Preparation and Characterization of Molarity Based ZnO Fine Powder by Hydrothermal Synthesis

Zon[1], Cho Cho Hmway[1], Htet Htet Nwe[2], Yin Maung Maung[1], Than Than Win[1] and Ko Ko Kyaw Soe[1]

[1]*Department of Physics, University of Yangon, Myanmar*

[2]*Department of Physics, Dagon University, Myanmar*

[1]dryinmgmg @g-mail.com

Abstract **- Crystalline zinc oxide fine powder has been prepared by hydrothermal method. Hydrothermal synth esized zinc oxide powder was prepared with zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$) and sodium hydroxide (NaOH), and methanol (CH_3OH) employed as solvent. Samples were prepared at different molarities (0.2 – 0.5) M for 6 h. Teflon-lined stainless steel container was used as a hydrothermal vessel. The temperature for synthesizing zinc oxide powder was around 120°C lower than that of conventional heating process. Subsequently, X-ray diffraction (XRD) was used to examine the phase formation and crystallographic properties of ZnO specimens. The concentration of zinc in zinc oxide was characterized by energy dispersive X-ray fluorescent (EDXRF). The results indicate that zinc oxide powder synthesized by hydrothermal method was fine powder.**

Keywords: **Hydrothermal method, Zinc oxide, phase formation, crystallographic properties**

I. INTRODUCTION

Zinc oxide (ZnO) is a wide band gap II-VI compound semiconductor with a direct bandgap of 3.37 eV at room temperature. With an electron binding energy of 60 meV and the superior properties such as anti-oxidation and chemical stability, ZnO is a promising optoelectronic material with great potential in applications for optical detector, gas sensor, solar cell, short-wavelength UV laser, and blue or green optoelectronic devices. In the present time, the synthesis of ZnO with novel shapes (e.g. wire, rod, lamina, and tube) has attracted widespread attention [1]. Now, ultrafine ZnO shows significant value in many fields consisting of ceramics, chemical industry, electronics, catalyst, optics and medical chemistry. It had attracted much attention and become the focus of the researchers all over the world. Ultrafine ZnO is able to grow with self-organizing ability. Under steady conditions, the interaction of molecules is evident, which makes molecules grow rigorously along with the epitaxial interface of crystal lattice to form homogenous structure. Ultrafine ZnO has not only strong ability to absorb electromagnetic wave, but also shield ultraviolet ray, absorb infrared ray, disinfect, etc [2].

ZnO is one of important ceramic materials, and has been found to have diversified applications in electronic devices such as gas sensors, varistors, and transducers. Different routes such as precipitation, spray pyrolysis[3], sol-gel synthesis [4], and thermal decomposition have been utilized for preparing ZnO powder; however, only a few studies have focused on the hydrothermal synthesis. Among the solution processing routes, recently the hydrothermal process has been proposed to be an effective method for synthesizing fine ceramic powder. The hydrothermal process in general progresses in a closed system at a high autogeneous pressure. By the benefit of the closed system with high pressure, the required temperature for preparing ceramic powder can be greatly reduced because of enhanced reactivity of reactive species, and fine particles with high sinter ability can be obtained. In addition, the evaporation of volatile species can be suppressed, and the stoichiometry of ceramics can be maintained [3].

Hydrothermal technique is a promising alternative synthetic method because of the low process temperature and very easy to control the particle size. The hydrothermal process have several advantage over other growth processes such as use of simple equipment, catalyst-free growth, low cost, large area uniform production, environmental friendliness and less hazardous. This method has been successfully employed to prepare nanoscale ZnO and other luminescent materials. The particle properties such as morphology and size can be controlled via the hydrothermal process by adjusting the reaction temperature, time and concentration of precursors [4]. This study was aimed at a new and simple low-temperature hydrothermal process for preparation of ZnO fine powder.

