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Synthesis of ZnSe nanocrystalline powders by mechanochemical reaction

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Abstract The ZnSe nanocrystalline powders were synthesized by mechanochemical reaction method. The powders milled at air atmosphere have the second phase ZnO, but that milled above 2 h at high N_2 atmosphere have not second phase ZnO. The phase structure of the ZnSe powder milled for 10 h at N_2 atmosphere is sphalerite structure. The average size of the as-milled and annealed ZnSe nanocrystalline powders is 5.17 and 8.88 nm respectively. The TEM analysis demonstrated that the size of agglomerated ZnSe crystalline is less than 100 nm, but the electron diffraction pattern showed that ZnSe clusters were a polycrystalline structure. The absorption spectrum of ZnSe samples was measured by UV–VIS–NIR Photometer Spectrum. It showed that the absorption edge of the ZnSe nanocrystalline powders by mechanochemical reaction comparing to ZnSe bulk materials had a red-shift. This result can be attributed to the residual stress and lattice aberrance of ZnSe nanocrystalline powders in milling process. The absorption edge of the annealed ZnSe powders was recovered owing to the residual stress was eliminated by annealing for 2 h containing nitrogen.

Keywords ZnSe · Nanocrystalline powders · Mechanochemical reaction

1 Introduction

Zinc selenide (ZnSe) is an important II–VI semiconductor material with good properties of physics and chemistry as well as wide band gap. It has attracted more and more attention due to its novel optical and transport properties and significant potential applications in the luminescence, laser and nonlinear optical regions. Various chemical methods have been employed to synthesize ZnSe nanocrystalline powders at room temperature, such as reduction methods [1], reverse micelle synthesis [2], sonochemical method [3], solvothemal method [4, 5] etc. The difficulty encountered in the methods mentioned above is often using toxic metalorganic reagents as precursors or need a complicated process.

In the recent years, the mechanochemical reaction is a novel technique to synthesis nanoparticle. It has been used to obtain a number of transition metals and ceramics nanoparticles involving the mechanical activation of solid-state reactions during ball milling. The synthesis and of powders through this technology and the influence of several different nominal compositions on the lattice parameter and average crystallite size were reported [6]. The aging at room temperature of products with equiatomic ZnSe were presented [7].

The principle of mechanochemical synthesis is that repeated cold welding and fracture of reacting particles during ball-powder collision result in continuously regenerating fresh interfaces between reacting phases and increasing the area of contact between reactant particles due to a reduction in size. This allows the reaction to continue without the necessity for diffusion through the product phases [8, 9]. Therefore, the reactions which normally require high temperature will occur at lower temperature during the high energy ball milling. This process has many advantages over both conventional solid-state reaction and the wet-chemical process including using low-cost raw materials, simplicity of the process and obtaining fine particles. In this paper, the mechanochemical

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synthesis has been used to prepare ZnSe nanocrystalline powders and the effects of milling time and atmosphere on the solid-state reaction during milling have been investigated. The residual stress of ZnSe nanocrystalline powders by ball milling and the influence of it on absorption optical spectrum were presented.

2 Experimental procedures

The high-purity zinc powders (99.999%, 100 mesh) was blended with selenium powders (99.95%, 100 mesh) to produce nominal equiatomic composition. High-energy ball milling was carried out using a Vario-Planetary Pulverisette 4 mill system (Germany FRITSCH Company). The milling ball and vial were made of tungsten carbide. About 25 g of each mixture and 50 milling balls of 10 mm in diameter were placed in the vial. The weight ratio of milling ball and mixture was controlled to 20:1. The starting mixture was milled dryly for 1–10 h under air and high purity N_2 (99.99%) atmosphere respectively. Then the powder milled for 10 h at N_2 atmosphere was annealed at 550°C under a flowing N_2 atmosphere for 2 h.

The phase structure and crystallization behavior of products were carried out by an X-ray diffractmeter (XRD) (RIGAKU D/MAX-2400, CuKá). The morphography of ZnSe nanocrystalline powders was observed by transmission electron microscope (TEM) (JXM-200CX, JEOL). The transmittance properties were measured by UV/VIS/NIR spectrophotometer (JASCO V-570) and the absorption edge was calculated.

