Inorg. Chem. **2000,** *39,* 2061−2064

Solvothermal Route to Tin Monoselenide Bulk Single Crystal with Different Morphologies

Bin Li,[†] Yi Xie,*[,†] Jiaxing Huang,[‡] and Yitai Qian[†]

Structure Research Laboratory and Department of Chemistry, Department of Chemical Physics,
University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Received August 11, 1999

Orthorhombic SnSe bulk single crystals with different morphologies were conveniently grown through solvothermal process at low temperature (180 °C). X-ray diffraction (XRD) patterns, scanning electronic microscope (SEM) images, electronic diffraction (ED), and X-ray photoelectron spectra (XPS) were used to characterize the products. In the solvothermal process, the solvent plays an important role in the growth of the single crystal. The morphology of the crystal is influenced not only by the kind of solvent but also by the concentration of the reactants in solvent. Single crystals with rodlike or platelike morphology can be conveniently obtained under controlled concentration of reactants in solvent.

Introduction

The IV−VI intermetallic compounds SnSe and $SnSe_2$ possess interesting semiconducting properties. SnSe belongs to the interesting class of isomorphic materials that are in many ways between two-dimensional (layer type) systems and three-dimensional crystals, and it exhibits a strong anisotropy of optical properties.[1] SnSe is a semiconductor with a band gap of about 1 eV and therefore should possess the potential to work as an efficient solar cell material.[2] It is also of interest to holographic recording systems[3] and electrical switching.[4] The SnSe bulk single crystals have mainly been grown by the Bridgman method[5,6] and vapor phase methods (such as the chemical vapor transport technique using ammonium chloride as a transporting agent,[7] the close-tube-vapor-transport technique,[8,9] and the direct vapor transport technique without transporting agent[1]). In those methods special and complicated devices are generally required and the crystal growth usually needs two steps: the formation of SnSe powders and the later crystal growth. Moreover, the growth temperature is high (>600 °C) and the temperature gradient has to be carefully controlled.

Microcrystalline selenides can be prepared by the hydrothermal process at 260−312 °C and 100 atm.[10] The high pressure makes the thermal process less safe. Recently, the solvothermal technique, which is carried out at low temperature and does not require organometallic precursors, has been developed as a mild and effective route to synthesize novel materials.[11] Such a process has allowed for the synthesis of several kinds of nanocrystalline selenides.[12−14] However, no reports on the preparation of single crystalline selenides by this mild method were found. Here, we extend the solvothermal technique to prepare single crystalline SnSe. We successfully obtained two kinds of SnSe bulk single crystals with rodlike and platelike morphologies under mild conditions (180 °C and less than 30 atm[11]) and found that the morphologies are influenced not only by the solvent but also by the reactant concentration. Inorganic materials with different morphologies, which have the same chemical composition, may exhibit different physical properties.[15] Therefore, the synthesis of these materials would be particularly interesting. Moreover, thin platelets (<50 μm) needed for the physical property measurements are usually obtained from a large-size crystal by the method of cleaving. The process of cleaving may introduce a large number of defects.[7] The thin platelets prepared by our solvothermal route provide desirable crystals to be used for the physical property measurements.

Experimental Section

Preparation of SnSe Bulk Single Crystal. SnSe bulk single crystals were grown in a 50 mL Teflon liner autoclave from stoichiometric selenium (99.95%) and anhydrous stannous chloride (99.95%) by a solvothermal route at 180 °C for 7 days. The anhydrous stannous chloride was prepared by fully mixing $SnCl_2{\cdot}2H_2O$ and acetic anhydride as a dehydrant with a molar ratio of 1:2 and then washing with ethyl ether. SnSe single crystals with two types of morphologies were grown as follows. For route I, selenium (0.39 g, 5 mmol) and $SnCl_2$ (0.95 g,

---

* To whom correspondence should be addressed. Address: Department of Chemistry, University of Science & Technology of China, Hefei, Anhui 230026, P. R. China. Phone: 86-551-3603987. Fax: 86-551-3631760. E-mail: yxie@ustc.edu.cn.

[†] Structure Research Laboratory and Department of Chemistry.

[‡] Department of Chemical Physics.

