



Magnetic Properties of Fe doped ZnO Nanosystems Synthesized by Solution Combustion Method

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Abstract

$Zn_{1-x}Fe_xO$ ($0.01 \leq x \leq 0.05$) nanosystems synthesized by a solution combustion method were characterized by different techniques. The structural characterization by XRD confirmed the phase purity of the samples. TEM measurement depicted the crystallinity of nanosystems prepared and EDS analysis conformed the elemental composition. The magnetic behaviour of the nanoparticles of ZnO with varying Fe doping concentration was investigated using a super conducting interference device (SQUID) which confirmed the ferromagnetic state for 5% Fe doped sample at room temperature. Local environment around Fe atoms has been probed by ⁵⁷Fe Mossbauer spectroscopy and measured isomer shifts confirmed the charge state of iron is Fe³⁺.

Keywords: ZnO, Fe-doping, solution combustion, mossbauer spectroscopy.

Introduction

Semiconductor nano-crystals have been extensively studied due to their size tunable optical and electrical properties and their potential applications to electronics and bio-technology¹. There is rapid growing interest in diluted magnetic semiconductors (DMS), where magnetic ions are doped into the semiconductors hosts, allowing us to design a new generation spin-tronic devices with enhanced functionalities^{2,3}. Spintronics is expected to improve upon traditional electronic and photonic devices, allowing for enhancement in the form of reduced power consumption, faster device operation, and new forms of information computation. In the recent years the researchers have paid much attention to the synthesis and characterization of II-IV semiconductor materials at nanometer scale, due to their ability to test the fundamental concepts of quantum mechanics and because of their key role in various applications such as solid-state lighting devices and sensors⁴. ZnO belongs to the list of most promising candidates for spintronics application due to friendly nature and also due to its potential as a suitable optoelectronic with a wide band gap (-3.3eV) and high exciton binding energy of 60meV⁵. Earlier first-principle electronic structure calculations suggested that TM (TM = Ti, V, Cr, Mn, Fe, Co, Ni, Cu) doped ZnO are ferromagnetic provided the TM doping produces carriers forming a partially filled spin-split impurity band in the nanoparticle form⁶⁻¹¹. The effect of Fe doping as a magnetism activator and as a compensator of n-type material is of great importance for II-VI semiconductors¹²⁻¹³. Earlier Fe doped ZnO nanosystems have been prepared by co-precipitation method^{4,9}, solid state method¹⁴, and sol-gel technique¹⁵. We have here presented a simple technique to synthesize ZnO: Fe nanoparticles.

Material and Methods

All materials used in this study were of analytical grade. $Zn_{1-x}Fe_xO$ ($0.01 \leq x \leq 0.05$) nanocrystalline samples with different fraction of iron were prepared by solution combustion of aqueous solutions containing required amounts of the corresponding metal nitrates, zinc nitrate, iron nitrate and glycine¹⁶. By merely changing the temperature conditions of previously described synthesis technique, O/F ratio was kept two using total oxidizing and reducing valencies of the oxidizer and the fuel. The resulting mixture was allowed to heat at 100^oC with constant stirring. Finally the dried powder was kept in a muffle furnace at temperature of 400±20^oC for 4 hours. The obtained product was yellowish in color and fluffy.

X-Ray powder diffraction analysis was conducted on XPERT-PRO Diffractometer (XRD) using Cu K α radiation. The phase structure of nano ferrites was analyzed by XRD. Simulation of crystal structure based on the measured X-ray diffraction (XRD) data was performed using Rietveld crystal structure refinement software FULLPROF 2007.

Crystal structure, morphology and quantitative composition of the nanocrystals were obtained using a transmission electron microscope (model PHILIPS CM 200) operated at 200KV accelerating voltage by dissolving the synthesized powder sample in the ethanol. Magnetization measurements were carried out using a super conducting interference device (SQUID) upto a field of 5000 Oe. Mössbauer spectra were recorded by using ⁵⁷Fe spectroscopy using cobalt as radioactive source with pc-based spectrometer equipped with weissel velocity at the room temperature and the experimental results were fitted with the NORMOS-SITE program.