3 Results and discussion

The phase composition of ZnSe powders milled under air atmosphere at different milling time was shown in Fig. 1. The results showed that the phase composition of the powders have second phase ZnO except the main phase ZnSe. The second phase ZnO has not disappeared with the increase of milling time. This result is ascribed to the fine zinc powders is easy to be oxided in milling process at air atmosphere. However, all the powders milled at high purity N_2 atmosphere have not second phase ZnO except the main phase ZnSe (Fig. 2). This result showed that the oxide of zinc powders is prevented by the N_2 atmosphere. So the pure ZnSe phase was obtained by milling for 2 h at N_2 protection atmosphere.

The phase structure and grain size was investigated using the ZnSe powders milled for 10 h at N_2 atmosphere. The phase structure of the ZnSe powder milled for 10 h at N_2 atmosphere is sphalerite (cubic ZnS structure). The apparently broadened diffraction peaks indicated that the

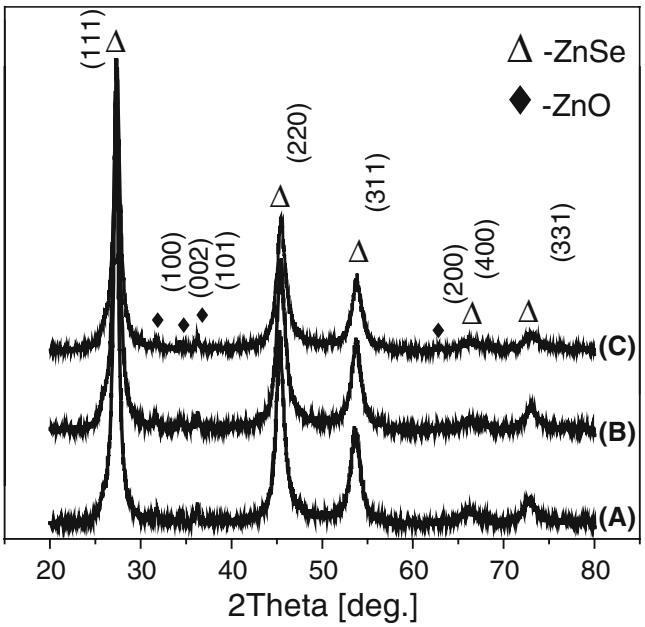

Fig. 1 XRD patterns of ZnSe powders under air atmosphere at different milling time: *A* 1 h, *B* 2 h, *C* 2.5 h

size of ZnSe grains were fine. The size of the as-milled and annealed ZnSe nanocrystalline powders was calculated according to Scherer's equation:

$$D = (0.89\lambda)/B\cos\theta$$

Where D, λ, θ represent the grain diameter, wavelength (λ=1.5406 Å) and diffraction angle, respectively. The full width at half maximum (B) was measured using peaks of high angles from 70° to 135° with scan rate of 3°/min. The size of crystallite obtained by the (331), (422), (511), (531) crystal plane and the average value were given in Table 1.

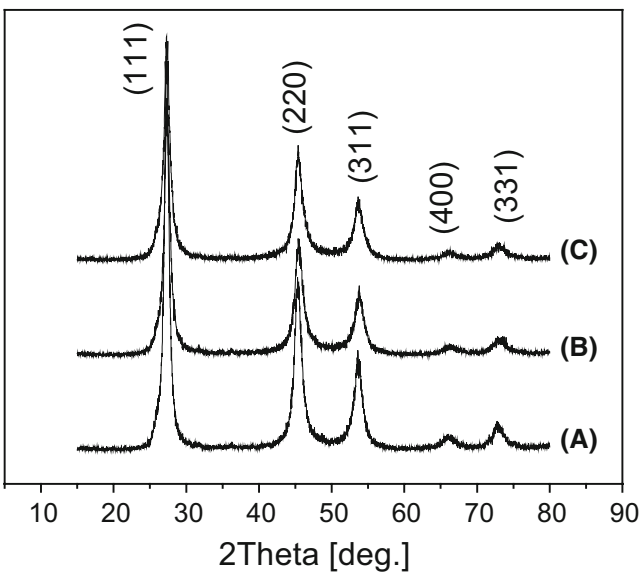

Fig. 2 XRD patterns of ZnSe powders under high N_2 atmosphere at different milling time: *A* 2 h, *B* 4 h, *C* 8 h

Table 1 The size of ZnSe grains at different condition.

