split} & \Gamma_{q} \\ &= \frac{A^{2} \left| M_{q} \right|^{2}}{\mathfrak{h}(2\pi)^{3} \mathfrak{h} v_{F}} \int_{0}^{\infty} k dk \int_{0}^{\infty} k' dk' \int_{0}^{2\pi} d\varphi \int_{0}^{2\pi} d\theta \left\{ \left[f_{k} - f_{k'} \right] \right. \\ &\times \delta \left(k - k' \right. \\ &\left. - \frac{1}{\mathfrak{h} V_{F}} \left(\mathfrak{h} \omega_{q} \right) \right) \right\} \end{split}$$
(3)

The linear approximation of the distribution function f(k) is given as $f(k)=f_0(\varepsilon(k)) + f_1(\varepsilon(k))$ (4) $f_1(k)$ is derived from the Boltzmann transport equation $f_1(k) = \tau \left[(\varepsilon(k) - \mu) \frac{\nabla T}{T} \right] \frac{\partial f_0}{\partial \varepsilon} v(k)$ (5)

 $v(k) = \partial \varepsilon(k)/\hbar \partial k$ is the electron velocity, μ is the chemical potential, τ is the relaxation time and ∇T is the temperature gradient. The unperturbed electron distribution function is given by the shifted Fermi-Dirac function i.e

$$f_0(\varepsilon(k)) = \{ exp[\beta(\varepsilon_\lambda(k) - \beta\varepsilon_F)] + 1 \}^{-1}$$
(6)

(K_B is the Boltzmann constant, T is the absolute temperature, ε_F is the Fermi energy and for BLG

 $\varepsilon_{\lambda}(k) = \frac{\hbar^2 k^2}{2m}$ (with Fermi velocity V_F = 10⁸m/sec with low energy excitation, electron chirality λ =1. At low temperatures (K_BT<<1), ε_F = μ , the Fermi- Dirac equilibrium distribution function become $f_0(\varepsilon(k)) = exp[\beta(\varepsilon(k) - \mu)]$ (7)

Inserting Equations (5) and (7) into (4) and putting $\mu=0$ for intrinsic graphene and using it in (3), we get



where
$$\Gamma_0 = -A m^2 q \Lambda^2 \sqrt{\beta} / 4\pi v_s \beta^{3/2} \rho \hbar^4$$

For an open circuit ($\Gamma_0=0$), the threshold temperature gradient ∇T^0 which gives the lower limit for amplification by external temperature gradient yield the following result

$$\nabla T^{0} = T \left(\frac{-4\left(-1+e^{\beta\omega}q^{h}\right)}{\sqrt{2}r \left(\frac{-2e^{\beta\omega}q^{h}\sqrt{\beta}\sqrt{-\omega}q^{h}\left(-3+2\beta\omega_{q}h\right)+}{3\sqrt{\pi}\left(\frac{-1}{\omega q^{h}}\sqrt{-\omega}q^{h}\right)+3\sqrt{\pi}\sqrt{\frac{-1}{\omega q^{h}}\sqrt{-\omega}q^{h}Erf\left[\sqrt{\beta}\omega_{q}\sqrt{\frac{-1}{\omega q^{h}}h}\right]} \right) \right)$$
(9)

The threshold temperature gradient ∇T^0 relate the thermal voltage $V_T = K_B T/e$ as

$$V_T = k_B \frac{\frac{-2e^{\beta \omega_q \hbar} \sqrt{\beta} \sqrt{-\omega_q \hbar}(-3+2\beta \omega_q \hbar) +}{3\sqrt{\pi} \left(-1+\sqrt{\frac{-1}{\omega_q \hbar}}\sqrt{-\omega_q \hbar}\right) + 3\sqrt{\pi} \sqrt{\frac{-1}{\omega_q \hbar}}\sqrt{-\omega_q \hbar} Erf\left[\sqrt{\beta} \omega_q \sqrt{\frac{-1}{\omega_q \hbar}}\right]}{-4(-1+e^{\beta \omega_q \hbar})e}$$
(10)

 $(\nabla V)_T = -S(\nabla T^0)$ (11) here the Seebeck coefficient (S) is given as S =

$$k_{B} \frac{\sqrt{2}\tau \left(\frac{-2e^{\beta\omega_{q}h}\sqrt{\beta}\sqrt{-\omega_{q}h}(-3+2\beta\omega_{q}h)+}{3\sqrt{\pi}\left(-1+\sqrt{\frac{-1}{\omega_{q}h}\sqrt{-\omega_{q}h}}\right)+3\sqrt{\pi}\sqrt{\frac{-1}{\omega_{q}h}\sqrt{-\omega_{q}h}}Erf\left[\sqrt{\beta}\omega_{q}\sqrt{\frac{-1}{\omega_{q}h}\hbar}\right]\right)}{-4\left(-1+e^{\beta\omega_{q}h}\right)e}$$

(12)

Numerical Analysis and Discussion

For the estimation of numerical values we use the same set of parameters as reported in Ref.[2].Using these values we plot in Fig. 1a the Eq. (7) the plot start rising with increasing values of ω_q For $\nabla T = 0$ K/m, there is only attenuation/absorption($\Gamma/\Gamma_0 > 0$). In reference [2] Subhana et.al. have reported for SLG amplification coefficient is found to be dependent on temperature as T³ but for BLG it is found to be depend on T power law from Eq.11. Thermal voltage V_T comes out to be 3.68489×10⁻⁸⁴µV.Seebeck effect comes out to be 1.14927 ×10⁻⁶¹µV/k.



Fig.1.(a) normalized plot of Γ/Γ_0 v/s ω_q for different value of T.1(b) normalized plot of Γ/Γ_0 v/s ∇ T for different values of ω_q . Amplification coefficient magnitude decreases with increasing the ω_q .



Fig .2. normalized plot of Γ/Γ_0 v/s ω_q for ∇T .

Conclusion

We concluded from our results that Bilayer graphene is much better thermoelectric material than Single layer graphene. These properties makes Bilayer graphene a worthy material for thermal systems like thermal amplifier, logic gates and signal manipulation devices. Due to high phonon frequencies graphene can be used as hypersound phonon laser (SASER).

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Designing an Efficeint Sensor Based on Penta-graphene for Detection of Formaldehyde

Nirmal Barman¹, Jyotirmoy Deb¹, and Utpal Sarkar^{1*}

Department of Physics, Assam University, Silchar-788011, India

*Corresponding author: utpalchemiitkgp@yahoo.com

Abstract

Here we have studied the adsorption of formaldehyde (H_2CO) on penta-graphene (PG) and finds its application as a gas sensor using density functional theory (DFT) calculation. It is found that formaldehyde is physisorbed on penta-graphene with small binding energy and a large binding distance. We find that the major contribution to the adsorption energy comes from the van der Waals London dispersion interaction (LDI). Our calculation suggest that penta-graphene is a promising material for designing gas sensor for detecting formaldehyde.

Introduction

From the last few decades, carbon allotrope, namely graphyne, fullerene, graphene, pentagraphene, pentagraphyne, twin-graphene, etc. [1-5] are more extensively used by the research community due to their unique properties and novel applications. These carbon allotropes are widely used in designing gas sensors [6-8]. Among these carbon allotropies, pentagraphene (PG) [1] having a tetragonal crystal structure formed by sp^2 and sp^3 hybridized C atoms and also an intrinsic quasi-direct-band-gap semiconductor. Literature survey reveals that PG shows great potentiality for detecting various gases such as CO, CO₂, H₂O, H₂S, NH₃, SO₂, and NO [9,10]. which motivate us to design gas sensors.

Formaldehyde (H_2CO) is one such highly toxic, volatile and strong odour, flammable gas. It has been found that formaldehyde gas can causes nausea, rare cancers, nasal tumor, myeloid leukemia, asthma like symptoms and also it may cause headache and respiratory disease. It is produced in industrial environments and also occurs naturally in the environment. Therefore, it is most important to control its exposure in both residential and industrial environments. So, we have studied here the possibility of using penta-graphene as a gas sensor for detecting formaldehyde.

COMPUTATIONAL DETAILS

DFT calculations are performed as suggested in the QUANTUM-ESPRESSO package [11]. Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional under generalized gradient approximation (GGA) has been adopted. Kinetic energy and charge density cut-off are set to 130 Ry and 520 Ry, respectively. The Brillouin zone (BZ) is sampled using $14 \times 14 \times 2$ k-point grid. To avoid interaction between the successive layers, a vacuum spacing of 15

Å is kept along Z-direction. We have incorporated the dispersion interactions due to van der Waals (vdW) forces using the DFT-D2 scheme. The adsorption energy [12-14] of formaldehyde on penta-graphene is calculated for the most stable configuration, which is given by the equation:

 $E_{ads} = E_{PG+H_2CO} - (E_{PG} + E_{H_2CO})$ (i)

where, E_{PG+H_2CO} , E_{PG} and E_{H_2CO} are the energy of the whole system, penta-graphene, and H₂CO molecules respectively.

