

Synthesis and Characterization of Zn_{1-x}Mn_xO Nanoparticles by Coprecipitation Method

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Abstract. Zinc Oxide Nanoparticles are materials that are developed in the nanotechnology today, because it has mechanical properties, electrical, and optical applicable to such conversion solar cells, thin-film UV protection, and gas sensors. To produce Zinc Oxide nanoparticles materials there are many ways including wet chemical methods, sol-gel, spray pyrolysis, physical vapor deposition, solvothermal, and hydrothermal [1]. Previous research has been done to synthesize ZnO nanoparticles by coprecipitation method. Synthesis and characterization Zn_{1-x}Mn_xO nanoparticles by coprecipitation method. This study is an extension of previous research. The study was conducted by using a powder material Dihidrat Zinc Acetate, Mangan powders, solvents HCl, and NH₄OH precipitating agent was stirred for 1 h at 65 °C and then heated in air at 100 °C and annealed 400 °C [2]. Zn_{1-x}Mn_xO nanoparticle synthesis performed with the variation of Mn doping (x=0,00, 0,01, 0,02, 0,03) to the solution precursor. Characterization testing performed using X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD data analysis performed using the Match software, X'Pert High Score Plus (HSP), and Material Analysis Using Diffraction (MAUD) and the analysis of crystal size by Scherrer method. The results showed that the Zn_{1-x}Mn_xO successfully synthesized. X-ray diffraction patterns suggest that Mn²⁺ ions were successfully incorporated into the lattice position of Zn²⁺ ions in ZnO host. Doping variations that have smaller radii than parent effect on the crystal lattice parameters. Lattice parameters of Zn_{1-x}Mn_xO produced decreased with increased doping Mn²⁺ are given. Decrease in the lattice parameter caused the smaller volume of the crystal cell. With the diminution of the volume of the crystal causes the crystal size is getting smaller.

Introduction

Nanoparticle Zinc Oxide is one of the nanoparticle semiconductor material which has been developed recently . Zinc Oxide Nanoparticles been developed in the field of nanotechnology because it has mechanical properties, electrical, and optical which can be applied to them for solar cells, catalysts, thin film UV protector, gas sensors, etc.. Zinc oxide nanoparticles have many ways to synthesize them with wet chemical methods, sol-gel, spray pyrolysis, physical vapor deposition, solvothermal , and hydrothermal.[1,2,3]

Coprecipitation method is one method of synthesis of inorganic compounds based on the deposition of more than one substance together when passing through the point of saturation . Coprecipitation method uses a low temperature in the process and can produce particle small size. So expect from this coprecipitation method produced smaller particle size and more homogeneous than the solid state method .

In a previous study conducted by R. Nurul synthesis ZnO used coprecipitation method. In the synthesis of ZnO is successfully performed using low temperatures and using variations of temperature , pH, and duration of stirring . This synthesis is an extension of previous studies which use temperature high enough to obtain ZnO nanoparticles.

In the present study will be conducted through the synthesis of Zn_{1-x}Mn_xO coprecipitation method. Given by the variation of Mn doping (x= 0,00, 0,01, 0,02, 0,03) in the ZnO precursor. Materials used powder Dihydrate Zinc Acetate, Mn powders, solvents HCl, and NH₄OH precipitating

agent. Characterization is done with some testing that is testing X-ray diffraction (XRD) and Scanning Electron Microscope test (SEM). The output of the X - Ray Diffractometry analyzed using the software *Match !* for phase identification, *MAUD* (Materials Analyzing Using Diffraction) to identify the size of the crystal phase in the sample , and *Reitica* to determine the crystal size or particle size.

In result Lattice parameters a, b, and c change with increasing doping , although the difference is very small. Due to a shift in the lattice, indicating that the doping Mn^{2+} has entered the parent compound ZnO and replaced most position of Zn^{2+} ions on the composition of the compounds $Zn_{1-x}Mn_xO$.

Methods

The materials used in this study are powder Zinc Acetate Dihydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$] (Merck), powder of pure Manganese (Mn) (Merck), HCl (Merck), and a solution of ammonium hydroxide (Merck).

