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Dilute Magnetic Semiconductor Fe Doped ZnO and CeO_2 Nano-crystals

Pushmita Bhattacharya

Department of Science & Humanities, Technique Polytechnic Institute, Hooghly, West Bengal, India
E-mail: bhattacharyapushmita@gmail.com

Abstract—*This paper consist information about ferromagnetism observed in Fe doped ZnO Nano crystal and Fe doped CeO_2 Nano crystal. This sort of diluted magnetic semiconductor forms the major focus for research. Doped magnetic semiconductors exhibit high Curie temperature that scales with the p-type charge carriers. Fe doped ZnO Nano crystals are structurally, vibrational, magnetically characterized and synthesized by using X-ray diffraction (XRD), transmission electron microscopy (TEM) & Raman Spectroscopy. Here the M-H curves exhibit ferromagnetism with slight paramagnetic behaviour with transition temperature equal to 464 K.Fe doped CeO_2 Nano crystals are successfully synthesized by XRD and is structurally characterized by TEM images. Here the M-H curves exhibit a weak ferromagnetic behaviour at room temperature. Within the framework of this paper, the EPR and Mossbauer indicates the presence of Fe in its both valence states i.e. Fe^{+2} & Fe^{+3}.The existence of Fe^{+3} is due to hole doping in the system created by the Zn^{+2} vacancies. This hole doping has a strong impact in stabilizing ferromagnetism in Fe doped ZnO and are shown in this paper.*

1. INTRODUCTION

According to earlier studies,Mn doped GaAs system has Curie temperature T_c 110K & that for Mn doped ZnTe & CdTe systems has Curie temperature only of order of few Kelvin. System having high Curie temperature at room temperature is under research to understand the origin of ferromagnetism in doped systems.Local spin density approximation(LSDA) suggests that ZnO is the most suitable material for spintronics application due to its high exciton binding energy of 60meV having a wide band gap of 3.3eV.For designing new spintronics devices,transition metals are doped with semiconducting oxides like ZnO,SnO_2 & TiO_2 to obtain 100% spin polarization & ferromagnetism behavior at room temperature.

In Fe doped ZnO system, the nature of magnetism has been studied both experimentally & theoretically. In Fe doped ZnO system, there are few evidences of ferromagnetism except with co-doping. This co-doping are associated with the formation of nonstoichiometric spinel ferrite phases. Recent investigations reveal the magnetic anisotropy of the dopant cation to be a signature of intrinsic ferromagnetism in dilute magnetic oxide materials. The initial works of Venkatesan et.al, suggests that Fe^{+2} doped ZnO systems are also highly anisotropic in nature. Due to its such nature, there is always possibility of obtaining high temperature ferromagnetism in Fe doped ZnO system which is essential for the development of high density magnetic storage media with Nano sized constituent particles.My present work concentrates on preparation of Fe doped ZnO system & its structural characterization with XRD & TEM,thereby producing a clear Nano crystal phase without any impurity phase. Magnetisation measurements show T_c=464K in such samples. Along with EPR & Mossbauer studies on the same sample reveal % of aligned moments & valence states of the transition metal ions.

2. STRUCTURAL CHARACTERIZATION

In this research paper, Nano crystalline 12% Fe doped ZnO samples is prepared by chemical pyrophoric reaction method. Depending upon the % doping, $Zn(NO_3)_2.6H_2O$ with $Fe(NO_3)_3.9H_2O$ are made to dissolve in distilled water then heated at 190ºC with constant stirring.

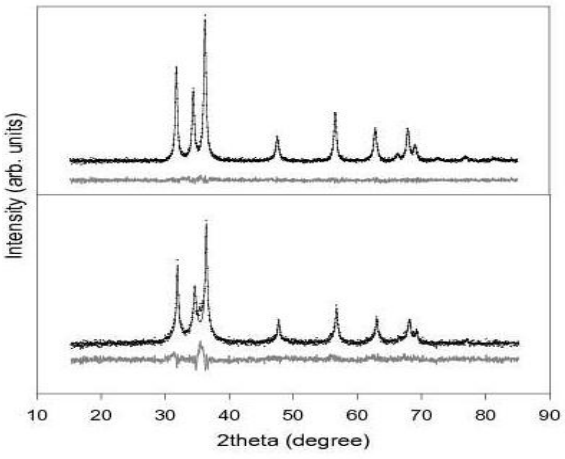

Fig. 1: Powder X-Ray Diffraction patterns for Pure ZnO & 12 % Fe Doped ZnO

To it tri- ethanol amine is added in 4:1 ratio with the metal ions to precipitate the metal ions with the amine.$HNO_3$is added to dissolve the precipitate forming a clear solution that is allowed to evaporate.

