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Effects of Li doping on structural, electronic, optical and magnetic properties of $Fe_{0.04}Zn_{0.96}O$ nanocrystalline samples

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ABSTRACT

Sol-gel synthesized nanocrystalline samples of $Li_xFe_{0.04}Zn_{0.96-x}O$ (x = 0.0, 0.02, 0.04 and 0.06) have been investigated through X-ray diffraction (XRD), X-ray absorption near edge spectroscopy (XANES), UV–visible absorption spectroscopy and magnetic measurements. First three samples, i.e., x = 0.0, 0.02 and 0.04, have been found to possess an impurity phase of $ZnFe_2O_4$. As determined from the Rietveld analysis, the presence of $ZnFe_2O_4$ phase has decreased on Li doping and for x = 0.06, it is negligibly small. XANES analysis shows that the majority of Fe ions is in Fe^{3+} state. From the UV–visible spectroscopy, the energy band gap (E_g) of pure ZnO has been estimated to be 3.064 eV, whereas on Fe doping E_g has increased. No significant change in E_g due to Li doping has been observed. Magnetization measurements have revealed that the samples containing $ZnFe_2O_4$ (x = 0.0, 0.02 and 0.04) phase exhibit strong ferromagnetic spin-glass behaviour at low temperature and a weak ferromagnetic ordering at the room temperature. However, the sample with x = 0.06 does not show any significant ferromagnetic ordering in the temperature range of 2–300 K. The observed magnetic ordering and spin-glass behaviour in first three samples have been attributed to the impurity phase of $ZnFe_2O_4$.

1. Introduction

Integrating magnetism with semiconductors to produce spintronic devices [1] has become a very interesting topic [2] in the field of materials research. Such systems can be achieved by adding a minute amount of transition metal (TM) elements to the oxide semiconductors. Such systems, known as diluted magnetic semiconductors (DMSs), can play an important role in future spintronic devices. The simultaneous use of both charge and spin degrees of freedom accommodated into a single material and the interplay between them will explore novel physics and new devices such as spin field-effect transistors, spin light emitting diodes and spin qubits for quantum computers. However, for their practical device applications, these DMS systems must exhibit ferromagnetic ordering above room temperature. Due to its promising electronic and optoelectronic properties, ZnO can be taken as a suitable candidate for realizing such TM doped diluted magnetic oxide (DMO) systems. Dietl et al. [3,4] theoretically predicted that room temperature ferromagnetism could be achieved in TM doped wide-bandgap p-type ZnO by increasing the p-d hybridization and reducing the spin-orbit coupling. However, according to donor impurity band exchange model of Coey et al. [5], ferromagnetic exchanges in wide band gap semiconductors like ZnO, GaN, etc., can be mediated by shallow donor electrons that form bound magnetic polarons (BMPs). These BMPs, in fact, overlap to create a spin-split impurity band. On the other hand, Sato et al. [6] suggested that TM:ZnO would show ferromagnetic ordering only when the carriers produced by TM doping formed a partially filled spin–split impurity band. Following these predictions, a substantial investigation has been done on ZnO based DMOs, and room temperature ferromagnetism has widely been observed in TM (e.g., Mn [7–11], Fe [12–19], Co [5,20,21], Ni [22,23], Cu [24–29] etc.) doped ZnO. Although a number of experimental reports and corresponding mechanisms are available in literature, the actual origin of the magnetic ordering in TM:ZnO systems is still a matter of debate.