The contribution to the total adsorption energy from London dispersion interaction (LDI) (E_L) [15] is calculated using:

$$E_L = E_{PG+H_2CO}^{disp} - (E_{PG}^{disp} + E_{H_2CO}^{disp}) \dots \dots \dots (ii)$$

where $E_{PG+H_2CO}^{\mu\alpha\beta}$, $E_{PG}^{\mu\alpha\beta}$ and $E_{H_2CO}^{\mu\alpha\beta}$ are the LDI contribution to the total energy of the system.

RESULTS AND DISCUSSION

We have taken a $2 \times 2 \times 1$ supercell of pentagraphene and adsorbed the formaldehyde molecule at different adsorption sites. Here we have chosen four different sites for the adsorption of formaldehyde on penta-graphene and the four sites are S1, S2, S3 and S4 that represents the configurations of the adsorption positions of H₂CO on C2 with facing H, H₂CO on C2 with facing O, H₂CO on C1 with facing H and H₂CO on C1 with facing O. The calculated adsorption energies and optimal distances are given in table 1. Based on adsorption energy it has been found that S3 configuration is the most stable configuration among the four considered configurations. The optimized structure of PG and most stable configuration of H₂CO adsorbed on PG is presented in Fig.1. It is physisorption where H₂CO interacts with the C1 atom of PG via its H atom with an optimal distance of 2.89 Å. We have reoptimized the S3 configuration by incorporating vdW correction. It has been found that



Fig.1 Optimized geometry of (a) PG and (b) the most stable adsorption structure of H₂CO on PG.

the adsorption energy is -0.027 eV without considering vdW corrections, whereas the value is found to be -0.281 eV when vdW correction is included. However, H₂CO is strongly physisorbed on PG having a lower optimal distance with vdW than without vdW. The negative value of adsorption energy with vdW correction indicates the stability of H₂CO molecule adsorbed PG, as a result, it would be used as a sensor. It is also clear that the stability of the system increases significantly on the incorporation of vdW correction. Next, we have analyzed the contribution of London dispersion interaction (LDI) to the adsorption energy. For H₂CO molecule adsorbed on PG, the London contribution (E_L) is -0.281 eV, calculated by equation (ii). The result reflects that the total adsorption is mainly contributed by the London dispersion interaction.

Table 1. Adsorption energy (E_{ads}) and optimal distance (D) for H₂CO molecule on PG for with vdW and without vdW

Configurations	Without vdW		With vdW	
	Eads (ev)	D	Eads (ev)	D
		(Å)		(Å)
S1	-0.025	3.09	-	-
S2	0.094	3.23	-	-
S 3	-0.027	2.89	-0.281	2.71
<u>S</u> 4	0.094	3.29	-	-

GAS SENSING MECHANISM

Here, we have studied the recovery time of our proposed gas sensor to check its performance. A good sensor has a short recovery time, which pertains to how fast the desorption of H₂CO molecule occurs from the PG surface [11-13]. The recovery time τ_{rev} is determined using the equation

$$\tau_{rev} = \nu^{-1} \exp(-\frac{E_{ads}}{K_B T}) \quad \dots \quad \text{(iii)}$$

where ν is the attempt frequency and taken as 10^{12} s⁻¹, K_B is the Boltzmann constant and T is the room

temperature (T=300K). The magnitude of τ comes out to be 0.052 µs and the magnitude is reasonable for rapid desorption thus ensuring its reusability as a sensor.

CONCLUSION

In this article, we have investigated the interaction of formaldehyde with penta-graphene and finds its potential application as a gas sensor. It has been found that the adsorption energy is more negative i.e, most stable when vdW is considered. It has also been found that for the adsorption of H_2CO on PG, the adsorption energy is mostly contributed from London dispersion interaction. Adsorption of formaldehyde on penta-graphene is physisorbed. Negative adsorption energy with low optimal distance along with short recovery time confirms its potentiality towards detecting formaldehyde.

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Oxidation Study of Titanium Carbide (Ti₃C₂T_x) Using A Thermo-gravimetric Analyzer

Shravani Kale¹, Vinila Bedekar² and S N Kale^{1*}

¹Department of Applied Physics, Defence Institute of Advanced Technology, Girinagar, Pune - 411025, INDIA ²Department of Physics, Indian Institute of Science Education and Research, Pune-411007, INDIA *Corresponding author: sangeetakale2004@gmail.com

Abstract

MXene is a novel 2D material to be utilized in many applications. Titanium carbide $Ti_3C_2T_x$, because of its versatile properties, is the most extensively researched MXene. Although it is an extremely promising candidate for several applications, such as superconductors, batteries, electromagnetic shielding, and sensors, its storage in the air is a challenge. We have synthesized $Ti_3C_2T_x$ with the HF etching technique to investigate this. XRD measurements ascertain the composition of the synthesized material to be the hexagonal structure of titanium carbide, while the imaging has been done by using FESEM. Here, we propose the study of the oxidation stages of $Ti_3C_2T_x$ in the air which are being examined using a thermo-gravimetric analyzer (TGA).

Structural Evolution of Molybdenum Phosphate

Garima Jain^a, Dr. A. Juliet Christina Mary^{a,b}, and Dr.A.ChandraBose^a*

^aNanomaterials Laboratory, Department of Physics, National Institute of Technology,

Tiruchirappalli, Tamil Nadu, India- 620015

^bDepartment of Physics, JayarajAnnapackiam College for Women (Autonomous),

Periyakulam, TamilNadu, India

^a*Corresponding author: acbose@nitt.edu

Abstract

Metal Phosphates, particularly the layered metal phosphides and phosphates, have gained much attention from the research community. Molybdenum phosphate is one of the promising class of transition metal phosphates (TMPOs). In this report we intend to study the synthesis, structural, and morphological variations of molybdenum phosphate nanomaterial. A facile hydrothermal approach is carried out for synthesizing molybdenum phosphate and investigated by X ray diffraction (XRD), Thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), Scanning electron microscope (SEM). The result indicates the formation of $(NH_4)_{2.6}$ ($H_3O_{0.4}$ ($PMo_{12}O_{40}$) Ammonium Oxonium Dodecamolybdophosphate which was further annealed at 250 °C, 350 °C, 450 °C temperatures to get the pure form.

Introduction

Recently phosphate-based materials have received more attention due to its outstanding performance in catalysis, ion exchange, proton conductivity, interface chemistry, and material science, also great promise for supercapacitor application [1]. Phosphates are expected to play a major role in the development of high-performance supercapacitors due to their high theoretical specific capacitance, high chemical stability, non-toxicity, high abundance and low cost. The nanostructures and mesostructures of metal phosphates are highly tunable for better access by electrolytes. Several transition metal phosphates open a framework with large channels and cavities, shown to possess excellent ion/charge conductivity [2,3]. Properties of phosphate which makes it more prominent:-

1.Phosphate refers to oxyanions of pentavalent phosphorus, which ranges from the simple PO³⁻ through ring and chain anions of infinite network.

2.Owing to the variations in their structural assemblies, the large number of cations to which they can coordinate, and the presence of additional anions or molecules, metal phosphates occur in large diversity.

In this work, we will focus on extensive recent progress on molybdenum phosphate and its structural evolution. Further phosphates as one of the newly developed materials show great promise for supercapacitors, with various advantages. Inspired by interests on the synthesis of 'Molybdenum phosphate' via hydrothermal approach.

Experimental Setup

Hydrothermal approach is preferred for synthesizing the metal phosphate materials. HNO₃ was dissolved in DD water with ammonium molybdate tetrahydrate (NH₄)₆Mo₅O₂₄·4H₂O. After this sodium di-hydrogen phosphate (NaH₂PO₄) is used which turns the solution in yellow colour. On transferring it to the hydrothermal chamber Yellow precipitate was observed when heated at 90°C. The material got washed with DD water and ethanol. A shiny yellow coloured powder is obtained by putting it in a vacuum chamber. We consider it as prepared material and further we keep it at various temperatures (250°C and 450°C) to study its properties.

Results and Discussion



Fig. 1. TG/DTA curves of as- prepared material

TGA/DTA studies of as-prepared material provide the change in weight loss at different temperature ranges. TGA demonstrates a small weight loss at 250 °C. At the end of 450 °C the material loses 5.6% of its remaining weight due to the decomposition of NH₄⁺ as shown in Fig.1, then it becomes constant till 780 °C after which a huge drop of 71.74% is obtained due to phase transition. From the DTA curve, the peak around 500 °C exhibits an exothermic change that occurs during the process while the downward peak near to 800 °C represents endothermic change.