After evaporation, the powder obtained was grinded then calcined 15hr in air at 390 ºC.TEM images suggests that powder samples are Nano crystalline with size varying from 2.5nm to 30nm..This structural characterization is done by Shimazdu X-ray diffract meter with Cu-Kα radiation and high resolution transmission electron microscope of 200 kV.Powder X-ray diffraction patterns [3] for pure ZnO & 12% Fe doped ZnO are shown in (Fig. 1).

Owing to Nano crystal size, the XRD peaks of the doped sample are somewhat flat. Here XRD for four different composition of $ZnO_{1-x}(Fe_2O_3)_x$ where x=0.00,0.04,0.10,0.12 are conducted(Fig. 2).

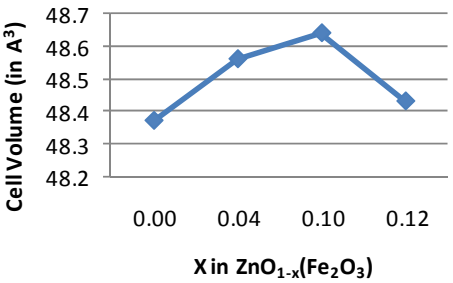

Fig. 2: Cell Volume vs. Fe Concentration

The dominant diffraction peaks lead to the hexagonal wurtzite structure. On increasing the% of Fe,the X-ray peak widths increases resulting in peaks lead to the hexagonal wurtzite structure. On increasing the% of Fe,the X-ray peak widths increases resulting in decrease in crystalline correlation. For Fe doped CeO_2, the XRD data were calculated using Panalytical X'pert MRD diffractometer(with CuKα radiation at 40kV,40mA).XRD results show that samples are in one phase identical to cubic CeO_2(Fig. 3).

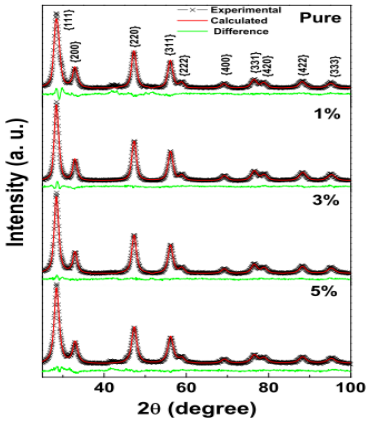

Fig. 3: Powder X-ray diffraction patterns for pure CeO_2 & Fe doped CeO_2[1]

For Fe doped ZnO, the low resolution TEM micrograph suggests particle diameter ranging from 2.5 to 30nm & high resolution TEM micrograph reveals all the nanoparticles are single crystalline nature and free from lattice defects. Selected Area diffraction Patterns (SAD) of each nanoparticle in the sample also indicates the single crystalline nature of each nanoparticle confirming the wurtzite phase.

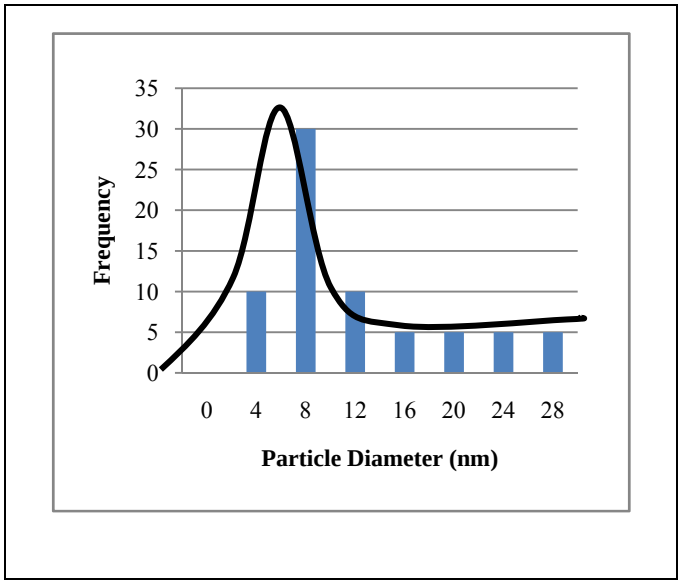

Fig. 4: Particle Diameter of Fe doped ZnO Nano Crystal

Fig. 4 gives information about the average diameter of nanoparticle to be about 8 nm. In order to analyse the particle size for Fe doped CeO_2 samples [1] TEM is employed that reveals the crystalline nature with spherical shape and average size of 9nm (Fig. 5)

