



Tailoring of Optical and Electrical Properties of Transition Metal Ions-Doped ZnO-Based Diluted Magnetic Semiconductor Nanoparticles†

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To tailor the optical and electrical properties, Fe-doped ZnO diluted magnetic semiconductor nanoparticles have been synthesized *via* surfactant assisted co-precipitation technique. The single phased samples are characterized by X-ray diffraction. The optical absorption has been studied from UV-VIS spectroscopy and the optical band gap has been estimated. The variation of band gap with the doping concentration has been plotted. To study the optical properties, photoluminescence and FTIR spectroscopy have been employed. DC resistivity has been investigated with variation of temperature. Activation energy of the samples has been calculated following the Arrhenius law.

Key Words: Nanoparticles, Diluted magnetic semiconductor, Band gap tailoring, DC resistivity.

INTRODUCTION

Diluted magnetic semiconductors (DMS)¹ is semiconductors with magnetic ordering. Hence both the charge and spin of the electron can be utilized in the emerging field of spintronics and many other spin-based devices²⁻⁴. Nanostructured diluted magnetic semiconductors with ferromagnetic ordering above the room temperature are important for their promising applications in the emerging field of spintronics and other applications. In nanostructure regime doping of semiconductors with transition metal elements (3-d) such as Mn, Fe, Co, *etc.* offers a viable means of tuning the optical band gap^{1,5-8}, as well as the ferromagnetism⁹⁻¹¹. On the other hand, the ability to tailor the physical properties of nanocrystals by simply changing their size and surface functionality renders nanocrystals attractive building blocks for functional devices.

Specifically, zinc oxide (ZnO), an optically transparent II-VI semiconductor, is a well-known piezoelectric and electro-optic material with hexagonal wurtzite structure (space group P6_{3mc}), wide direct band gap ($E_g \sim 3.37$ eV), exciton binding energy of ~ 60 meV and friendly environment, has been identified as a promising host material after theoretical studies have predicted ferromagnetism above room temperature for several transition metal doped ZnO-based diluted magnetic

semiconductors^{12,13}. Thereafter, quite controversial results on transition metals doped ZnO have been reported¹⁴⁻¹⁶. Therefore, in spite of significant progress and exciting experimental results in recent years the origin of ferromagnetic ordering in diluted magnetic semiconductors nanostructures remains poorly understood.

Hence, though magnetism in transition metal-doped ZnO nanoparticles is an interesting and controversial issue to be solved, tailoring of the optical band gap has immense importance for device applications. This is the reason that we concentrate on the optical and magnetic properties of Fe-doped ZnO (*i.e.* Zn_{1-x}Fe_xO) nanocrystals.

EXPERIMENTAL

To synthesize Zn_{1-x}Fe_xO ($0 \leq x \leq 0.06$) samples (named as F0, F0.5, F1, F1.5, F2, F4 and F6 for Fe-concentration $x = 0, 0.005, 0.01, 0.015, 0.02, 0.04$ and 0.06 , respectively) we follow Liu *et al.*¹⁷. Appropriate proportions of Zn(NO₃)₂·6H₂O (99.9 % purity) and Fe(NO₃)₃·9H₂O (99.9 % purity) powders were thoroughly mixed and dissolved in water to obtain a homogeneous solution. The mixture was then poured into citric acid [C₆H₈O₇] (99.5 % purity) while stirring. The solution was dried at 80 °C to obtain xerogel and the swelled xerogel

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was completed at 130 °C. After ground, the powders were sintered at 600 °C for 10 h under air atmosphere.

Structural characterization of $Zn_{1-x}Fe_xO$ samples was performed by X-ray diffractometer (model: Miniflex-II, Rigaku, Japan) with CuK_{α} radiation ($\lambda = 1.5406 \text{ \AA}$). Fourier transmission infrared (FT-IR) spectra of the samples (as pellets with KBr) were recorded using FT-IR spectrometer (Spectrum One, Perkin Elmer Instrument, USA) in the range of 4000–400 cm^{-1} . The optical absorption spectra were measured in the range of 300–800 nm using UV-VIS spectrometer (Carry 100, Varian, USA). The photoluminescence (PL) spectra were taken by a fluorescence spectrometer (LS-45, Perkin Elmer, USA). The resistivity was measured by four probe method.