II. EXPERIMENTAL PROCEDURE

The raw materials of zinc acetate dihydrate ($Zn(CH_3COO)_2.2H_2O$), sodium hydroxide (NaOH) and methanol (CH_3OH) were chosen as starting chemicals. In order to synthesize the ZnO fine particles, the solution of $Zn(CH_3COO)_2.2H_2O$ (0.1 M) was prepared in 50ml methanol

under stirring. 25ml of NaOH (varying from 0.2M to 0.5M) solution prepared in methanol was added to this solution under continuous stirring. These solutions were transferred into Teflon-lined stainless steel vessel. Then these mixture solutions were heated at 120°C for 6 h. It was then allowed to cool at room temperature. Finally, ZnO fine powders were obtained. In this process, the samples at different molarities from 0.2M to 0.5M were obtained. The synthesized samples were characterized by X-ray diffraction (XRD) analysis. The XRD analysis was carried on the samples for investigation structural properties. The quantitative analysis of the samples was obtained by XRF analysis. Fig 1 showed the experimental procedure of ZnO powder preparation. Table 1 showed the concentration of hydrothermal synthesized ZnO powder. The apparatus used for hydrothermal synthesis was shown in Fig 2.

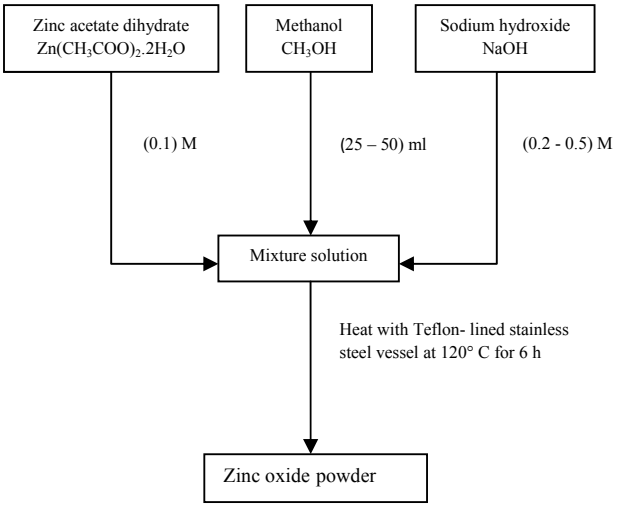


Fig 1 Experimental procedure of Zinc oxide powder preparation

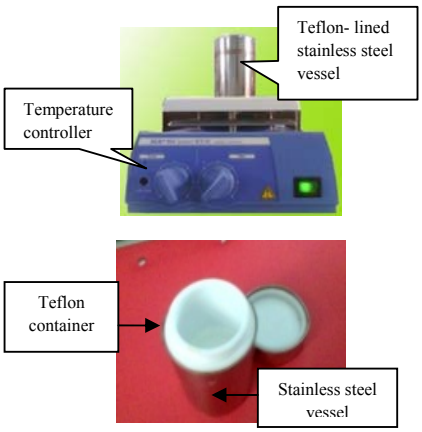


Fig 2 Photos of heating process & Teflon lined stainless steel vessel for preparation of ZnO powder by hydrothermal synthesis

TABLE I
CONCENTRATION OF HYDROTHERMAL SYNTHESIZED ZNO POWDER

No.	Molarity (M)	Zinc acetate dihydrate in 50ml methanol (g)	Sodium hydroxide in 25ml methanol (g)
1.	0.2	1.097	0.199
2.	0.3	1.097	0.299
3.	0.4	1.097	0.399
4.	0.5	1.097	0.499

III. RESULTS AND DISCUSSION

A. *XRD analysis*

XRD analysis was carried out to study the phase formation and crystallographic properties such as crystallite size and lattice parametres of ZnO fine powder. XRD profiles of ZnO samples at different molarities (0.2-0.5) M were shown in Fig 3 (a-d). These samples were prepared at constant temperature 120°C for 6 h. Specimens were scanned from 30° to 70° in diffraction angle, 2θ with step-size of 0.02°. The standard or reference profile was # 75-0576 > ZnO JCPDS library file. Fig 3(a) indicated the XRD spectrum of ZnO powder at 0.2 M. On this XRD spectrum, nine peaks were well-consistent with the ZnO JCPDS library file. They were (100), (002), (101), (102), (110), (103), (200), (112) and (201) peaks. The peaks (100), (002), (101) were situated between 30° and 40° of 2θ angle, (102) peak was between 40° and 50°, (110) peak was between 50° and 60°, and the peaks (103), (200), (112) and (201) were between 60° and 70° respectively. The XRD diffraction peaks belonging to (100), (002) and (101) planes of ZnO hexagonal phase were observed in all the XRD profiles of ZnO samples. The intensity of (002) diffraction was the weakest among them. Fig 3(b-d) showed the XRD spectrum of ZnO powder at (0.3-0.5) M. On these spectrums, the most intense peak was caused by the (101) reflection. The dominant peak was also (101) reflection. In addition, some extra peaks were formed on all XRD spectra and they were unidentified. The crystallite size was calculated by Debye- Scherrer formula

