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# Application and preparation of ZnSe nanometer powder by reduction process

Jun Che*, Xi Yao, Haiqing Jian, Minqiang Wang

*Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, PR China*

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**Abstract**

In this paper, we discussed the ZnSe synthesized from $H_2SeO_4$ and $Zn(Ac)_2{\cdot}2H_2O$ as raw materials by coprecipitation process. When $Zn(Ac)_2{\cdot}2H_2O$ dissolved in different solvents, the precipitated crystalline size and morphology of $ZnSeO_4$ were different after $H_2SeO_4$ added. X-ray diffraction (XRD) method has been used to investigate the crystalline size, crystalline morphology, and phase structure of $ZnSeO_4$. Then ZnSe was synthesized from $ZnSeO_4$ by reduction method using carbon monoxide. The structural variation of the ZnSe powder with different annealing temperature was studied. The lowest temperature for the formation of single-phase ZnSe nanocrystals was found to be 460 °C and the average crystallite diameter in the powder annealed at 460 °C was around 25 nm and it can be composed with organic glass. XRD and spectrum analysis showed that stable nanocomposite can be obtained from the mixture.


*Keywords:* B. Nanocomposite; ZnSe; Nanocrystalline

## 1. Introduction

The research of nanometer sized crystallites provides an opportunity to observe the evolution of material properties with size. Semiconductor quantum structure of a three-dimensional confinement have been known as one of the most important candidates for nonlinear optical applications because of their large nonlinearity and fast response [1]. Especially, zinc selenide (ZnSe) as an important II–VI semiconductor materials with wide band gap are used as luminescence, laser and nonlinear optical material. When embedded in transparent optical media, the quantum dots of semiconductor also show a dielectric confinement effect that results in an enhanced field intensity near, at, and inside the particle surface. This local field enhancement may have a profound influence on the photophysical and nonlinear optical integration making it possible and enable the use of a low laser power.

There are many methods to synthesize ZnSe nanocrystalline powder, such as sonochemical methods [2], complex pyrogenation [3], reverse micelle synthesis [4], solvothemal method [5] etc. We selected the ZnSe synthesized from selenic acid and zinc acetate dihydrate as raw material by coprecipitation process. Ethanol or deionized water was used as solvent to dissolve zinc acetate dihydrate and selenic acid. When zinc acetate dihydrate reacts with selenic acid in the solution, zinc selenate sediment was formed. Then again, zinc selenide was synthesized by zinc selenate. The carbon monoxide gas was used as reductive agent. We can represent this reaction as follows:

$$Zn(Ac)_2 + H_2SeO_4 = ZnSeO_4 + 2HAc$$
$$ZnSeO_4 + 4CO = ZnSe + 4CO_2$$

## 2. Experimental procedures

Firstly, the stoichiometric amount of selenic acid and zinc acetate dihydrate, respectively, were added into the solvent at room temperature in a beaker. Then they were mixed and stirred with high speed. The production was moved in a flask and dehydrated under lower vacuum. Fig. 1 shows the X-ray diffraction (XRD) pattern of the zinc selenate powder using different solvent.

* Corresponding author. Fax: +86-29-82668794.
*E-mail address:* chejun@mailst.xjtu.edu.cn (J. Che).

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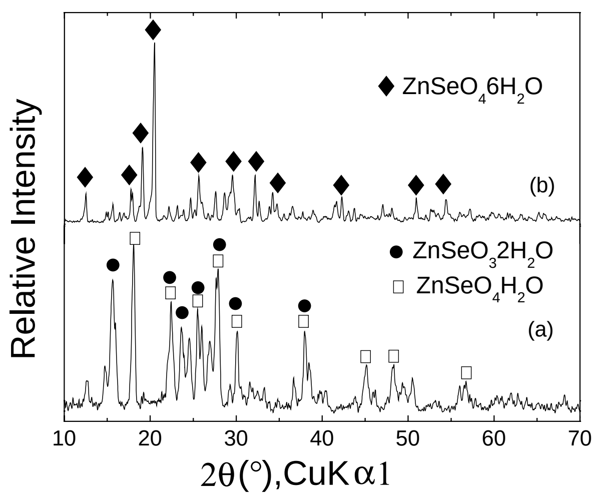


Fig. 1. XRD pattern of $ZnSeO_4$ powder by different solvent: (a) water (b) ethanol.

