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CONCENTRATION EFFECT OF ZINC ACETATE DIHYDRATE AS PRECURSOR IN PREPARING ZINC SELENIDE THROUGH HYDROTHERMAL METHOD

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Zinc Selenide has been synthesized through hydrothermal method using Zinc Acetate Dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$) and Se powder as the precursor. In a typical synthesis, Zn^{2+} and Se^{2-} ion have been prepared separately and charged into a teflon-lined stainless steel autoclave. The ZnSe are characterized by X-ray diffraction (XRD), Field Emission Microscopy (FESEM), ultraviolet–visible spectroscopy (UV-Vis) and photoluminescence (PL). From the Pure ZnSe with main XRD peak at 2θ = 27.29°, 45.30°, 53.62°, 65.88°, 72.68° has been synthesized with the optical band gap energy (E_g) of 2.50 eV with emission peak at 486 nm.

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1. Introduction

Selenium based chalcogenide materials are getting attention since the past decade as the increasing demands on high-performance electronics, high mobility semiconducting materials which compatible with conventional metal oxide semiconductors. Selenium based chalcogenides included zinc selenide, iron selenide, copper selenide, copper zinc selenide, copper zinc tin selenide and etc. These materials are widely use in solar cells [1], light- emitting diodes (LED) [2], diode lasers [3] and infrared optical material [4].

In this research, ZnSe is synthesized as it is a yellow II-VI semiconductor with wide band gap. There are various methods has been used to synthesize ZnSe. These methods are sol-gel methods [5,6], hydrothermal method [7] and chemical vapour deposition (CVD) [8,9]. In the present study, we report the synthesis of ZnSe via hydrothermal route in presence of ethylene diamine tetraacetic acid. Hydrothermal method has been chosen due to its advantages of low temperature reaction, simple equipment and also an effective method to form well-crystallization structure with fewer defects.

This project aims to investigate the concentration effect of zinc acetate dihydrate in synthesizing ZnSe and study the optical phenomenon for optoelectronic devices. Characterizations such as UV-Vis spectroscopy, photoluminescence (PL) and FESEM have been used to examine the absorption value, band gap energy (E_g), emission peak and the particle size of ZnSe powder.

2. Experimental procedure

All chemicals were analytical grade and used without further purification. Zinc acetate dihydrate ($Zn(O_2CCH_3)_2(H_2O)_2$, $\geq$ 98%), selenium (Se, $\geq$ 99%), ethylene diamine tetraacetic acid

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(EDTA, ≥99%) was purchased from HmBG and sodium hydroxide (NaOH, 99%) was purchased from Fisher Scientific.

$Zn(O_2CCH_3)_2(H_2O)_2$ and Se powder were used as the precursors. 0.4 g $Zn(O_2CCH_3)_2(H_2O)_2$ powder and 3.2 g NaOH were dissolved in 20 ml of distilled water and stir for 50 min. At the same time, 0.5 g Se powder and 3.2 g NaOH were added into 20 ml distilled water under stirring condition. Both solutions were mixed and then EDTA was added into the mixture. The samples have been prepared based on the mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$: Se as shown in Table 1. The number of mole of $Zn(O_2CCH_3)_2(H_2O)_2$ was vary from 0.25 to 4 while the number of mole of Se remain constant.

Table 1. The mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se.

Mole Ratio	Number of mole (mmol) $Zn(O_2CCH_3)_2(H_2O)_2$	Se
0.25:1	1.5	6.0
0.5:1	3.0	6.0
1:1	6.0	6.0
2:1	12.0	6.0
3:1	18.0	6.0
4:1	24.0	6.0

The final mixture was transferred into Teflon-line autoclave and hydrothermal reaction was conducted in oven (Memmert oven UNE 200) at 180°C for 32 h. The product was naturally cooled to room temperature and centrifugation process was carried out. The light yellow powders were dried at 60°C for 24h.

The crystal structure of the sample is identified using X-ray diffraction (X'pert Pro Panalytical PW3040) with CuK_α radiation at 40kV, 40mA. The optical properties was characterized by ultraviolet-visible NIR (Shimadzu UV-6000) and photoluminescence (Perkin Elmer LS 55 Luminescence) with excitation at 370 nm at room temperature. The morphology properties were investigate using FESEM (HITACHI SU8000).