Results and Discussion

The XRD patterns of the Fe doped ZnO nano-crystalline samples with different atomic fraction of dopant ion ($0 \leq x \leq 0.05$) which are denoted hence onwards as ZF, ZF1, ZF2, ZF3, ZF4, ZF5 respectively as shown in figure-1. It reveals that, there is no change in the wurtzite structure of ZnO after Fe doping. The average particle size calculated is found to be in the range of 10-21nm. Since the difference in radii between Zn^{2+} (0.60 \AA) and Fe^{3+} (0.63 \AA) is considerable, significant changes in the lattice constants are expected for Fe doped samples. The crystal structure of the sample ZF1 at room temperature is determined to be wurtzite structure of $P6_3mc$ with its lattice constant $a_0 = 3.253 \text{ \AA}$ and $c_0 = 5.210 \text{ \AA}$ by Rietveld refinement (figure-2). The determined Bragg constant R_B and R_F have values 2.43% and 1.93% respectively. The lattice constant a_0 is found to increase from 3.250 to 3.253 \AA and c_0 is found to decrease from 5.211 to 5.210 \AA with increase of Fe concentration.

Low resolution Transmission electron micrographs of the sample ZF1 is presented in figure-3 (a-b). The particles are more or less spherical having a distribution of size between 8-21 nm. The average particle size obtained matches well with size estimated from XRD. The elemental composition of the sample was checked by energy dispersive X-ray analysis (figure-3(c)), which confirms the presence of only Zn, Fe and O in the sample. The selected area electron diffraction (SAED) pattern shows the crystalline nature of the sample (figure-3(d)).

Figure-4 shows the results of the M-H measurements of the samples ZF1 to ZF5 at room temperature. A clear hysteresis loop has been observed for sample ZF5. From the loop remanant magnetization and the coercive field were estimated to be 0.002 emu/g and 162 Oe, where it is 0.0002 emu/g and 5 Oe (bulk sample) under the application of field of 20,000 Oe but the saturation didn't take place¹⁰. Whereas M_r and H_c has found to be 0.008 and 98 Oe (nano-particles) by applying high field upto 20,000 Oe⁹. The narrow hysteresis implies a small amount of dissipated energy in repeatedly reversing the magnetization which is important for quick magnetization and demagnetization of the samples synthesized. The ferromagnetic behaviour can be attributed the presence of small magnetic dipoles located at the surface of nanocrystals, which interacts with their nearest neighbours inside the crystal. As a result of which the interchange energy in these magnetic dipoles making other neighbouring dipoles oriented in the same direction, so the population of magnetic dipoles oriented in the same direction will increase at the surface. Thus, the sum of the total amount of dipoles oriented along the same direction will increase subsequently. In short, the crystal surface will be usually more magnetically oriented. Since the particle size play a crucial role in magnetism, so it can be expected for zf1 that somekind of superparamagnetic character (almost zero coercive field) exists in the sample which is expected because of smaller size of particles (less than 10 nm from TEM). As the size of particles increase this superparamagnetic character begin to cease and paramagnetic type of character appears. However it is still

unclear what factor is playing the role for ferromagnetic state for zf5 at room temperature.

Temperature dependent magnetization $[M(T)]$ curves in field cooled (FC) and zero field (ZFC) conditions in the presence of a dc magnetic field of 100 Oe for ZF5 sample is shown in figure-5. The outward concave nature of magnetization curve confirms the low carrier density and the localized nature of the carrier as well. The strong irreversibility persists even above the room temperature, signifying the surface effect of nanoparticles. However the spectra for ZF1 is quiet typical as supported by M-H spectra.

Figure-6 shows the Mossbauer spectra for all the samples for ZF1-ZF5 shows doublet for all cases. Isomer shift (IS) ranges from 0.09 mm/s to 0.12 mm/s, and Quadrupole splitting (QS) from .68 mm/s to 0.90 mm/s indicating Fe^{3+} nature of the Fe atom in ZnO. No signature of Fe^{2+} has been found in any of these spectrum. Similar kind of behavior had been found in Fe doped ZnO nanoparticles synthesized in using chemical pyrophoric reaction method with IS ~ 0.56 mm/s and QS ~ 0.73 mm/s reported recently¹⁷. Whereas coexistences of Fe^{3+} (QS ~ 0.81 mm/s) and Fe^{2+} (QS ~ 2.00 mm/s) state has been found in the Fe-doped ZnO polycrystalline sample prepared by solid state reaction method¹⁴. Lower value of IS in our case indicates lower s electron density in the sample. The increasing QS indicate the enhancement of electric field gradient around Fe probe atoms as more Fe atoms are introduced in the ZnO lattice. In a Fe-doped ZnO system, the valence state of Fe is expected to be +2 if Fe simply substitutes for Zn. Fe^{3+} nature may be due to the presence of nearby cationic vacancies at the substitutional sites, which trigger the conversion of Fe^{2+} to Fe^{3+} to neutralize the charge imbalance. In view of this, the substitution of Fe^{3+} for Zn^{2+} Carrier-mediated ferromagnetism has a possibility to explain the observed magnetic behavior in Fe doped ZnO. The theory based on interaction between magnetic polarons is another candidate. Disorder defects may also be an important factor for the observed ferromagnetism in $Zn_{1-x}Fe_xO$ nanoparticles. Formation of Fe cluster can be other candidate. A detailed research is required on this problem to clarify the doubt.

