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Investigation of Microstructure and Magnetic Properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ ($x = 0, 0.05, \text{ and } 0.09$) prepared by Solid-state Reaction Method

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Abstract

In this study, we investigated the microstructure and magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ ($x = 0, 0.05$, and 0.09) powders prepared by the solid-state reaction method. The starting material, which consisted of ZnO, Mn, and Fe powders, were wet milled for 3 hours using high-energy milling. We then used an X-ray diffractometer (XRD), scanning electron microscope, and vibrating sample magnetometer to investigate the effects of doping and co-doping on the microstructure, morphology, and magnetic properties, respectively. The XRD results suggest that Mn and Fe ions had substituted into the ZnO matrix, as illustrated by the resulting single-phase polycrystalline hexagonal wurtzite structures. The diffraction intensity was observed to decrease as the Mn composition increased. The analysis showed that the lattice parameters decreased due to Mn^{2+} and Fe^{3+} ion substitution in the ZnO matrix. The co-doping of Mn-Fe ions in the ZnO structure enhanced the magnetic properties, particularly due to the $\text{Zn}_{0.89}\text{Mn}_{0.09}\text{Fe}_{0.02}\text{O}$ composition. The increase in the Mn dopant and Mn-Fe co-dopant concentrations strongly contributed to the improved morphology and magnetic properties. Therefore, we can conclude that the presence of Mn and Fe co-dopants in the ZnO system contributed to its magnetic properties, as confirmed by high-saturation magnetization.

Keywords: dopant, high-energy milling, microstructure, solid-state reaction, ZnO

Introduction

Zinc oxide is a semiconductor with a hexagonal structure, wide direct band gap (3.3 eV), and an exciton binding energy of 60 MeV at room temperature. This type of semiconductor is an environmentally friendly and low-cost host material that can be processed with different metal ions, including transition metal (TM) elements such as Cr, Mn, Fe, Ni, Co, and others [1–4]. Among all the TM impurities, Mn is widely used for doping into ZnO, because its radius (0.066 nm) is equivalent to that of Zn atoms (0.060 nm) and it has high solubility [5].

However, Fe-doped ZnO has difficulty obtaining a high Curie temperature (T_c) due to the low solubility of Fe in ZnO and the occurrence of phase separation, which tends to form a cluster or a secondary-phase ZnFe_2O_4 at doping concentrations $>2\%$ [6]. Several research methods have been used in the co-doping of Mn-Fe into ZnO thin films to improve the magnetic saturation,

including the sol-gel technique [7], solid-state reaction [8], and solid-state sintering at low temperature [9]. These methods have showed that ZnO co-doped with Mn and Fe can increase the magnetic saturation, as compared to that achieved when using only Mn as a dopant. Co-doping two different TM impurities into the ZnO wurtzite structure is an effective approach for increasing its ferromagnetic properties and Curie temperature [10].

To the best of our knowledge, there has been no discussion of the physical aspects of the co-doping (Mn-Fe) effect with Mn variation into ZnO and the resulting magnetic properties by the solid-state reaction method. The advantages of the solid-state reaction are its relative simplicity, low cost, and easy synthesis as compared to other methods such as ion implantation and thin-film deposition. In this study, we employed the solid-state reaction method to fabricate $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ ($x = 0, 0.05$, and 0.09), which are commonly classified as diluted magnetic semiconductors.

Our findings suggest that Mn and Mn-Fe co-dopants directly influence the microstructure and morphology of ZnO as well as enhancing its ferromagnetic properties.

Experiments

The starting materials used in the synthesis of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ were ZnO (> 99.9%), Mn (> 99.9%), and Fe (> 99%) powders. Table 1 lists the various compositions of the dopant and co-dopants used in this study. The Mn dopant and Mn-Fe co-dopant were mixed and milled by high-energy milling, with a powder-to-ball ratio of 1:10. The wet milling process was performed with the addition of a 20-ml toluene solution for 3 h and drying in ambient air at 100 °C for 1 h. Subsequently, the dried powder was put into a mold with a diameter of 12 mm, then pressed in a hot press at a pressure of 1.5 tonf/cm² and temperature of 150 °C. The microstructures of the Mn dopant and Mn-Fe co-dopant were characterized using X-ray diffraction (XRD, Smartlab Rigaku Cu-K α radiation wavelength λ = 1.5406 Å). The magnetic properties were measured using a vibrating sample magnetometer (VSM250, Dexion Magnet Ltd.), and the surface morphology was determined using a scanning electron microscope (SEM, Hitachi 3500 SU).