3. Results and discussion

The X-ray diffraction (XRD) studies were done on zinc selenide powder synthesized through hydrothermal route at different concentration ratio of zinc acetate dihydrate $Zn(O_2CCH_3)_2(H_2O)_2$ with selenium (Se). Fig. 1 shows the XRD patterns of samples prepared by $Zn(O_2CCH_3)_2(H_2O)_2$:Se from 0.25:1 to 4:1 mole ratio. The main peaks are sharp and narrow with peaks centered at 27.3°, 45.3°, 53.6°, 65.9° and 72.7°. The spectra are closely matched with ICSD (reference no. 98-009-1262) which indexed the sample as cubic zinc blended system. The XRD results that obtained in the experiment was similar with result that obtained by Yang *et al.* [10] and Peng *et al.* [11] through solvothermal and hydrothermal method, respectively.

The crystallite size of ZnSe powder has been calculated using Scherer equation, $d = K\lambda/\beta\cos\theta$ in Xpert HighScore Plus software (Version 3.0e) with five main peak at 2θ, which is 27.3°, 45.3°, 53.6°, 65.9° and 72.7 for each sample. The crystallite size obtained is in the range of 50.0 nm to 62.9 nm as shown in Table 2. The highest crystallite size is 62.9 nm for sample ratio 3:1 and the lowest is 50.1 nm for sample ratio 0.25:1. From the results obtained, it can be conclude that the concentration ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se did not influence the crystallite size of the ZnSe.

Table 2. Crystallite size of ZnSe powder prepared with different mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se

$Zn(O_2CCH_3)_2(H_2O)_2$:Se ratio	Crystallite size (nm)
0.25:1	50.1
0.5:1	58.5
1:1	50.3
2:1	55.9
3:1	62.9
4:1	58.4

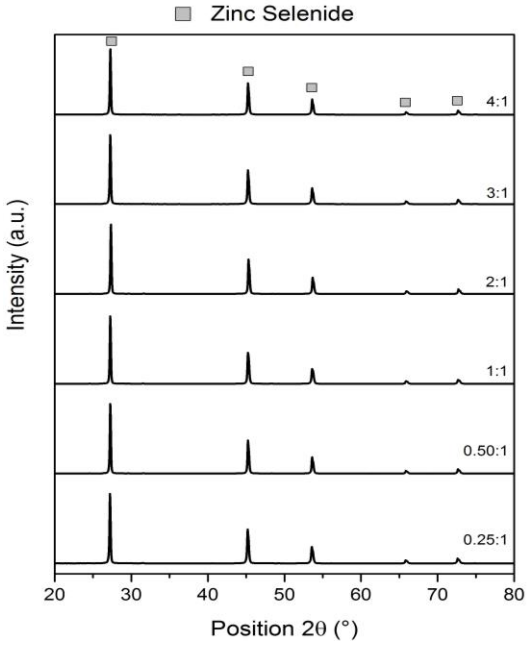


Fig. 1. XRD pattern of ZnSe powder prepared with different mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se.

For optical properties, ZnSe synthesized with different mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se were monitored with UV-Vis spectroscopy as shown in Fig. 2. The absorption spectrum for all different concentration ratio $Zn(O_2CCH_3)_2(H_2O)_2$:Se is at value 460 nm. As reported by Li et al. [12] the absorption peak for ZnSe is around 400 nm to 450 nm, but a slightly different absorption value (460 nm) have been observed in our sample due to the factor such as the starting material, reaction temperature, time reaction and the method used is different.

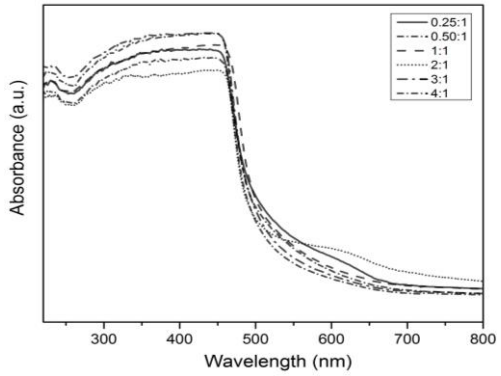


Fig. 2. UV-Vis absorption spectrum of ZnSe powder with various mole ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se.

