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Iron doped ZnO nanocrystals and their structural, optical and magnetic behavior

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ABSTRACT

This present investigation deals with the synthesis of Fe doped ZnO nanocrystals by chemical method of microwave irradiation technique and the special attention is given to structural, optical and magnetic behavior. The X-ray diffraction analysis confirmed the single phase ZnO wurtzite structure without any impurity or secondary phase formation. The shifting of [1 0 1] peak in the higher angle side is due to the smaller cation of Fe^{3+} than Zn leads to the change in lattice parameters. The formation of metal oxide bond at 450 cm^{-1} is confirmed by Fourier transform infrared spectrum and the Raman modes ~324 cm^{-1}, 432 cm^{-1} and 564 cm^{-1} correspond to ZnO is identified by micro Raman spectrum. The band gap energy of the samples increases with the increase of Fe concentration due to the increase of crystal size. The ZFC–FC curve confirms the absence of Curie temperature below 350 K. The room temperature magnetization measurement shows the paramagnetic behavior in all samples.

1. Introduction

Diluted magnetic semiconductors (DMSs) produced by doping very small amount of magnetic impurities in semiconductors have currently attracted much attention as materials for spintronic applications [1]. Unlike the diluted magnetic semiconductors based on III–V or II–VI semiconductors showing ferromagnetism only at very low temperatures, these oxide based DMSs exhibit ferromagnetism at higher temperature and even well above room temperature. Development of room temperature ferromagnetic semiconductor materials is essential for advancing spintronics technology. These materials would open prospects for room temperature performance of spin-injection devices. They are also optically transparent enabling them to be promising candidates for magneto-opto-electronic applications. However, it is also important to study ferromagnetic properties in nanocrystalline materials as they will be potentially useful for ferrofluids, magnetic recording, and biomedical applications. Some reports showed room temperature FM in the absence of secondary phases or cobalt clusters [2–4] while some showed no ferromagnetism at room temperature [5] and some showed that the observed FM originates from metallic cobalt clusters [6], Wi et al. [7] reported that for ZnO systems with V, Cr, Fe, Co, and Ni doping, ferromagnetism can be achieved without any need of carriers-doping. Theoretical studies show that the ferromagnetism comes from inhomogeneous distribution of magnetic elements in a host lattice [8], shallow donor electrons [9], strong near range magnetic interaction between cations, a long-range coupling between cation and oxygen vacancy pairs [10]. Sample morphology and intrinsic defects are crucial for magnetic behavior. The role of oxygen ion vacancy is important in magnetic state; annealing in vacuum, changes the paramagnetic state to ferromagnetic state, due to increase in oxygen ion vacancy in the crystal system [10]. Most of the reports have contradicting results and there is no theory was given to explain the origin of ferromagnetism and it is still unclear.

2. Materials and method

In this work, we report the synthesis and characterization of Fe doped ZnO using simple method of microwave irradiation technique with particle size ~40 nm. Zinc acetate dihydrate, $Zn(Ac)_2{\cdot}2H_2O$ (99.9%, HPLC Co.), Ferric Chloride hexahydrate $Fecl_3{\cdot}6H_2O$, (99.9% HPLC Co.), Urea, NH_2 CO NH_2 (99.9% HPLC Co.) and ethylene glycol (99.9% HPLC Co.) were used as received, without further purification. In a typical experiment, $(1-x)$ mole% of $Zn(Ac)_2{\cdot}2H_2O$ and x mole% of $FeCl_3{\cdot}6H_2O$ were dissolved in 50 mL of ethylene glycol under vigorous stirring at room temperature at 10 min a clear transparent solution was obtained. The solution was

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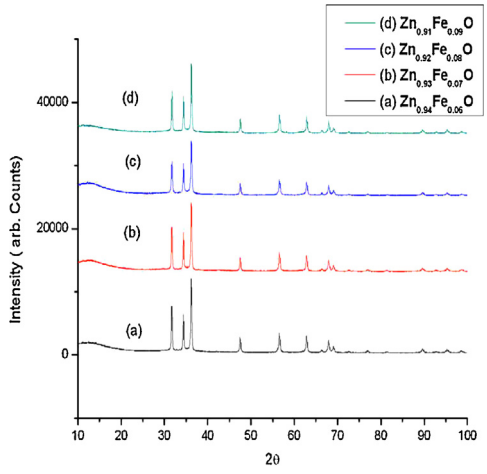

Fig. 1. XRD pattern of Zn1-xFexO ($0.06 \leq x \leq 0.09$) samples.

