

Synthesis and phases of ZnSe prepared by hydrothermal method

LIU KEGAO*, ZHANG LI, JI NIANJING^a, LIU HONG^a

School of Materials Science and Engineering, Shandong Jianzhu University, Fengming Road, Jinan 250101, China

^aState Key Laboratory of Crystal Materials, Shandong University, 27 Shandan Road, Jinan 250100, China

ZnSe powders with single phase were synthesized by hydrothermal co-reduction method from ZnCl₂ and SeO₂ using hydrazine hydrate as reductant. The effects of temperature, reacting time and solute concentration on synthesis of ZnSe powders were investigated. The phases of the products were characterized by X-ray diffraction (XRD), the morphology and sizes were characterized by field emission scanning electron microscope (FESEM). The experimental results show that, the there strong XRD peaks of these products with cubic zinc blende structure are corresponding to (111), (220) and (311) crystal planes. The solute concentrations have no obvious effect on phase crystallization of ZnSe. The temperature and reacting time in reaction are the two key factors to affect ZnSe crystallization. Well-crystallinity ZnSe nano-powders with single phase can be produced under conditions of higher temperature and longer reacting time. The ZnSe products show small particles with sizes of about 20~200 nm, which become larger as the reacting temperature increased.

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II-VI family Compound ZnSe with direct transition band structure is an important wide bandgap semiconductor with a band-gap about 2.7eV. ZnSe can exist in two crystal structures of zinc blende and wurtzite structure and has excellent optical and electrical properties [1-4]. It has wide application in photoelectron field, for example, it can be used for producing blue and green light emitting diodes, laser device, and photovoltaic devices [5-7]. ZnSe with high light absorption coefficient is the ideal film solar cell absorber layer material since its intrinsic absorbed spectrum falls into the most intense region of the solar spectrum. ZnSe has wider forbidden band width than CdS (2.4eV) which is used widely currently. Due to its high degree lattice match with CIGS (Cu₂InGaSe₄), it is suitable to be used as buffer layer material for CIGS thin film solar cell and to prepare CIGS thin film solar without non-toxic Cd [8,9]. The ZnSe thin film synthesized using chemical bath deposition by Rumberg group has been used as the buffer layer of Cu(In,Ga)(Se,S)₂ battery with conversion efficiency high up to 9.6% [10]. ZnSe nanoneedles were prepared using laser beam deposition method by L. Chen group and used as the cathode to prepare polymer/inorganic composite solar cells to improve the performance of the battery. It proved that the ZnSe nanoneedles have a potential application value in polymer/inorganic solar cell [11]. A kind of new battery with ZnO/ZnSe core/shell nanowire array was synthesized by Yong Zhang group, it used ZnSe as the absorbent layer due to its high light absorption rate [12].

The methods for preparing different kinds of nano

ZnSe such as nanoneedles, nanowire array and hollow nanospheres include solvothermal method [13], chemical bath deposition [8], laser beam deposition [11], sol-gel [14] and vacuum thermal evaporation [15], etc. The high-quality ultra-narrow single-crystal nanowires were obtained successfully first by Hao Wei's group via a one-pot solution-based method [16]. The ZnSe microspheres were synthesized through the process of dissolving single mass of Zn and Se respectively in a solution of NaOH and heating at 150 °C for 24h [17]. Well-crystallized ZnSe nanoparticles were prepared by Shakir's group using microwave heating process in first time, these products with band gap 2.99 eV show obvious blue shift [18]. Nano-powders of ZnSe were successfully prepared by hydrothermal method under conditions of different temperatures, and solute concentrations and reacting time in this work.

1. Experimental details

For prepare ZnSe powder, ZnCl₂ and SeO₂ with a ratio of 1:1 were added into a stainless steel autoclave with a Teflon liner of 20 mL capacity. The autoclave was filled with 1:2 ratio of deionized water and absolute ethyl alcohol up to 80% of the total volume. After ultrasonic agitation for about 30 min, 1 mL hydrazine hydrate (N₂H₄·H₂O) and 1 mL HCl were poured into the reactants. The autoclave was sealed and heated at temperatures of (160 °C, 180 °C and 200 °C) for 10~90 h in an electric furnace. Af-

ter heating, it was cooled down to room temperature naturally. The products were collected by filtration, washed with deionized water and absolute ethanol, and then dried at 70 °C. The phases of powder samples obtained were analyzed by X-ray diffraction (XRD) on a model of Bruker D8 Advance XRD system with Nifiltered Cu K α ($\lambda=1.5059$ Å). The size and morphology of the products were observed by a model Hitachi S-4800 field emission scanning electron microscope (FESEM).

2. Results and discussion

2.1 Synthesis of ZnSe by hydrothermal co-reduction

Fig. 1 shows the XRD patterns of Zn-Se powders prepared at different temperatures. According to the standard XRD pdf card of ZnSe (No.37-1463), it indicates that these products belong to cubic zinc blende. The diffraction peaks at the 2θ angles of 27.1°, 45.1°, 53.4° were corresponded to (112), (204) and (312) crystal planes respectively. These results are in good agreement with other papers reported [17-19]. It indicates that the synthesized ZnSe crystals have good crystallinity according to their sharp, high and symmetrical XRD peaks. Fig.1 indicates that the diffraction peaks of the samples synthesized at 180 °C and 200 °C are higher than that synthesized at 160 °C obviously. In addition, the product with Se impurity synthesized at 160 °C shows yellowish green color which is different from yellow color of other examples. It can be seen that well-crystallinity ZnSe nano-powders with single phase can be produced at higher temperatures.