The first process of the dissolution of the powder [$Zn(CH_3COO)_2 \cdot 2H_2O$] and pure Mn powder with each composition ($x = 0.00, 0.01, 0.02, 0.03$) conducted by adding 37 % HCl solution that has been diluted into 0.5 M HCl solution with stirring Forum using a magnetic stirrer with a temperature of 48 °C treatment. Then, the addition of 0.5 M NH_4OH solution little by little (titration), so the solution mixed. After the precursor solution pH was tested using a test paper (universal indicator). The addition of concentrated NH_4OH solution with a pH titration method to achieve the desired precursor solution (pH 9). After the precursor solution is at the desired pH , then the next step is the precursor solution was stirred using a hot plate while. After filtering the precipitate was formed. After the precipitate formed was filtered washed with a solution of distilled water and drying process is carried out in an oven with a temperature of 100 °C for 15 hours. Then performed with the calcination temperature of 400 °C for 3h.

Result and Discussion

1. XRD diffraction patterns of $Zn_{1-x}Mn_xO$ results ($x = 0, 0.01, 0.02, 0.03$)

Diffraction patterns of $Zn_{1-x}Mn_xO$ ($x = 0, 0.01, 0.02, 0.03$) synthesized by coprecipitation method shown in Figure 1.1.

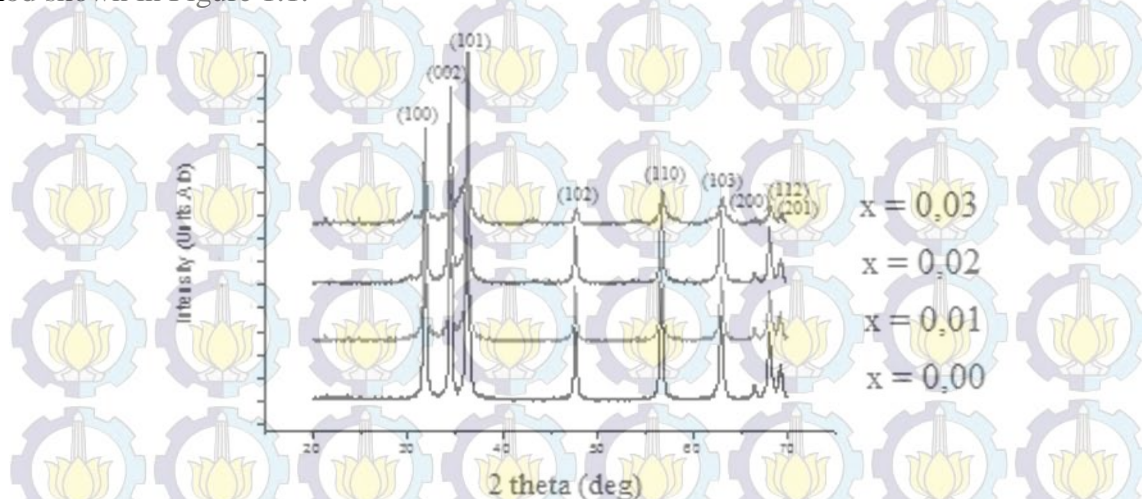


Fig 1.1. The diffraction pattern of ZnO nanoparticles synthesized with Mn^{2+} dopant composition variation

Figure 1.1 shows the diffraction patterns of $Zn_{1-x}Mn_xO$ with Mn^{2+} ions doping variation, the variation of the diffraction pattern from a low of doping $x = 0$ to $x = 0.03$ which is the highest.

The results of the analysis with the software *Match !* In accordance with the data PDF (Powder Diffraction File) 00-079-0208 of ZnO phase seen that the inorganic phase is formed Zinc Oxide (ZnO) is hexagonal shaped with Zincite crystal structure.

From Figure 1 the results obtained diffraction peaks conformance with the database ZnO on (hkl) (100), (002), (101), (102), (110), (103), (200), (112), and (201) which occupies the location of $2\theta = 31,91^\circ, 34,58^\circ, 36,38^\circ, 47,68^\circ, 56,73^\circ, 63,01^\circ, 66,50^\circ, 68,07^\circ$ and $69,23^\circ$. Furthermore, it appears also a shift in the lattice parameter. This indicates the success of doping Mn^{2+} entry in the parent compound ZnO.

