Structural, Optical, and Magnetic Properties of Mn-doped ZnO Nanoparticles Synthesized by Coprecipitation Method

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Abstract. Many studies have been conducted to produce ZnO including in the form of powder and film. This paper reports the characteristics of structures, optics, and magnetics of $Zn_{1-x}Mn_xO$ nanoparticles synthesized by coprecipitation method. The range of x value was maintained in the range of 0 to 0.03. The X-RD data analysis showed that all samples formed in nanosized. The lattice parameters sifted for all x values indicating the Mn ion was inserted into ZnO replacing Zn ion. The optical properties presented that the increase of Mn ion decreased the gap energy nanoparticles. Furthermore, the addition of Mn ion in the samples resulted in different magnetic properties.

Keywords: $Zn_{1-x}Mn_xO$, SEM, band gap energy, magnetization, coprecipitation

1. Introduction

Diluted Magnetic Semiconductors (DMS) attract many researchers' attention because they have optical and magnetic properties that have potential applications in spintronic devices [1]. One material of concern is the wurtzite zinc oxide phase with a wide band gap. Previous research has been done with the characterization of the optical properties of ZnO with the known energy gap of 3.30 eV. The Mn doping transition metals in ZnO give the best results because Mn has the highest magnetic moment and has the most stable polarization regions. Some Zn can be substituted with Mn ions which can provide ferromagnetic properties [2,3]. Many studies have been conducted to produce ZnO including in the form of powder and film [4]. In general, Mn substitution into ZnO can be formed in the system of $Zn_{1-x}Mn_xO$.

Regarding the synthesis of nanoparticles, coprecipitation has been chosen by many experts due to its excellent properties compared to other methods. Practically, among other traditional synthetic methods, coprecipitation provides a simple route with low cost for large-scale production. Furthermore, such method also does not need expensive raw materials. Regarding the superior of such method and to produce better properties of $Zn_{1-x}Mn_xO$ nanoparticles, in this work, We investigate the influence of Mn

concentration on their microstructural and magnetic properties. The optical band gap also reported accordingly.

2. Methods

We conducted the synthesis of $Zn_{1-x}Mn_xO$ by coprecipitation method for x value of 0-0.03. We used powder dehydrate zinc acetate, manganese powders, solvents HCl, and NH_4OH for raw precursors. It was stirred for 4h at 80ºC followed by heated at 100 ºC for 24 hrs in air. The processed we continuously stirring under magnetic stirrer to reach the desired pH using. It was filtered, and the precipitate is washed using a distilled water and dried with a temperature of 100 °C. It was calcined at 400 °C for 3 hours. The obtained $Zn_{1-x}Mn_xO$ nanoparticles were characterized their structure, optic, and magnetic properties. Characterization was performed using X-ray diffractometer (X-RD) to determine the lattice parameters of the associated crystal structure. The magnetic properties of the samples were performed using a Vibrating Sample Magnetometer (VSM). We used UV-Vis to define energy gap (Eg), and Scanning Electron Microscope (SEM) to identify their particle formed of the $Zn_{1-x}Mn_xO$.

3. Results and Discussion

From the X-ray diffraction patterns obtained from the labs, were further analyzed using Rietica software according to the model. A final step of the Rietveld refinement is depicted in Figure 1. There are three patterns on Figure 1, i.e., the observed pattern, calculated-model, and the difference which are represented by a black cross, solid red line, and solid green line respectively. The blue marker of vertical lines states the Bragg's position. Every peak associated with the Braggs' plane of Miller's (hkl) indices.