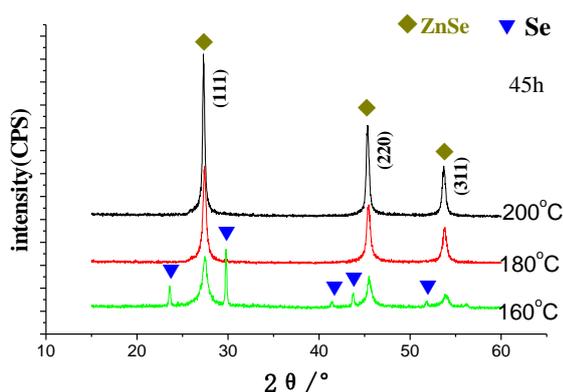


Fig. 1. XRD patterns of the Zn-Se powders prepared at different temperatures.

Fig. 2 shows XRD patterns of the Zn-Se powders prepared with different time at 200 °C. It can be seen that the products with single phase ZnSe prepared with 22.5 h and 45 h have crystallized well while the impurity Se has been found in the product prepared with 11 h. It indicates that the product crystallized better as the reacting time increased.

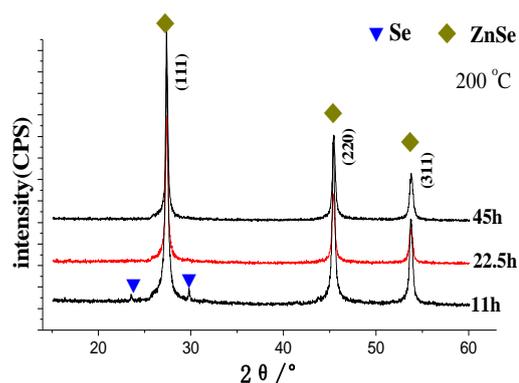


Fig. 2. XRD patterns of the Zn-Se powders prepared with different reacting time.

The XRD patterns of the Zn-Se powders prepared with different solute concentrations under other same conditions of 200 °C and 90 h are shown in Fig. 3. It can be seen that the intensities of the diffraction peaks are high and sharp for the products prepared with 0.02 mol/L and 0.08 mol/L solute concentrations, which demonstrates that the powder products with single phase ZnSe crystallized well. So we can say that the solute concentrations have no obvious effect on phase crystallization of ZnSe under the experimental conditions in this work.

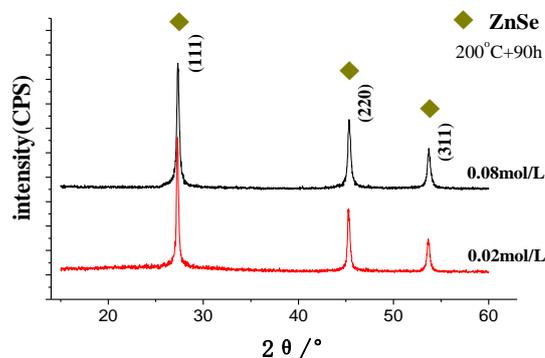
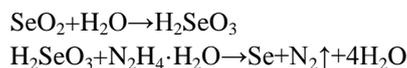
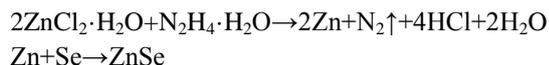


Fig. 3. XRD patterns of the Zn-Se powders prepared with different solute concentrations.

So the temperature and time are the two key factors to affect ZnSe crystallization. Raising temperature and prolonging time in reaction are conducive to prepare ZnSe powders with single phase and high crystallinity. The reaction mechanism is proposed as follows: When all the reactants are put into the autoclave and heated, Zn atoms and Se atoms are easily reduced by hydrogen decomposed from $N_2H_4 \cdot H_2O$, because their positive electrode potentials are much higher than hydrogen. The as-reduced Zn atoms and Se atoms are very active and can easily combine to be ZnSe molecules [20, 21]:





2.2 The morphology of ZnSe powders

Fig. 4a and b are the images of the same ZnSe powder prepared at 180 °C for 45 h, the other two images are for the same product prepared at 200 °C for 45 h. These powder products prepared by hydrothermal co-reduction show rough surface grains with different sizes which vary with reacting conditions. These ZnSe grains show irregular shapes or spheres can be observed at lower magnification in Fig. 4a and c, their sizes of 300 nm~2 μm in diameters are similar in spite of different reacting temperatures. While the small grains are still made up of further smaller nano-particles observed at higher magnification. It indicates that 20~50 nm in sizes are for the smaller nano-particles prepared at 180 °C in Fig.4a and 50~200 nm for those prepared at 200 °C in Fig.4c, which indicates that the sizes of ZnSe grains become larger as the reacting temperature increased.