RESULTS AND DISCUSSION

The XRD pattern for $Zn_{1-x}Fe_xO$ ($0 \leq x \leq 0.06$) samples is presented in Fig. 1. The single phase samples have hexagonal wurtzite structure according to the standard JCPDS file for ZnO (JCPDS 36-1451). The mean particle size, d , of the nanoparticles are estimated using the Debye-Scherrer's equation¹⁸. Fig. 2 shows the variation of particle size with the concentration of Fe. It is observed that the average particle size is decreasing with the increase of Fe-concentration. This result is consistent with the observation of Mishra *et al.*¹⁹, which may be because of decrease in nucleation and subsequent growth rate due to higher ionic radius of Fe^{2+} (0.78 \AA) cation compared to Zn^{2+} (0.74 \AA)⁹.

Since, fourier transform infrared spectroscopy (FTIR) gives information about functional groups present in a compound, the molecular geometry and inter- or intra-molecular interactions, we have employed the FTIR to study the vibrational bands of the $Zn_{1-x}Fe_xO$ samples at room temperature. Normally the band frequencies within 1000 cm^{-1} should be attributed to the bonds between inorganic elements. Fig. 3 shows the FTIR spectra of $Zn_{1-x}Fe_xO$ samples. The most prominent band at around 460 cm^{-1} is assigned to stretching vibration of ZnO, in the octahedral coordinations which also confirms wurtzite structure formation^{20,21} of the samples. The UV-visible spectra of the samples obtained by dispersing $Zn_{1-x}Fe_xO$ nanoparticles in distilled water and using distilled water as the reference are shown shown in Fig. 4. Optical band gap (E_g) is obtained from the extrapolation of the linear portion of the $(\alpha h\nu)^2$ vs. $h\nu$ plot using Tauc's relation²². Fig. 5 shows the variation of the optical band gap (E_g) with the Fe-concentration (x). The red shift of the band gap E_g edge with incorporating Fe into ZnO has been observed and interpreted as mainly due to the $sp-d$ exchange interactions between the band electrons and the localized d -electrons of the Fe^{2+} ions substituting Zn ions. The $s-d$ and $p-d$ exchange interactions lead to a negative and a positive correction to the conduction-band and the valence-band edges, resulting in a band gap narrowing²³. Photoluminescence (PL) spectroscopy is an important tool to study the optical properties of a semiconductor. Photoluminescence intensity may be directly correlated with the defect density in a fluorescent material. The room temperature photoluminescence spectra of Fe-doped ZnO nanocrystalline samples are shown in Fig. 6. As can be seen from the figure, all the samples have shown a dominant peak around 400 nm. This peak in the UV region,

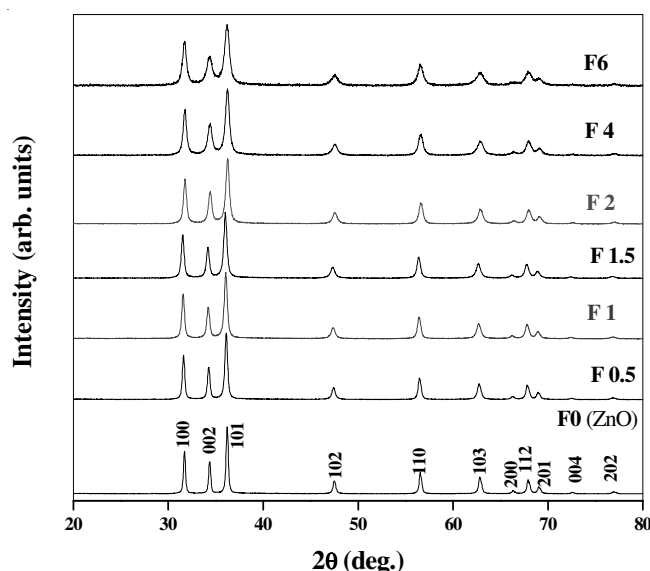


Fig. 1. X-ray Diffraction pattern of single phased $Zn_{1-x}Fe_xO$ ($0 \leq x \leq 0.08$) samples.