$$G = \frac{\beta \lambda_{CuK_\alpha}}{FWHM \cos\theta_B} \quad \text{---------- (1)}$$

Where β = Scherrer constant ≈ 0.899

G = Crystallite size

λ_{CuK_α} = wavelength of Cu K_α = 1.54056 Å

FWHM = Full Width at Half Maximum

θ_B = Bragg angle

Table 2 described the some unique features about XRD analysis. Lattice constants "a" and "c" were calculated by using well known analytical method. The lattice parametres and lattice distortions for ZnO powder were given in Table 3. The change in covalent bond length and position parametres with respect to molarities were quoted in Table 4. The position parametres (u-parametres) and bond length (BL) were calculated by the following equation (2)

$$BL\,(\text{Å}) = \sqrt{\frac{a^2}{3} + \left(\frac{1}{2} - u\right)^2 c^2} \quad \text{---------- (2)}$$

Where u = position parametres = $\frac{a^2}{3c^2} + 0.25$

Table 5 presented the lattice parametres and lattice distortion of ZnO by Xiao-yi S et al, 2010 [2]. Table 6 showed the crystallite sizes of ZnO at different molarities reported by Aneesh P M et al, 2007 [4]. The standard values of ZnO were shown in Table 7 [5]. The lattice parametres of ZnO in JCPDS files # 361451 were a = 3.249 82 Å and c = 5.206 61 Å. Concerning with Table 3, 5 and JCPDS files, the observed lattice parametres were found to be little different in those of references. According to Table 2 and 6, the observed value of crystallite size of ZnO at 0.2 M & 0.4 M were in good agreement with those of Aneesh P M et al, 2007 and were not matched at 0.3 M & 0.5 M. From Table 3 and 7, the observed values of lattice parametres and lattice distortion were in good agreement with the standard values of ZnO.

TABLE II.
SOME UNIQUE FEATURES ABOUT XRD ANALYSIS

Molarity (M)	Dominant peak	CuK_α(Å)	FWHM (degree)	2θ (degree)	Crystallite size (nm)
0.2	(101)	1.54	0.053	36.64	15.5
0.3	(101)	1.54	0.034	36.40	24.2
0.4	(101)	1.54	0.038	36.39	21.5
0.5	(101)	1.54	0.024	36.42	34.5

TABLE III
LATTICE PARAMETRES AND LATTICE DISTORTIONS OF ZNO POWDER AT DIFFERENT MOLARITIES

Molarity (M)	Lattice parametre (Å)		Lattice distortion ($\frac{c}{a}$)
	a - axis	c - axis	
0.2	3.21	5.22	1.63
0.3	3.23	5.25	1.63
0.4	3.22	5.28	1.64
0.5	3.21	5.31	1.65

TABLE IV
POSITION PARAMETRES AND BOND LENGTHS OF ZNO AT DIFFERENT MOLARITIES

Molarity (M)	Position parametre (Å)	Bond length (Å)
0.2	0.377	1.96
0.3	0.377	1.97
0.4	0.376	1.97
0.5	0.375	1.97

TABLE V
LATTICE PARAMETRES AND LATTICE DISTORTION OF ZNO BY XIAO-YI S ET AL, 2010 [2]

Molarity (M)	Temperature (°C)	Annealing time (h)	Lattice parametre (Å)		Lattice distortion ($\frac{c}{a}$)
			a-axis	c-axis	
2, 5, 10	140	12	3.249	5.206	1.547