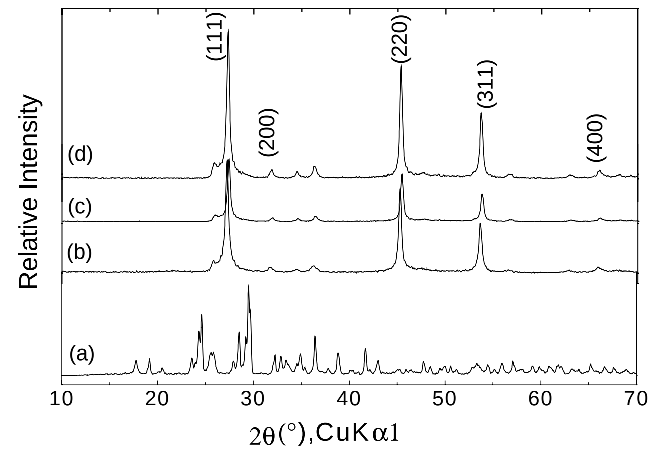


Fig. 2. XRD pattern of ZnSe powder at different temperature for 25 min by different solvent: (a) 420 °C, by water; (b) 460 °C, by water; (c) 500 °C, by water; (d) 500 °C, by ethanol.

The zinc selenate was put into a quartz crucible. Then the quartz crucible was placed in a tube furnace. The tube furnace was sealed off and air was removed by a vacuum pump. After 10 min pumping, the tube furnace was begin to heat up with the rate of 5 °C/min and carbon monoxide gas was aerated simultanety. The zinc selenate was finally heated to different temperatures at the same rate and held for 20–25 min. Then they were cooled down to room temperature. The XRD patterns of zinc selenide by different solvent and at ditterent heat-treatment temperatures were shown in Fig. 2.

The composite process was that dissolved zinc selenide in methyl methacrylate and it was dispersed by ultrasonic device. Then a monomer and initiator of polymerization was added and mixed at 80 °C under stirring. A viscous liquid was formed in water-bath by polymerizing at 90 °C from the mixture solution. After injected into forming module, the mixture was baked at 110 °C and cooled down. This process can be used to prepare bulk and thick film.

## 3. Results and discussions

The XRD patterns of Fig. 1 show that the phase-formation characteristics of zinc selenate is a mixture of zinc selenate hydration ($ZnSeO_4{\cdot}H_2O$) and zinc selenous dihydrate ($ZnSeO_3{\cdot}2H_2O$) by ethanol, but it basically is zinc selenate hexahydrate ($ZnSeO_4{\cdot}6H_2O$) by water solvent. Although the phase-formation characteristics of productions is different, it does not affect on synthesis of zinc selenide.

Fig. 2 show the XRD patterns of zinc selenide powders annealed at different temperature for 25 min by different solvent. Samples annealed at temperatures lower than 460 °C exhibit that zinc selenide has not formed. When the annealing temperature reaches 460 °C or above, the pure zinc selenide phase is observed. The pure zinc selenide phase-formation characteristics are simple cubic sphalerite. The average crystallite size in the zinc selenide powder prepared is calculated from the full-width at half-maximum (FWHM) of the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (4 0 0) X-ray diffraction parks using Scherrer's equation:

$$D = \frac{K\lambda}{B\cos\theta}$$

where $D$ is the grain diameter; $\lambda$, wavelength (=1.5418 Å); $\theta$, diffraction angle; $B$, FWHM of diffraction peak; and $K$, Scherrer's constant (=0.89). The crystallite diameter obtained by the (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (4 0 0) and its average value is given in Table 1.

It shows that the size of zinc selenide nanocrystalline powder by water solvent is thinner than the size of zinc selenide nanocrystalline powder by ethanol solvent in the

Table 1
Crystallite size of ZnSe nanocrystalline powder by different condition

| ZnSe sample | Various parks crystallite diameter (nm) | | | | | |
|---|---|---|---|---|---|---|
| | (1 1 1) | (2 0 0) | (2 2 0) | (3 1 1) | (4 0 0) | Average |
| Ethanol solvent, 500 °C | 31.23 | 28.98 | 40.17 | 41.54 | 39.85 | 36.35 |
| Water solvent, 500 °C | 24.59 | 24.85 | 26.78 | 28.01 | 26.10 | 26.07 |
| Water solvent, 460 °C | 24.59 | 17.35 | 24.13 | 28.78 | 26.53 | 24.28 |
| In perspex | 17.17 | – | 18.07 | 18.69 | – | 18.18 |