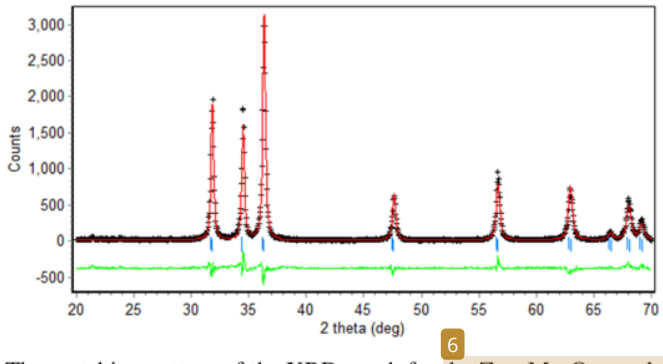

Figure 1. The matching pattern of the XRD graph for the $Zn_{1-x}Mn_xO$ sample for (x = 0.00) with the ZnO database using Rietica.

From Figure 2 it is obtained the suitability of the peak diffraction results with PDF (Powder Diffraction File) 00-079-0207 data from the ZnO phase at (hkl) of (100), (002), (101), (102), (110),(103), (200), (112), and (201) which associated of their peak position of 2θ at 31.59˚, 34.29˚, 36.08˚, 47.40˚, 56.39˚, 62.70˚, 66.19˚, 67, 77˚ and 68.98˚.

Further inspection of Figure 2, we found that there is no additional peak exist except the sample with high doped of Mn ion. This phenomenon indicates that the manganese ions substituted for the Zn site in the crystal cell. Since the replacement is local and changes only a small electronic environment crystal field, the crystal system does not change from the original wurtzite system. The kinetics of diffusion during the coprecipitation as well as the heating might be different compared to the pristine formula. Mn dopant may reduce the crystallite size of the compound, due to the new environment and thermoelectrical interaction among the available ions. These condition expressed by the lowering intensity or broadening of the peak. It is found that inducing Mn to give rise to decrease (1 0 1) intensity. As Mn increase, the order of the crystalline state may

decrease due to the increase of lattice strain as well as the decrease of the grain size. The peak indicated by * on the sample with x = 0.03 show an impurity corresponding to the data of PDF (Powder Diffraction File) 00-028-1468 is $ZnMnO_3$ phase [5]. We understand that the solubility of Mn into ZnO should be lower than 0.03 molar ratio.

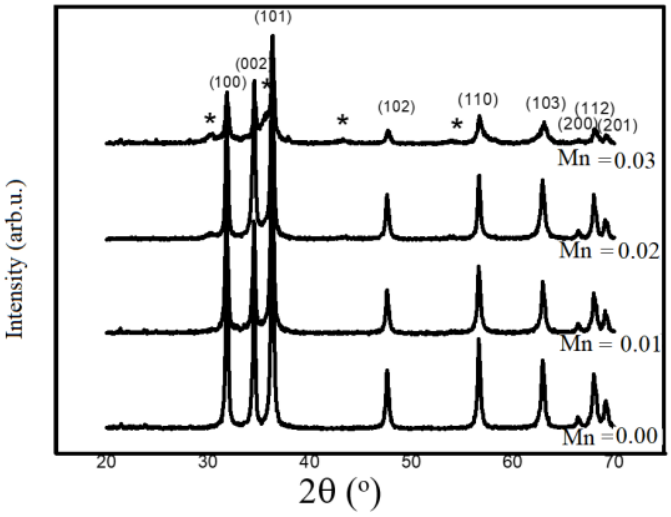

Figure 2. X-ray diffraction patterns of $Zn_{1-x}Mn_xO$.

The addition of doping, there is a change in the size of the crystal (analyzed using MAUD). The increasing of Mn dopant give rise to the size of the crystal gets smaller. The large crystal size indicates that the crystal is perfect and has a high diffraction peak. If the Mn dopant given too large in the ZnO parent compound can make the crystal break, and the size of the crystal becomes small due to the addition of more doping, and the size of the doping ion radius is also more significant.