Sample condition	Diameter (nm)					
Crystal face	(331)	(422)	(511)	(531)	(620)	Average
Milling 10 h (as-milled)	5.33	5.11	5.83	4.69	4.90	5.17
Milling 10 h (annealed)	9.18	8.69	9.60	9.03	7.92	8.88

The result showed that the average size of the as-milled and annealed ZnSe nanocrystalline powders is 5.17 and 8.8 nm respectively. So the ZnSe nanocrystalline was obtained by milling for 10 h at N_2 atmosphere. The increase of the average size of the annealed ZnSe nanocrystalline powders may be ascribed to the residual stress originated from the milling process was eliminated by annealing.

The absorption edge of ZnSe materials can be measured by UV/VIS/NIR absorption spectra. The absorption edge can be confirmed by second derivative of the absorption spectrum [10]. The measurement results were showed in Fig. 3 and the calculated results were showed in Fig. 4. From Fig. 4, the absorption edge of ZnSe bulk materials is at 478 nm, and the absorption edge of the as-milled ZnSe nanocrystalline powder is at 508 nm. The shift of optical absorption edge for as-milled ZnSe nanocrystalline powders is attributed to residual stress and lattice aberrance of ZnSe nanocrystalline powders in milling process. The residual stress was caused by the repeated cold welding and fracture of reacting particles through ball-powder collision continuously. As the size of the as-milled ZnSe powders decreased to several nanometers, the specific surface area largely increased. It leads to increase of dangling bond, stoichiometric or external defects [11],

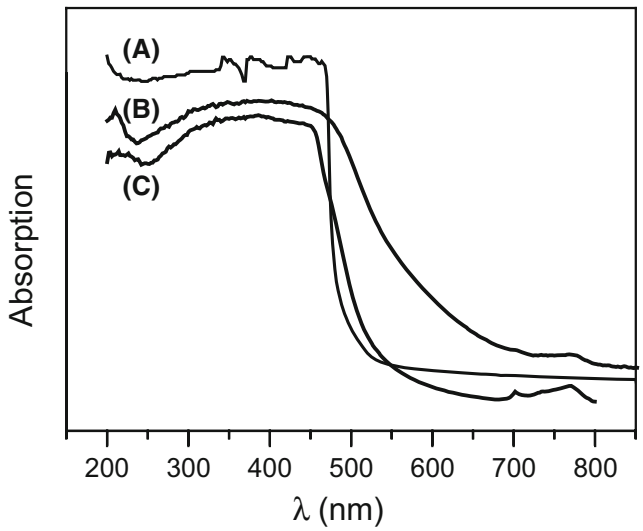

Fig. 3 Optical absorption spectrum of ZnSe samples: *A* ZnSe bulk materials, *B* the as-milled powders, *C* the powders annealed at 550°C

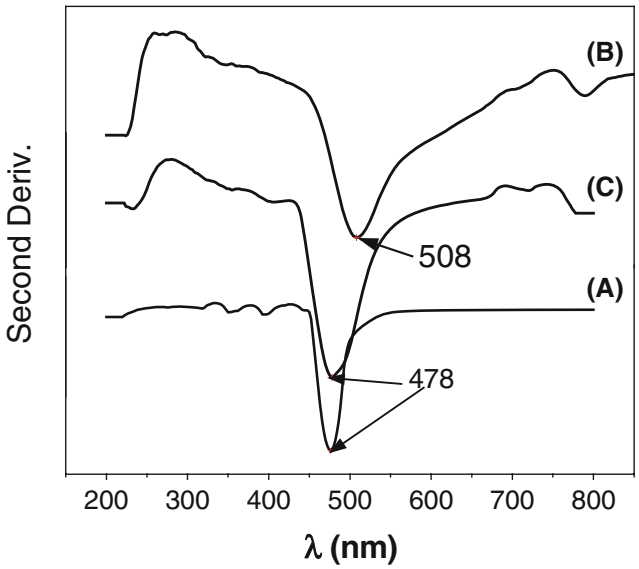

Fig. 4 Second derivative of absorption spectrum of ZnSe samples: *A* ZnSe bulk materials, *B* the as-milled powders, *C* the powders annealed at 550°C