TABLE VI
CRYSTALLITE SIZES OF ZNO AT DIFFERENT MOLARITIES BY ANEESH P M ET AL, 2007 [4]

Molarity (M)	Temperature (°C)	Annealing time (h)	Crystallite size (nm)
0.3	100 - 200	6	7 – 16
0.2, 0.4, 0.5	200	12	12 - 24

TABLE VII
THE STANDARD VALUES OF LATTICE PARAMETRES AND LATTICE DISTORTION OF ZNO [5]

Lattice parametres(Å)		Lattice distortion ($\frac{c}{a}$)
a - axis	c - axis	
3.25	5.2	1.633

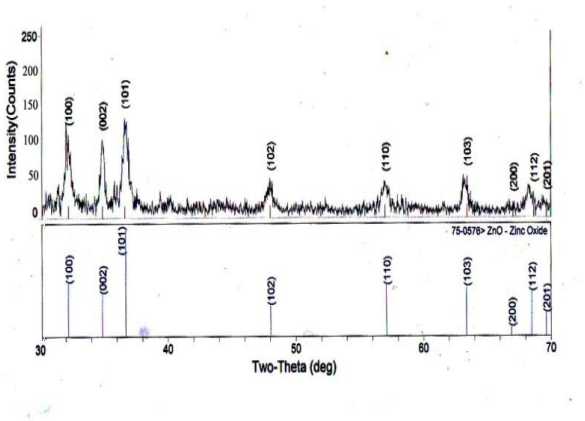


Fig 3(a) XRD spectrum of ZnO powder at 0.2 M

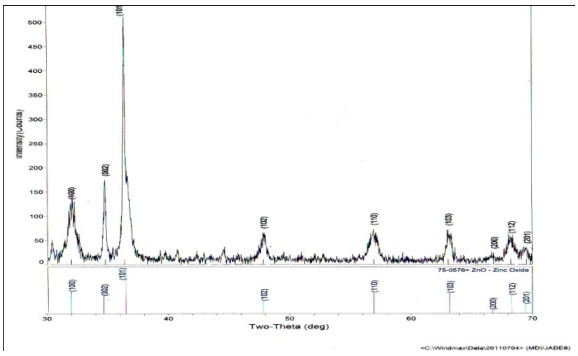


Fig 3(b) XRD spectrum of ZnO powder at 0.3 M

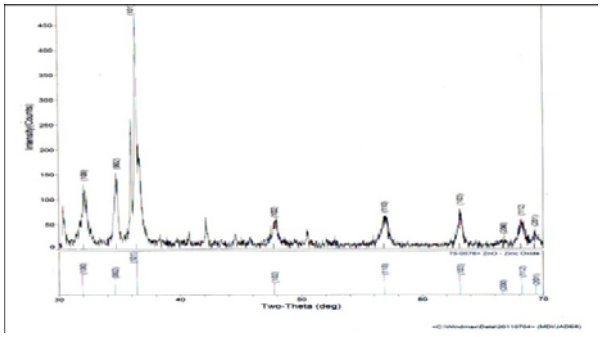


Fig 3(c) XRD spectrum of ZnO powder at 0.4 M

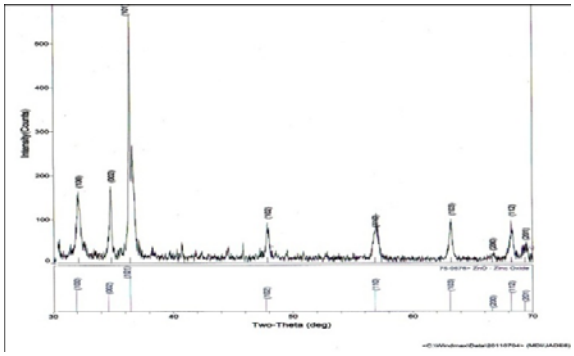
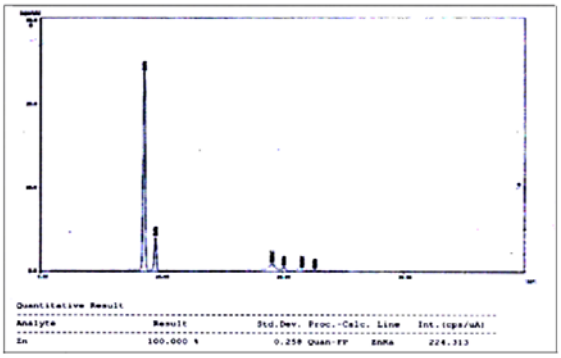