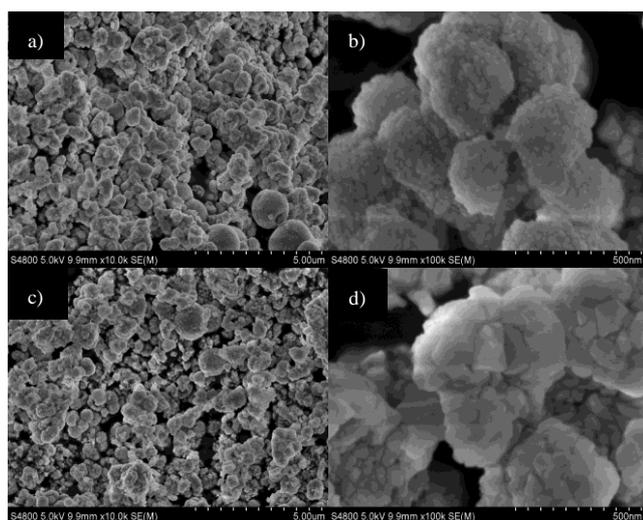


Fig. 4. SEM images of ZnSe synthesized at 180 °C and 200 °C.

3. Conclusions

ZnSe powders with single phase and high crystallinity are synthesized by hydrothermal co-reduction method at temperatures of 160~200 °C using ZnCl₂ and SeO₂ as raw materials. The three strong XRD peaks of these products with cubic zinc blende structure are corresponding to (111), (220) and (311) crystal planes. The solute concentrations have no obvious effect on phase crystallization of ZnSe. The temperature and reacting time in reaction are the two key factors to affect ZnSe crystallization. Well-crystallinity ZnSe nano-powders with single phase can be produced under conditions of higher temperature and longer reacting time. The ZnSe products show small particles with sizes of about 20~200 nm, which become

larger as the reacting temperature increased.

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References

- [1] S. Venkatachalam, D. Mangalaraj, Sa. K. Narayandass, et al. *Physica B*, **358**, 27 (2005).
- [2] Hua Gong, Zhonghai Lin, Guangmei Zhai, et al. *Ceramics International*, **34**, 1085 (2008).
- [3] Minqiang Wang, Xiao Huo, Jianping Li, et al. *Ceramics International*, **34**, 1081 (2008).
- [4] Jiang Haiqing, Che Jun, Li Zhimin, et al. *Trans. Nonferrous Met. SOC. China*, **16**, 419 (2006).
- [5] J. J. Andrade, A. G. Brasil Jr., P. M. A. Farias, et al. *Microelectronics Journal*, **40**, 641 (2009).
- [6] NoSung Myoung, Dmitri V. Martyshev, Vladimir V. Fedorov, et al. *Journal of Luminescence*, **133**, 257 (2011).
- [7] J. Hoya, J. I. Laborde, L. C. Damonte. *International journal of hydrogen energy*, **37** 14769 (2012).
- [8] R. B. Kale, C. D. Lokhande, R. S. Mane, et al. *Applied Surface Science*, **252**, 5768 (2006).
- [9] A. Rumberg, A. Gerhard, A. J. Ager-Waldau, et al. *Solar Energy Materials & Solar Cells*, **75**, 1 (2003).
- [10] A. Rumberg, Ch. Sommerhalter, M. Toplak, et al. *Thin Solid Films*, **361-362**, 172 (2000).
- [11] L. Chen, J. S. Lai, X. N. Fu, J. Sun, et al. *Thin Solid Films*, **529**, 76 (2013).
- [12] Yong Zhang, Zhiming Wu, Jinjian Zheng, et al. *Solar Energy Materials & Solar Cells*, **102**, 15 (2012).
- [13] Sunirmal Jana, In Chan Baek, Mi Ae Lim, et al. *Journal of Colloid and Interface Science*, **322**, 473 (2008).
- [14] Minqiang Wang, Yaohui Xue, Zhonghai Lin, et al. *Materials Letters*, **62**, 574 (2008).
- [15] Linyu Yang, W. J. Wang, B. Song, et al. *Journal of Crystal Growth*, **312**, 2852 (2010).
- [16] Hao Wei, Yanjie Su, Shangzhi Chen, et al. *Materials Letters*, **67**, 269 (2012).
- [17] Hua Gong, Hui Huang, Minqiang Wang, et al. *Ceramics International*, **33**, 1381 (2007).
- [18] Mohd. Shakir, S. K. Kushwaha, K. K. Maurya, et al. *Solid State Communications*, **149**, 2047 (2009).
- [19] Huiling Li, Biben Wang, Lijun Li. *Journal of Alloys and Compounds*, **506**, 327 (2010).
- [20] Kegao Liu, Hong Liu, Jiyang Wang, et al. *Journal of Alloys and Compounds*, **484**, 674 (2009).
- [21] Kegao Liu, Hong Liu, Jiyang Wang, et al. *Materials Letters*, **63**, 512 (2009).

*Corresponding author: liukg163@163.com