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Investigation on Fe-doped ZnO nanostructures prepared by a chemical route

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ABSTRACT

$Zn_{1-x}Fe_xO$ ($x = 0.03$, 0.05 and 0.07) nanoparticles synthesized by a chemical route were characterized by different techniques. The structural characterization by XRD and TEM confirmed the phase purity of the samples and indicated a reduction in particle size with increase in the dopant (Fe) concentration in ZnO. The optical characterization of the nanoparticles by FTIR, PL and UV–visible spectroscopy confirmed the formation of wurtzite structure and incorporation of Fe in the ZnO lattice. Magnetization measurements by VSM and Faraday balance techniques indicate presence of room temperature ferromagnetism in the Fe-doped ZnO samples. Local environment around the Fe atoms has been probed by ^{57}Fe Mössbauer spectroscopy and the measured isomer shifts confirmed the charge state of iron as Fe^{3+}. Positron annihilation lifetime spectroscopy (PALS) measurements confirm the presence of cation vacancies in the nanoparticles and indicate a reduction of overall defect concentration with incorporation of Fe atoms in the ZnO structure.

1. Introduction

The current decade has witnessed vast research interest in semiconductor oxides (SnO_2, TiO_2, ZnO etc.) because of their potential use as multifunctional materials and special applications in different kind of devices [1]. Among this group of materials, zinc oxide (ZnO) has attracted great attention due to its widespread applications in opto-electronic devices such as light emitting diodes, ultraviolet laser devices, varistors, thermoelectric devices etc. ZnO is a direct wide band gap (3.37 eV) semiconductor having high excitonic binding energy (60 meV) [2].

ZnO has been doped with transition group elements to exploit the spin of an electron associated with its charge for potential applications in spintronics and the observation of room temperature ferromagnetism in transition metal (TM) doped samples had initiated a surge of intense research activities [3,4]. Thereafter, several groups have supported the observation of room temperature ferromagnetism in transition metal ion doped ZnO samples [5–8]. But quite a few controversial results have also been reported. Jin et al. did not observe any signature of ferromagnetism in their transition metal doped ZnO thin film prepared by the laser molecular beam epitaxy method [9]. Sati et al. however have shown intrinsic ferromagnetism in $Zn_{1-x}Co_xO$ epitaxial thin films [10]. Kim et al. have found room temperature ferromagnetism in $Zn_{1-x}Co_xO$ thin film and suggested that it results from impurity present in the sample in the form of Co clusters [11]. Kolesnik et al. did not find ferromagnetism in transition metal ion doped polycrystalline single phase ZnO sample but the observed ferromagnetic order in cobalt and iron doped ZnO samples prepared under selected synthesis conditions was assigned to the secondary phases present in the samples [12]. An experimental and theoretical study on $Zn_{1-x}Co_xO$ ($x = 0.05$, 0.1 and 0.15) polycrystalline samples by Risbud et al. has shown that the nearest-neighbour interaction in the system is antiferromagnetic and ferromagnetic order can occur only in the presence of additional hole doping [13]. A thorough computational study by Spaldin on Co- and Mn-doped ZnO system also showed that ferromagnetism is not possible without additional carrier doping; doping ZnO simultaneously with Co and Cu was shown to be necessary to achieve ferromagnetism [14]. Later, an experimental work by Jayakumar et al. had shown existence of room temperature ferromagnetism in ZnO samples doped simultaneously with Co and Cu whereas the sample doped with only Co was paramagnetic [15]. However Shim et al. reported that room temperature ferromagnetism in ZnO co-doped with Fe and Cu was due to a secondary $ZnFe_2O_4$ phase [16]. Experimental work by Hong et al. indicated that the presence of defects such as vacancies might be responsible in getting magnetic order in ZnO [17]. Similar conclusion was made by Sundaresan et al. where the presence of vacancies at the surface of the nanomaterials was argued to be the reason for getting room temperature ferromagnetism [RTFM] in nonmagnetic oxides [18]. A theoretical study by Wang et al. on ZnO thin film and nanowire has shown that presence of Zn vacancy is essential to obtain magnetism in ZnO that has not been doped with any transition metal impurity [19]. Karmakar et al. had reported weak ferromagnetism at room temperature in Fe-doped ZnO nanocrystals; the presence of Fe^{3+} in such system was argued to be due to hole doping in the system by Zn