Room temperature ferromagnetism in Fe:ZnO has been reported by many groups [12–15]. But the results are conflicting and quite inconsistent. Han et al. were unable to produce room temperature ferromagnetism in pure Fe:ZnO bulk samples prepared by a solid-state reaction method and they suggested that an additional doping of Cu might be necessary to achieve room temperature ferromagnetism in Fe:ZnO [16]. As an alternative mechanism, a double exchange interaction has also been proposed for Fe:ZnO co-doped with Cu [18,19]. However, Shim et al. found that the ferromagnetic ordering in Fe and

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Cu co-doped ZnO was due to the formation of the secondary phase of $ZnFe_2O_4$ [17]. Therefore, the occurrence of ferromagnetic ordering in Fe:ZnO may be due to metallic clusters and secondary-phase formation or it may have an intrinsic origin. In this present work, we report that the observed ferromagnetism in Fe:ZnO is due to the formation of a secondary phase of $ZnFe_2O_4$. First we prepared Fe:ZnO which contained a small amount of $ZnFe_2O_4$ phase. Then we removed that secondary phase by Li doping. We observed that on diminishing of $ZnFe_2O_4$ phase, the ferromagnetism also vanished. Moreover, a spin-glass behavior in the samples containing $ZnFe_2O_4$ phase was also found. We claim that the simultaneous presence of strong ferromagnetism and spin-glass character in Fe:ZnO is due to the formation of $ZnFe_2O_4$ impurity phase.

2. Experimental procedure

Standard Pechini sol-gel process was used to synthesize nanocrystalline $Li_xFe_{0.04}Zn_{0.96-x}O$ (x = 0.0, 0.02, 0.04 and 0.06) samples. Zinc oxide (ZnO), Lithium nitrate [$LiNO_3$] and Iron nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] were used as precursors. Three separate solutions of (a) Zinc oxide in nitric acid, (b) Lithium nitrate and (c) Iron nitrate in double distilled water were prepared and they were mixed together in appropriate stoichiometric ratios to maintain the doping concentrations of Li and Fe. A solution of citric acid and glycerol was prepared to serve as gelling agent. The gelling agent was added to the mixed aqueous solution of precursors followed by stirring at 80 °C to form a gel which was further dried to produce the powders. These powders were heated at 450 °C to remove the trapped carbonate and nitrate phases. The samples with x = 0.0, 0.02, 0.04 and 0.06 have been denoted by S1, S2, S3 and S4 respectively.

An X-ray diffractometer (PANalytical, XPERT-PRO) with Cu K_α radiation (1.5416 Å) was used to investigate the crystallinity, phase purity and phase quantification. A step size of 0.003° and counting time of 35 s per step were used for all samples. Fullprof 2.05 (2011) program was utilized for Rietveld refinement. The XANES spectra were taken at the Energy-Scanning EXAFS beamline in fluorescence mode at Synchrotron Source (2.5 GeV, 100 mA). The optical absorption spectra were taken by using a UV–Visible spectrometer (PerkinElmer-Lambda35) at room temperature. All magnetic measurements were carried out with a Superconducting Quantum Interference Device Vibrating Sample Magnetometer (SQUID-VSM-050), Quantum Design.