The optical band gap are estimated by using classical Tauc equation approach [11]:

$$\alpha E_p = K (E_p - E_g)^n \quad (1)$$

where α is absorption coefficient, E_p is photon energy, E_g is optical band gap, K is constant and n is different possible electronic transitions with has value ½ (direct) and 2 (indirect). The optical band gap energy (Eg) for sample with different concentration ratio $Zn(O_2CCH_3)_2(H_2O)_2$:Se have been tabulated in Table 3. The optical band gap (E_g) value for ZnSe is 2.50 eV for all mole ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se from 0.25:1 to 4:1. The absorption spectrum and optical band gap obtained indicated that the concentration of precursor does not influence the optical properties of the material.

Table 3. Optical band gap energy (E_g) value with different mole ratio of $Zn(O_2CCH_3)_2(H_2O)_2$:Se.

$Zn(O_2CCH_3)_2(H_2O)_2$:Se ratio	Optical band gap energy E_g (eV)
0.25:1	2.50
0.5:1	2.50
1:1	2.50
2:1	2.50
3:1	2.50
4:1	2.50

Fig. 3 shows the photoluminescence emission peak monitored by luminescence spectrometer (Perkin Elmer LS 55 Luminescence) for sample prepared with precursor $Zn(O_2CCH_3)_2(H_2O)_2$. The sample is excited with excitation source at 370 nm in powder form. All results obtained shows single emission peak at around 486 nm (blue region) for all sample with concentration ratio $Zn(O_2CCH_3)_2(H_2O)_2$:Se from 0.25:1 to 4:1. It is similar to the result obtained by Feng at al. [13,14] and Zhou et al. [15] at 472 nm and 458 nm in the range blue region peak (450 nm to 490 nm), respectively. Fig. 4 shows the emission peak for the sample prepared at different concentration ratio $Zn(O_2CCH_3)_2(H_2O)_2$ from 0.25:1 until 4:1. The intensity of the emission peak is increasing as the concentration of $Zn(O_2CCH_3)_2(H_2O)_2$ varied with Se. The results show that the emission peaks are centered at 486 nm which is having the peak energy of 2.55 eV.

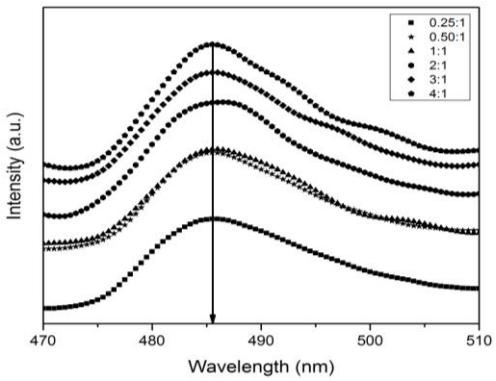


Fig. 3. Photoluminescence (PL) emission peak of ZnSe powder with various mole ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se.

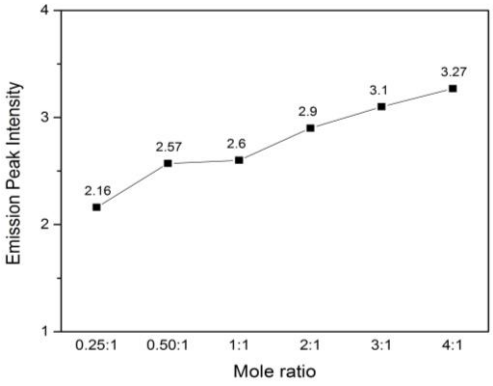
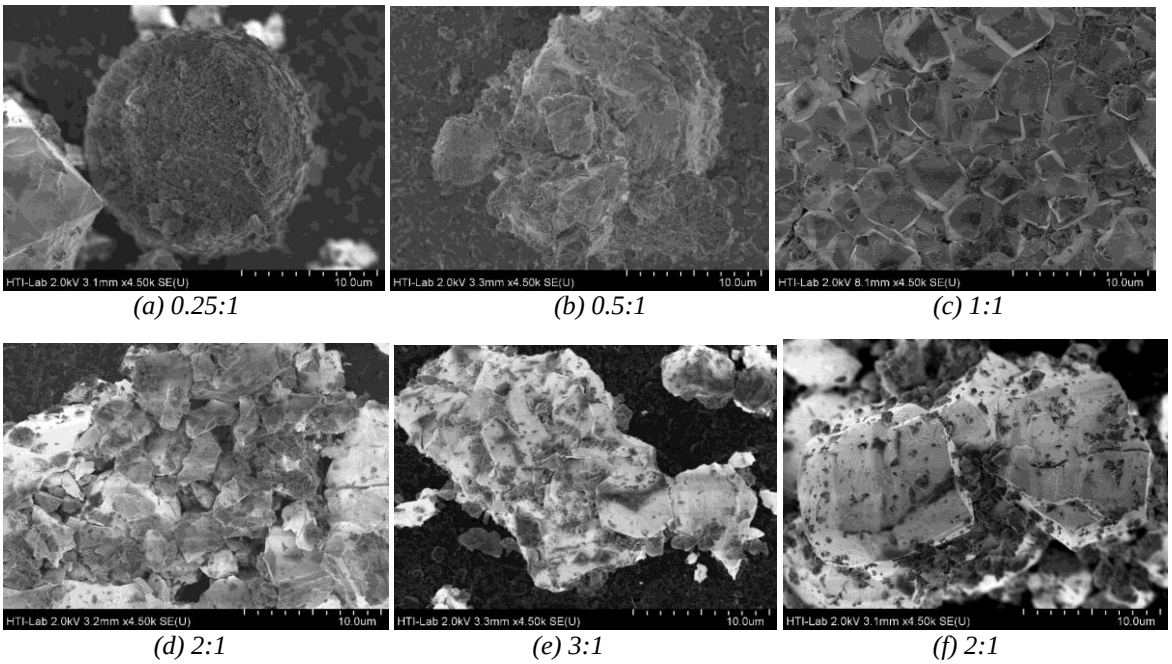