FTIR spectra corresponding to the as prepared, 250 °C, and 450 °C annealed samples are shown in Fig.2. The main peaks at 591 and 863 cm⁻¹ represent the Mo=O stretching vibrational band, 495 cm⁻¹ corresponding to PO_4^{3-} , and 774 cm⁻¹ corresponds to O=P-O vibrational band. After annealing the sample at 450 °C, the intensity of the amine groups is reduced, and the intensity of the major peaks corresponding to Mo=O and O=P-O functional groups are increased. These results are correlated with TG/DTA analysis and XRD analysis.



Fig. 2. FTIR spectra of the as prepared and annealed materials

The XRD pattern of as-prepared material is shown in Fig.3. confirms the cubic crystal structure of Ammonium Oxonium Dodeca Molybdophosphate $(NH_4)_{2.6}(H_3O)_{0.4}$ (PMo₁₂O₄₀) material. At 250 °C only the XRD intensity gets reduced. At 450 °C, the material gets transformed into MoO₃ and P₂O₅. The color of the material is also changed to greenish black in color. It confirms the orthorhombic crystal structure formation of the MoO₃ material. The symbol (*) represents the formation of hexagonal P₂O₅ phase. These results concluded that the ammonium is fully removed after 250 °C and the material gets dissociated at 450 °C. The aim of the work is to obtain molybdenum phosphate.



Fig. 3. XRD patterns of as prepared and annealed material

Morphological study of the as-prepared material is shown in Fig.4(a-c), which represents uniform hollow spherical structures in micrometer range. The surface of the microspheres exhibits micro pores which provide active sites for ion diffusion and charge transport, and can be used as an effective supercapacitor material.



Fig. 4. SEM images of the as prepared material at different magnifications

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Effect of Carbon Cloth Substrate on Field Emission Properties of Bi₂S₃ Nanostructure

Pankaj Kolhe¹, A. B. Kanawade¹, Ajay Nimbalkar¹, Prashant Bankar², Pallavi Mutadak², Mahendra More², Namita Maiti^{3*}, Kishor Sonawane^{1*}

¹Department of Physics, Fergusson College (Autonomous), Pune- 411004, India ²Centre for Advanced Studies in Materials Science and Condensed Matter Physics, Department of Physics, Savitribai Phule Pune University, Pune-411007, India

³Laser & Plasma Technology Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

*Corresponding author: kmsonawane@gmail.com (Dr. Kishor Sonawane); nmaiti@barc.gov.in (Dr. Namita Maiti)

Abstract

In present study, Bi_2S_3 nanostructures are grown on carbon cloth via facile hydrothermal route in order to investigate their FE properties. The physico-chemical properties of synthesized Bi_2S_3 nanostructures were studied using X-ray diffraction (XRD), scanning electron microscopy (SEM) etc. The SEM micrograph illustrates the Bi_2S_3 nanorods are vertically grown on carbon cloth. The FE study reveals, Bi_2S_3 nanorods grown on carbon cloth delivers maximum current density of 2167 μ A/cm² at an applied electric field of 3.2 V/µm with lower turn-on (defined at 10 μ A/cm²) field of 1.48 V/µm than pristine Bi_2S_3 nanostructure. The emission current stability tested at a pre-set value of ~1 and 5 μ A over 4 hours duration is observed to be very good. The FE properties of Bi_2S_3 nanostructure grown on carbon cloth are superior to nanostructure in powder form which is attributed to the high aspect ratio of the vertically oriented nanorods,. The outcome of FE properties indicates the potential applicability of Bi_2S_3 nanostructure emitter grown on carbon cloth in the practical application in FE based vacuum micro/nano-electronic devices.

Keywords: Bi2S3 Nanostructure; Carbon Cloth Substrate; Field Emission Properties

Substrate Dependent Growth Study of ZnIn₂S₄ Nanostructures: Single Step Hydrothermal Approach

Prashant K. Bankar^{*1}, Pallavi R. Mutadak¹, Pankaj S.Kolhe², Prashant S. Badgujar¹

Kishor M. Sonawane^{2,} and Mahendra A. More¹

¹Centre for Advanced Studies in Materials Science and Condensed Matter Physics, Department of Physics, Savitribai Phule Pune University, Pune – 411 007, India.

²Deparment of Physics, Fergusson College affiliated Savitribai Phule Pune University, Pune 411004, India

*Corresponding author: bankarprashant26@gmail.com

Abstract

The unique structural features and fascinating physicochemical properties of 2D nanostructured materials have shown great application in charge storage, optoelectronics and photoconduction device. Zinc Indium Sulfide ($ZnIn_2S_4$) is the only member of the ternary metal sulfides family with a layered structure. Amongst the methods used for synthesizing $ZnIn_2S_4$ structures, the hydrothermal technique offers a simple, cost-effective and environmentally friendly route for materials synthesis. To study the effect of substrate on the formation of hydrothermally grown $ZnIn_2S_4$ on several types of substrates were used. The structures of the $ZnIn_2S_4$ were systematically studied by scanning electron microscopy (SEM) and XRD. It was demonstrated that the type of substrates used had a great influence on the morphologies, density and alignment of the $ZnIn_2S_4$ formed. The ordered structure of nanometric dense $ZnIn_2S_4$ has been prepared on the conductive substrate for practical application in nano electronic devices.

A Comparison of Transient Optical Response of a Monolayer MoS₂ near to its A, B, and C Excitons

Durga Prasad Khatua^{1,2,*}, S. Gurung^{1,2,*}, A. Singh¹, S. Khan¹, and J. Jayabalan^{1,2,*}

¹Nano Science Laboratory, MSS, Raja Ramanna Centre for Advanced Technology, Indore, India-452013.
 ²Homi Bhabha National Institute, Training School Complex, Anushakti Nagar, Mumbai, India – 400085.
 *Corresponding author: <u>khatuadurgaprasad03@gmail.com</u>; <u>ijaya@rrcat.gov.in</u>

Abstract

Ultrafast carrier dynamics study has been performed on monolayer MoS_2 at three excitonic transition energies by pumping and probing with corresponding photon energy. Measurements at A and B excitons peaks show an initial negative maximum in $\Delta T/T$ which recovers within the first few picoseconds. At a later time, a positive maximum in $\Delta T/T$ has been observed only in the case of measurement at A exciton. At C exciton, $\Delta T/T$ remains positive throughout the first 15 ps. The recovery of $\Delta T/T$ in the case of both A and B excitons are of similar time scales, whereas C takes a much longer time. The origin of such transient changes in transmission has been explained through various ultrafast physical processes in the MoS₂.

Introduction

Transition metal Dichalcogenides (TMDCs) are emerging as fascinating materials for various applications like optoelectronics, spintronics, etc. due to their interesting electronic and optical properties [1]. The importance of TMDC materials lies in the fact that they are indirect bandgap materials in bulk down to few layers while it possesses a direct bandgap in monolayer form [2, 3]. Some other attractive properties that make it fascinating are large binding energy excitonic states, Trion states, optically controllable valleys, and spin [3, 4]. Among these various TMDC materials, Molybdenum Disulfide (MoS₂) has attracted the attention of many researchers in recent times since its monolayer has a direct bandgap of 1.8 eV and exciton binding energy 0.4 - 1.1 eV which is much larger than conventional semiconductor materials [2]. For various applications in Valleytronics, spintronics, sensing, laser, etc., it is necessary to understand the dynamics of charge carriers in MoS₂ for which ultrafast pump-probe spectroscopy is a powerful tool. Many researchers have studied the carrier dynamics of MoS₂ monolayer at different excitation energies but there is no direct observation of carrier dynamics when excitation and probing are done at given excitonic transition energy with high excitation density.

In this work, we report the experimental carrier dynamics measurements which have been carried out on monolayer MoS_2 near its A, B, and C exciton peaks individually by pumping and probing at the corresponding transition energies at the same carrier densities. We show that the observed carrier dynamics in each of these excitonic states are very different from each other.

Experimental Technique

Transient transmission measurements had been carried out in a pump-probe setup developed using an optical parametric amplifier (OPA) pumped by a femtosecond oscillator-amplifier system whose full-width half maxima (FWHM) is 35 fs. For the measurements, wavelength near A (668 nm), B (628 nm) and C (400 nm) exciton of MoS2 monolayer has been obtained from the OPA. In this setup, OPA beam is divided into two parts using an 80% transmission beam splitter. Among these two beams, the higher pulse energy beam is used as the pump and lower energy as the probe. To match the optical path length of the beams, probe beam is passed through a mechanical translation stage. Both the beams are overlapped at the sample position using two parabolic mirrors. Same optical path length has been confirmed using autocorrelation technique at the sample position where FWHM of the laser pulse is measured to be 43 fs. Size of the pump and probe beams were measured using CCD camera which are 72 µm and 24 µm respectively. To select a flake for the measurement, a microscope with a 50X objective was used. Using this setup, a monolaver has been chosen in which carrier dynamics has been studied using a highly sensitive detection system comprising of lock-in amplifier and boxcar combination [5].

