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Synthesis and Characterization of Al doped ZnO (AZO) by Sol-gel Method

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Abstract. Al doped ZnO (AZO) nanoparticles have been successfully synthesized by the simple sol-gel method. The starting materials of Al doped ZnO were $Zn(CH_3COO)_2 \cdot 2H_2O$ and $Al(OH)(CH_3COO)_2$. Preparation of AZO using polyethylene glycol as a surfactant. The solution of precursors was stirred at 60 °C for 2 hour in the conditions of Al contents are 0%, 2%, 3% and 4% (g/mL), respectivelly. In the last step reaction, gelation occurred from solution to sol gel. The sol gel then were dried at 60 °C following by annealing process for crystalization. By this simple sol gel method, the nanoparticles have been produced. The characterizations were conducted X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Fourrier Transform Infra-Red (FTIR) and X-Ray Fluorescence (XRF). XRD analysis reveals that all samples has crystallizes in polycrystalline nature and exhibit no other impurity phase. The variation of Al doped ZnO slighly affect the crystallinity and crystal size. Both crystallinity and crystal size decrease with increasing of Al content in AZO. Morphology of AZO shown the particle distribution more equitable with increased Al content. The synthesized AZO gaved shift peak absorption of asymetric and symetric vibrations of Zn-O-Zn around wavelengths of 680 cm^{-1} and 1630 cm^{-1} atributed of the uptake of the Al-O-Al bond instead Zn-O-Zn. XRF analysis shown that the increase ratio of Al entering into Zn influenced the Al dopant concentration.

1. Introduction

ZnO is a semiconductor which has direct band gap. The value of the energy band gap of ZnO monocrystalline is between 3.1-3.3 eV at room temperature and 3.44 eV at a temperature of 4 K and for polycrystalline ZnO films is between 3.28 to 3.30 eV [1]. ZnO exhibited some properties such as optical, acoustic, and attractive electrical hence it has a number of potential applications in the fields of electronics, optoelectronics and sensors. In addition, ZnO has several advantages such as stable chemical structure, non-toxic, and can be used as an additive in a variety of materials, as well as low cost material due to these materials have highly abundance in nature [2].

Due to it has large energy band gap, the ZnO has transparent to visible light (400-700 nm). Moreover, the wide bandgap ZnO only 5% efficiency of photocatalytic of sunlight. In order to be an affective, it is necessary to minimize the energy gap and increase the absorption of light. One this way is doping. Doping can be defined as the addition of impurities in the material hence modified of its electronic properties [3]. The material used as a doping material (Group III) such as Gallium (Ga), Fluorine (F), Indium (In), Manganese (Mn) and Aluminum (Al). Aluminum (Al) as a doping due to the seed has a morphology that increase the surface area coating and more efficient photocatalytic activity [4]. Selection of aluminum as a dopant also has advantages such as high conductivity, high transparent and low resistivity [5].

There are several methods to synthesis AZO such as sol-gel [6], spray pyrolysis [7], precipitation [8], and hydrothermal processes [9]. Among these methods, sol-gel method is in great demand due to it has thin and large layer, simple, and low cost [10]. Based on these issues, this study has been synthesis ZnO by sol-gel method. The study of temperature effect on crystalization ZnO as well as AZO, calcination treatments were done at 400 °C, 500 °C and 600 °C. In addition, to determine the effect of Al dopant like structural characteristics and physical properties, we investigated the synthesis of AZO by add the various Al dopand about 0%, 2%, 3% and 4% (w/v).