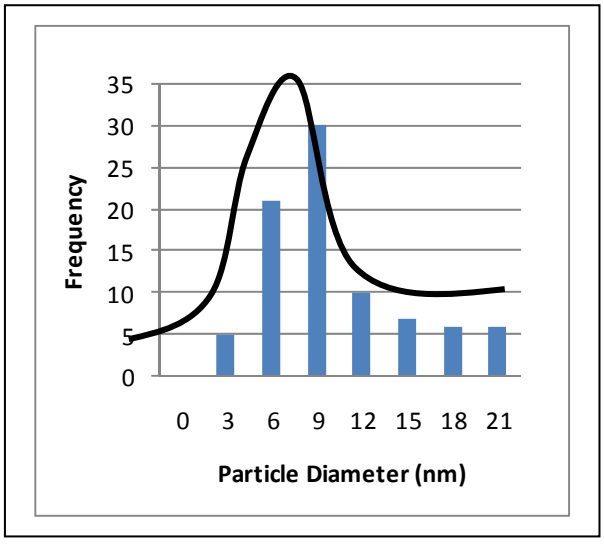

Fig. 5: Particle Diameter of Fe doped CeO2 Nano Crystal

3. MAGNETIC MEASUREMENTS

For obtaining ferromagnetism at room temperature for 12% Fe doped ZnO Nano crystals the magnetic measurements were carried out using a Quantum design MPMS SQUID Magnetometer & a Vibrating sample magnetometer(VSM).Temperature depending parameter of magnetization was observed both in ZFC(Zero-field cooled) and FC(Field cooled) conditions for the sample having four different field values like H=100Oe.1000Oe,2000Oe,5000Oe that reveals the system will be weakly ferromagnetic at room temperature & the ZFC curves have a cusp that shifts towards low temperature with the increase in applied field due to super paramagnetic behavior or field-induced cross- over from ferromagnetic(FM) to Spin- Glass(SG) state[3]. The fact that the magnetic behavior is weakly ferromagnetic & not super paramagnetic, the M vs. H hysteresis loops as presented in the experiment represents a well-defined hysteresis at room temperature with field values of 95.8Oe and magnetization of 0.0866emu/gm. The corresponding values at 10K are 355.6 & 0.355 emu/gm. In, the low temperature loops for 2K,10K,25K, the paramagnetic contribution was found to be high due to presence of disordered Fe^{+3} spins in the Nano crystal and at 300K it decreases. Saturation in magnetization was found at 2K and achieved at very high field. Magnetic moment per Fe at 2K is $\sqcup$ 1.18$\mu\beta$ and that value decreases down to 0.08 $\mu\beta$ at room temperature. This data supports the weakly ferromagnetic nature of the nanoparticle. For $Ce_{1-x}Fe_xO_2$ samples, the M vs H curves with x=0.01 & 0.03 shows the presence of a weak ferromagnetic behaviour & not super paramagnetic behaviour. It is also observed[1] that $Ce_{0.99}Fe_{0.01}O_2$ sample presents higher magnetization than in $Ce_{0.97}Fe_{0.03}O_2$ sample. This observation suggests the formation of ferromagnetic clusters due to non- homogenous Fe ions in CeO_2 latice.

4. EPR MEASUREMENTS

EPR is used to observe the origin & nature of ferromagnetism in a nanoparticle. Temperature dependent changes in the line width, line position & integrated intensity provides information about the range of magnetic ordering, spin fluctuations, spin glass behavior and the oxidation state of the dopant cation involved in the spin coupling.

5. MOSSBAUER SPECTROSCOPY

To determine the oxidation state of Fe in ZnO lattice.,

Mossbauer spectroscopy is recorded for ^{57}Fe sample using a conventional constant acceleration velocity drive. Temperature is maintained between 4K-300K using a flow cryostat continuously.[3] Record of these spectra is done in transmission geometry keeping $^{57}Co(Rh)$ as source. The Mossbauer spectra in the aforesaid range of temperature reveal the presence of uncoupled Fe^{+3} that indicate paramagnetic doublet's existence. This doublet becomes more & more asymmetric with decrease in temperature due to change in magnetic environment of the sample. The low temperature Mossbauer data for 12K indicates the presence of quadrupole splitting [3]for both Fe^{+3} & Fe^{+2} whose values are 0.73mm/s & 1.4mm/s respectively. Here Fe^{+2} signals is difficult due to its very short spin-lattice relaxation time. Thus Mossbauer measurements give information about the existence of both Fe^{+3} & Fe^{+2} within the sample.

6. CONCLUSIONS

Here Fe doped ZnO Nano crystals & Fe doped ZnO Nano crystals are successfully synthesized & structurally characterized by XRD & TEM images. The magnetic measurements showed the presence of ferromagnetic behavior at room temperature along with the formation of magnetic clusters. The average particle for CeO_2 Nano crystals is 9 nm whereas that of ZnO is 8nm.An EPR &. Mőssbauer measurement indicates the existence of both valence state Fe^{+3}& Fe^{+2}.

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