Results and Discussion

Figure 1(a) shows the diffraction patterns of pure ZnO, $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, and the Mn-Fe co-dopant $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ for x = 0, 0.05, and 0.09, respectively. These results indicate that all the samples had a hexagonal wurtzite structure according to ICDD Card No. 01-0780-3315, with the dominant peaks in the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (104) planes. Figures 1(b) and 1(c) show specific observations of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$, respectively, in the (002) plane for the various concentrations of Mn and the Mn-Fe co-dopant. We can see that no secondary phase is observed, as compared to a previous work that used the co-precipitation method and found evidence of a secondary phase of Mn_3O_4 [11]. The authors of another study reported that the use of the solid-state reaction method resulted in the appearance of secondary phases of Mn_2O_3 at x = 0.2 [12].

Interestingly, we found the (002) peak intensities of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ to be lower than that of pure ZnO and that these peaks were shifted to a higher 2θ angle, as shown in Figures 1(b) and 1(c), respectively. This trend is in contrast with the findings based on the sol-gel method with x = 0.01–0.1 [13,14] and those based on the solid-state reaction method with x = 0.02, 0.04, and 0.06 [15], which demonstrate peak shifts to a lower 2θ angle. However, our findings showed adequate agreement with previous work that had used the solid-state reaction method, with shifts to a

Table 1. Concentrations of Mn Dopant and Mn-Fe Co-dopant in ZnO Ferromagnetic Materials

Mn-doped	$\text{Zn}_{1-x}\text{Mn}_x\text{O}$	$\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$
x = 0	ZnO	$\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$
x = 0.05	$\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$	$\text{Zn}_{0.93}\text{Mn}_{0.05}\text{Fe}_{0.02}\text{O}$
x = 0.09	$\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$	$\text{Zn}_{0.89}\text{Mn}_{0.09}\text{Fe}_{0.02}\text{O}$

Figure 1. (a) XRD Spectra of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$, and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ (x = 0, 0.05, and 0.09), (b) and (c) Details of 2θ from the (002) Plane for Most Dopant and Co-dopant Concentrations, Respectively

higher 2θ angle when using concentrations of x = 0.02, 0.05, and 0.1 [12]. Accordingly, the diffraction peaks shifted to higher angles for all Mn^{2+} doping concentrations as a result of the occupancy of Zn^{2+} sites by Mn^{2+} , which causes lattice distortion by tensile stress [16]. The XRD pattern of $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ shifted to a 2θ angle of 35.35° when the Mn-Fe co-dopant was incorporated into ZnO.

Furthermore, an increase in the Mn-Fe co-dopant concentration resulted in a decrease in peak intensity, particularly at a concentration of x = 0.09. The 2θ angle peak shifted to a higher 2θ angle, as depicted in Figure 1b. It has been reported that this angle peak shifted to lower 2θ angles than those of undoped ZnO [7–9]. Other authors have reported a shift in the co-doping (Cr-Ni) angle peak to a higher 2θ angle [2].

Based on the above XRD patterns, we can determine lattice parameters such as the lattice constant, lattice parameter ratio, d-spacing, volume, crystal size, and strain. Lattice parameters a and c in the hexagonal structure can be calculated from the (100) and (002) planes using the following equations:

$$a = \frac{\lambda}{\sqrt{a} \sin \theta} \sqrt{h^2 + hk + k^2}, \quad (1)$$

$$c = \frac{\lambda}{2 \sin \theta} l \quad (2)$$

To determine the d-spacing and volume (V) of the lattice, we used the following equations:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}, \quad (3)$$

$$V = \frac{\sqrt{3}}{2} a^2 c, \quad (4)$$

where λ is the wavelength, θ is the Bragg angle of diffraction, and h, k, l are the Miller indices. Table 2 shows the calculated lattice parameters. We found the lattice parameters a and c of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ with a wavelength of $\text{Cu-K}\alpha = 1.54056 \text{ \AA}$ decreased as the Mn and Fe content increased, as compared to those in the standard ICDD Card No. 01-0780-3315. This trend indicates that Zn^{2+} ($0.74 \text{ \AA}$) was successfully substituted by Mn^{2+} ($0.70 \text{ \AA}$) and Fe^{3+} ($0.60 \text{ \AA}$) ions, which both have lower ionic radii, and resulted in decreases in the lattice parameter values. Khalid *et al.* reported that a decreasing lattice parameter could be caused by an oxygen vacancy [17]. Alternatively, this tendency could be caused by a defect in which Mn was only partially doped and did not substitute but only adhered to the surface of ZnO [12]. The ratio of c/a tended to be approximately constant for both the pure and doped samples, which suggests that the dopant atoms were well incorporated into the ZnO crystal lattice without altering the overall crystal structure [18]. To determine the crystallite size (D) and strain (ϵ), the following equations were used, respectively:

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (5)$$

$$\epsilon = \frac{\beta}{4 \tan \theta} \times 100\%, \quad (6)$$

where β is the FWHM of a plane (002). As we can see in Table 2, the crystal size (D) and strain (ϵ) of the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ sample are respectively around 43.735–45.326 nm and 0.258–0.267%. However, these quantities for

the $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ sample are around 44.298–48.051 nm and 0.243–0.264 %, respectively. It can be seen that the lattice strain generally increased for the $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ sample by the increased addition of the Mn dopant, which indicates that the Mn^{2+} ions were successfully substituted into the ZnO structure. The difference in the radii of Zn^{2+} and Mn^{2+} will result in lattice distortion in the ZnO system [19]. Different amounts of Mn^{2+} ions that substitute for the Zn^{2+} ions cause changes in the lattice distortion by the change in the lattice strain. The contribution of the Mn dopant to the $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ sample resulted in a rather erratic trend of the lattice strain. Even so, the addition of Fe co-dopant scaled up the lattice strain values. The crystallite size tended to decrease with increases in the Mn doping, which could be due to the relatively small grain growth compared to pure ZnO nanocrystals [20].

Figure 2 shows plots of the hysteresis loops of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$. As shown in the figure, zinc oxide is primarily a diamagnetic material with a negative susceptibility value. Interestingly, Mn doping on $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ tends to produce ferromagnetic characteristics. The induced ferromagnetism observed in doped metal oxides may be due to the formation of some intrinsic defects (such as zinc vacancy (V_{Zn}), zinc interstitials (Zn_i), oxygen antisite (O_{Zn}) or oxygen interstitials (O_i) [19,21]. Moreover, ferromagnetism is reported to emerge in diluted magnetic semiconductors for one of the following three reasons: (1) the formation of secondary phases that do not match; in our case the XRD results in Figures 1(b) and 1(c) confirm the absence of a secondary phase [10]. (2) Dopant peaks are present; but no peak corresponding to the dopants are observed [22]. (3) RKKY interaction occurs between the conductive electrons of the host and the spin-polarized electrons of the dopant [23].

It is well known that magnetic properties are possible in ZnO due to the interaction of the spin polarization of the conductive electrons in the ZnO host lattice [24]. Other researchers have reported that the magnetization of ZnO becomes possible with higher or lower ferromagnetic properties with the presence of magnetic impurities that may not be detected by XRD [6]. It has also been demonstrated that either the secondary-phase $\text{Mn}_{2-x}\text{Zn}_x$

Table 2. Crystal Parameters of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ ($x = 0, 0.05$, and 0.09)

Sample	a ($\text{\AA}$)	c ($\text{\AA}$)	c/a	d ($\text{\AA}$)	V ($\text{\AA}^3$)	β (deg)	D (nm)	ϵ (%)
ZnO	3.248	5.201	1.601	2.601	47.505	0.184	45.326	0.258
$\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$	3.241	5.194	1.603	2.597	47.236	0.190	43.735	0.267
$\text{Zn}_{0.91}\text{Mn}_{0.09}\text{O}$	3.237	5.186	1.602	2.593	47.054	0.187	44.466	0.262
$\text{Zn}_{0.98}\text{Fe}_{0.02}\text{O}$	3.245	5.199	1.602	2.600	47.405	0.173	48.051	0.243
$\text{Zn}_{0.93}\text{Mn}_{0.05}\text{Fe}_{0.02}\text{O}$	3.238	5.189	1.603	2.595	47.110	0.188	44.298	0.264
$\text{Zn}_{0.89}\text{Mn}_{0.09}\text{Fe}_{0.02}\text{O}$	3.238	5.189	1.603	2.595	47.109	0.181	46.038	0.254

$O_{3-\delta}$ or extrinsic sources are responsible for the ferromagnetic properties in Mn-doped ZnO [25]. The ferromagnetic properties of $Zn_{0.98-x}Mn_xFe_{0.02}O$ are minimal when the addition of doping Mn is $x = 0.05$ and maximal when the concentration of Mn doping is $x = 0.09$. The sol-gel method on a thin film can be used to determine the magnetic saturation value, which was found to nearly double when $x = 0.01$ to $x = 0.03$ and was almost the same when $x = 0.04$ and 0.05 [7]. Table 3 summarizes the magnetic saturation values of Mn and the Mn-Fe co-dopant into ZnO, which are much higher than that of pure ZnO and those reported previously [8,9]. On the other hand, Ashraf *et al.* used the sol-gel method in thin-film samples and reported a similar ratio for the Mn concentration $x = 0.03$ [7].

