

Structural and Magnetic Characterization of Mn and Fe-doped ZnO Nanopowders

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Abstract. The $\text{Zn}_{1-x}\text{A}_x\text{O}$ ($\text{A} = \text{Mn, Fe}$ and $x = 0 - 0.03$) nanopowders, have successfully been synthesized by coprecipitation method. The starting materials of dihydrate zinc acetate, iron and mangan powders were employed using HCl and NH_4OH as solvent and precipitating agents respectively. The solution was stirred at 48°C for 4h to induce a precipitation and the resulted precipitate was then heated at 100°C for 24h in air followed by annealing at 400°C for 3h. Based on the XRD spectra, the doped samples with x up to 0.02 form the single wurtzite phase of ZnO with crystal size around 20-60 nm, where the dopants, both Mn and Fe, have partially substituted Zn. Meanwhile, samples with $x = 0.03$ were observed to contain impurity phases. The magnetization for the magnetic field up to 1 tesla visualizes a monotonically increased weak-ferromagnetism for Fe doping, while exhibits from diamagnetic, paramagnetic to weak-ferromagnetic behaviors for Mn doping. This magnetic interaction becomes complicated by the presence of magnetic impurities due to Mn dopant.

1. Introduction

Dilute magnetic semiconductors (DMSs) have gained a considerable attention from scientific community because of their wondering optical and magnetic properties which have applications in 'Spin electronics' also known as spintronics [1]. After these predictions about the dilute magnetic semiconductors, simulations of Sato and Katayama-Yoshida [2] showed that Ferromagnetic could also be achieved in V, Cr, Fe, Co, and Ni doped ZnO. Over last decade, most of the research efforts were devoted to Mn and Co doped ZnO systems [3]. Very few studies were reported for Fe doped ZnO ;however, reports showed inconsistency in magnetic behavior of Fe doped ZnO. Zinc ionic can substitution with mangan ionic which give ferromagnetism behaviour [4].

In this research, a series of The $\text{Zn}_{1-x}\text{A}_x\text{O}$ ($\text{A} = \text{Mn, Fe}$ and $x = 0 - 0.03$) nanopowders, have successfully been synthesized by coprecipitation method. The influence of Fe concentration and Mn concentration on the structural and magnetic properties of the samples was presented and discussed. Considering their essential importance for applications in spin-optoelectronic devices in the future, the optical properties of the films were also studied.

2. Experimental

The study was conducted by using a powder material Dyhidrat Zinc Acetate, Iron powders, Mangan powders, solvents HCl, and NH_4OH precipitating agent. The synthesis process by mixing Zinc Acetat Dyhidrat powders and (Mn, Fe) powders with HCl and NH_4OH . The Solution was stirred for 4h at 84



°C and then heated in air for 24h at 100 °C and annealed for 3h at 400 °C. $\text{Zn}_{1-x}\text{A}_x\text{O}$ ($\text{A} = \text{Mn, Fe}$) nanoparticle synthesis performed with the variation of (Mn, Fe) dopant ($x = 0,00, 0,01, 0,02, 0,03$) to the solution precursor. Characterization testing performed using X-ray diffraction (XRD), *Vibrating Sample Magnetometer* (VSM), and Scanning Electron Microscopy (SEM). XRD data analysis performed using the Match software, Rietica, and Material Analysis Using Diffraction (MAUD). The crystal structure of the $\text{Zn}_{1-x}\text{A}_x\text{O}$ ($\text{A} = \text{Mn, Fe}$) nanoparticle was determined by XRD. Magnetic measurements were carried out on an vibrating sample magnetometer (VSM) with the magnetic field applied parallel to the sample.

3. Result of Discussion

Figure 1 shows the X-ray diffraction patterns of the $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.