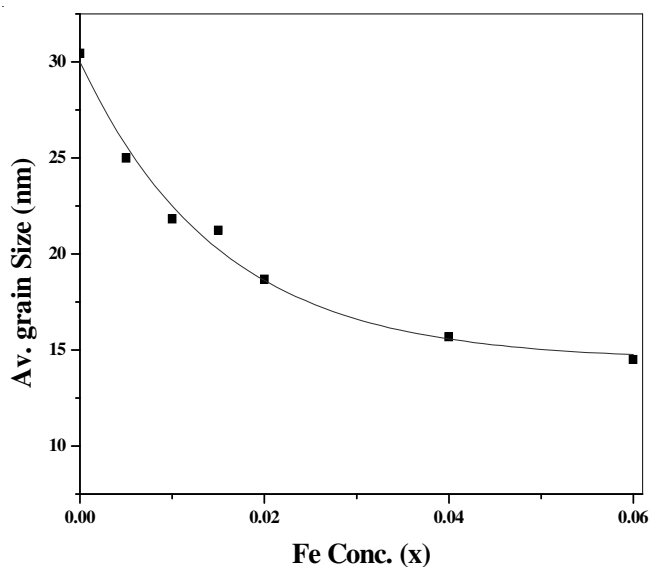


Fig. 2. Variation of average grain size with Fe-concentration (x)

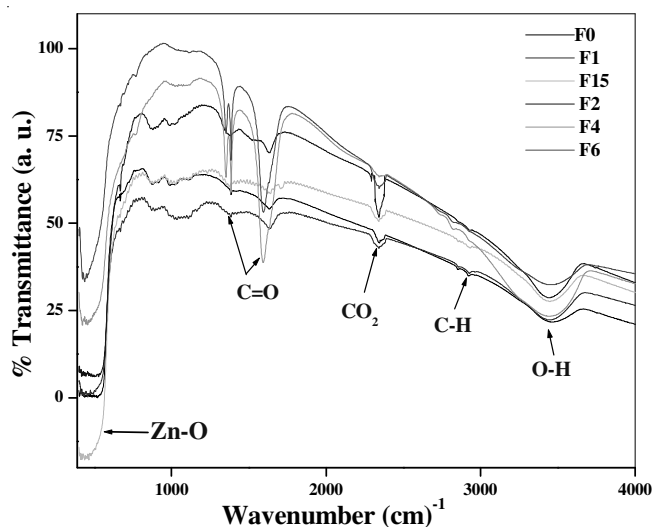


Fig. 3. FTIR spectra of $Zn_{1-x}Fe_xO$ ($0 \leq x \leq 0.06$) samples showing wurtzite structure