Results and Discussion

Figure.1(a) shows the transient transmission measured near the A-exciton of monolayer MoS_2 . With the arrival of the pump pulse, the transmission through the samples starts decreasing reaching a maximum change


Figure 1. Ultrafast transient transmission measured on monolayer MoS₂ near the peak of (a) A exciton, (b) B exciton, (c) C exciton using corresponding excitation energy as pump and probe.

within the pulse duration. This first negative dip recovers within first ps, however later times the $\Delta T/T$ starts increasing and shows a positive peak at about 3.5 ps. The recovery of the positive peak is much slower compared to that of the first peak. At high excitation densities, the bandgap of a material decreases due to band gap renormalization (BGR) [6, 7]. Such reduction in band gap causes the absorption to increase leading to a reduction in transmission. The first negative peak observed in case of A- and B-excitons in the present case are attributed to BGR. Appearance of the second peak is attributed to the band filling effect assisted by the reabsorption of hot phonons by the carriers in trapped and defect states [8]. When measured near the B-exciton peak, the initial change in transmission is negative (Fig.1(b)) similar to that of A-exciton. This negative peak recovers much slowly within first 4 ps. However, unlike the case of Aexciton, the measurement near B-exciton did not show any change in the sign of $\Delta T/T$. The behavior of $\Delta T/T$ measured near the C exciton is very different from that of the other two, shown in Fig.1(c). With the arrival of the pump pulse, the transient $\Delta T/T$ in case of Cexciton starts increasing slowly reaching a positive peak by about 0.6 ps which is much longer than the pulse duration. The observed positive change of $\Delta T/T$ in case of C-exciton is attributed to band filling effect. The decay time of this peak is also much longer than A and B excitons. Single exponential fit shows that the recovery/decay time for the A, B and C exciton is 0.4 ps, 1 ps, and 5.5 ps respectively. Since the excitation energy of photon in this C exciton case is large, a much larger number of hot phonons are released during the thermalization process which can lead to a slower carrier relaxation process [6, 8].

Conclusion

In conclusion, in this article, we report the ultrafast carrier dynamics study performed on monolayer MoS_2 at its three excitonic transition energies individually, by pumping and probing at corresponding photon energies. Near A exciton, an initial negative peak is

observed due to the BGR effect which decays within 1 ps following by a positive peak due to the reabsorption of hot phonons by the carriers trapped in surface and defect states. This positive peak relaxes slowly due to high density of phonons in longer time scale. In the B exciton case, an initial negative peak appears as that of A exciton which is due to the BGR effect with no appearance of any second peak. In the C exciton case, the initial change in the transmission is positive and decays slowly compared to the other two cases which is due to the buildup of a high density of hot phonons in the carrier thermalization process.

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Impressive Electronic and Optical Properties of HfN₂/ MoSe₂ Heterostructure: A Density Functional Theory Study

Jayanta Bera¹, Atanu Betal¹, and Satyajit Sahu^{1*}

¹Department of Physics, Indian Institute of Technology Jodhpur, Jodhpur, Rajasthan-342037, India

*Corresponding author: satyajit@iitj.ac.in

Abstract

The electronic and optical properties of bilayer $HfN_2/MoSe_2$ Van der Waals heterostructure have been investigated using density functional theory (DFT). The $HfN_2/MoSe_2$ heterostructure has been constructed by two types of stacking (AA' and AB) of single layer MoSe_2 and HfN_2. Both the stacking has direct band gap though AB stacking has a slightly higher band gap than AA' stacking. It is also observed that the AB stacking is more sensitive to the spin orbit coupling (SOC) effect. The $HfN_2/MoSe_2$ heterostructures have high value of absorption coefficient in the visible and ultraviolet regions. Our theoretical investigation suggests that $HfN_2/MoSe_2$ heterostructure can be very promising candidate in nano electronics and optoelectronics for visible and ultraviolet photodetector.

Introduction

Two dimensional transition metal di-chalcogenides (TMDCs) have drawn much attraction in the last decade because of their excellent electronic, optical, thermoelectric and mechanical properties^{1–3}. Like TMDCs, transition metal di-nitrides (TMDNs), where chalcogen atoms are replaced by nitrogen atoms, become very popular recently because of their high thermoelectric, photovoltaic and piezoelectric performance. The construction of heterostructure by TMDC and TMDN is a trending research in recent days. The intrinsic properties of HfN₂ monolayer, as well as strain and electric field modulated thermoelectric, optical and piezoelectric properties of HfN₂/MoTe₂ Van der Waals heterostructure has been investigated recently⁴.

In this work, we have investigated the electronic and optical properties of $HfN_2/MoSe_2$ Van der Waals heterostructure with two different types of stacking AA' and AB. The effect of spin orbit coupling (SOC) on electronic band structures has also been studied. Our computational investigation suggests that $HfN_2/MoSe_2$ heterostructures can be very promising candidates in nano-electronics and optoelectronics for visible and ultraviolet photodetectors.

Computational details

First principle calculations were performed using (DFT) in Quantum espresso (QE) code and generalized gradient approximation (GGA) - Perdew-Burke-Ernzerh (PBE)⁵ as exchange and correlation functional for the wave function. A sufficient vacuum of 17 Å along Z direction was created to avoid any interlayer interaction to realize the effect of bilayer.

Grimme's DFT-D2⁶ was implemented to realize the Van der Waals interactions between two layers. The kinetic energy cut-off of 60 Ry and a dense k-mess of $24 \times 24 \times 2$ was used for the calculations. The force convergence threshold for geometry optimization was kept 0.01 eV/Å. The optical properties were calculated using time dependent density functional theory (TDDFT) in SIESTA code. More details of the calculation of optical properties can be found in our previous work⁷.



Fig. 1. Optimized unit cell structure of (a) AA' and (b) AB. Top view of a 4×4 supercell of (c) AA' and (d) AB.

Results and discussions

The optimized lattice constants of AA' stacked and AB stacked HfN₂/MoSe₂ heterostructure as shown in fig.1, are a = b = 3.38 Å and 3.376 Å respectively. Whereas the monolayer MoSe₂ and monolayer HfN₂ have lattice constant of 3.32 Å and 3.42 Å respectively. So, the lattice constants of HfN₂/MoSe₂ heterostructures are in between that of MoSe₂ and HfN₂, as expected. The electronic band structure of AA' and AB stacked

HfN₂/MoSe₂ heterostructure have been calculated along the high symmetry path $\Gamma \rightarrow K \rightarrow M \rightarrow \Gamma$ in hexagonal Brillouin zone. The valence band maxima (VBM) and conduction band minima (CBM) both lie on K point resulting in a direct band gap in both the structures. The calculated values of direct band gap are 0.97 eV and 1.29 eV respectively for AA' and AB stacking without SOC as shown in fig. 2. So it is seen that AB stacking has higher band gap than that of AA' stacking. The effect of SOC on electronic properties has been investigated on both the structures. For AA' stacking there is negligible effect of SOC on the electronic band structure as the VBM and CBM do not split significantly. The splitting in VBM is only 42 meV while CBM splits by 19 meV with SOC in AA' stacking. However, there are a significant splitting in VBM and CBM in AB stacking with SOC as shown in fig. 2b. The VBM splits by 189 meV while CBM splits by 198 meV in AB stacking with SOC resulting a reduced band gap of 1.0 eV. The AB stacking is more sensitive to the SOC in comparison to AA' stacking.



Fig. 2. Electronic band structures of AA' and AB stacking with and without SOC.

To investigate the optical properties of the structures, we have plotted imaginary part of the dielectric function (Imɛ) and absorption coefficient of AA', AB, monolayer MoSe₂ and monolayer HfN₂ as a function of incident photon energy as shown in fig. 3. The imaginary part of dielectric function starts rising from 0.8 eV for both of the stacking. The first peaks of Ime have been observed at 1.73 eV and 1.72 eV while the highest values of ImE have been found at 2.31 eV and 2.30 eV for AA' and AB stacking respectively. In case of monolayer MoSe₂ and HfN₂ Ime start increasing from 1 eV and 3.5 eV respectively. So it is clear that there is a red shift in Ime and higher values of Ime have been observed in HfN2/MoSe2 heterostructures compared to MoSe₂ and HfN₂ single layer. A similar trend has been observed in the absorption spectra of the structures as shown in fig. 3b. The absorption starts from infrared region for both the structures and first absorption peak has been observed at 1.78 eV which is in the visible region. A second absorption peak has been observed at 2.4 eV. As photon energy increases the absorption coefficient also increases for both the structures and the highest absorption peak has been found at 6.3 eV, which is in the ultraviolet region. The $HfN_2/MoSe_2$ heterostructures have higher values of absorption coefficients than that of monolayer $MoSe_2$ and HfN_2 . These results suggest that $HfN_2/MoSe_2$ heterostructure can be a promising candidate in optoelectronics for near IR, visible and ultraviolet light detection.