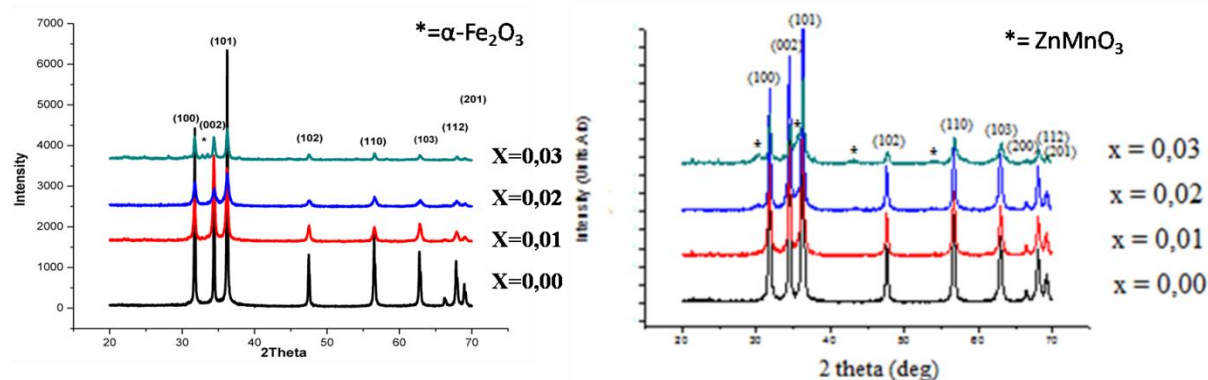


Figure 1. XRD spectra of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.

All of the diffraction peaks can be indexed to the wurtzite structure of ZnO (space group P63mc). With increasing Fe concentration x in the $\text{Zn}_{1-x}\text{Fe}_x\text{O}$, the clear shifts of the (002) peaks to higher angles are observed. This phenomenon indicates a reduction in the lattice constant with Fe doping, which is expected as smaller Fe ions are incorporated into the Zn sites of the ZnO lattice without changing the wurtzite structure. Also, the (002) peak exhibits an increased line broadening as x increases, suggesting a significant lattice-defect formation by Fe doping. In order to properly substitute Zn^{2+} ionic sites with maintaining charge neutrality of the sample, Fe ions need to have a valence of +2. It is noted that the ionic radius of Fe^{2+} is larger than that of Zn^{2+} by about 5%, whereas that of Fe^{3+} is smaller by about 10% [5]. The lattice parameter should not decrease with enhancing x if there is Fe^{2+} that replaces the site of Zn^{2+} . Therefore, it can be inferred that Fe^{2+} and Fe^{3+} ions coexist in the $\text{Zn}_{1-x}\text{Fe}_x\text{O}$, Fe^{2+} and Fe^{3+} ions are expected to distort the lattice structure for holding charge neutrality. The higher concentrations of Fe may provide more chances for Fe to substitute Zn^{2+} sites, resulting in the lattice constants further shrink with the increase of the Fe concentration x . Considering that both the valence state and the ionic radius are the major factors determining the solubility of the dopant [5], high Fe solubility ($x=0.02$) for the present $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ samples is attributable to the existence of the Fe^{2+} ions with high density. They do not show any secondary phases such as FeO, Fe_3O_4 and ZnFe_2O_4 in the detection of our diffractometer. This may be attributed to the limitation of XRD characterization that small amount of impurities cannot be detected. However, for highly doped sample ($x=0.03$) we observe the appearance of a spinel $\alpha\text{-Fe}_2\text{O}_3$ phase are marked with *. $\alpha\text{-Fe}_2\text{O}_3$ exhibits weak-ferromagnetism. The analysis of diffraction data was carried out using Rietica software for calculate lattice parameter, and MAUD software for calculate crystal size. The cause of shift in (002 and 101) reflection peak is because of variation in lattice spacing a , c and crystal size as shown in Table 1.

