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Mn doping in ZnO nanoparticles: effects investigated by positron lifetime and Doppler broadening studies

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Positron lifetime and Doppler broadening measurements in nanocrystalline zinc oxide (ZnO) indicated the negatively charged trivacancy-type defects $V_{Zn+O+Zn}$ as the predominant positron trapping sites within the nanocrystallites. They got converted to neutral divacancies (V_{Zn+O}) on doping with manganese (Mn). Further doping resulted in the reduction of the size of the nanocrystallites. At still increased doping concentrations, a new phase $ZnMn_2O_4$ was formed. It had a normal spinel structure with positron trapping centers at some of the tetrahedral and octahedral sites. X-ray diffraction and transmission electron micro-scopy studies confirmed these findings.

1 Introduction ZnO is an n-type semiconductor with a wide band gap (3.37 eV) and has applications in technological areas like surface acoustic wave filters and solar cells. When it is composed of grains of nanometer sizes, there are issues like defects and changes in properties that need in-depth investigation. In this work, we focused on the defects in nanocrystalline ZnO doped with different concentrations of Mn and report the results of positron lifetime and Doppler broadening measurements.

2 Experimental details Weighted amounts of manganese acetate and zinc acetate were mixed with 2 g urea at room temperature in an agate mortar. The mixture was heated at 150 °C. It first got dissolved to become a gel. The temperature was kept on until the gel became dry and it was collected, ground and annealed at 550 °C for 0.5 hour to obtain the desired phase material in nanocrystalline form. The samples were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM) to ensure phase purity and determine grain sizes (Table 1).

For positron annihilation measurements, a 400 kBq strong ^{22}Na source in thin (~ 2 μm) Ni foil was kept immersed in the sample, taken in a glass tube and maintained under dry vacuum. Positron lifetime spectrometer had an experimental time resolution 200 ps and about 1.5×10^6 counts were collected in a spectrum. The spectra were analyzed using PALS fit [1]. Doppler broadening measurements were made using a HPGe detector of resolution 1.14 keV at 511 keV. The S para-meter is defined as the ratio of counts under 511±0.64 keV to that under 511±8 keV.

3 Results and discussion The average grain sizes of samples of different concentrations of Mn are all below the thermal diffusion lengths for positrons in ZnO (~ 52 nm [2, 3]). Positron lifetime data analysis gave four components, the longer ones τ_3 (fixed at 500 ps) and τ_4 being the lifetime of positrons trapped in the defects at the grain surfaces and of orthopositronium atoms formed in the intercrystalline regions. A defect-specific lifetime τ_2 originates from the annihilation of positrons at vacancy-type defects within the grains. These vacancies arise from non-stoichiometric deficiencies characteristic of semiconductor systems. ZnO is known to contain vacancies left by missing Zn^{2+} and O^{2-} ions. Since vacancies are charged opposite to ions, the negatively charged Zn^{2+} vacancies will offer attractive potential to trap positrons unlike the O^{2-} vacancies, which are positively charged.

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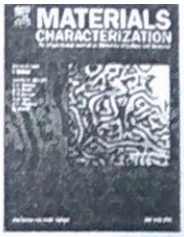

Effect of neodymium doping on structure, electrical and optical properties of nanocrystalline ZnO

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ABSTRACT

In this paper, we report effect of Nd doping on structure, electrical and optical properties of nanocrystalline ZnO prepared through a modified ceramic route. The X-ray diffraction and transmission electron microscopy studies reveal that annealed samples are single phase, pure nanocrystalline ZnO. The optical band gap for different compositions, estimated from ultraviolet–visible spectroscopy study, shows a little increasing tendency while doped with Nd for the samples annealed at lower temperature. The dc electrical conductivity of the samples decreases with the increase in Nd concentration. The ac electrical measurements prove the hopping conduction as the dominant mechanism. The results are being explained on the basis of band structural change due to Nd doping in the host lattice and by Correlated Barrier Hopping model.