(1) Agarwal, A.; Patel, P. D.; Lakshminarayana, D. *J. Cryst. Growth* **1994**, *142*, 344.
(2) Loferski, J. J. *J. Appl. Phys.* **1956**, *27*, 777.
(3) Valiukonis, G.; Guseinova, D. A.; Krivaite, G.; Sileika, A. *Phys. Status Solidi B* **1986**, *135*, 299.
(4) Chu, D.; Walser, R. M.; Bene, R. W.; Courtney, T. H. *Appl. Phys. Lett.* **1974**, *24*, 479.
(5) Agnihotri, O. P.; Jain, A. K.; Gupta, B. K. *J. Cryst. Growth* **1979**, *46*, 491.
(6) Bhatt, V. P.; Gireesan, K.; Pandya, G. R. *J. Cryst. Growth* **1989**, *96*, 649.
(7) Agarwal, A. *J. Cryst. Growth* **1998**, *183*, 347.
(8) Maier, H.; Daniel, D. R. *J. Elect. Mater.* **1977**, *6*, 693.
(9) Yu, J. G.; Yue, A. S.; Stafsudd, O. M. *J. Cryst. Growth* **1981**, *54*, 248.
(10) Cambi, L.; Elli, M. *Chim. Ind.* **1968**, *50*, 94.
(11) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206 and references therein.
(12) Li, Y.; Ding, Y.; Qian, Y.; Zhang, Y.; Yang, L. *Inorg. Chem.* **1998**, *37*, 2844.
(13) Li, Y.; Ding, Y.; Qian, Y.; Zhang, Y.; Yang, L. *Inorg. Chem.* **1998**, *38*, 1382.
(14) Wang, W.; Geng, Y.; Yan, P.; Liu, F.; Xie, Y.; Qian, Y. *J. Am. Chem. Soc.* **1999**, *121*, 4062.
(15) Hulliger, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 143. Yu. S.; Wu, Y.; Yang, J.; Han, Z.; Xie, Y.; Qian, Y. *Chem. Mater.* **1998**, *10*, 2309.

10.1021/ic990964v CCC: $19.00

Table 1. Reaction Conditions and Results of the Experiments

no.	solvents	$SnCl_2$/Se/sol[a]	temp (°C)	time (h)	product[b]	morphology
1	en	2.5:2.5:597	180	168	SnSe	polycrystalline powder
2	en	3.3:3.3:597	180	168	SnSe	platelike single crystals
3	en	5:5:597	180	168	SnSe	rodlike single crystals
4	en	6.6:6.6:597	180	168	SnSe	polycrystalline powder
5	en	3.3:3.3:597	140	12	SnSe	platelike nanocrystals
6	en	4:4:597	140	12	SnSe	rod and platelike nanocrystals
7	en	5:5:597	140	12	SnSe	rodlike nanocrystals
8	diethylamine	5:5:383	180	36	SnSe	spherical nanoparticles
9	pyridine	3:6:496	180	24	$SnSe_2$	spherical nanoparticles
10	benzene	3:6:450	180	24	$SnSe_2$	spherical nanoparticles

[a] The sol represents the solvents, and the ratios are molar ratios. [b] All the SnSe and $SnSe_2$ as-prepared are, respectively, orthorhombic and hexagonal phases.

5 mmol) were successively loaded into a 50 mL Teflon liner autoclave, which was then filled with 40 mL of ethylenediamine. All of the above steps were carried out on a bench top. The autoclave was sealed and maintained at 180 °C for 7 days and then cooled to room temperature. The precipitate was filtered and washed with ether, distilled water, and absolute ethanol several times to remove the byproducts. Rodlike crystals, metallic light-gray in color with a high reflective luster, were obtained and then dried in a vacuum at 60 °C for 4 h. For route II, with all the other conditions constant, when an amount of selenium and $SnCl_2$ added was 0.26 g (3.3 mmol) and 0.63 g (3.3 mmol), respectively, platelike SnSe single crystals were obtained. Contrast experiments under different conditions were also made. The detailed conditions and results of the experiments are listed in Table 1.

Characterization of Products. The phases and the crystallographic structure of the products were determined by X-ray diffraction (XRD) using a Japan Rigaku D/max-γA X-ray diffractometer with Cu Kα radiation (λ = 1.541 78 Å). The scan rate of 0.02° s^{-1} was applied to record the patterns in the 2θ range of 10−70°. The morphology and size of bulk single crystals were observed using scanning electronic microscopy (SEM), which was performed on an X-650 scanning electron microanalyzer. To study the structure of single crystals, electronic diffraction (ED) was used. Patterns were taken on a Hitachi model H-800. Further evidence for the purity and composition of the products was obtained by X-ray photoelectron spectra (XPS). XPS was collected on an ESCALAB MK II X-ray photoelectron spectrometer, using nonmonochromatized Al Kα X-rays as the excitation source. The Sn 3d and Se 2p core level regions were also examined. To examine the morphology and particle size of SnSe nanocrystals obtained, transmission electron microscope (TEM) images were taken on a Hitachi model H-800, using an accelerating voltage of 200 kV.

