THE INFLUENCE OF PH VALUES ON THE CRYSTALLITE SIZE OF ZnO SOLVOTHERMAL SYNTHESIS

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Abstract

Zinc oxide (ZnO) is a semiconductor material that widely used in various applications due to its unique properties. Synthesis of ZnO by solvothermal method has been conducted with controlled pH values. The variations of pH value were 10, 11 and 12 by adjusting NaOH content. Crystall structure of the synthesis products after heat treatment at 110oC and 600oC has been characterised by X-ray Diffratometer (XRD). Crystallite size of ZnO was calculated by Scherrer equation. Crystall phase of ZnO has been observed on all pH value variations at 110 oC with 22,98-37,06 nm of crystallite size, whereas ZnO has been observed on all pH value variations at 600 oC with 41,39-71,77 nm of crystallite size.

Keywords: *ZnO, pH values, crystallite size, solvothermal*

Introduction

Zinc oxide (ZnO) as semiconductor material has high stability in chemical, mechanical, photoradiation and thermal, board band gap energy and good in electrochemical and photochemical properties (Kołodziejczak-radzimska, 2014). As a semiconductor material, ZnO is widely used as promising materials for electronic and optoelectronic applications such as laser diodes, photoelectrodes, LEDs and gas sensors. Besides electronic application, ZnO is also catalyst that has lewis acid and basic for organic compounds synthesis (Kothandapani, 2016). In health and environmental application like medicine, biomedical diagnosis and therapy, water treatment, waste photodegradation, ZnO has antimicrobial (Król, 2017), antioxidant (Zare, 2017) and photocatalytic properties (Atchudan, 2017). According to versatile applications, ZnO is still attractive materials to be investigated especially in synthesis development.

Synthesis of ZnO by solvothermal method is an alternative method to produce single-crystalline nanostructure, controlled size and shape (Rai, 2013). In addition, solvothermal synthesis is able to produce fine and uniform nanoparticle (Sari, 2015). This method performance is influenced by reaction environment such as precursor, solvent and additives (An, 2015). Precursor, solvent and additives affect microstructures, morphology and the properties of product (Zare, 2017). Synthesis of ZnO by solvothermal method basicly is conducted in base environment. As an important factor, the influence of pH on ZnO synthesis has been investigated in this work.

In this research, ZnO has been synthesized by facile solvothermal method in various pH then continued with heat treatment process at 110°C and 600°C. The influences of pH have been studied by X-

ray diffraction method to study the crystall structures and crystallite size. Crystallite size average was calculated using Scherrer method.

Materials and Methods

Materials

Zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$, 99%), sodium hydroxide (NaOH, 98%), ethanol absolute were purchased from Sigma-Aldrich, that used without further purification.

Methods

Synthesis of ZnO

Synthesis of ZnO has started by dissolving of 2 gram $Zn(CH_3COO)_2.2H_2O$ in 100 mL ethanol absolute until homogenous. The solution of NaOH 2 M in ethanol was then added drop wise into $Zn(CH_3COO)_2$ to adjust pH values to 10, 11 and 12 while still stirred constantly and heated at 75 °C for 8 hours. The mixtures were then digest at room temperature for 24 hours. The percipitates were formed during this process then filtered and washed with demineralised water. After this, the precipitates were heated at 110°C and 600°C for 5 hours, respectively.

Characterisation of ZnO

Phase and crystall structure was analyzed on a X-ray diffractometer (XRD) X'PERT-PRO PA using CuKα radiation (λ = 1,5418 Å) for 2θ values for 20-80°. Crystallite size was measured by X-ray peak profile analysis and calculated by Debye-Scherrer equation (Thomas, 2014).

$$D = \frac{K\,\lambda}{\beta_{hkl}\,Cos\theta} \quad (1)$$

where D is crystallite size, K is Scherrer constant equal to 0,90, λ is X-ray wavelength for CuKα radiation equal to 1,5418 Å, β_{hkl} is full width at half maximum (FWHM) of XRD peak and θ is diffraction angle.

Results and Discussion

Herein, white powders of ZnO were sucessfully synthesised by solvothermal method at all variations of pH value and at all temperature heat treatment. These results are following precipitation reaction of $Zn(OH)_2$ then transformed to ZnO by heating process (Kołodziejczak-radzimska, 2014)

Elimination of $Na(CH_3COO)$ and H_2O as side products was conducted by washing and heating process so that can produce single product of ZnO. Figure 1 shows the difractogram of ZnO with similar XRD peaks pattern of all pH variation at 110°C. The XRD peaks pattern are indexed to JCPDS 36-1451 that confirm the hexagonal wurtzite phase of ZnO. There are no other crystalline phase detected that mean this synthesis method produce single crystalline phase of ZnO. Besides all pH variation show similar pattern, the XRD peak intensity ratio are quite similar at all pH variations