1. Introduction

ZnO is a wide band gap semiconductor with a direct bandgap of 3.4 eV and a large exciton binding energy of 60 meV [1]. ZnO is now being potentially used as an important electronic and photonic material for ultraviolet light-emitters, varistors, gas sensors, acoustic wave devices, etc. [2–10]. Recently, ZnO nanoparticles have attracted considerable attention due to the unique physical properties caused by the size effect (quantum confinement) and their potential applications in nanodevices. For realization of devices, based on ZnO or doped ZnO, one of the prerequisites is to tailor its properties according to the need. Two most important ways of tailoring the properties are either to synthesize alloys of ZnO with specific concentrations of materials or by varying the grain size in the nanometer range.

Different synthesis methods like combustion [11], co-precipitation/sol–gel [12], low-temperature solution processing technique [13], solid state reaction method [14], etc., have been adopted for the synthesis of doped ZnO nanoparticles. Several studies have also been conducted on the structural, optical, electrical and magnetic properties of ZnO nanoparticles [14–24]. It has been proved that the physical and chemical properties of ZnO are greatly influenced by doping of the foreign metals ions. For example, in the field of spintronics, transition metal-doped ZnO provides efficient injection of spin polarized carriers. Recent experiments have shown that the introduction of rare earth ions such as Gd/Nd/La in wide band gap semiconductors introduced a magnetic moment [15,16]. Ungureanu et al. [15] studied the electrical and magnetic properties of Nd-doped ZnO thin films and showed that the resistivity of Nd-doped ZnO reduces by increasing the thickness of the film. Xu et al. [16] investigated the effect of codoping of Nd and Mn ions in the ZnO matrix and showed the room temperature (RT) ferromagnetism. It was also suggested that co-doping of Nd ions in the Mn-doped ZnO is one of the possible ways to introduce new energy levels in the band gap and to mediate the electron spins of the magnetic dopants [16]. Some recent theoretical calculations using density functional theories [17] explained suitably the high electrical conductivity and high transparency of the Si or Nb-doped polycrystalline ZnO. Thomas et.al. [18] have recently showed how the doping of Ag can pave a path towards

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UNUSUAL MAGNETIC PROPERTIES OF NANOCRYSTALLINE $GdFeO_3$ PREPARED BY SOLID STATE REACTION ROUTE AT LOWER TEMPERATURE

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Unusual magnetic properties of nanocrystalline orthoferrite, $GdFeO_3$, synthesize by conventional solid state reaction (SSR) route based on stoichiometric mixing of Fe_2O_3 and Gd_2O_3 is reported here. The structural characterization of these nanoparticles was carried out by using X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) techniques. We observe that the $GdFeO_3$ phase start to precipitate at 1173 K which is rather lower for a SSR route. XRD and HRTEM studies confirm the growth of highly crystalline single phase $GdFeO_3$ nanoparticles. Magnetic behavior shows the coexistence of weak ferromagnetism along with antiferromagnetic interaction. The field dependence magnetization delineates hysteresis loop at room temperature which is better at lower temperature.

Keywords: Nanocrystalline orthoferrite; $GdFeO_3$; HRTEM; magnetic study.

$GdFeO_3$, a rare-earth based perovskite is a class of material having potential for various applications such as gas separators, sensor and magneto-optic materials, etc.[1–4] The orthoferrite $GdFeO_3$, has a distorted structure with an orthorhombic unit cell (space group Pbnm).[5,6] Fe spins ($S = 5/2$) order antiferromagnetically at the Néel temperature $T_N^{Fe} = 661$ K with a weak ferromagnetic moment due to the Dzyaloshinskii-Moriya interaction.[7,8] Furthermore, in this compound, ferroelectric polarization and magnetization are successfully controlled by magnetic and electric fields respectively, thus could have an important role towards the application of multiferroics to practical devices. The phase-selective synthesis of $GdFeO_3$ is challenging because of co-existence of undesirable phases i.e., $Gd_3Fe_5O_{12}$ and Fe_3O_4. Also, the garnet phase ($Gd_3Fe_5O_{12}$) is thermodynamically more stable than $GdFeO_3$.[9] Presence of these undesirable phases affects almost all the physical and chemical properties of materials. Hence, a number of preparative methods have been explored to synthesize this garnet-free pure perovskite phase.