Fig. 4. Emission peak intensity vs mole ratio of $Zn(O_2CCH_3)_2(H_2O)$: Se.

Fig. 5 shows FESEM morphology for ZnSe powder synthesis through hydrothermal method with concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$: Se from 0.25:1 until 4:1 at 4500 x magnification. From the observation, the ZnSe powder synthesized with $Zn(O_2CCH_3)_2(H_2O)$ have some evolution of shape without specific shape. These phenomena happen due to the environment of the experiment and amount of molecules or atom of Zn and Se are different for each concentration ratio. From Fig. 5(a), the particles agglomerates into spherical shape but start to change into cubic structure as the concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se increase up to 1:1 (Fig. 5(c)). As the concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se increased up to 4:1, particles formed cubic shapes as indicated at Fig. 5(f). The highest average particle size is (6.60 ± 0.49) μm for sample with $Zn(O_2CCH_3)_2(H_2O)$:Se concentration ratio 4:1 and the lowest is (0.08 ± 0.02) μm for sample with $Zn(O_2CCH_3)_2(H_2O)$:Se ratio 0.25:1. Others average particle size is reported as (0.1 ± 0.01) μm, (2.4 ± 0.13) μm, (2.3 ± 0.22) μm for concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se 0.5:1, 1:1, 2:1 and 3:1 respectively. The average particle size increased as the concentration ratio of the precursor $Zn(O_2CCH_3)_2(H_2O)$:Se increased. As conclusion, when the concentration of the precursor ratio is different, the shape of formation of ZnSe will be affected, where it changed from sphere to irregular shape and also the diameter size of the particle [10,16].



(a) 0.25:1 *(b) 0.5:1* *(c) 1:1*

(d) 2:1 *(e) 3:1* *(f) 2:1*

Fig. 5 FESEM image for ZnSe powder with different mole ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se.

4. Conclusions

In summary, ZnSe was successfully synthesized via hydrothermal method with different concentrationratio of $Zn(O_2CCH_3)_2(H_2O)$:Se at temperature 180°C for 32 hours. From the XRD result, pure ZnSe with main XRD peak at 2θ = 27.29°, 45.30°, 53.62°, 65.88°, 72.68° which match to ICSD (reference no: 98-009-1262) with zinc blende structure is observed for sample prepared at concentration ratio 0.25:1, 0.5:1, 1:1, 2:1, 3:1 and 4:1. From the absorption result, the peak is at 460 nm with optical band gap energy (E_g) at 2.5 eV.

The emission peak at 486 nm in blue region had been observed for all concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se. The average particle size is from (0.08±0.02) μm to (6.60±0.49) μm from concentration ratio of $Zn(O_2CCH_3)_2(H_2O)$:Se from 0.25:1 to 4:1. The optimum condition to synthesize pure ZnSe is at ratio 1:1 with absorption spectrum at 460 nm and optical band energy at 2.50 eV. The emission peak is at 486 nm (blue region) and average diameter size at (2.4±0.13) μm. The effect of increasing the zinc acetate dihydrate concentration in synthesizing ZnSe has increasing the intensity of the absorption spectrum and the shape of the samples at room temperature.

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