Table 1. Crystal size of $Zn_{1-x}Mn_xO$ as a function of Mn dopant

No	dopant Mn^{2+} (x)	Crystal size (Å)
1	0.00	612.15
2	0.01	514.60
3	0.02	477.99
4	0.03	ZnO = 252.89
	0.03	$ZnMnO_3$ =907.07

We employed the Tauc plot method by using the equation $(h\nu\alpha)^{1/n} = A(h\nu - Eg)$ [6] to find the optical gap energy. In the previous study which was carried out by [7] the gap energy (Eg) found in the $Zn_{1-x}Mn_xO$ sample of its multilayers thin layer decreased from 3.30 eV to 3.18 eV with increasing Mn fraction. The inferred optical band gap of current work of $Zn_{1-x}Mn_xO$ (x = 0-0.03) is shown in Figure 3 falls to 3.28 eV to 3.05 eV as Mn increases. This can be explained because of the strong exchange *sp-d* interaction between the charge carriers (electron) that is located around the *sp* shell with the electron localized to the *d* shell of Mn as a result of the interaction with Zn site on the ZnO lattice.

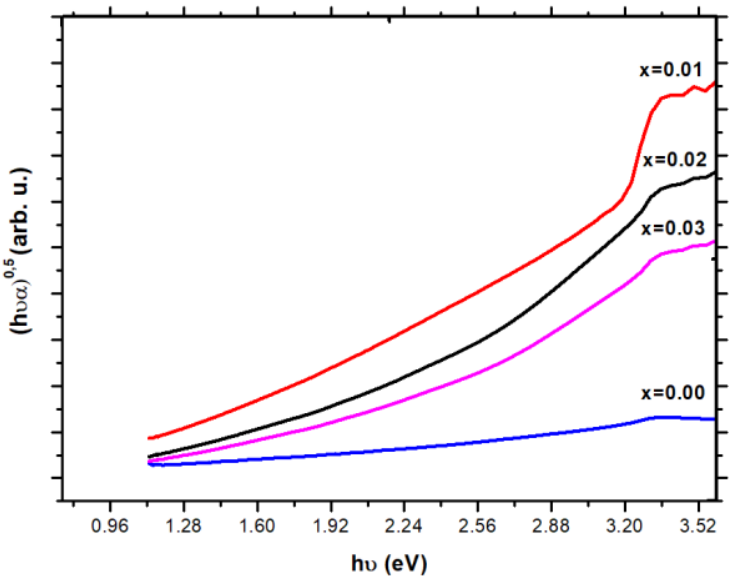

Figure 3. Relationship between υ dan $(h\upsilon\alpha)^{1/2}$ to determine the optical band gap energy value at $Zn_{1-x}Mn_xO$ ($x = 0, 0{,}01, 0{,}02, 0{,}03$)

The magnetic properties of the $Zn_{1-x}Mn_xO$ sample by using coprecipitation synthesis method, VSM characterization was needed in the sample. We present four observed curves from the VSM measurement. The resulted magnetization-applied field (M-H) curves of the $Zn_{1-x}Mn_xO$ samples is displayed in Figure 4. The interesting various M-H curves is shown by associated Mn content. The ZnO samples without doping belong to a weak paramagnetic. This weak paramagnetic property appears possible due to the intrinsic defects in ZnO in the form of oxygen vacancies.

A slight change of M-H curve is shown by the sample with x = 0.01. The small amount of x = 0.01 just transforms the sample into diamagnetic nature [8]. When Mn composition x = 0.02 doped on ZnO, resulting curve appears curved superparamagnetic. This arises because the superparamagnetic properties of Mn dopant given to the parent compound ZnO more than Zn positions are replaced by Mn where Mn^{2+} ions have a magnetic moment more than Zn^{2+} ions. To cause an increase in an increasing number of magnetic moments in $Zn_{1-x}Mn_xO$ and bring superparamagnetic properties. In ZnO doped by Mn with x = 0.03 express a curve which indicates a hysteresis. It means showing weak ferromagnetic properties in the sample. The magnetic phase transformation due to Mn induce into ZnO is representing a complex magnetic interaction. The magnetic interaction is supposed not only come from the decrease the size but also the intrinsic lattice and magnetic interactions provided by Mn dopant [1]. The ZnO sample has intrinsically already had an oxygen vacuum. It could also understand that the Mn content is strongly related to its magnetic moment as well as the possible existing of oxygen vacancy [9].