Attempts to obtain $GdFeO_3$ in nanocrystalline form have recently been performed by the sol–gel,[10] sonochemical,[11] ball milling[12] and heterobimetallic precursor methods.[9,13] Chavan and Tyagi used a combustion method to produce $GdFeO_3$ nanoparticles with sizes in the 40–65 nm range.[14] The most prominent methods that have been reported like

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Applied Crystallography

Structural characterization of manganese-substituted nanocrystalline zinc oxide using small-angle neutron scattering and high-resolution transmission electron microscopy

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A series of zinc oxide (ZnO) nanoparticles, substituted with manganese dioxide, have been synthesized through a modified ceramic route using urea as a fuel. X-ray diffraction and high-resolution transmission electron microscopy studies indicate that the sizes of the ZnO particles are of nanometer dimension. Particles remain as single phase when the doping concentration is below 15 mol%. Small-angle neutron scattering indicates fractal-like agglomerates of these nanoparticles in powder form. The size distributions of the particles have been estimated from scattering experiments as well as microscopy studies. The average particle size estimated from small-angle scattering experiments was found to be somewhat more than that obtained from X-ray diffraction or electron microscopy measurement.

1. Introduction

Zinc oxide (ZnO), with a bandgap of 3.37 eV and a large exciton binding energy (~60 meV) at ambient temperature, is a promising candidate for optoelectronic applications, field-emission displays, gas sensors *etc.* (Wang *et al.*, 2004; Rao & Rao, 1999; Park *et al.*, 2004). Transition metal ion (TMI)-doped ZnO, a promising dilute magnetic semiconductor (DMS), has drawn considerable attention because of its potential applications in various spintronic devices, such as spin-value transistors, spin polarizing light-emitting diodes and nonvolatile storage devices (Akai, 1998; Ohno, 1998; Litvinov & Dugaev, 2001). When prepared in nanocrystalline form, reduced dimensionality and confinement effects may be explored in order to develop a better understanding of the capabilities of such material. The Curie temperature (T_c) reported in the literature for these DMSs is quite low compared with room temperature, and is normally below 150 K (Matsukura *et al.*, 1998; Nazmul *et al.*, 2003). However, in order to achieve good performance in spintronic devices, a semiconductor with high T_c is required for all practical situations. Recent theoretical predictions of higher T_c (above room temperature) by Dietl *et al.* (2000) have given renewed impetus to the study of Mn-doped ZnO. Several researchers have, therefore, investigated TMI-doped ZnO and other DMS systems. They have reported ferromagnetic behavior above room temperature (Ogale, 2003; Ueda *et al.*, 2001). It is also reported that the growth of these DMS materials is always associated with some secondary magnetic phases. Realization of high-temperature ferromagnetization in DMS is definitely an important achievement. However, further studies are still required in order to explain the appearance of carrier-induced ferromagnetization in these DMSs. Some researchers believed that the secondary phase of TMI clusters and their spinel oxide composites might be responsible for the observed ferromagnetism (Kundaliya *et al.*, 2004; Zheng *et al.*, 2004; Coey *et al.*, 2005; Sharma *et al.*, 2003; Rao & Deepak, 2005). Thus, we felt it important to examine the structure and the