The XRD results also indicate that the Mn^{2+} ions systematically substituted for the Zn^{2+} ions in the sample without changing the wurtzite structure, as shown in the inset of Figure 1. The most intense diffraction peak (101) is clearly evident with a slight shift into low angular scale, whereas the corresponding intensity decreases compared with undoped ZnO. Furthermore, the intensity of the diffraction peaks decreases, and the width broadens due to the formation of smaller grain diameters as

a result of an increase in disorder on Mn^{2+} doping. But, high Mn solubility ($x=0.03$) for the present $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ samples is attributable to the existence of ZnMnO_3 phase [6]. In our experiment, Fe and Mn dopant influence the crystalline size of ZnO, because the creation of new nucleation centers from the dopant atoms is retard for the growth of ZnO crystals. So that crystal size of ZnO with dopant (Fe or Mn) less than ZnO undoped. This is probably connected with due to the difference of ionic radius between dopant (Fe or Mn) and Zn^{2+} .

Table 1. Lattice parameters and crystal size for $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$

Lattice Parameter	Dopant	x=0	x=0.01	x=0.02	x=0.03
a=b (Å)	Mn	3.2559	3.2494	3.2509	3.2449
	Fe		3.2514	3.2506	3.2524
c (Å)	Mn	5.2149	5.1998	5.2056	5.1863
	Fe		5.2054	5.2054	5.2099
Crystal size (nm)	Mn	61.2	51.4	47.7	$\text{ZnO} = 25.2$ and $\text{ZnMnO}_3 = 90.7$
	Fe		32.8	38.1	43.5

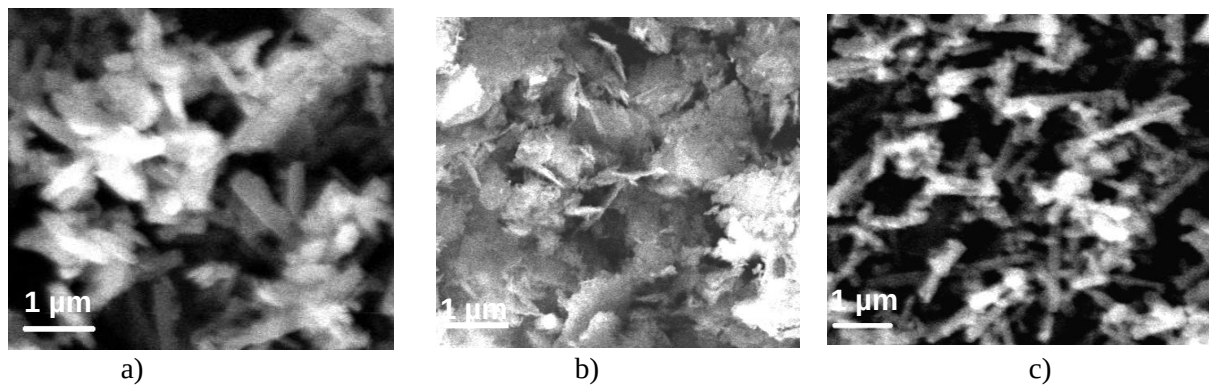


Figure 2. SEM images of : (a) ZnO , (b) $\text{Zn}_{0.99}\text{Fe}_{0.01}\text{O}$, and (c) $\text{Zn}_{0.99}\text{Mn}_{0.01}\text{O}$.

The surface morphology of undoped (a), Mn doped (b) and Fe doped (c) is shown in Fig. 2(a)–(c). It is seen that the average size of the particles is in sub-micrometre size. Pure ZnO showed rod-like structures and as dopant (Mn and Fe) content increased, rod-like structures transformed into sheets- and plates-like. Further increase of dopant (Mn and Fe) causes a transformation from sheets and plates to spheres with finer grains. The defects caused by dopants may be responsible for deformation of structures, and hence different morphology.

Magnetic characterizations for $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ were done by using VSM at room temperature. Fig. 3a shows the hysteresis graph for $\text{Zn}_{1-x}\text{Fe}_x\text{O}$. It has been observed that our samples did not show full saturation; this effect appears due to the ambiguous nature of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ phase which contributes in both ferromagnetic and paramagnetic behaviors. It has also been shown in previous studies that the ZnFe_2O_4 phase exhibits anti-ferromagnetic and $\alpha\text{-Fe}_2\text{O}_3$ phase exhibits weak-ferromagnetism behavior which may suppress the magnetic signal [7]. However, the increase/decrease in the lattice parameter with increasing doping percentage indicates that it is not only due to Fe^{2+} ions and Fe^{3+} ions substitution in the ZnO lattice, but also due to any secondary phases such as FeO, $\alpha\text{-Fe}_2\text{O}_3$, Fe_3O_4 and ZnFe_2O_4 [8]. The magnetization for the magnetic field up to 1 tesla visualizes a monotonically increased weak-ferromagnetism for Fe doping.