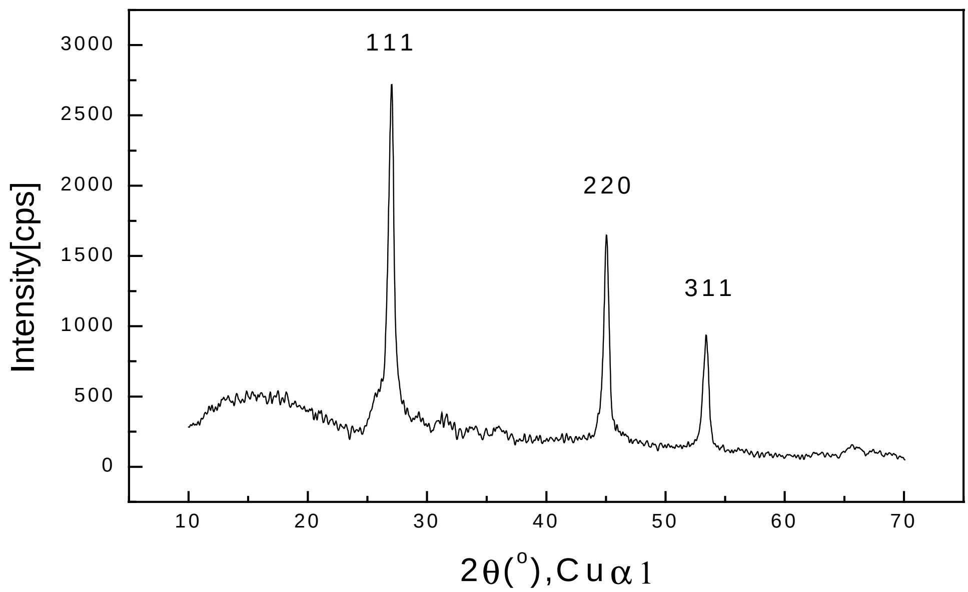


Fig. 3. XRD pattern of ZnSe 0–3 composite.

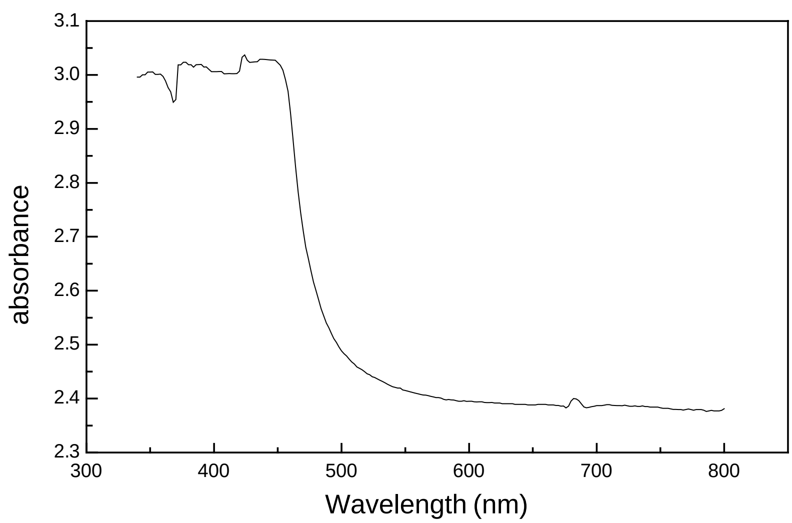


Fig. 4. Absorption spectrum ZnSe/perspex composite sample.

table. The pure zinc selenide nanocrystalline powder can be obtained in this process. At 460 °C or above, the size of powder ranges from 20 to 30 nm by water solvent, but it is 30–40 nm by ethanol solvent.

The XRD pattern of zinc selenide and organic glass composite is showed in Fig. 3. From the figure we can find that the zinc selenide do not react with the methyl methacrylate in the mixture. The average crystal size of zinc selenide in composite is relative smaller than that in pure zinc selenide powder calculated using the Scherer's equation.

Fig. 4 shows the absorption spectrum of the zinc selenide and it's organic glass composite measured by spectrophotometer. The value of absorption edge is 480 nm, similar to that of the pure zinc selenide, and the absorption increases sharply, which shows the zinc selenide is pure. The absorption edge does not take any blue-shift effects. The reason is that the crystal size of zinc selenide is about 18.18 nm, larger than the excitonic Bohr radius of zinc selenide.

## 4. Conclusion

The nanocrystalline of zinc selenide can be obtained from zinc selenate, which is prepared by coprecipitated process, by the reduction process using carbon monoxide gas. The lowest temperature for the formation of single-phase ZnSe nanocrystals is found to be 460 °C and the average crystallite diameter of the powder at 460 °C is around 25 nm. XRD and spectrum analysis show that stable nanocomposite can be obtained in the mixture of zinc selenide and organic glass.

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