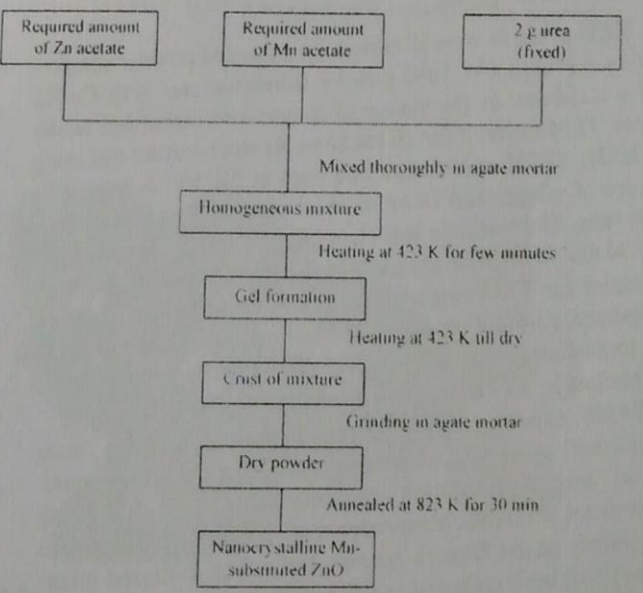

Figure 1
Flowchart of sample preparation.

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Influence of annealing on structure and optical properties of Mn-substituted ZnO nanoparticles

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The influence of annealing on crystal growth and the micro- and mesoscopic structures of Mn-substituted nanocrystalline zinc oxide (ZnO) has been investigated using X-ray diffraction, high-resolution transmission electron microscopy and small-angle neutron scattering (SANS). Average particle sizes and their distributions have been estimated from scattering experiments as well as a microscopy study, and found to be in the nanometre range. The SANS study indicates that the fractal dimension, which describes the nature of the agglomerate, is almost unchanged up to an annealing temperature of 1023 K. However, at 1223 K, the fractal dimension increases to 3. An attempt has also been made to understand the influence of the annealing temperature on the growth of the structural morphology of the aggregates by performing a simulation based on a diffusion-limited aggregate model. By showing the variation of the band gap estimated from UV–visible absorption spectra with particle size, an attempt has been made to establish a structure–property correlation.

1. Introduction

Zinc oxide (ZnO), a wide band-gap (E_g = 3.37 eV) semiconductor with a fairly large exciton binding energy (60 MeV) at room temperature, is a promising material for opto-electronic devices, field-emission displays, gas sensors, solar cells *etc.* (Pan *et al.*, 2001; Sebastian & Ocampo, 1996; Guo *et al.*, 2001; Corcoran, 1990; Krishnamoorthy *et al.*, 2002; Zheng *et al.*, 2011). Both pure and doped ZnO are important for various technological applications in catalytic, electrical, opto-electronic (Sebastian & Ocampo, 1996; Guo *et al.*, 2001) and quantum devices (Corcoran, 1990; Krishnamoorthy *et al.*, 2002). In the manufacture of devices, based on ZnO or doped ZnO, one of the prerequisites is to engineer the band gap of this material. The two most important ways of achieving this are either to synthesize alloys of ZnO with specific concentrations of materials or to vary the grain size in the nanometre range.

Substitution of manganese into a ZnO matrix offers an interesting way to alter various physico-chemical properties (Meulenkamp, 1998; Ranjani *et al.*, 2004), such as tuning of the band gap of the host material in the range of 3.3–3.7 eV. The synthesis of controlled nanocrystalline structures allows one to investigate the effects of reduced dimensionality and confinement in order to develop a better understanding of the capabilities of such a substituted material. It is worth mentioning that Mn-substituted ZnO, a dilute magnetic semiconductor, is a potential candidate for spintronic devices. While the preparation of pure ZnO with a higher Mn substitution is challenging, the micro- and mesoscopic structural characterization of such nanoparticles is highly desirable in order to establish a correlation between the structure and its properties.