From the results of research conducted diffraction pattern of a shift in the lattice parameter. For the analysis of the shift of the lattice on the sample $Zn_{1-x}Mn_xO$ used *Reitica* software. In Table 1 are given the results of the analysis of the lattice parameters of the samples $Zn_{1-x}Mn_xO$ using *Reitica*.

Table 1. Results of lattice parameters by the *Reitica* analysis

Lattice parameter:	x = 0,00	x = 0,01	x = 0,02	x = 0,03
a=b (Å)	3,2518	3,2598	3,2512	3,2509
c (Å)	5,2062	5,2172	5,2056	5,1961
$\alpha=\beta$ (°)	90	90	90	90
γ (°)	120	120	120	120

Lattice parameters a, b, and c change with increasing doping, although the difference is very small. Due to a shift in the lattice, indicating that the doping Mn^{2+} has entered the parent compound ZnO and replaced most position of Zn^{2+} ions on the composition of the compounds $Zn_{1-x}Mn_xO$. It also can be explained by reviewing the ionic radii of Mn^{2+} ($r=0,91$ Å) is larger than the radius of Zn^{2+} ion ($r=0,74$ Å) because dopant ionic radius is smaller, resulting in cell volume of the compound material will also change. Changes in the lattice parameters a, b, and c are not regular because it is in the form of hexagonal lattice of ZnO not be cubic. The shift in the lattice parameter of each graph is shown in Figure 1.1. shows most of the shift towards the left. This is because the radius of the dopant ion Mn^{2+} is greater than the radius of Zn^{2+} ions. But look at the graph with the composition of dopant Mn ($x=0,03$) the shift is not seen, this is due to the difficult nature of Mn has to substitute into a compound and the nature of the coordination number of Mn which has more than one. At the peak of the graph is the graph looks widened, this is due to the greater number of dopants, but given the size of the crystals can be changed.

The output graph pattern matching the *Reitica* software is shown in Figure 1.2. Based on Figure 1.2 appears a pattern matching the measured diffraction data in accordance with the model

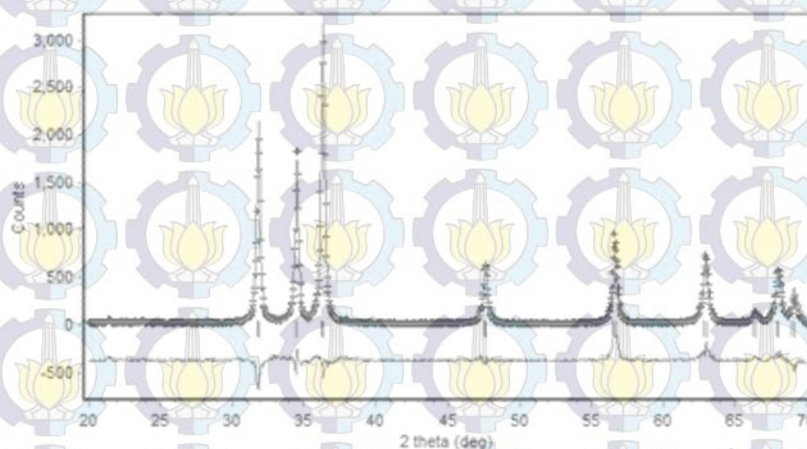


Fig 1.2. XRD pattern of the graph matching to sample $Zn_{1-x}Mn_xO$ for ($x = 0.00$)

2. Analysis of the Software Material Crystal Size Analysis Using Diffraction (MAUD)

XRD test results that produce the pattern of diffraction peaks crystallization describe the level of a material. In addition, the diffraction peaks indicating the size of the crystal phases in a sample.

The wider the diffraction peaks, the crystal size will be smaller. For the analysis of crystal size on the sample $Zn_{1-x}Mn_xO$ used software MAUD.

Example plot smoothing the measured data samples $Zn_{1-x}Mn_xO$ with $x = 0,00$ is shown in Figure 2.1. From the results of the matching between the calculated diffraction pattern with diffraction patterns obtained measured value output smoothing results on any smoothing parameters. The results of the analysis with MAUD smoothing performed on samples of ZnO can be declared acceptable if the Sig < 2 %.

The output graph pattern matching the MAUD software is shown in Figure 2.1. Based on Figure 2.1 appears a pattern matching the measured diffraction data according to the model. Of all the measured diffraction data matching with the model are not all acceptable. There is some research data that resulted in sig > 2 %, so that the analysis can not be said to be acceptable or non- acceptable.