3. Results and discussion

3.1. Structural analysis

XRD patterns of the pure ZnO as well as all doped/co-doped samples are depicted in Fig. 1a. Patterns as obtained from theoretical calculation using Rietveld method are also shown (solid red line) in Fig. 1a. Along with the wurtzite ZnO phase, a secondary phase of $ZnFe_2O_4$ has been detected in the samples S1, S2 and S3 (clearly visible in Fig. 1b shown for sample S1 only) and the peaks at $2\theta = 29.9°$ and 35.2° belong to this secondary phase of $ZnFe_2O_4$. However, in sample S4, no impurity phase of $ZnFe_2O_4$ has been identified in the XRD pattern. From the Rietveld analysis, we have extracted the structural parameters of all samples and they are tabulated in Table 1. It has been found that the pure ZnO has highest unit cell volume and it significantly decreases on 4 at% Fe doping (S1). Apart from the substitutional incorporation of Fe ions into Zn sites with tetrahedral symmetry (FeO_4) and formation of $ZnFe_2O_4$ phase, a fraction of Fe ions can also occupy the interstitial positions with octahedral symmetry (FeO_6) in ZnO lattice. As discussed later (in XANES part), almost all Fe ions are in Fe^{3+} state. Therefore, this decrease in unit cell volume is due to the incorporation of smaller Fe^{3+} ions (ionic radius = 0.49 Å) into Zn^{2+}(ionic radius = 0.60 Å) sites. However, on Li doping, a further decrease in unit cell volume has been observed for sample S2 and then it gradually increases up to sample S4. This clearly indicates that in sample S2, 2 at% Li doping has enhanced Fe^{3+} incorporation into Zn^{2+} site which in turn causes a decrease in unit cell volume. Since, the size of Li^+ ion (ionic radius = 0.59 Å) is comparable to that of Zn^{2+}, therefore, the incorporated Li^+ ions should not change the unit cell volume of ZnO significantly. So, due to increasing Li doping, we must not expect any appreciable change in the unit cell volume. Therefore, in samples S3 and S4, a gradual increase in unit cell volume can be interpreted as the reduction in substitutional incorporation of Fe^{3+} in presence of higher concentration of Li dopant. This might have caused an increase in Fe^{3+} incorporation into the interstitial positions. Another noteworthy point is that the unit cell volumes of all Li and Fe co-doped ZnO samples (S2-S4) are smaller than the unit cell volume of Fe:ZnO (S1). This is an indication of Li assisted higher Fe incorporation into ZnO lattice. But, the trend of increasing unit cell volume as a function of Li doping also puts an upper limit of Li doping to get enhanced Fe incorporation as compared to Fe:ZnO. Phase quantification has also been done from the Rietveld analysis for the samples S1–S4. From Table 1, we observe that the contribution of $ZnFe_2O_4$ phase is highest (5.6%) in sample S1 and it significantly decreases on Li doping. Sample S4 possesses negligibly small amount (~0.01%) of $ZnFe_2O_4$ phase. The average crystallite size has been estimated using the Scherer's formula [30]:

$$D = \frac{K\lambda}{\beta \quad \cos\theta} \tag{1}$$

where the Scherer constant K is taken to be 0.94, λ is the wavelength of the Cu-K_α radiation (1.5416 Å), and β is the full width at half maximum (FWHM-in radians) of the diffraction peak corresponding to the Bragg diffraction angle (2θ). The estimated average crystallite size is given in Table 1. For pure ZnO, the average crystallite size is about 81.2 nm, whereas for samples S1–S4, no much variation (65.8–67.4 nm) has been observed. The observed decrease in average crystallite size can be attributed to the strain produced by the smaller size of Fe dopant in the host ZnO matrix.

3.2. Electronic properties

The oxidation state of doped Fe ions has been investigated by XANES measurement. The XANES spectrum of any element is very sensitive to its oxidation state. Fig. 2 depicts the normalized XANES spectra of all samples (S1–S4) measured at Fe K-edge. For comparison, reference spectra of Fe metal foil (Fe°), FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}) are also shown in Fig. 2. The positions of the main absorption edges of XANES spectra of Fe K-edge of samples S1–S4 are much closed to the reference spectrum of Fe_2O_3. This clearly indicates that the most of the Fe ions in all samples are in Fe^{3+} state. The feature (small peak) before the main absorption edge is called pre-edge. In the inset of Fig. 2, the pre-edges of all XANES spectra of samples S1–S4 are shown in an enlarged view. Pre-edge is a characteristic of transition from Fe:1 s orbital to O:2p-Fe:3d hybridized orbitals. In an isolated Fe atom, the dipole selection rule restricts the transitions from 1 s to 3d orbitals. However, in this present case, this selection rule is not valid for Fe:3d orbitals hybridized with O:2p orbitals in ZnO. Therefore, the presence of the pre-edge peak clearly indicates the hybridization of Fe:3d-O:2p orbitals due to the substitution of Fe ions at Zn sites. Moreover, the area under the pre-edge peak provides a rough estimation of the number of transitions from Fe:1 s to Fe:3d-O:2p hybridized orbitals. From the inset of Fig. 2, the area under the pre-edge peak increases on Li doping. This may be due to the increasing concentration of Li^+(hole dopant) ions which in turn generates a fraction of Fe ions with higher oxidation states. Fe ions with higher oxidation states will have more empty Fe:3d-O:2p hybridized orbitals and therefore, the number of transitions should also increase.