Fig. 3. Imaginary part of the dielectric function (ImE) and optical absorption spectra of bilayer AA', AB stacking, monolayer MoSe₂ and HfN₂.

In conclusion, the electronic and optical properties of HfN₂/MoSe₂ Van der Waals heterostructures with AA' and AB stacking, have been investigated using DFT. Both the heterostructures are direct band gap semiconductor though AB stacking has larger value of band gap than that of AA' stacking. The calculation of optical properties implies that HfN₂/MoSe₂ heterostructures can absorb a wide range of spectra in near IR, visible and ultraviolet regions. Our computational investigation suggests that HfN₂/MoSe₂ heterostructures can be very promising candidates in nano electronics and optoelectronics for visible and ultraviolet photodetectors.

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Study of the electrical modulus spectrum to the analysis of electric relaxation and conductivity effect in Graphene Oxide – PAA Composite

T.N. Ghosh^{1*}, A.K. Bhunia², S.S. Pradhan³, S.K. Sarkar³, S.C. Saha⁴

¹Department of Electronics, Midnapore College (Autonomous), Midnapore 721101, West Bengal, India

²Department of Physics, Government General Degree College at Gopiballavpur-II, Jhargram 721517, West Bengal,

India

³ Department of Physics, Midnapore College (Autonomous), Midnapore 721101, West Bengal, India, ⁴Department of Electronics, Vidyasagar University, Midnapore 721102, West Bengal, India

*Corresponding author: tilak.narayan.ghosh@midnaporecollege.ac.in

Abstract

In this report, we mainly focused the analysis of electric modulus and AC conductivity of the two-graphene oxide (GO)–Poly (acrylic acid) (PAA) nanocomposite to study the electrical properties and relaxation effect. Maximum peak of the frequency dependence imaginary component of the electric modulus has been changed with the change in temperature (20 to110 °C) and GO contents (wt 5% and 10%) in the nanocomposites. The observation showed that activation energy (E_A) decreases whereas relaxation time increases with the increase of the GO content from 5 wt% to 10 wt% within the PAA-GO composites. AC conductivity within both sample increases with the increase of temperature and frequency in the range 10^{-4} to 8×10^{-4} S/m. The E_A value decreases from 0.256 to 0.121eV with the increase of the GO content.

Introduction

Graphene, an exceptionally thermal and electrical conductive material, is the initial twodimensional (2D) atomic crystal. Its ascent, status and possibilities, and guide are audited in [1]. It is a 2D atomic crystal of sp² bonded carbon atoms with a honeycomb structure. Graphene oxide (GO) is an antecedent of synthetically changed over Graphene and has been broadly read for its interesting properties. These properties incorporate high charge mobility, mechanical adaptability, thermal stability, and chemical stability. GO has a two-dimensional monolayer structure and contains different oxygen functional groups, for example, carboxyl, epoxy, and hydroxyl groups [2]. GO is very much dispersed in water, chemically versatile and mechanically strong for additional alteration as a promising competitor for composite fillers [3].

Utilizing a polymer as a lattice permits simple and minimal effort preparing one can utilize handling strategy for example, arrangement mixing, expulsion, hot pressing or moulding successfully. Inferable from their superb properties (e.g., high electric breakdown field, low dielectric loss, adaptability, simple handling, and minimal cost), polymer and polymerbased dielectrics offer an alluring option in contrast to the conventional ceramic dielectrics in numerous fields [4]. The electrical, dielectric, optical, magnetic, thermal, and various properties of the polymer are improved with the low content of the fillers because of the splendid properties of Graphene-based materials like GO, rGO [5]. In this work, we report about the AC conductivity andelectrical modulus spectrum to the analysis of electric relaxation and conductivity effect in Graphene Oxide–PAA with GO weight percent 5and 10% and the relaxation mechanism from the concept of relaxation time and activation energy. Two different weight percent of GO loaded PAA was prepared by simple chemical solution casting method.

Experimental

There are various techniques for nanocomposite manufacture - solution mixing, melt blending, insitu polymerization, latex technology and so on. We orchestrated the GO polymer nanocomposites following the solution mixing method. We initially depict the method for water dissolvable polymers PAA. Graphite oxide powder, prepared by modified Hummers technique [5] was scattered in water and shed by ultrasonication. This dispersion was ultracentrifuged to remove unexfoliated particles. By the repeated use of these two procedures finally a stable aqueous dispersion of Graphene oxide (GO) was prepared. The polymer PAA was dissolved in water at room temperature. The requisite amounts of the GO dispersion and polymer solution are mixed by constant stirring. The mixture was poured into petridishes. After the evaporation of water thin films are formed. The thin films of GO-PAA nanocomposites were peeled off form the petridishes. The electric modulus of the thin films was investigated with the help of LCR meter (HIOKI 3536 LCR METER), frequency range 1 Hz-1 MHz, and temperature range 20 to 110° C.

Results and discussion

The variation of imaginary part (M") of the electrical modulus with frequency from 1Hz to 1MHz under different temperatures varies from 20^oC to 110^oC for the different GO-PAA nanocompites are shown in Fig.1(i). The peak value gradually shifted toward higher frequency with the increment of the temperature in all of the composites. The peak values arise at different frequencies at a particular temperature for different wt% GO content PAA nanocomposites. Thus, peak shifting depends on temperature as well as GO contents. This temperature and GO content dependent peak shift arise may be due to variation of carrier relaxation and charge transport process.



Fig. 1. (i) Frequency dependence of the imaginary component of the electric modulus at temperatures from 20 to110 °C (ii) Plot of ln (τ_M) vs. 1/T for and (iii) Scaling of the electric modulus M" for (a) PAA-GO 5% wt (b) PAA-GO 10wt%

The carrier relaxation life time (τ_M) is studied from the relation [2]:

 $\omega_{\text{max}}\tau_{\text{M}}=1 \text{ or } \tau_{\text{M}}=1/(2\pi f_{\text{max}}).$

The τ_M value forPAA-GO with rGO5wt% varies from 3×10^{-5} to 7.56×10^{-6} sec with the temperature changes from 20 to 110^{0} C. The same value for PAA-GO with GO content 10wt% varies from 7.45×10^{-5} to 1.5×10^{-5} sec with the said temperature range. The temperature

(T) dependent relaxation process can be expressed by the following Arrhenius law [2]:

$\tau_{\rm M} = \tau_0 \exp\left(E_{\rm A}/kT\right)$

where E_A = activation energy, τ_0 = pre-exponential factor/characteristic life time. The variation of $ln(\tau_M)$ with 1/T and its corresponding straight-line fittings (Fig.1(ii)) E_Aand τ_0 . Their values are tabulated in Table-1.The E_A value decreases from 0.256eV to 0.121eV whereas characteristic life time increases from 1.5×10^{-7} sec to 9.5×10^{-7} sec with the increment of GO content from 5 wt% to 10wt%. AC conductivity (σ_{ac}) within 5 wt% to 10 wt% samples (Fig.2) increases with the increase of temperature and frequency in the range 10^{-4} to 8×10^{-4} S/m.



Fig. 2. Frequency dependence AC conductivity (σ_{AC}) vs. frequency at different temperature for (a) PAA-GO 5%wt (b) PAA-GO 10wt%

Table 1. Activation energy an	nd relaxation life time and
range of conductivity	

Sample	E _A (eV)	τ ₀ in sec	Range of σ _{AC} (S/m)
PAA-GO 5%wt	0.256	1.5×10^{-7}	10^{-4} to 6×10^{-4}
PAA-GO 10% wt	0.121	9.5×10^{-7}	10^{-4} to 8×10^{-4}

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Stability and Electronic Structure of Novel Allotrope of Two-Dimensional Platinum Disulfide

Pooja Jamdagni^{1,3*}, Sunita Srivastava¹, Ravindra Pandey² and K. Tankeshwar³

¹Department of Physics, Guru Jambheshwar University of Science and Technology, Hisar, Haryana 125001 ²Department of Physics, Michigan Technological University, Houghton, MI, USA 49931 ³Department of Physics, Central University of Haryana, Mahendragarh, Haryana 123031

*Corresponding author: j.poojaa1228@gmail.com

Abstract

The stability and electronic structure calculations of the novel monolayer allotrope of PtS_2 have been performed using density functional theory and the G_0W_0 method. Stability analysis reveals that the monolayer allotrope is free from imaginary modes that suggest its dynamical stability. The electronic structure calculations show an indirect band gap of 1.57 eV and 3.04 eV at the GGA-PBE and G_0W_0 level of theory, respectively. The strong hybridization of Pt-d and S-p states forms the top of the valence band and the bottom of the conduction band. The bands nearest to the Fermi level are independent of SOC effects. However, strong splitting of Pt-d bands below the Fermi level has been observed. These characteristics make monolayer PtS_2 a candidate material for optoelectronic applications.