2. Experimental

2.1 Synthesis of Al doped ZnO nanoparticle

Al doped ZnO (AZO) samples were prepared by a simple sol-gel method. 0.5 M of zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Aldrich) was dissolved in 30 ml of ethanol. Then, 10 ml of Polyethylene Glycol 1000 (PEG) was add into solution. The solution was stirred at 60 °C for 2 hour. To prepare the AZO nanoparticles, different amounts of Aluminum acetate ($Al(OH)(CH_3COO)_2$, Aldrich) were dissolved in a solution of zinc acetate dihydrate and polyethylene glycol to gain concentration at 0% (AZO 0%), 2% (AZO 2%), 3% (AZO 3%) and 4% (AZO 4%) (g/mL), respectively. Then, the solution was stirred at 60 °C for 1 hour till gel formation. After that, the solution was placed in an oven at 60 °C until the solvent evaporated. Finally, it was putted into an oxidizing furnace to perform heat treatment at 400 °C, 500 °C, and 600 °C. The final products were nanoparticles of Al doped ZnO (AZO).

2.2 Characterization

Crystal structures of the prepared AZO samples were examined by X-ray diffraction (XRD, Bruker D8 Advance) in the diffraction angle range 2θ = 10-80 °. The effect of doping concentration on crystallite size was also investigated and the crystallite size was calculated using the Scherrer's formula :

$$D\ (nm) = \frac{k\,\lambda}{B\cos\theta} \tag{1}$$

where D is the average of crystallite size, β is the full width at the half maximum of the diffraction peak, θ is the Bragg angle, λ is the wavelength of X-ray used and *k* is a constant.
The morphology of the synthesized AZO particles was visualized by Scanning Electron Microscopy (SEM). Fourrier Transform Infra-Red (FTIR) analyzed the groups of Al doped ZnO (AZO). XRF was also utilized to analyze the composition of various species in Al doped ZnO particles.

3. Result and Discussion

3.1 Effect of Annealing Temperature with Al doped ZnO

Annealing temperature can influence to rate of evaporation and crystallization process of the particles produced. The characterization results were shown in Fig. 1, which shows that the crystalline structure in accordance with the wurtzite hexagonal structure (JCPDS 80-0075). In Fig.1, it can be seen that the particles formed was Al doped ZnO and crystallinity of particle increase with increase annealing temperature. At high temperature, 600 °C, peak of ZnO seem sharp and clear, the particles have a high crystallinity. This is due to the higher temperature affect evaporation process and interparticle reaction more perfect, so can increased of crystalline formation [11]. These results are according with Zhang et al. (2013) [12] increase in temperature affects the formation of defects in ZnO crystals, such as substitution of Zn^{2+} atom by atom Al^{3+} is more easily and produce larger crystal size.

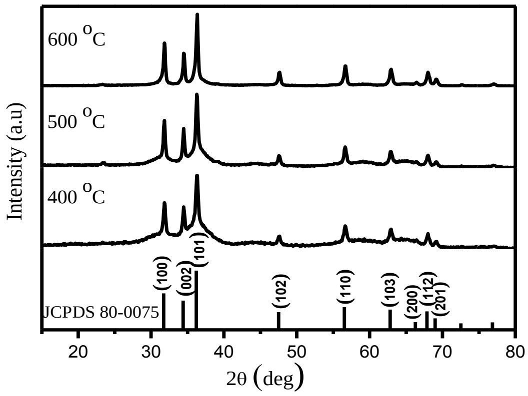


Figure 1. XRD patterns of 2% Al doped ZnO at various temperatures.

From these results, it was found that the optimum temperature to produce a large crystal size and fewer impurities at temperature 600 °C which shown in Table 1. This is because of the higher temperature, the higher particle nucleation rate and crystalite growth faster.

Table 1. Crystallite size of AZO 2% at various temperatures.

Temperatur (°C)	**Crystallite size (nm)**
400	1.290
500	12.659
600	20.247

3.2 Effect of Al doping

Fig. 2 shows the XRD pattern of Al doped ZnO with concentration addition of Al 0%, 2%, 3% and 4% w/v, respectively. Al dopant decreased the crystallinity described by broadening of peak width. In this study, the crystallinity of the highest AZO was obtained on the addition of Al dopants 2%. Increasing the concentration of the Al dopant will form stresses by difference size of ion Zn and Al growing and the formation of aluminium at the grain boundaries at a concentration of dopant higher [13].