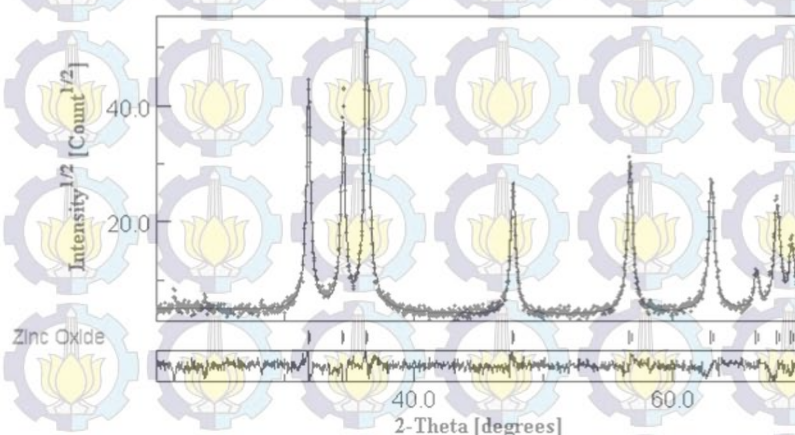


Fig 2.1. XRD pattern of the graph matching to sample $Zn_{1-x}Mn_xO$ for ($x = 0.00$) by MAUD

The following table crystal size of the analysis using Maud.

Table 2. Value $Zn_{1-x}Mn_xO$ crystal size variations in the composition of the dopant ions to Mn^{2+}

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	290,07

From the analysis using MAUD, with the addition of doping the crystal size changes. With increasing doping makes the smaller crystal size. Large crystal size indicates that the crystal is perfect and has a high diffraction peaks. If the Mn dopant is too large given the parent compound ZnO crystals can make and break the crystal size becomes small due to the addition of more doping and size of ionic radii of dopant also greater. Causing the diffraction peak and decline widened. Here is a graphic image between the variation of doping with crystal grain size.

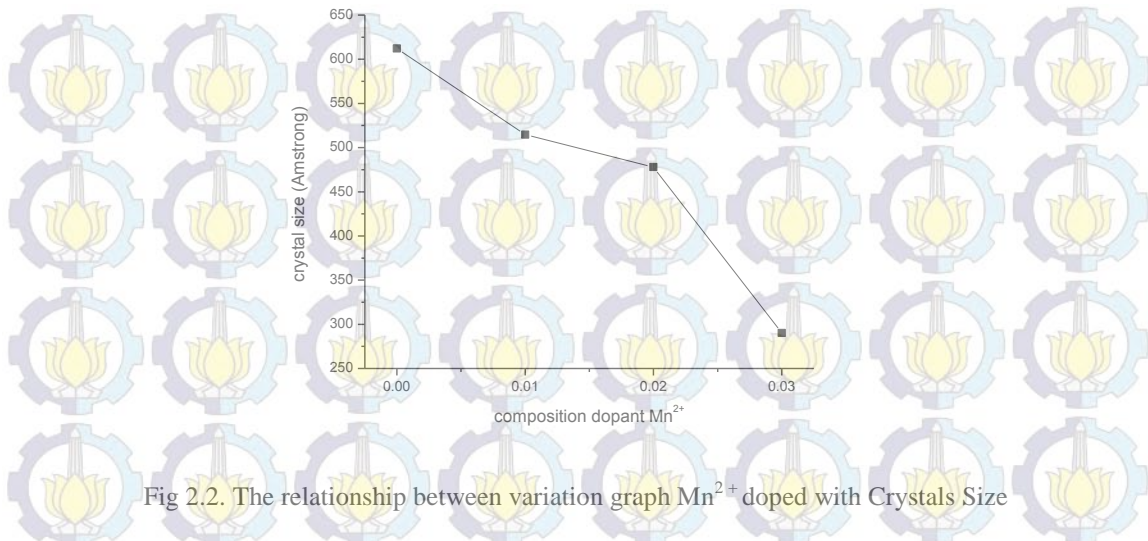


Fig 2.2. The relationship between variation graph Mn²⁺ doped with Crystals Size

3. Results of Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy Testing is performed to determine the morphology of the particles Zn_{1-x}Mn_xO with variations in the composition of the dopant ions Mn²⁺. Based on the test results of the SEM can be seen that the morphology of the particles Zn_{1-x}Mn_xO the nanowire can be seen in Figure 3.1, 3.2, 3.3, and 3.4. Previous research conducted by Lee Sul in 2008 that can synthesize ZnO nanoparticles using sample polyols obtained ZnO nanowire.