Scattering experiments employing neutrons and X-rays on condensed matter systems provide quantitative structural information on microscopic and mesoscopic length scales (Sehgal *et al.*, 2005; Berret *et al.*, 2006; Fresnais *et al.*, 2008). Small-angle neutron scattering (SANS) is a powerful and non-destructive technique to probe mesoscopic density fluctuations in condensed matter on length scales ranging from a nanometre to a few hundreds of nanometres (Sköld & Price, 1987; Strunz *et al.*, 2007; Wyslouzil *et al.*, 1997; Rajh *et al.*, 1999; Roy *et al.*, 2009). While conventional X-ray powder diffraction yields information regarding an average structure of atomic organization over a length scale of typically a unit-cell dimension, SANS probes mesoscopic inhomogeneities up to 100 nm or even more.

Various methods have been utilized to grow ZnO nanocrystals, including sol–gel (Ray *et al.*, 2007), spray pyrolysis (Madler *et al.*, 2002), double-jet precipitation (Zhong & Matijević, 1996), mechano-chemical preparation (Shen *et al.*, 2006), ion implantation (Amekura *et al.*, 2005) *etc.* However, so far there have been no reports on the micro- and mesoscopic structural characterization of Mn-substituted nanocrystalline ZnO using scattering techniques. In this paper we report the effects of annealing on the micro/mesoscopic morphology and optical properties of Mn-substituted nano-

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PREPARATION AND MICROSTRUCTURAL CHARACTERIZATION OF NANOCRYSTALLINE Mn-DOPED ZnO

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Mn-doped ZnO, a dilute magnetic semiconductor (DMS), has been prepared in nanocrystalline form by using a soft chemical route. The concurrent diffusional growth of both nanocrystalline Mn-doped ZnO and secondary spinel phase $ZnMn_2O_4$ in annealed samples have been studied by using a modified Rietveld method and transmission electron microscope (TEM). Rietveld analysis reveals that both the compounds start growing when Mn concentration is lower and the volume fraction of crystalline spinel phase $ZnMn_2O_4$ decreases sharply when Mn concentration increases. TEM study indicates that average particle sizes of both the phases are in nanometer dimensions and are highly crystalline in nature. Magnetization increases initially and then almost saturates with the increase of Mn concentration. The enhanced magnetization could be a combined effect of Mn ions and surface ferromagnetism of nanoparticles.

Keywords: Nanocrystalline; Mn-doped ZnO; Rietveld analysis; TEM.

1. Introduction

There has been tremendous interest in dilute magnetic semiconductors (DMSs) because of their use in spintronic devices like spin-value transistors, spin polarizing light-emitting diodes and nonvolatile storage devices.[1–8] The Curie temperature values reported for these DMS are quite low, normally below −123°C.[7,8] However, for achieving good performance in spintronics devices, semiconductors with high Curie temperature (Tc) is required. A major breakthrough, the theoretical prediction of higher Curie temperature (above room temperature) by Dietl *et al.*,[9] has given renewed impetus to the study of DMS especially, Mn-doped GaN/ZnO.[10–12] The experimental effort essentially centers on to show the appearance of magnetization in these DMS.[1,8] But of particular interest to emerging technologies are DMS nanostructures, including

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Mn SUBSTITUTION EFFECTS AND ASSOCIATED DEFECTS IN ZnO NANOPARTICLES STUDIED BY POSITRON ANNIHILATION

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Nanocrystalline ZnO particles substituted with different concentrations (0–30%) of Mn were synthesized by using a modified ceramic route and characterized by X-ray diffraction, transmission electron microscopy, selected area electron diffraction and energy dispersive X-ray analysis methods. Positron lifetime and coincidence Doppler broadening measurements were used as probes to identify the vacancy-type defects present in them and monitor the changes while doping. The predominant positron trapping center in the undoped ZnO is identified as the trivacancy-type cluster $V_{Zn-O+Zn}$ which is negatively charged, and it transformed to the neutral divacancy V_{Zn-O} on doping with Mn^{2+} ions. The intensity of the defect-specific positron lifetime component got reduced initially indicating partial occupancy of the vacancies by the doped cations but then recovered on further doping due to the additional Zn vacancies created as a result of the increasing strain introduced by the Mn ions of larger radius. The creation of a new phase $ZnMn_2O_4$ thereafter changed the course of variation of the annihilation parameters, as the positrons got increasingly trapped in the vacancies at the tetrahedral and octahedral sites of the spinel nanomanganite.