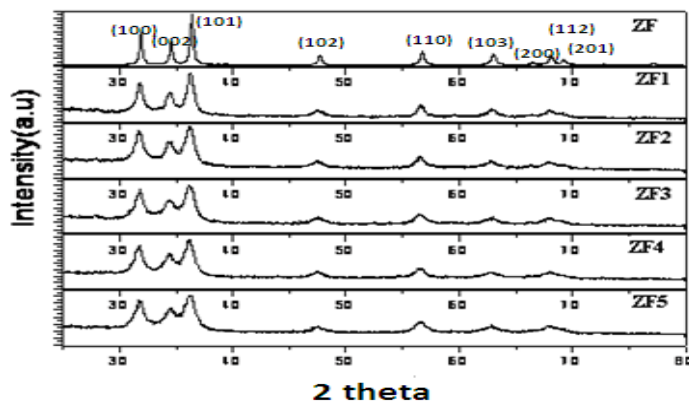


Figure-1
 XRD patterns of ZF, ZF1, ZF2, ZF3, ZF4 and ZF5

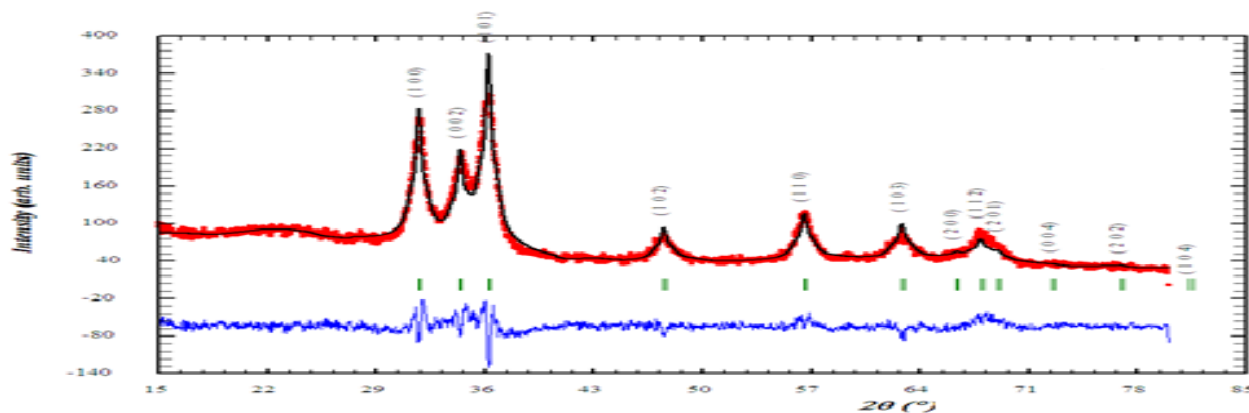


Figure-2
 Refined XRD pattern of ZF1

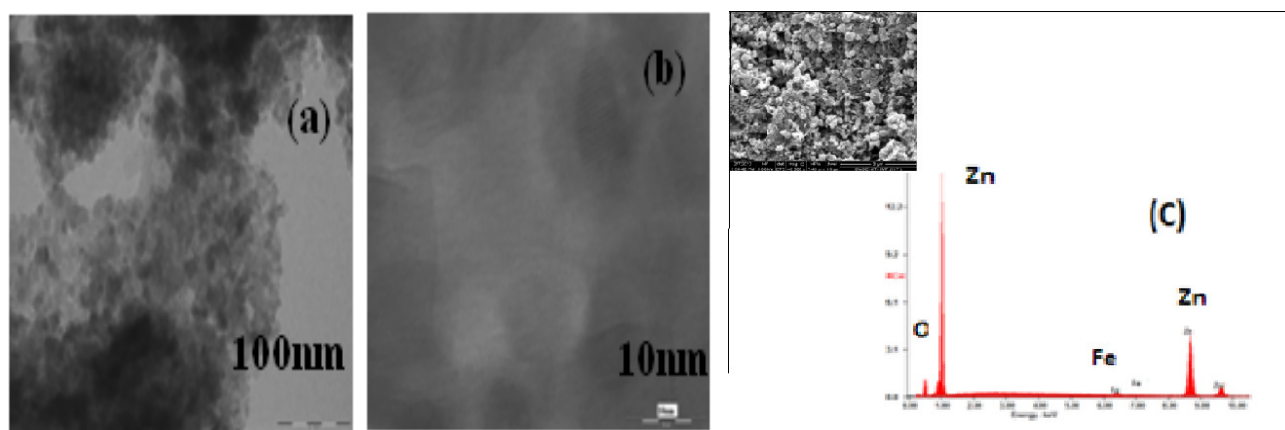