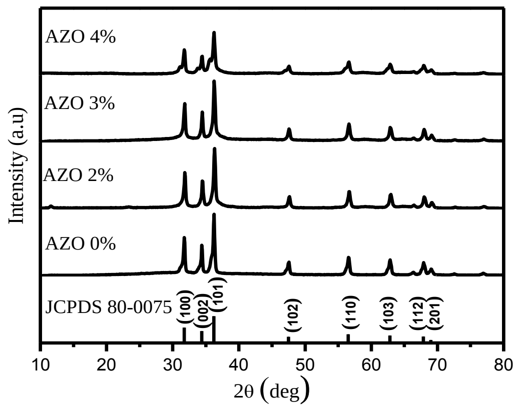


Figure 2. XRD patterns of Al doped ZnO nanoparticle.

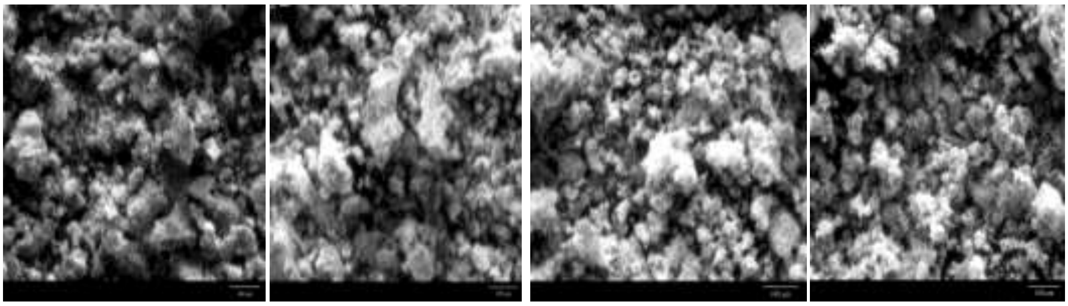
All peaks were well matched with hexagonal structure of ZnO using standard data (JCPDS-80-0075). There is no other impurity peaks in XRD pattern which indicates the purity of nanoparticle formation as Al_2O_3. These result indicate that Al atoms into the structure of ZnO and ZnO is substituted in the lattice because of the size of atoms Al (0.54 Å) is smaller than that of Zn (0.74 Å). So that it can be seen that the Al doped ZnO substituting Zn atoms without changed the structure of the crystals formed. The crystallite size of AZO samples was also estimated from the XRD results by using Scherrer's equation and the results were listed in Table 2. The crystallite size of AZO particles decreased with increasing Al concentration and becomes 12-23 nm.

Table 2. Crystallite size of AZO particles.

Al content (%)	**Crystallite size (nm)**
0	28.651
2	20.247
3	20.215
4	10.779

From the results of XRD analysis, slit diffraction lower yield crystalline diameter size is smaller, so the degree of crystallinity is also low. This is due to the replacement of the position of Zn by Al during formation Al doped ZnO. Radius of Zn^{2+} ions is greater than Al^{3+} (r_{Al} = 0.054 nm and r_{Zn} = 0.074 nm), so it cause decrease the size of Al doped ZnO [15].

The study of morphology and structure were investigated using Scanning Electron Microscopy and shown in Fig. 3 for 2%, 3% and 4% Al doped ZnO. It was seem that agglomeration increases with increasing concentration of Al. The study of morphology and structure were investigated using Scanning Electron Microscopy and shown in Fig. 3. It was seen that agglomeration increases with increasing concentration of Al. Pure zinc oxide (AZO 0%) show that particle morphology broken, irregular and round shape was intact. With the addition of the dopant concentration of 2%, AZO particles ranging round and flat surface. The same result also occurs in the dopant concentration of 3% and 4%.