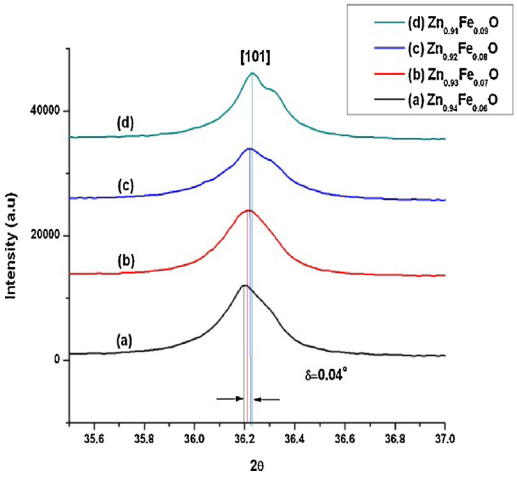

Fig. 2. Peak shifting in the diffraction peaks of Zn1-xFexO ($0.06 \leq x \leq 0.09$).

kept into a domestic microwave oven of 500 W, in which, due to the micro wave heating, the solvents were allowed to evaporate until the precipitates were formed. The precipitates were carefully collected and washed with deionized water several times to remove the ions possibly remaining in the final products, and then washed with acetone a few times to remove the water content present in the product. The advantages of microwave irradiation technique are that it is easiest, energy-saving, and quick method for large scale production of nanomaterials. The final dry powdered samples were further examined by the following measurements.

The X-ray diffraction spectrometer (XRD) and transmission electron microscope (TEM) were used to examine phase segregation and size of the grown crystals. The surface analysis were performed by Atomic force microscope (AFM). FTIR spectral analysis were used to find the formation of metal oxide and other functional groups present in the sample. The Micro-Raman spectroscopy was employed to find the vibrational mode present in the sample at room temperature. The optical behavior of the samples was examined by UV–vis spectrophotometer in the wavelength range of 200–800 nm. Vibrating sample magnetometer (VSM) is employed to measure the magnetic properties.

3. Result and discussion

The XRD pattern of $Zn_{1-x}Fe_xO$ ($0.06 \leq x \leq 0.09$) samples shown in Fig. 1 exhibits single phase ZnO wurtzite structure without any impurity phase. The decrease of lattice parameters indicates the substitution of Fe ions in Zn site of ZnO wurtizite structure. The significant increase in intensity and the sharpening of diffraction peaks with increasing Fe concentration indicate that the size of the nanoparticles increases with increasing Fe concentration. This is due to distortion in the host ZnO lattice, the introduction of foreign impurity i.e. Fe doping or due to lattice strain. However, it is clear from Fig. 2 that the diffraction peak shifted toward the higher angle indicating an increase in strain in the NCs. This might be due to the

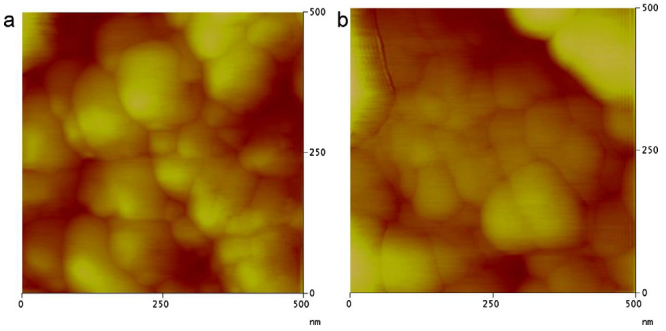

Fig. 3. (a) & (b) AFM images of 6 and 9 at % Fe doped ZnO nanocrystals.

valence state of Fe ions in ZnO. About 0.04° peak shift is observed for the successive Fe doped ZnO NCs indicating that the Zn cations have been successfully substituted with smaller cations of Fe^{3+} which is in good agreement with decrease in the lattice parameters. The average crystallite sizes were calculated from Debye–Scherer's formula (Eq. (1)) with respect to the [1 0 1] peak and are tabulated with respect to the dopant concentration shown in Table 1 and are in the range between 26 and 35 nm [11].

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

The surface microstructure and morphology of the samples were studied by atomic force microscopy (AFM). Fig. 3(a) and (b) shows the two dimensional images of 6 and 9 at% Fe doped ZnO crystals clearly indicate the existence of polycrystalline nature. The crystals are in regular geometrical shape with random distribution. It appears that the incorporation of cobalt atoms does not significantly affect the microstructure and surface morphology. It may be noted that all the crystals have an rms roughness in the range of 12–35 nm and have an average grain size in the range of 30–70 nm.

Table 1
Average crystallite sizes w.r.to dopant concentrations of Fe in ZnO.

Lattice parameters (Å)	Pure ZnO (Å) pdf 89–1397	Different mole% of Fe doped ZnO			
		6%	7%	8%	9%
a (Å)	3.253	3.2520 ± 0.0031	3.2508 ± 0.0031	3.2504 ± 0.0026	3.2499 ± 0.0021
c (Å)	5.213	5.2118 ± 0.0022	5.2115 ± 0.0022	5.2089 ± 0.0022	5.2067 ± 0.0022
c/*a* ratio	1.6025	1.6026 ± 0.0007	1.6031 ± 0.0007	1.6025 ± 0.0007	1.6021 ± 0.0007
Volume of the unit cell (Å)^3	47.77	47.733	47.694	47.659	47.624
Crystal size (nm)		26.64	28.84	32.2	34.95