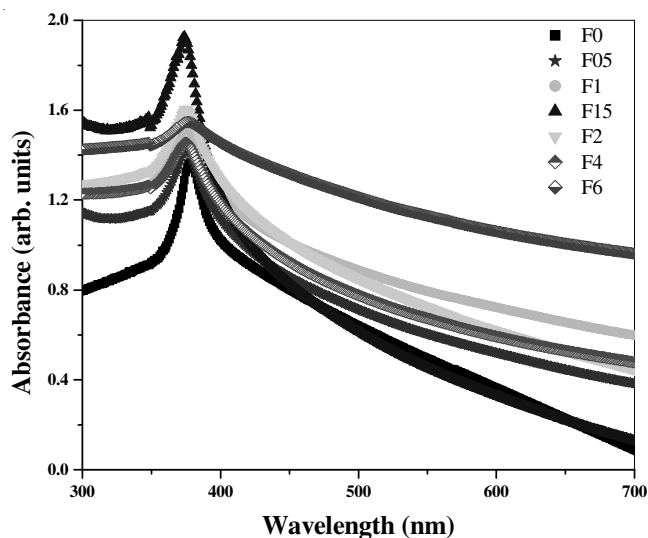


Fig. 4. Absorbance spectra of the samples

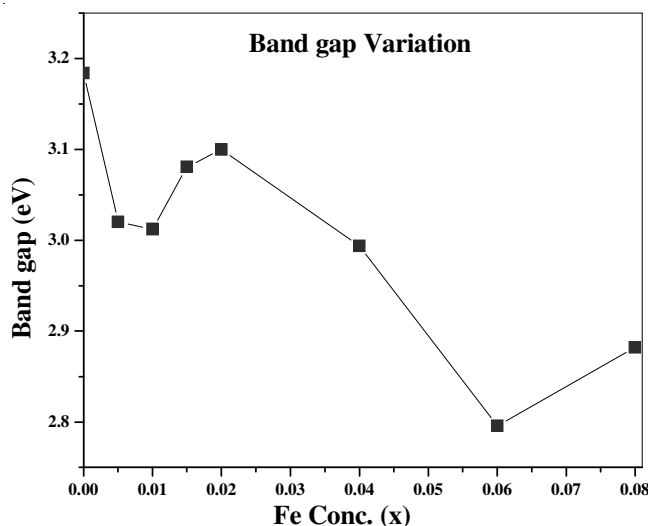
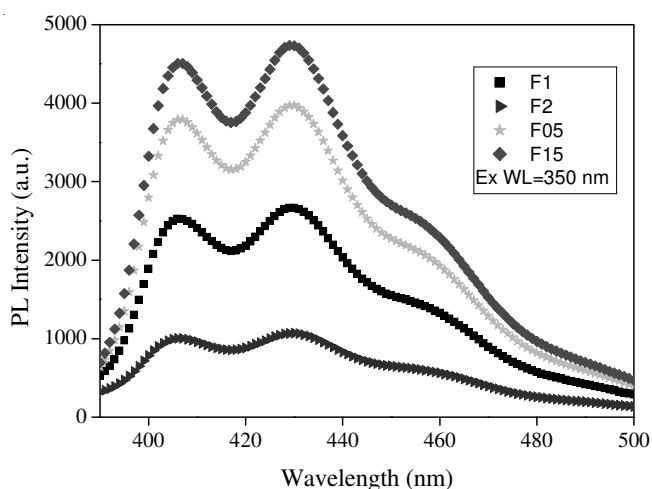
Fig. 5. Variation of the optical band gap (E_g) with the Fe-concentration (x)

Fig. 6. Room temperature photoluminescence spectra of some selected samples

originates from the recombination of free excitons through an exciton-exciton collision process, is typically observed in ZnO nanocrystalline materials and has been assigned to the near band edge emission since the energy corresponding to this

peak is almost equal to the band gap energy of bulk ZnO.²⁴ The other peaks such as the violet-blue ~ 430 nm peak is due to oxygen vacancies and the blue emission ~ 455 nm is due to negatively charged Zn vacancies. The measurement of resistivity with the variation of temperature was carried out for these samples. Fig. 7 shows the semiconducting nature of a typical sample. The activation energy (~ 0.3611 eV) of the samples were estimated from Arrhenius equation.

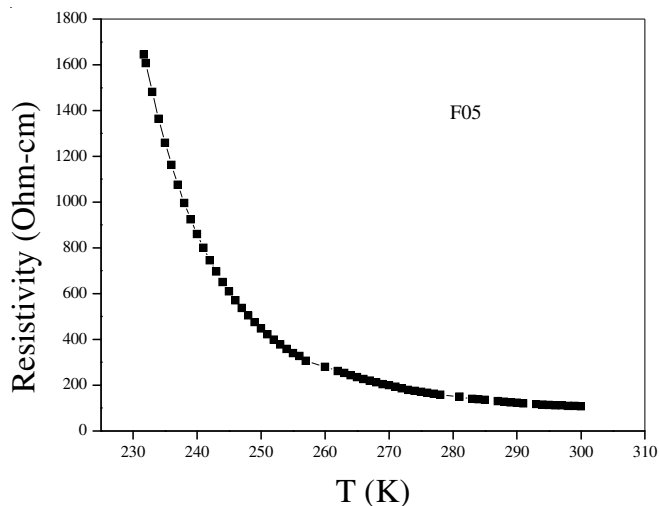


Fig. 7. Temperature variation of resistance of a typical sample F05

Conclusion

Sol-gel derived single phased Fe-doped ZnO nanocrystalline samples of wurtzite structure are characterized. Average grain size is estimated by X-ray diffraction. The average grain size of the samples decreases with increasing Fe-concentration. The wurtzite structure was confirmed by FT-IR. Photoluminescence measurements gave a red-shift of the band edge emission peak in the Fe-doped samples and showed signature of the presence of defects in the samples. The optical band gap has been estimated from UV-VIS absorption. The DC electrical conductivity has been investigated with the variation of the temperature. Activation energy of the samples has been calculated following the Arrhenius law.

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