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vacancies that can favour stable ferromagnetic ordering in the Fe-doped samples [20]. Straumal et al. claimed that room temperature ferromagnetism in pure and Mn-doped ZnO thin film is associated with vacancies at grain boundaries [21]. Tamura et al. found RTFM in Fe-doped ZnO thin film while Mn- and Co-doped ZnO did not show any ferromagnetic behavior and suggested that half filled 3D band in the mid-gap of ZnO is responsible for RTFM in the case of Fe-doped ZnO [22]. Singhal et al. have reported weak ferromagnetism at room temperature in colloidal Fe-doped ZnO nanocrystals and described this as its intrinsic property [23]. A recent report on polycrystalline Fe-doped ZnO nanorod by Kumar et al. has shown weak ferromagnetic behavior at room temperature [24].

Such controversial results clearly indicate that the cause of room temperature ferromagnetism in diluted magnetic semiconductor is still debated and further experimental and theoretical studies are needed to arrive at a definite conclusion. Since nanostructured materials contain a large concentration of defects in the form of vacancies at the grain boundaries they are ideal materials to study the role of vacancy in getting room temperature ferromagnetism in different oxide systems. In the present work, a comprehensive study was carried out on Fe-doped ZnO nanostructures prepared by a chemical route. Different techniques were used to confirm the existence of room temperature ferromagnetism in the samples and ascertain the presence of vacancies in them as reported by many workers. The structural characterization of the samples was carried out by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The optical characterization of the samples was done by Fourier transform infrared (FTIR) spectroscopy, photoluminescence (PL) and UV–visible spectroscopy. Magnetic properties of the Fe-doped samples were carried out by a vibrating sample magnetometer and a Faraday balance magnetometer. Local structure around the doped Fe atoms was investigated using ^{57}Fe Mössbauer spectroscopy. The samples were also studied by positron annihilation lifetime spectroscopy (PALS) technique to ascertain the presence of cation vacancy in the system. Room temperature ferromagnetism has been observed in the Fe-doped samples. The presence of cation vacancy in ZnO structure as detected by positron annihilation technique has been shown to be a possible reason for getting room temperature ferromagnetism in the Fe-doped samples.

2. Experimental

$Zn_{1-x}Fe_xO$ ($x = 0.03, 0.05$ and 0.07) nanocrystalline samples with different atomic fraction of iron were prepared by the chemical coprecipitation method.

Required amount of $Zn(NO)_3{\cdot}6H_2O$ and $Fe(SO_4){\cdot}7H_2O$ were dissolved in Milli-Q water. The solution was stirred vigorously at 60 °C and then it was cooled down to room temperature. After that, sodium dodecyl sulphate (SDS) was added to the solution and the whole solution was hydrolyzed by dropwise addition of NaOH under vigorous stirring. The obtained precipitate was washed several times and was heat-treated in air at 200 °C for eight hrs. The percentages of Fe and Zn in the samples were checked by a PerkinElmer make inductively coupled plasma atomic emission spectrometer (ICP-AES). The phase purity of the prepared samples was established by X-ray diffractometry (Bruker D8 Advance diffractometer using a Cu Kα source, $\lambda = 1.54056$ Å) and their morphological characterizations were made by transmission electron microscopy (JEOL 2010, operated at 200 kV). The selected area electron diffraction (SAED) measurements and energy dispersive X-ray analysis (EDX) of the samples were also carried out.