Figure-3
 (a-b) TEM images of ZF1, (c) EDS spectrum of ZF1, (d) SAED pattern of ZF1sample

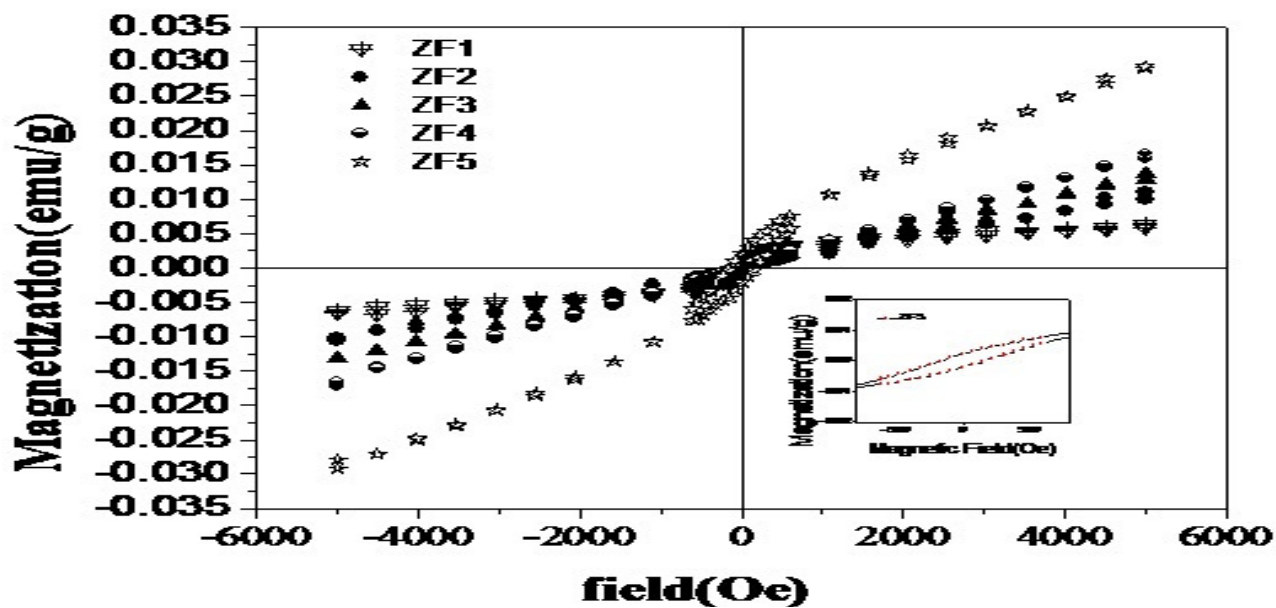


Figure-4
 (a) Magnetization spectras of ZF1, ZF2, ZF3, ZF4 and ZF5, (b) of ZF1 near origin