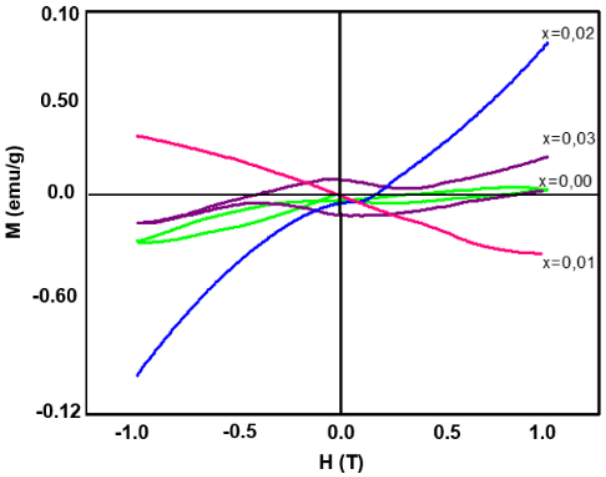

Figure 4. The magnetization curve of $Zn_{1-x}Mn_xO$.

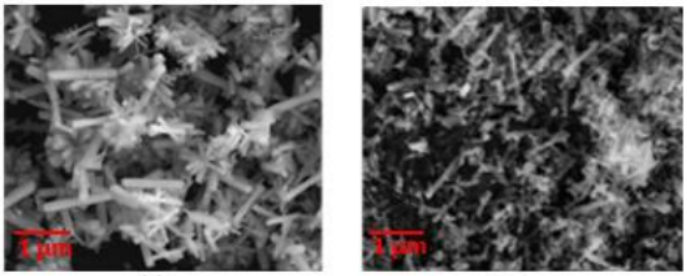

Figure 5. SEM images of (a) ZnO, (b) $Zn_{0.99}Mn_{0.01}O$ with a magnification of 10.000×

The morphological shape of the $Zn_{1-x}Mn_xO$ particles with various compositions of Mn^{2+} ion dopants as shown in Figure 5. Based on the results of SEM testing, it can be seen that the morphological form of $Zn_{1-x}Mn_xO$ particles, namely nanowire can be seen in Figure 5. The surface morphology of (5. a) un-doped and (5.b) Mn-doped exist mostly in the rod shape with the average size of the rod of about 1 nm (diameter) x 1 µm (length). From the SEM image, we found that the more Mn incorporated, the morphology produced more subtle. This phenomenon of lowering the size of-of $Zn_{1-x}Mn_xO$ by increasing manganese dopant from SEM images is similarly obtained from X-ray analysis.

4. Conclusion

We may conclude that the crystallite size of the $Zn_{1-x}Mn_xO$ reduces by the increase of Mn^{2+} dopant. We further found that the energy gap of $Zn_{1-x}Mn_xO$ decrease by increasing the Mn^{2+} dopant into $Zn_{1-x}Mn_xO$ nanoparticles. An interesting feature occurred on magnetization curves in each doping level composition. At the dopant level of x = 0.00, the magnetization curve shows weak paramagnetic properties, while at x = 0.01 it behaves diamagnetic properties, and at x = 0.02 it was showing superparamagnetic properties. We further obtained at x = 0.03 the magnetization showed ferromagnetic properties. We also found from the SEM images analysis, the morphology of $Zn_{1-x}Mn_xO$ sample fell to a nanorod and indicated that with more and more compositions of Mn, the morphology produced more subtle. This is because the particle size of $Zn_{1-x}Mn_xO$ getting smaller with increasing doping.

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Acknowledgments

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