Fourier transform infrared (FTIR) spectra of all samples were taken with a PerkinElmer spectrum GX spectrometer in the frequency range of 2500–400 cm^{-1} with a resolution of 4 cm^{-1}. Photoluminescence (PL) spectra were recorded in a PerkinElmer LS-55 luminescence spectrometer. UV–visible absorption spectra were taken on a Shimadzu UV-1601 PC spectrophotometer. Dc magnetic susceptibility measurements of the samples were carried out in the temperature range 300–14 K with a sensitive Faraday balance magnetometer. The low temperature environment was created with the help of a closed cycle helium cryo-cooler of APD, USA. Magnetization measurements were taken by a vibrating sample magnetometer (VSM) of Cryogenics, UK. Mössbauer measurements were carried out in a standard PC based multichannel analyzer with 1024 channels working in the constant acceleration mode. A 10 mCi ^{57}Co in Rh matrix was used as the radioactive source. The system was calibrated with a high purity iron foil of thickness 12 μm. The low temperature measurements were recorded by using a Janis, USA make closed cycle refrigerator fitted with a special anti-vibration stand. The spectra thus obtained were fitted using a least squares fitting programme assuming Lorentzian line shapes [25]. Positron annihilation lifetime measurements were carried out using a fast–fast coincidence system consisting of two 1 in. tapered off BaF_2 scintillators coupled to XP 2020Q photo multiplier tubes. The prompt time resolution of the system using a ^{60}Co source with ^{22}Na gate was 260 ps. The lifetime spectra were deconvoluted using the code PATFIT 88 after incorporating necessary source corrections [26].

3. Results and discussion

3.1. Structural studies

The XRD patterns of Fe-doped ZnO nanocrystalline samples with different atomic fraction of dopant ion ($x = 0.03, 0.05$ and 0.07 which are denoted hence onwards as ZF 3, ZF 5 and ZF 7 respectively) are shown in Fig. 1. The observed diffraction peaks have been compared with the standard JCPDS files of ZnO, which indicates formation of wurtzite phase in all the samples. In the sample ZF 3, no additional peak apart from that corresponding to ZnO is detected. In the samples ZF 5 and ZF 7 a peak of small intensity is seen at 32.7° ($d = 0.1753$ Å) which could not be identified. In the sample ZF 7, the additional peak at 35.25° ($d = 0.1873$ Å) has been identified as due to a small fraction of $ZnFe_2O_4$ secondary phase. No peak corresponding to α-Fe, α-Fe_2O_3, γ-Fe_2O_3 or Fe_3O_4 could be detected in any of the samples. A shift towards lower angle has been observed for all strong peaks with increase in Fe concentration in the ZnO structure. Similar observation has been reported by other workers also and

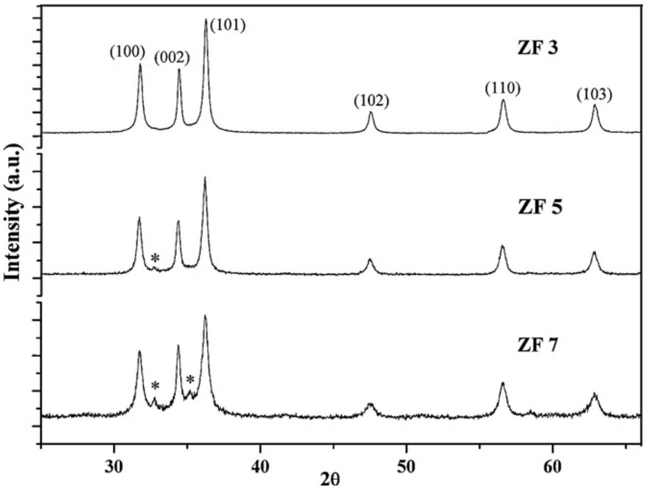

Fig. 1. XRD patterns of the prepared samples. The mark (*) represents impurity phase in the samples.