Antibacterial Behavior of Salt Assisted Chemically Exfoliated MoS₂ Nanosheets Against Pathogenic Strains

Rajwinder Singh¹, Sushil Kumar², Virender Singh², Kanishk¹, J.S. Shahi¹ and Sanjeev Kumar²

¹Department of Physics, Panjab University Chandigarh-160014 ²Department of Physics, Goswami Ganesh Dutta Sanatan Dharma College, Chandigarh-160047

*Rajwinder Singh: rajwinder.rv@gmail.com

Abstract

The 2D MoS2 nanosheets have been fabricated by systematic salt assisted exfoliation of bulk powder. The synthesized nanostructures were characterized using x-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) measurements. The interlayer spacing obtained from HRTEM analysis of exploited nanosheets is in good agreement interlayer planes spacing of the XRD analysis. The antibacterial potential of synthesized 2D nanostructure were evaluated against one gram positive (Bacillus Subtilis) and two gram negative (Escherichia Coli and Pseudomonas Aeruginosa) pathogenic strains. The experimental results clearly showed significant resistance of exfoliated MoS₂ nanosheets against Bacillus Subtilis and, minute effect on Escherichia Coli and Pseudomonas Aeruginosa at low concentrations. The antibacterial behaviour is attributed to generation of reactive oxygen species (ROS) on MoS₂ nanosheets surfaces.

Introduction

The contamination of drinking water with various pathogenic stains is a serious problem of global concerns [1]. The use of nanomaterial photocatalysts in various forms has emerged as a cost-effective and environmentally friendly solution for cleaning of water from health hazardous pathogens. Recently, various antimicrobial nanomaterials viz, gold nanoclusters, silver nanoparticles and graphene oxide nanostructures have been explored as antimicrobial agents [2-3]. The metal ions released from nanostructures can have serious side effects on human health and the environment [4]. Therefore, the search for cost-effective and environmentally friendly antimicrobial nanomaterials without any adverse sideeffects are highly demanding.

During the past decade, 2D nanomaterials have emerged as a novel class of antibacterial agents against various pathogenic strains [5]. The graphene based 2D nanostructures have been extensively explored for antibacterial applications [6]. Recently, 2D MoS₂ semiconductor nanosheets exhibit the tremendous applications in the field of hydrogen evolution. photovoltaics, sensing and as supercapacitor electrode materials. MoS₂ nanosheets have large surface area and high conductivity that can be tuned from indirect band gap to direct band gap relative to graphene 2D structure which makes it a more promising material as compared to graphene. The ability of the MoS₂ nanosheets to generate ROS and adverse physical effect on the bacterial infection makes these very useful as an antimicrobial agent [7-8].

Till date, limited studies have been reported related to the antimicrobial potentials of 2D MoS_2 nanosheets. In the present work we have studied the antibacterial of exfoliated MoS_2 nanosheets from bulk powder against Escherichia Coli, Bacillus Subtilis and Pseudomonas Aeruginosa.

Preparation of Material

To prepare the MoS_2 nanosheets from bulk powder, we mixed the known amount of bulk powder, sodium Dodecylbenzene and Sodium Chloride in 100ml deionized water. This overall mixture was then allowed to stir at 1200 rev/min with the help of a magnetic stirrer for 4 hours at 80° C. The obtained solution was mixed with N, N dimethylformamide and then kept under ultrasonication for about 6 hours to obtain MoS₂ nanosheets. The solution was then washed with water several times with the help of centrifuge at 6000 revolutions /min to get the purified yield of nanosheets for 20 minutes for each process. All the materials used for the exfoliation of MoS₂ bulk powder was of analytical grade.

Characterization and antibacterial activities of MoS₂ nanosheets

The synthesized nanocomposites were characterized using XRD, HRTEM and EDX measurements. The antimicrobial performances MoS₂ nanosheets were checked against one gram positive (Bacillus Subtilis) and two gram negative (Escherichia Coli and Pseudomonas Aeruginosa) pathogenic strains using well-known disc diffusion method.

Results and discussions

X-ray diffraction (XRD) measurements were performed using Rigaku Mini Flex 600 X-ray diffractometer in the range of $2\theta = 10-80^{\circ}$ with step size of 0.02. The XRD diffraction pattern for MoS₂ bulk powder are shown in Fig. 1. XRD Peaks at 35.4° ,38.72°, 58.12° represents the plane (100), (103), (110) respectively.



Fig. 1. XRD spectra of MoS_2 bulk powder. Inset in the picture shows the exfoliated MoS_2 nanosheets.

The purity of synthesized materials was tested using energy dispersive X-ray spectroscopy (EDS) measurements. The EDS measurements showed the intense characteristic X-ray peaks of Mo and S element and no other peaks corresponding to foreign impurities. Morphology of the synthesized nanocomposites was noticed from high-resolution electron transmission microscopy (HRTEM) micrographs shown in Fig. 2. These micrographs clearly reveal successful synthesis of exfoliated MoS₂ nanosheets.



Fig. 2. HRTEM images of exfoliated MoS₂ nanosheets.

Antibacterial performances of exfoliated MoS_2 nanosheets were estimated from the zones of inhibition formed around the agar diffusion wells as shown in Fig. 3.



Fig. 3. Zones of inhibition formed on agar (I) Bacillus Subtilis, (II) Escherichia Coli and (III) Pseudomonas Aeruginosa stains.

The measured diameter of zones of inhibition from the agar disc after 24 hours in 37°C incubation of these nanosheets are reported in Table 1.

Table 1. Measured zones of inhibition from disc.

% conc. in	Inhibition zones in mm		
DMSO	B. Subtilis	E. Coli	P. Aeruginosa
100	25	-	-
75	25	-	-
50	23	-	-
25	16	14	13

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Electrical Properties of Carbon Dots Extracted From Biomass

Ashwini Nawade¹ and Sabyasachi Mukhopadhyay¹

¹Department of Physics, SRM University-AP, Andhra Pradesh

*Corresponding author: ashwini_nawade@srmap.edu.in

Abstract

We report optoelectronic properties of carbon dots, extracted from microbial biomass as obtained after protein purification under centrifuge method. Electrical properties of synthesized carbon nanodots was examined in thin film form, when sandwiched between transparent conducting substrate and thermally deposited aluminum electrode on it. Optical absorption and photoluminescence studies of carbon nanodots depict semiconducting nature of the materials, which was further confirmed by electrical measurements. Our studies open up a new form of semi-conducting organic nanocarbon materials (after inorganic carbon nanotubes and graphene) for their applications in chemical sensor, bio-imaging, nano-medicine, light-emitting diode (LED) and renewable energy resources.

Introduction

Carbon dots are detected as novel zerodimensional carbon-based nanomaterials recognized for their small size and strong fluorescence characteristics.¹ The use of colloidal quantum carbon dots (QDs) in films for electronic and optoelectronic applications was proposed soon after the discovery of a quantum size effect in these semiconductor nanostructures.²

This class of materials was firstly reported by Sun et al. in 2006 as carbon dots, owing to its nanometersize diameter.³ The carbon dots that were prepared from carbon nanotubes exhibited bright and colorful optical photoluminescence. These intriguing properties emerge from the quantum confinement effect, which typically occur in C-QDs with a diameter of around 10 nm.⁴ Since then the advantages of inexpensive solution processed colloidal C-QDs with their tunable band gap, a small exciton binding energy and high photoluminescence (PL) quantum yields have been explored in thin film optoelectronic devices, for example, in solar cells and light-emitting diodes.5

Here, we report a new synthesis method for developing fluorescent carbon nanodots utilizing microbial biomass. Biomass, known as a fuel that is developed from organic materials, a renewable and sustainable source of energy used to create electricity or other forms of power. The optical absorption and photoluminescence studies of synthesized carbon nanodots exhibit semiconductor properties, which we proposed to utilize as photosensitive films. In order to integrate the carbon nanodots prepared from biomass in electronic devices, we have explored their electrical properties across thin film developed by solvent evaporation method.

Material and Methods

For preparation of carbon dots, organic biomass as obtained from waste yeast (after cell rapturing and protein purification under centrifuge method) was dissolved in distilled water and sonicated for 30 minutes until it is completely dispersed. Later it was heated for 5 hours at 200 °C in acidic medium. The prepared solution was cleaned with 0.2 micron syringe filter to remove unreacted yeast cell membranes. The filtered solution was examined under UV-VIS spectrometer (TECAN Spark M) for optical absorption and photoluminescence (PL) studies.