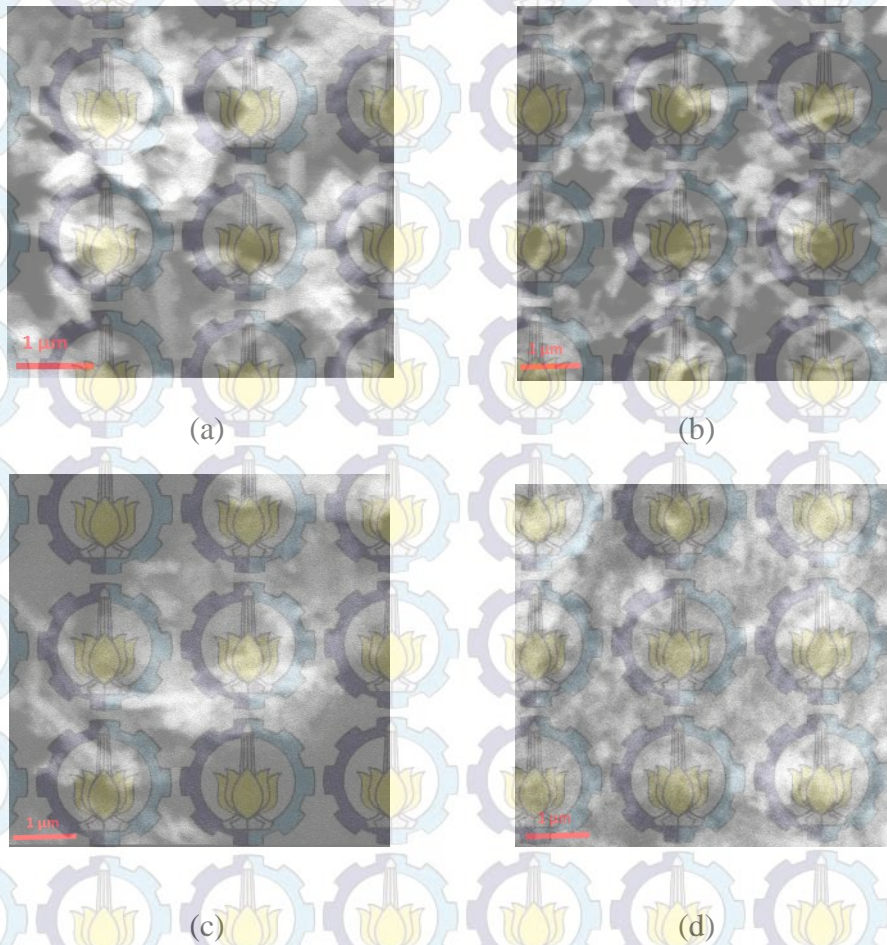


Fig 3.1. SEM with a magnification 27.500 times of composition Zn_{1-x}Mn_xO (a) dopant ions Mn²⁺ (x=0,00) (b) dopant ions Mn²⁺ (x=0,01) (c) dopant ions Mn²⁺ (x=0,02) (d) dopant ions Mn²⁺ (x=0,03).

From the SEM results indicated that the more a given Mn dopant composition, morphology produced more subtle. This is because the particle size of $Zn_{1-x}Mn_xO$ getting smaller with increasing doping.

Summary

Based on the results of the study entitled " Synthesis of Nanoparticles $Zn_{1-x}Mn_xO$ by Coprecipitation Method " it can be concluded that the synthesis of $Zn_{1-x}Mn_xO$ nanoparticles have been successfully carried out. There was a shift in the lattice parameters so that the resulting diffraction pattern can be indicated that the success of doping Mn^{2+} entry in the parent compound ZnO . Increasing Mn^{2+} dopant ions in $Zn_{1-x}Mn_xO$ cause a decrease in crystal size.

References

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