(a) (b) (c) (d)

Figure 3. SEM image of Al doped ZnO (a) 0% (b) 2% (c) 3% (d) 4%

Characterization of a finger vibration Al doped ZnO can be viewed using FTIR (Figure 4). Based on Fig. 4, AZO 0%, 2%, 3% and 4% gave the same weak absorption spectras at a wavenumber of 420 cm^{-1} atribute as a bending of Zn-O-Zn. The synthesized AZO gaved shift peak absorption of asymetric and symetric vibrations of Zn-O-Zn around wavelengths of 680 cm-1 and 1630 cm-1 atributed of the uptake of the Al-O-Al bond instead Zn-O-Zn. There are absorptions at the wavelength of 1360 cm^{-1} from an asymmetric stretching vibration Zn-O-Zn due to interference by Al atoms.

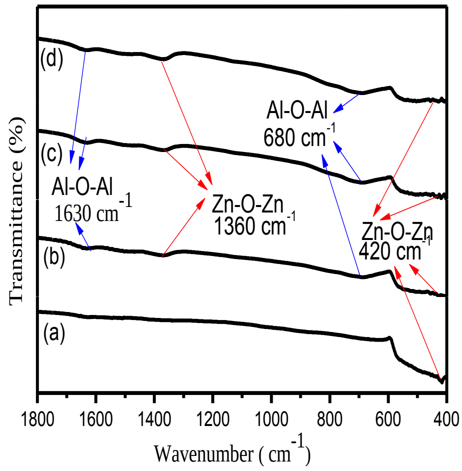


Figure 4. IR Spectra of Al doped ZnO (a) 0% (b) 2% (c) 3% (d) 4%

To check the chemical composition of the material were analyzed using X-Ray Fluorescence (XRF). Table 3. shows the results of the composition of materials Al doped ZnO. The Al doped ZnO contain elements of C, O, Zn, Al and Mg. Mg is fewer element in synthesized AZO nanoparticles. From the Table 2. shows that mass (%) of Zn decrease with increase Al doping concentration in AZO.

Table 3. XRF analysis result of Al doped ZnO (AZO).

Sample	Mass (%)						
	ZnO	Al_2O_3	MgO	Zn	O	Al	Mg
AZO 2 %	88.83	8.24	0	71.37	22.26	4.36	0
AZO 3%	85.39	10.53	1.09	68.60	23.09	5.57	0.66
AZO 4%	82.19	12.98	1.77	66.03	23.95	6.87	1.07

Furthermore, the calculation of ratio of Al/Zn in AZO 2%, AZO 3% and AZO 4% were shown in Fig. 5. the increasing Al dopand had beed added was capabled increase substitution of Zn atoms by Al. Replacement Zn by Al on AZO 2% have a ratio of Al /Zn = 0.061; on AZO 3% have a ratio of Al /Zn = 0.081 and on AZO 4% have a ratio of Al /Zn = 0.104.

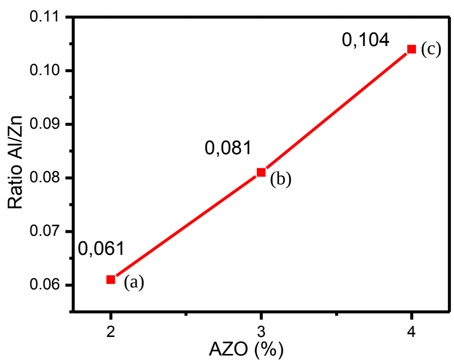


Figure 5. Influence of ratio Al addition in ratio of Al/Zn in AZO (a) 2%, (b) 3%, and (c) 4%

4. Conclusion

Al doped ZnO (AZO) were synthesized by sol-gel method. The structural and optical properties of AZO nanoparticle have been investigated. Annealing temperature influenced the crystalline quality of Al doped ZnO, where increasing of annealing temperature was followed by increase of crystallinity Al doped ZnO. The variation of Al content did not significantly influence the phase structure or the crystalline quality. SEM images of the samples show the agglomeration increases with increasing Al concentration. FTIR showed a new absorption at a wavelength of 680 cm^{-1} and 1630 cm^{-1} which is stretching vibration of symmetry and asymmetry of the Al-O-Al. XRF analysis shown that ratio of Al/Zn increase with increase Al doping concentration.

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