Fig 3(d) XRD spectrum of ZnO powder at 0.5 M

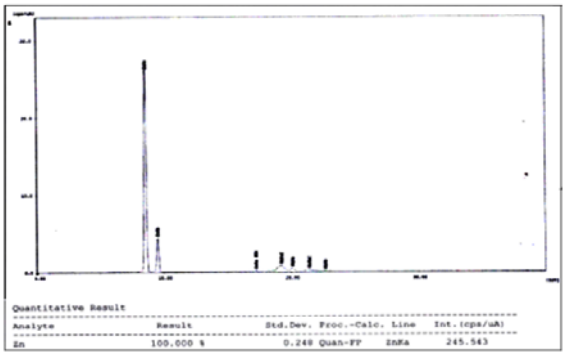
B. XRF analysis

XRF was employed to study the elemental analysis of ZnO specimens. As a result of XRF, the concentration of Zn in ZnO powders was 100.000% at different molarities (0.2 - 0.5) M. Fig 4(a-d) showed the XRF spectrums of ZnO powder at (0.2 - 0.5) M.



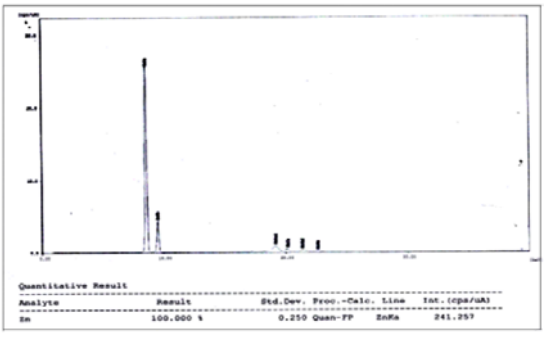
Quantitative Result
Analyte Result
Zn 100.000%

Fig 4(a) XRF pattern of ZnO at 0.2 M



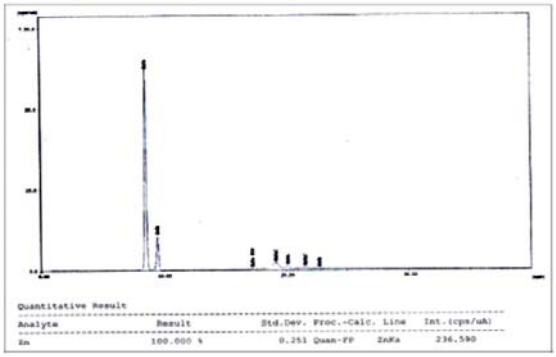
Quantitative Result
Analyte Result
Zn 100.000%

Fig 4(b) XRF spectrum of ZnO powder at 0.3 M



Quantitative Result
Analyte Result
Zn 100.000%

Fig 4.(c) XRF spectrum of ZnO powder at 0.4 M



Quantitative Result

Analyte	Result
Zn	100.000%

Fig 4(d) XRF spectrum of ZnO powder at 0.5 M

IV. CONCLUSION

The concentration of NaOH influenced on the crystallite size of ZnO powder. The XRD analysis demonstrated that the ZnO powder had the hexagonal wurtizite structure and the particle size changed with the concentration of NaOH. When the concentration of NaOH was increased from 0.2M to 0.3M, the crystallite size of ZnO powder increased, while that of NaOH was increased from 0.3M to 0.4M, the crystallite size decreased. However, as the concentration of NaOH was increased from 0.4M to 0.5M, the crystallite size increased again. It was found that the crystallite size of ZnO powder depended on the NaOH concentration. According to XRF analysis, the concentration of Zn in all ZnO samples at (0.2 - 0.5) M was examined to be 100.000%. It definitely meets the standards of the requirements for hydrothermal synthesis of low temperature and of low cost.

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