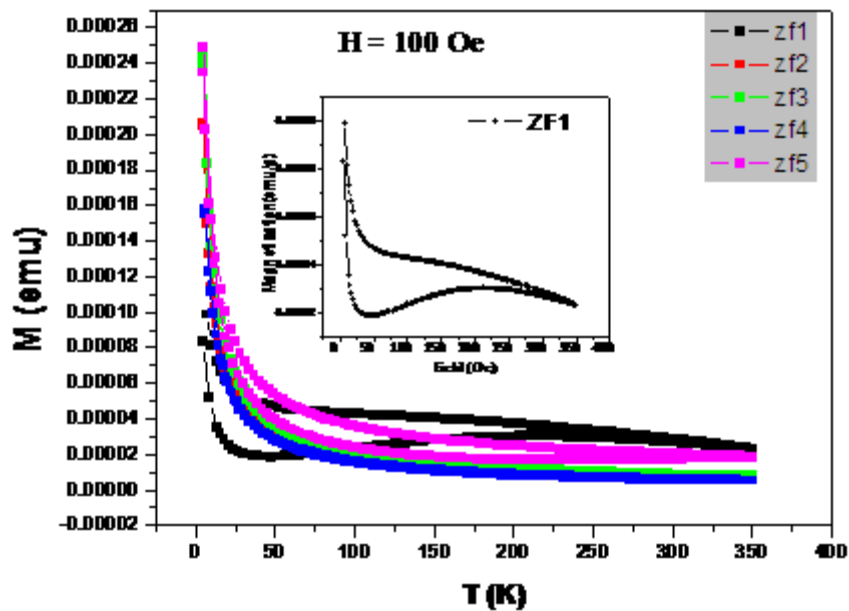


Figure-5
 FC and ZFC curve of ZF5, the inset displays curve for ZF1

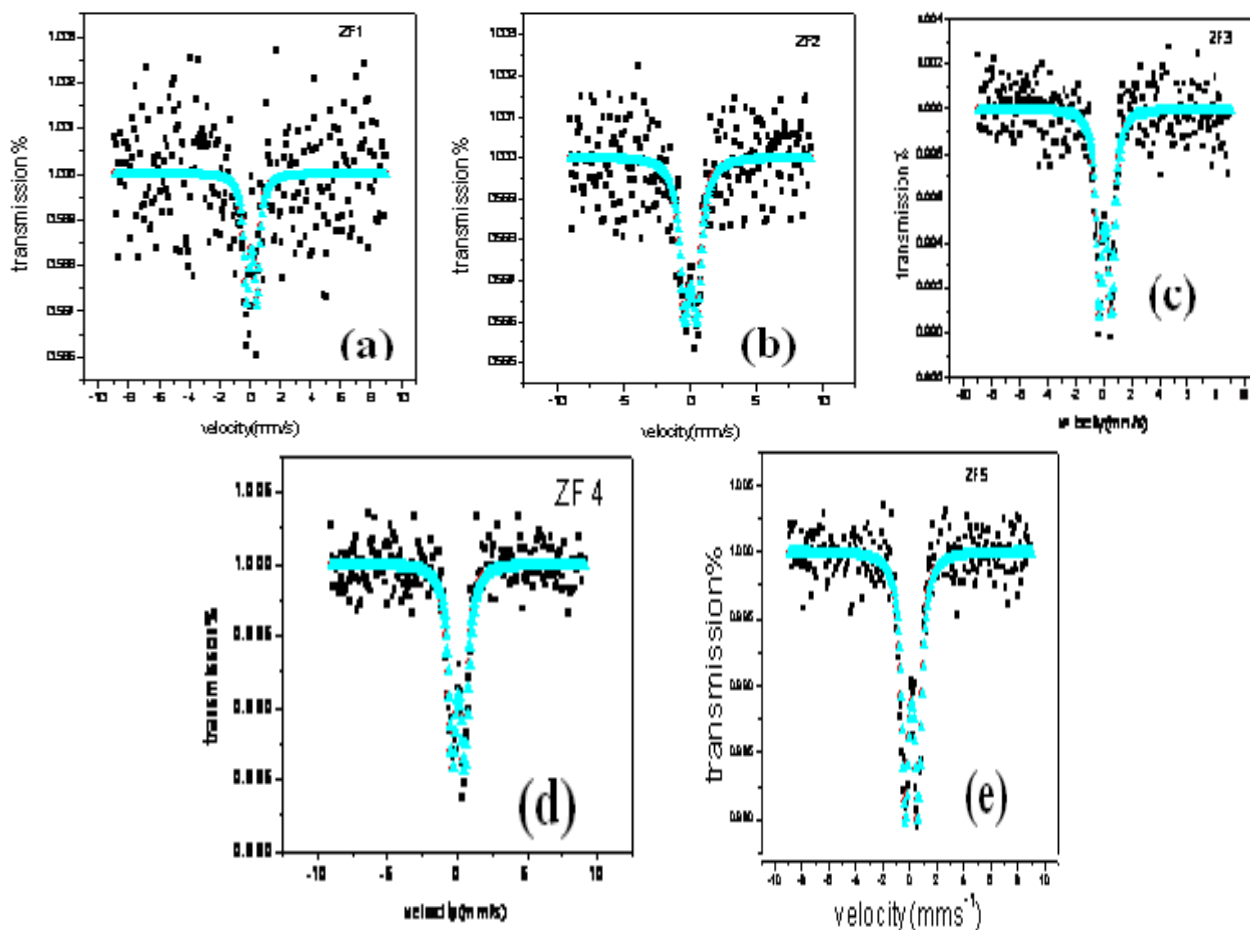


Figure-6
 Mossbauer spectra of $Zn_{1-x}Fe_xO$ nanoparticles (ZF0, ZF1, ZF2, ZF3, ZF4 and ZF5)