Approximately 200µl filtered solution was dropcasted on the pre-cleaned (fluorine doped) Fluoride-Tin Oxide (FTO) coated glass substrate to form thin films via solvent evaporation method under a vacuum condition. For top electrode, aluminum film of thickness ~ 50 nm, was deposited via Physical vapor deposition. (As shown in device schematic **Fig. 1**) Current-voltage measurements across FTO and Aluminum coating were carried out by Source Measurement Unit (SMU) within \pm 2V for around 50 junctions.



Fig. 1. Schematic diagram for used carbon nanodot-based detector

Results and Discussion

Fig 2 depict optical absorption (black) and PL (blue) of carbon nanodots in solution at visible regime. For photoluminescence measurements, carbon nanodots solution was excited at its absorption regime (400 nm) with 450 nm cut-off collection filter, which provides emission maximum nearly at 485 nm.



Fig. 2. Absorbance and photoluminescence spectra of green emitting carbon dots

Following the optical properties of carbon nanorods, we have prepared device with drop casted films with solution concentration of about 3.5 mg/ml of carbon nanodots in water. The current voltage behavior of carbon nanodots film, before and after filtration was plotted in Fig 3. The current-voltage characteristics carbon nanodots clearly exhibit of their semiconductor properties for electrical transport measurements with a symmetric behavior both in the negative and positive applied bias. The change in electrical properties due to the size of carbon nanodots is clearly reflected in Fig. 3. The carbon nanodots of bigger size depict higher current, but provides large variation in the current over different junctions. It could be due be due to the variation in the energy levels of the nanodots and the impurity present in the solution. The film prepared with filtered solution provides more uniformity in the junction current for nearly equal energy levels of the carbon nanodots and in absence of organic nonconducting materials in the film. Following our electrical measurements, currently we are exploring the optoelectronic current-voltage properties of the carbon nanodots films where, we are illuminating the junctions with commercially available blue diodes. We will further explore the small single optical pulse measurements utilizing lock-in and optical chopper method, which will demonstrate the use of carbon nanodots for photodetector applications.



Fig. 3. IV characteristics for different sizes of carbon dots

Conclusion

We have explore electrical properties of carbon nanodots by incorporating it in electronic devices in its drop casted thin film form. Our ongoing studied with these devices will help us to understand the charge transport mechanism across these nanodots assemblies and to utilize it as biomass based photodetector.

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Enhanced gas response of mechanically activated WS₂ flakes towards NO₂ gas at room temperature

Simon Patrick¹, M. Krishnamohan¹, S Harish¹, J. Archana¹, M. Navaneethan^{1,2}

¹ Functional Materials and Energy Devices Laboratory, Department of Physics and Nanotechnology,

SRM Institute of Science and Technology, Kattankulathur-603 203, India

² Nanotechnology Research Center (NRC) SRM Institute of Science and Technology, Kattankulathur-603 203

* Corresponding Author: mani.krishnamohan@gmail.com

Abstract

Activated WS2 is prepared using ball milling technique and characterized its nature using XRD and Raman spectra. The WS2 samples were coated as sensing films and its chemiresistive properties towards NO2 gas molecules were analyzed. The 1h WS2 sampled showed effective response with enhanced response and recovery time. Due to long time, mechanical disruption of the 2h WS2 sample lead to decreased response rate compared to pure and 1h WS2 samples. Therefore, controlled activation of layered structures enhances its effective properties towards real life application.

Electronic and Optical Properties of 2D Janus BiTeCl Compound

Poonam Chauhan, Jaspreet Singh and Ashok Kumar^{*}

Department of Physics, Central University of Punjab, Bathinda, Punjab, India 151401

*Corresponding author: ashokphy@cup.edu.in

Abstract

Taking inspiration from the successful experimental synthesis of two-dimensional Janus BiTeCl and BiTeBr compounds, we report electronic and optical properties of monolayer BiTeCl using state-of-the-art density functional theory. The spin–orbit coupling effect show significant reduction of band gap of BiTeCl monolayer. The calculated direct bandgap value of BiTeCl is 0.84eV with GGA-PBE+SOC functional as compared 1.7 eV at GGA-PBE level of theory. The optical absorbance spectra of BiTeCl lie in the UV-visible region having a peak at 2.7 eV. The moderate value of band gap and strong light absorption ability makes BiTeCl monolayer to be a potential candidate for the future electronic and optical devices.

Introduction

Named after the two-faced Roman god, 'Janus', a new class of 2D materials came into light which contain two different types of atoms on two side of surface. After the successful fabrication of Janus graphene, revolutionary change comes in the synthesis of Janus materials. The opening of the band gap in Janus graphene leads to the use of graphene in various electronic devices [1, 2]. Besides Janus graphene. other Janus materials that are experimentally synthesized are WSSe and MoSSe [3]. Recently in 2020, layered 2D Janus BiTeX (X =Cl, Br) was synthesized experimentally [4]. The experimentally synthesized BiTeCl contains triatomic layer of metal, halogen and chalcogen atoms. Stacked by weak van der Waals (vdW) interactions their atomic arrangements lead to the large induced electric field along the stacking direction.

Motivated from the experimental synthesis of 2D Janus BiTeCl, we have investigated the BiTeCl monolayer using the first principles calculations. The structure, electronic and optical properties of BiTeCl monolayer under the consideration of the spin-orbit coupling effect have been reported in this paper. The investigation of these properties suggests BiTeCl to be potential candidate for the applications in optoelectronics.

Computational Method

The electronic structure calculations were carried out by using the Quantum Espresso simulation package [5] which is based on the density functional theory (DFT). The non-conserving pseudopotentials with generalized gradient approximation are used in our calculations. The exchange-correlation part is contributed by Perdew-Burke-Ernzerhof (PBE) functional that also include spin-orbit coupling (SOC) effect which has been taken care due to heavier bismuth atom. The Monkhorst-Pack scheme for k–point sampling of Brillouin zone integration is adopted with $24 \times 24 \times 1$ k-mesh grid. The plane wave cutoff of 80 Ry is taken for calculation. The convergence threshold of 10^{-4} eV and 10^{-3} eV/Å on total energy and force has been employed in structural relaxations, respectively. For optical calculations, we have used a dense k-point mesh of 40x40x1 with an optical broadening of 0.1 eV. For the 2D slab, the vacuum distance of ~14Å has been used in z-direction.

Results and Discussion



Fig. 1.(a) Top view,(**b**)Side view , (**c**) Electronic band structure of BiTeCl monolayer at GGA+PBE+SOC level of theory and (**d**) Electronic band structure of BiTeCl monolayer at GGA+PBE

level of theory. BiTeCl possess a trigonal structure having a hexagonal unit cell contains 3 atoms per unit cell. (Fig. 1(a,b)). The crystal structure of BiTeCl is asymmetric with Bi atom is stacked in between the Te and Cl layer. The lattice constant value of BiTeCl monolayer is calculated to be 4.31 Å which is consistent with the other reported value [6].

The electronic direct band gap of 0.84 eV (Fig. 2) has been obtained with PBE+SOC level of theory. Note that the value of band gap without SOC is calculated to be 1.7 eV that suggest the importance of SOC coupling effects in Bi-based compounds.

Optical Properties

Further, we have done the qualitative analysis of optical properties of BiTeCl using random phase approximation method in terms of optical absorbance and electron energy loss spectrum (EELS). The optical absorbance, $A(\omega)$, of BiTeCl is calculated from the imaginary part of the dielectric function (ε_i) as [7]:

$$A(\omega) = \frac{\omega}{c} L \varepsilon_i(\omega) \qquad a)$$

where L is the length of the supercell along the zaxis. The peaks in the optical absorbance spectra (Fig. 2(a)) obtained at 2.71eV (in-plane) and 3.63eV (out-of-plane), respectively. The in-plane peak lies in the UV-visible region imply its practical applications in optoelectronic devices. The absorption edge observed at ~0.8 eV which is consistent with the calculated band gap. The calculated in-plane and out of plane static dielectric constant value comes out to be 4.33and 1.91, respectively. The energy loss spectrum of the BiTeCl has been calculated from the real and imaginary parts of the dielectric function as [8]:

$$Im\left\{\frac{-1}{\varepsilon(\omega)}\right\} = \frac{\varepsilon_i(\omega)}{\varepsilon_r^2(\omega) + \varepsilon_i^2(\omega)} \qquad \qquad b)$$

The sharp electron energy loss structure peaks are obtained at 4.9eV and 4.5 eV, respectively, for inplan and out-of-plan direction. These low energy plasmonic frequencies correspond to the excitation of π ($\pi \rightarrow \pi^*$) electrons.



Fig.2.(a) Optical absorbance and (b) Electron energy

loss spectra of BiTeCl monolayer at GGA-PBE+SOC level of theory.