Single cristallinity of hexagonal wurtzite phase of ZnO showed on Figure 2. Peak intensity of XRD increased at all pH value along the increasing of temperature from 110°C to 600°C. Similar results with heat treatment at 110°C, XRD peak intensity ratio are quite similar at all pH value that indicates similar shape and morphology formation (Jaimeewong, 2016)

$$Zn(CH_3COO)_2 + NaOH \longrightarrow Zn(OH)_2 + 2\ Na(CH_3COO) \quad (2)$$

$$Zn(OH)_2 \xrightarrow[\Delta]{} ZnO + H_2O \quad (3)$$

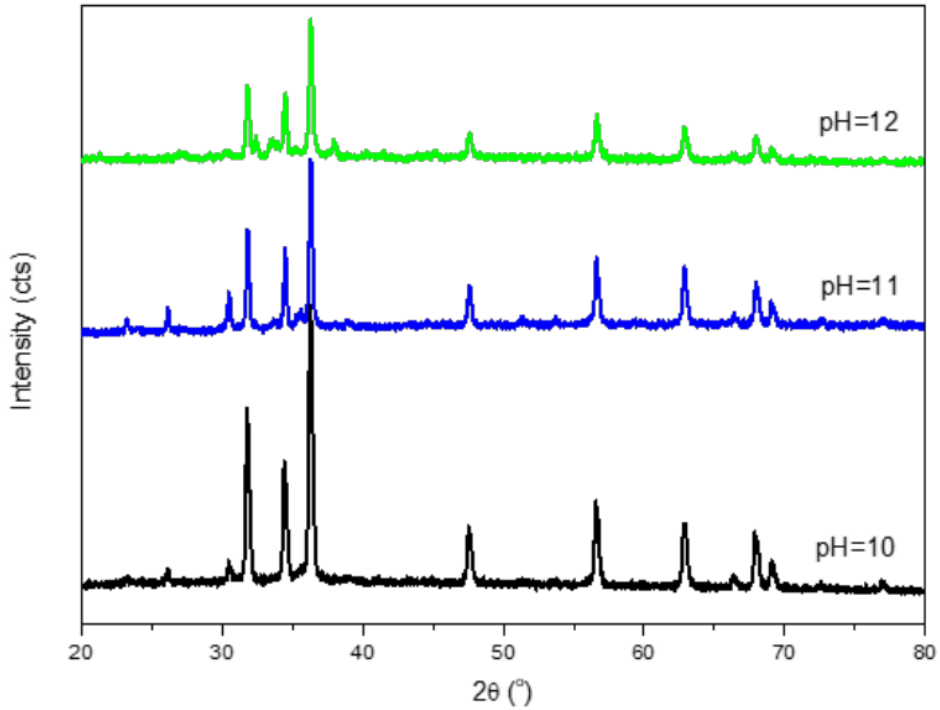

Figure 1. XRD difractograms of ZnO products of different pH variation at 110°C

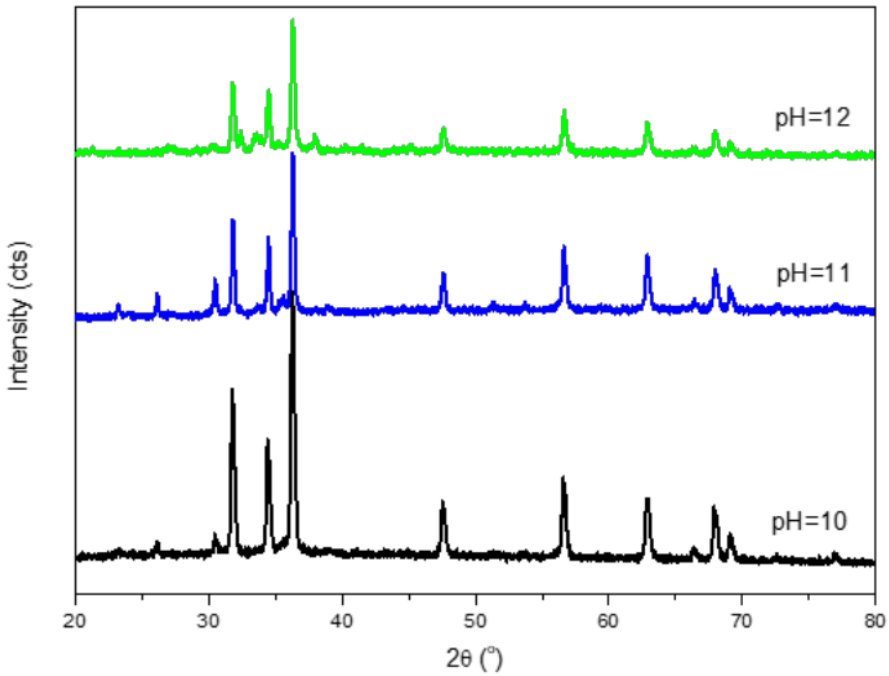

Figure 2. XRD difractograms of ZnO products of different pH variation at 600°C

Table 1. Crystallite size average of ZnO

Temperature (°C)	Crystallite Size Average (nm)		
	pH =10	pH = 11	pH =12
110	22,98	37,06	26,12
600	71,77	54,23	41,39

The influence of pH value variations to crystallite size of ZnO can be oberved on Table 1. At 110°C, there are no corelation results about the influence of pH value to ZnO crystallite size due to the diffrence of products transformation to ZnO. The product formation before heat treatment at pH 10 are dominantly $Zn(OH)_2$, product at pH 11 are dominantly $Zn(OH)_2$ and $Zn(OH)_3^-$ and product at pH =12 are dominantly $Zn(OH)_3^-$(Pandit, 2017). The increased of heat temperature increase the crystallite size of ZnO because the inccreased of aggregation process (Jaimeewong, 2016). The influence of pH value observed the decreased of the crystallite size from 10 to 12. The function of NaOH on solvothermal method as mineraliser and catalyst (An, 2015) can be the reason about the decreased of the crystallite size.

Conclusions

To conclude, ZnO have successfully been synthesized by solvothermal method. ZnO were formed in all of pH values variation at both 110°C and 600°C temperature of heat treatment. Synthesis of ZnO at pH = 10 at 600°C resulted highest XRD peak intensity and greatest crystallite average size to 71,77 nm.

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