In Fig. 3b, when ZnO was doped by Mn, the magnetization curve generated was different for each composition of dopant. On the curve with $x = 0.01$, it can be seen that the curve indicates a nature of diamagnetic. A few of Mn dopants will occupy some Zn position in this doping state. When $x = 0.02$,

a curve featuring a superparamagnetic behavior is observed. Further, for $x = 0.03$, the ZnO behaves as weak ferromagnetic. This magnetic interaction becomes more complicated by the presence of magnetic impurities due to Mn dopant [9].

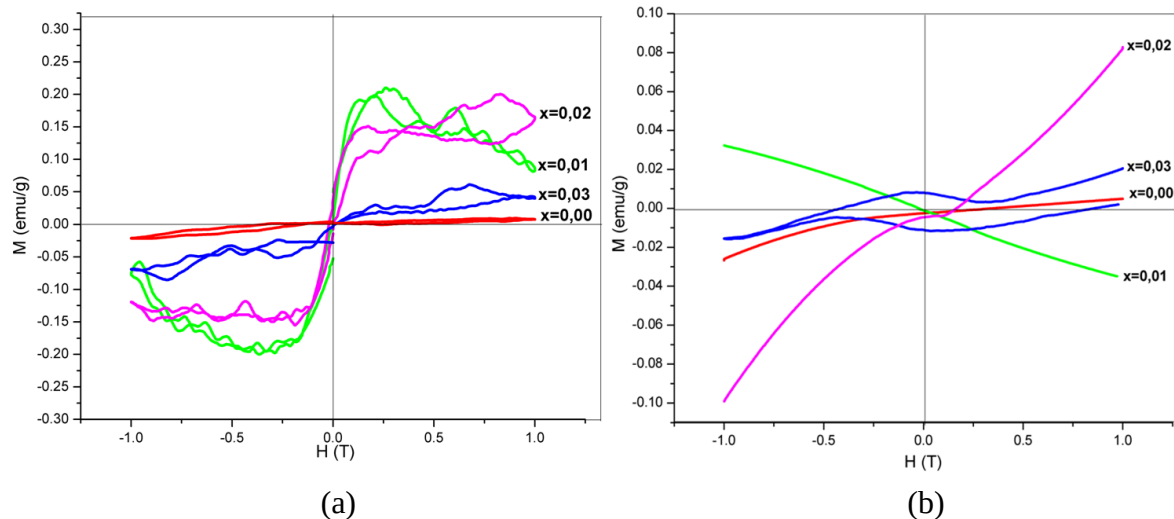


Figure 3. The magnetization curve of : (a) $\text{Zn}_{1-x}\text{Fe}_x\text{O}$, and (b) $\text{Zn}_{1-x}\text{Mn}_x\text{O}$.

4. Conclusion

A series of $\text{Zn}_{1-x}\text{Fe}_x\text{O}$ and $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ with the atomic fraction, x , in the range of 0–0.03 were synthesized by coprecipitation method. A systematic study was done on the structural and magnetic properties as a function of dopant concentration. XRD results indicated that there are not any secondary phases and Fe^{2+} as well as Fe^{3+} substituted for Zn^{2+} of ZnO host, while Mn^{2+} ions systematically substituted for the Zn^{2+} ions in the sample without changing the wurtzite structure for Mn doping. The magnetization for the magnetic field up to 1 tesla visualizes a monotonically increased weak-ferromagnetism for Fe doping, while exhibits from diamagnetic, paramagnetic to weak-ferromagnetic behaviors for Mn doping. This magnetic interaction becomes complicated by the presence of magnetic impurities due to Mn dopant.

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