Conclusions

In summary, the first-principles calculations have been performed to investigate the electronic and optical properties of experimentally synthesized BiTeCl monolayer. BiTeCl is an asymmetric triatomic layer hexagonal Janus compound. The direct band gap value of 0.84 eV is calculated withGGA+PBE+SOC method. BiTeCl shows strong absorption in UV-Visible region. The moderate band gap and strong UV-visible absorption suggests the application of 2D Janus BiTeCl compound in optoelectronics. Motivating from its experimental synthesis and the theoretical properties, there is a greater possibility for the existence of such type of materials. This will motivate the researchers to further explore these types of materials.

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Magnetic Properties of Cr₂O₃ Nanosheets

Sweta Das¹, Hemant Kumar^{1*}, and Niharika Mohapatra^{1*}

¹School of Basic Sciences, Indian Institute of Technology Bhubaneswar, Jatni, Odisha 752050

*Corresponding author: niharika@iitbbs.ac.in

Abstract

We present a study of the structural, morphological and magnetic characterization of the magnetoelectric Cr_2O_3 nanosheets, synthesized by a rapid thermal annealing method. The crystal structure of these nanosheets is found to be rhombohedral with space group R-3c. The results of magnetic measurement of these nanosheets reveal antiferromagnetic behavior with the Neel temperature ~285 K. Moreover, the low temperature isothermal magnetization behavior was shown to exhibit small hysteresis loop and absence of spin flop transition, which is in contrast to the magnetic properties of the bulk and nanoparticle Cr_2O_3 samples.

Introduction

Last few years have witnessed tremendous research progress in the field of two dimensional (2D) materials owing to their size dependent electronic and optical properties[1]. The well-studied materials belonging to the class of 2D materials include graphene and its analogous hexagonal boron nitride (hBN), transition metal dichalcogenides (TMDCs) and transition metal oxides (TMOs), which are mostly non-magnetic and therefore not suitable for spintronics application.

In recent years Cr based TMOs have attracted research attention due to their interesting magnetic properties in the nanometer range[2]. Bulk Cr₂O₃ is antiferromagnetic in nature and when it is reduced to nanometer range it exhibits weak ferromagnetic behavior[3]. This weak ferromagnetism increases with decreasing size of particles. Experimental as well as theoretical studies on the magnetic properties in this nanometer range is very useful for nano-spin-electronics and memory devices.

In this paper, we have conducted a detailed characterization study of Cr_2O_3 nanosheets prepared by the rapid thermal annealing method. The results of magnetic measurements show that these nanosheets are antiferromagnetic in nature with Neel temperature (T_N) as 285 K with a spin glass type freezing below ~15 K.

Experimental

The nanosheets of Cr_2O_3 were prepared by rapid annealing method [4]. The $CrCl_3.6H_2O$ crystals in a quartz crucible were directly placed in a muffle furnace, which was pre-heated to 430°C. After annealing for 15 minutes at the same temperature, the sample was rapidly quenched to room temperature. The obtained metal oxide product at this stage contains incompletely reacted intermediate compounds. To remove water-soluble impurities the quenched sample was dispersed in deionized water. Subsequently, the dispersed product was centrifuged three times for 5 minutes each. The first two times the centrifuge was done with distilled water and the third time with ethanol at 5000 r.p.m.. Finally, the sediment was collected and dried at 100 °C to obtain the Cr_2O_3 nanosheets.

The phase identification and crystal structure analysis were performed using Bruker D8 advance Xray diffractometer. In this XRD Cu-K α radiation with wavelength λ =1.540 nm is used. The surface morphology was analyzed by field emission scanning electron microscopy (FESEM) imaging. All the magnetic measurements were done in a Vibratingsample magnetometer (VSM) which is attached to the commercial Physical Property Measurement System (PPMS, Quantum Design, USA).

Result And Discussion

The room temperature powder XRD spectrum of obtained nanosheets of Cr_2O_3 were collected in the 20 range of 20° - 70° (Fig. 1(a)). All the diffracted peaks perfectly match with ICSD file No. 202619, which indicates that the crystal structure of Cr_2O_3 nanosheets is rhombohedral with space group R-3c while no unidentified impurity peaks appear in the XRD spectrum.

The field emission scanning electron microscopy (FESEM) was performed in a surface scan mode and is shown in the fig.1 (b). From the FESEM image it is confirmed that by this rapid thermal annealing method we got nanosheets of Cr_2O_3 and the layers obtained are estimated to be of few nanometres range



Fig. 1. (a)XRD pattern and (b)FESEM image of Cr_2O_3 nanosheets

The temperature dependence of the magnetic susceptibility, γ (=*M*/*H*), measured in an applied field of 5 kOe is shown in Fig. 2. An irreversibility in the zero-field-cooled (ZFC) and field-cooled (FC) curves below 285 K and a kink in the ZFC curve at the same temperature indicate the onset of frustrated antiferromagnetic ordering (T_N) . Nevertheless, the systematic increase in both ZFC and FC susceptibility below T_N may be attributed to the uncompensated spins located at the surface of the nanosheets. Additionally, we notice a small peak featured around 15 K presumably signifying the freezing of the uncorrelated spins. To verify this assumption, we measured isothermal magnetization at selected temperatures as shown in the inset of Fig.2. It may be ascertained from the figure that the M-H behaviour at 100 K is typical to that of an antiferromagnet while a hysteresis loop was observed at 10 and 2 K. With a small amount of retentivity and coercive field, the M-H behaviour suggests spin-freezing characteristics below 15 K. It is worthwhile to mention that the remnant magnetization (0.061 emu/gm) and coercive field (1045 Oe) is much higher than that of the nanoparticles of Cr₂O₃[5] indicating a higher fraction of uncompensated spins in the 2D layers. We further tried to explore the presence of spin flop transition in the antiferromagnetically ordered state. In contrast to

the bulk and nano-particles of Cr_2O_3 , which generally exhibit spin-flop transition, we did not observe any signal of spin-flop from the dM/dH plots (not shown here). These findings suggest the magnetic properties of Cr_2O_3 nanosheet synthesized here significantly differs than that of the bulk



Fig. 2. ZFC and FC curve of Cr_2O_3 nanosheets at 5kOe. The inset shows the Magnetic Hysteresis loop measured at 2, 10 and 100 K.

Conclusion

In this study we have synthesized Cr₂O₃ nanosheets by rapid thermal annealing method, which were found to retain the same rhombohedral crystal structure as that of the bulk sample (space group: R-3c). Magnetic characterization of these nanosheets indicate antiferromagnetic behaviour with the Neel ~285 The temperature as Κ. presence of uncompensated spins was ascertained from irreversibility in the ZFC and FC susceptibility behaviour and small hysteresis loop in the magnetization, which undergo spin glass type freezing below ~15 K. Unlike to the bulk Cr₂O₃ samples, these nanosheets do not exhibit spin-flop transition.

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Single-electron transistor based on Bi₂Te₃ and Sb₂Te₃ island

S. Majumder¹, S. J. Ray¹

¹Department of Physics, Indian Institute of Technology Patna, Bihta 801106, India

*Corresponding author: ray@iitp.ac.in

Abstract

Topological insulators are a new class of material where the bulk is insulating in nature but the time-reversal symmetry-protected surface states are conducting in nature. In this work, we have compared the operation and performance of a single electron transistor based on two topological insulators: Bi_2Te_3 and Sb_2Se_3 . From the analysis of the gate voltage-dependent total energy, the electrostatic coupling between the gate electrode(s) and the island (α_{avg}) and the electrostatic polarization parameter (β_{avg}) towards the total energy were calculated to be 0.23667, 0.04 eV⁻¹ for Bi₂Te₃-SET and 0.159, 0.03 eV⁻¹ for Sb₂Se₃-SET. Also, from the charge stability diagram, we found the first addition/ejection of an electron occurs at a slightly lower voltage for Sb₂Te₃-SET and the separation between the voltage at which the addition/ejection of electron happens is also slightly higher for the same.

Flicker Noise in an Electrolyte Gated Large Area Gr-FET

Rafiqul Alam*, Shubhadip Moulick, and Atindra Nath Pal

S N Bose National Centre for Basic Sciences, Department of Condensed Matter Physics and Material Sciences,

JD Block, Salt Lake sector-III, Kolkata-700106

*Corresponding author: rafiqul629@bose.res.in

Abstract

Here, we report low frequency noise measurement in a top gated CVD graphene device using a lock in amplifier-based ac technique at room temperature. We tune the carrier density of graphene by electrolyte-gating through which a wide range of carrier density can be accessed due to formation of nanometer thick Debye layer at the gate interface, offering large capacitance. The power spectral density mostly follows 1/f type behavior. By varying the carrier density, the noise magnitude shows a dip near the charge neutrality point and increases with density. The behavior is unusual compared to the reported data on exfoliated graphene device and can be explained through the charge exchange between the interfacial traps and graphene.