Figure 3(a) shows the SEM characterization results for of $Zn_{1-x}Mn_xO$ and $Zn_{0.98-x}Mn_xFe_{0.02}O$ using the Mn dopant variations $x = 0$ and 0.09 . These variations approximately represent the effective addition of the dopant and co-dopant on microstructural properties of the samples. We can see that the SEM images of the samples at $15,000\times$ magnification show the occurrence of agglomeration, which was primarily due to the Van

Figure 2. Magnetic Hysteresis Loops of $Zn_{1-x}Mn_xO$ and $Zn_{1-x}Mn_xFe_{0.02}O$ ($x = 0$ and 0.09). Inset Shows the Hysteresis Loop of Pure ZnO

Table 3. Magnetic Properties of $Zn_{1-x}Mn_xO$ and $Zn_{0.98-x}Mn_xFe_{0.02}O$ ($x = 0, 0.05$, and 0.09)

Sample	Magnetic properties		
	M_s (emu/g)	M_r (emu/g)	H_c (Oe)
$Zn_{0.95}Mn_{0.05}O$	0.391	0.048	382
$Zn_{0.91}Mn_{0.09}O$	0.833	0.119	156
$Zn_{0.98}Fe_{0.02}O$	1.661	0.307	246
$Zn_{0.93}Mn_{0.05}Fe_{0.02}O$	1.582	0.141	194
$Zn_{0.89}Mn_{0.09}Fe_{0.02}O$	1.718	0.288	178

Der Walls forces among the ions [26]. This agglomeration caused the particle size to become heterogeneous, ranging from 150 nm to 500 nm, which represents an extension of the nanoparticles size range (100 nm). Figure 3(b) shows histograms of the particle-size distributions from 100 random sampling points for each sample with the fitted Gaussian distribution indicated by the black dashed line. The particle-size distributions of the samples without the addition of Mn dopant ($x = 0$) tend to be narrow around the peak, which occurs at 245.0 nm and 262.5 nm for the $Zn_{1-x}Mn_xO$ and $Zn_{0.98-x}Mn_xFe_{0.02}O$ samples, respectively. From the histograms, it can be concluded that an increase in the Mn dopant to $x = 0.09$ caused the peaks to become larger in size, i.e., 287.5 nm and 275 nm for $Zn_{1-x}Mn_xO$ and $Zn_{0.98-x}Mn_xFe_{0.02}O$, respectively. Therefore, it can be understood that increases in the Mn dopant and Fe co-dopant concentrations increased the average of particle size, with the stronger effect achieved by the Mn dopant.

Figure 3. (a) SEM Images of $Zn_{1-x}Mn_xO$ and $Zn_{0.98-x}Mn_xFe_{0.02}O$ for $x = 0$ and $x = 0.09$ and (b) Their Corresponding Particle-size Distributions

Conclusion

In this study, $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ and $\text{Zn}_{0.98-x}\text{Mn}_x\text{Fe}_{0.02}\text{O}$ ($x = 0, 0.05, \text{ and } 0.09$) were successfully synthesized using the solid-state reaction method. The resulting XRD patterns showed a single-phase polycrystalline hexagonal wurtzite structure. More detailed observations indicated that different concentrations of Mn ions can substitute for Zn ions in the ZnO lattice. Interestingly, the lattice parameter ratio c/a remained approximately constant for the pure, doped, and co-doped samples, which suggests that the dopant atoms had been well incorporated into the ZnO crystal lattice without altering its overall crystal structure. In addition, the presence of the Mn and Fe co-dopant in the ZnO system contributed to its magnetic properties, which was confirmed by high-saturation magnetization. From the SEM characterization results, we can conclude that increases in the Mn dopant and Fe co-dopant concentrations increased the average particle size, and that the effect of the Mn dopant was more significant.

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