Keywords: ZnO; nanoparticles; doping; substitutional effects; defects; positron annihilation.

1. Introduction

The interest in the remarkable optical and physical properties of zinc oxide (ZnO) has still not diminished despite the availability of published research works in abundance on these topics in existing literature.[1–3] ZnO is a wide bandgap semiconductor that has been extensively studied due to its intrinsic properties and potential uses in a variety of devices, such as field-effect transistors, resonators, gas sensors and solar cells.[4–6] Besides, it is also a good

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Structural Characterization of Borate Glasses Containing Zinc and Manganese Oxides

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Abstract

We have investigated the effect of inclusion of two transition metal ions (TMI) on structure and optical properties of borate glass system having composition $x\mathrm{MnO_2} - y\mathrm{ZnO} - (100 - x - y)\ \mathrm{B_2O_3}$ ($9 \le x \le 12$, $36 \le y \le 48$) prepared by melt quenched route. Thermal study by using a differential scanning calorimeter (DSC) reveals that the glass transition temperature (Tg) and crystallization temperature (Tc) of the glasses increases with the increase of borate content in the system. Fourier transform infrared (FTIR) spectra indicate that inclusion of TMI produces BO_3 and BO_4 structural units by breaking the boroxol (B_3O_6) ring. The optical band gap energy estimated from ultraviolet-visible spectra shows a decreasing tendency when TMI are incorporated in the borate structure.

Keywords: Borate Glass, Differential Thermal Analysis (DTA), Infrared (IR) Spectroscopy, Optical Band Gap

1. Introduction

Glasses are receiving considerable attention due to their unique properties like hardness, good strength, transparency and excellent corrosion resistance. X-ray diffraction (XRD), infra-red spectroscopy (IR), differential scanning calorimetry (DSC) studies has been extensively employed over the years to investigate the structure of glasses [1-4]. Borate glasses, in particular, have been the subject of numerous infra-red studies due to their structural peculiarities [5-8]. In pure B_2O_3 glass structure most of the boron is involved in B_3O_6 (boroxol) ring. Addition of modifier breaks boroxol ring and thereby produced BO_3 and BO_4 units [6,8]. In addition, modifier also changes the physical properties along with structural modifications.

Recently, the study of oxide glasses doped with transition metal ions (TMI) has received considerable attention due to their attractive combination of physical and chemical properties. TMI doped borate glasses have application in microelectronics, optical glasses and solid state laser [9-11]. Continued effort for the development of new glassy materials either by doping or by adding TMI, and the study of their novel properties is highly relevant due to their potential applications in various technological fields [12,13]. Keeping in mind the very fact of creating novel functionalities we have chosen an uncommon glass system. We report here the preparation, structural characterization and optical properties of manganese and zinc oxide containing B_2O_3 glass with an intention to precipitate Mn-doped ZnO crystal in the borate glass matrix, which may lead to a new composite spintronics material.

2. Experimental Procedure

2.1. Preparation

Multicomponent transition metal oxide glasses containing MnO_2-ZnO-B_2O_3 having different compositions, presented in **Table 1**, have been prepared from analytical grade precursors MnO_2, ZnO and B_2O_3. Batches of 5 gm sample were prepared by taking weighted amounts of three oxides in an alumina crucible and melting mixture in a precisely controlled high temperature furnace (Thermolyne type 46100) at a temperature 1200°C in ordinary air atmosphere. Melted mixtures were repeatedly swirled to ensure complete homogenization. The