Conclusion

We have successfully synthesized Fe doped ZnO nanosystems by solution combustion method using glycine as fuel. XRD spectra for all samples shows the wurtzite structure. TEM and SAED measurements confirmed the crystallinity and particle size determined is in good agreement with those calculated from XRD. EDS analysis showed that elemental composition contains only Fe, Zn and O. M-H studies of the samples confirmed the ferromagnetic state for the 5% Fe doped sample. Measured isomer shifts confirmed the Fe³⁺ charge state of iron using Mossbauer spectroscopy.

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References

1. Taguchi S., Tayagaki T. and Kanemitsu Y., Luminescence and magnetic properties of Co doped ZnO nanocrystals Mater, *Sci. Eng.*, **6**, 012029 (2009)
2. Furdyna J.K., Diluted magnetic semiconductors, *J.Appl. Phys.*, **64**, R29 (1988)
3. Ohno H., Science Making Nonmagnetic Semiconductors Ferromagnetic, **281**, 951 (1998)
4. Nakamura S., *Science*, **281**, 956 (1998)
5. Ezenwa I.A., Synthesis and optical characterization of zinc oxide thin film, *Research Journal of Chemical Sciences*, **2**(3), 26 (2012)
6. Sato K. and Yoshida H.K., Material Design for Transparent Ferromagnets with ZnO-Based Magnetic Semiconductors, *Jpn. J. Appl. Phys.*, **39**, L555 (2000)
7. K. Sato and H. K. Yoshida, Stabilization of Ferromagnetic States by Electron Doping in Fe-, Co- or Ni-Doped ZnO, *Jpn. J. Appl. Phys.*, **40**, L334 (2001)
8. Kodama R.H., Berkowitz A.E., McNiff Jr E.J. and Foner S., Surface Spin Disorder in NiFe₂O₄ Nanoparticles, *Phys. Rev.Lett.* **77**, 394 (1996)
9. Sharma P.K., Dutta R.K., Pandey A.C., Layek S. and Verma H.C., Effect of Iron Doping Concentration on Magnetic Properties of ZnO nanoparticles, *JMMM*, **321**, 2587 (2009)
10. Kumar S., Gautam S., Kim Y.J., Koo B.H., Chae K.H., Lee C.G., Ferromagnetism in Fe doped ZnO synthesized by co-precipitation method, *J.Ceram.Soc.Japan*, **117**(5), 616 (2009)
11. Diet T., Ohno H., Matsukura F., Cibert J. and Ferrand D., Science Zener Model Description of Ferromagnetism in Zinc-Blende Magnetic Semiconductors, **287**, 1019 (2000)
12. Hua-Wei Zhang, Zhi-Ren Wei, Zhi-Qiang Li and Guo-Yi Dong, Room-temperature ferromagnetism in Fe-doped, Fe- and Cu-codoped ZnO diluted magnetic semiconductor, *Material Letters*, **61** 3605 (2007)
13. Park S.L., Ahn G.Y. and Kim C.S., Interpretation of ferromagnetic Fe doped ZnO by Mössbauer spectroscopy, *J.Appl.Phys.*, **101**, 09H113 (2007)
14. Ahn G.Y., Park S.I., Shim I.B. and Kim C.S., Mössbauer studies of ferromagnetism in Fe-doped ZnO magnetic semiconductor, *J.Magn.Mater.*, **282**, 166 (2004)
15. Liu H., Yang J., Zhang Y., Yang L., Wei M. and Ding X., Structure and magnetic properties of Fe-doped ZnO prepared by the sol-gel method, *J. Phys.: Condens. Matter*, **21** 145803 (2009)
16. Dinesha M.L., Jayanna H.S., Ashoka S. and Chandrappa G.T., Temperature dependent electrical conductivity of Fe doped ZnO nanoparticles prepared by solution combustion method, *Journal of Alloys and Compounds*, **485**, 538-541 (2009)
17. Karmakar D., Mandal S.K., Kadam R.M., Paulose P.L., Rajarajan A.K., Nath T.K., Das A.K., Dasgupta I., and Das G.P., *Phys. Rev. B.*, **75**, 144404 (2007)