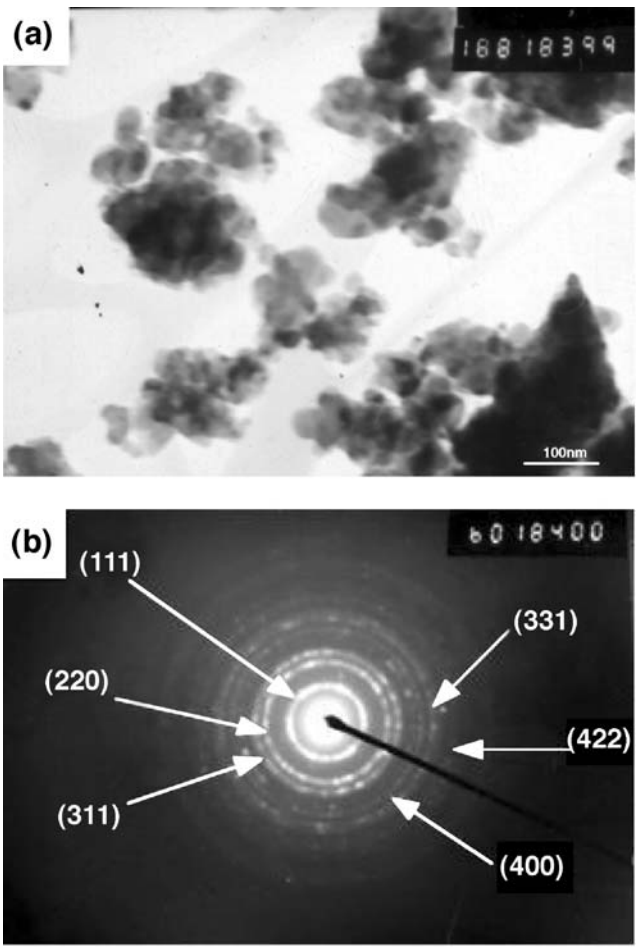

Fig. 5 TEM image (**a**) and electron diffraction pattern (**b**) of the as-milled ZnSe nanoparticles

which induce to lattice aberrance of ZnSe crystal. Otherwise, huge residual stress was aroused from plastic distortion, and then dislocation was aroused, which is the one of significant reasons of lattice aberrance.

The absorption edge of the annealed ZnSe nanocrystalline powders was at 478 nm (shown in Fig. 4). The absorption edge recovered for the annealed ZnSe nanocrystalline powders, this showed that the residual stress and lattice aberrance of the as-milling ZnSe nanocrystalline powders was eliminated after annealed at 550°C.

The TEM images of the as-milled ZnSe nanoparticles are shown in Fig. 5(a). It showed that the ZnSe crystalline aggregated to form particles clusters. The average size of these clusters was about 100 nm. The electron diffraction pattern also showed that ZnSe clusters were a polycrystalline structure (see Fig. 5(b)). It showed that ZnSe particles clusters were consist of many fine grains. The size of ZnSe crystalline was about 10 nm. This result is near to the calculated size (8.88 nm) of the annealed ZnSe powders according to Scherer's equation.

4 Conclusions

In this paper, the pure sphalerite structure ZnSe nanocrystalline powders have been prepared by the mechanochemical reaction method. The average size of the as-milled and annealed ZnSe nanocrystalline powders is 5.17 and 8.88 nm respectively. The TEM analysis demonstrated that the size of agglomerated ZnSe crystalline is less than 100 nm, but the electron diffraction pattern showed that ZnSe clusters were a polycrystalline structure. The absorption edge of the ZnSe nanocrystalline powders by mechanochemical reaction comparing to ZnSe bulk materials had a red-shift. This result can be attributed to the residual stress and lattice aberrance of ZnSe nanocrystalline powders in milling process. The absorption edge of the annealed ZnSe powders was recovered owing to the residual stress was eliminated by annealing for 2 h at N_2 atmosphere. The mechanochemical reaction method is a simple, efficient method to prepare ZnSe nanocrystalline powders. But the ZnSe nanocrystalline powders prepared by this method exists residual stress and lattice aberrance, which can be eliminated by annealing.

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