Results and Discussion

The single crystals grown through both routes are metallic light-gray with a high reflective luster. The single crystals grown by routes I and II display rodlike and platelike morphologies, respectively. However, it is found that the XRD patterns of the polycrystalline powder ground from the two kinds of bulk single crystals have little difference in relative intensity, and both can be represented by Figure 1A. The lattice parameters measured for the samples are found to be a = 11.49 Å, b = 4.16 Å, and c = 4.45 Å, which are in good agreement with the reported data for SnSe (a = 11.496 Å, b = 4.151 Å, and c = 4.444 Å),[16] and all the reflection peaks in the pattern can be indexed to the orthorhombic SnSe phase. The XRD pattern of a single rodlike SnSe single crystal as prepared only exhibits four peaks at 15.4°, 31.2°, 47.4°, and 64.8°, which can be assigned to the orthorhombic 200, 400, 600, and 800, respectively (Figure 1B). Moreover, the other relatively strong reflection peaks in polycrystalline power diffraction are absent in this pattern. The XRD pattern of a single platelike single crystal as prepared is the same as that of a single rodlike single crystal. The above results show that the (100) face of the SnSe crystals parallels the shaft of the rodlike single crystal and the plane of the platelike single crystal, respectively.

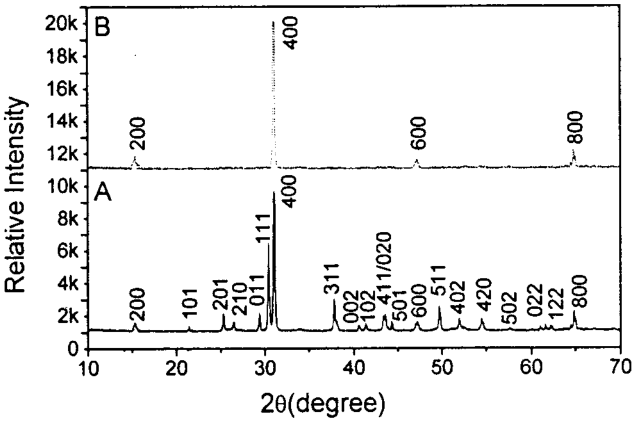

Figure 1. (A) X-ray powder diffraction pattern of SnSe single crystals as-prepared. (B) X-ray diffraction pattern of a single SnSe bulk single crystal as-prepared.

The SnSe single crystals synthesized by route I display rodlike morphology with a length of ca. 0.8−1.5 cm and a radius of ca. 60−100 μm, the latter of which was determined by the SEM image as shown in Figure 2A. From the SEM study, the SnSe single crystals synthesized by route II show platelike morphology with the dimensions of 1200 μm × 300 μm and a thickness of 10 μm. A typical SEM image is shown in Figure 2B. The thin platelets provide desirable crystals to be used for the physical property measurements. Both of the SnSe single crystals have the same electron diffraction pattern. A typical pattern of the crystals (Figure 3), using gold as a standard sample, showed that the materials were single crystals.

The quality of the samples was also characterized by XPS. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C_{1s} to 284.60 eV. Figure 4A shows the XPS survey spectra of the sample prepared in ethylenediamine. No obvious impurities (e.g., chloride ion or elemental selenium) could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 atom %). The Sn 3d core level spectrum (Figure 4B) indicates that the observed value of the binding energy for Sn $3d_{5/2}$ (485.6 eV) is in agreement with the literature values,[17] and no evidence for Sn^{4+} (487.0 eV) could be observed. The Se $2p_{3/2}$ binding energy of 54.05 eV, given by the Se core level spectrum, is also consistent with those

---

(16) Joint Committee on Powder Diffraction Standards (JCPDS) 14-159.

(17) Wanger, C. D., Riggs, W. M., Davis, L. E., Moulder, J. F., Muilenberg, G. E., Eds. *Handook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corp.: Eden Prairie, MN, 1978.

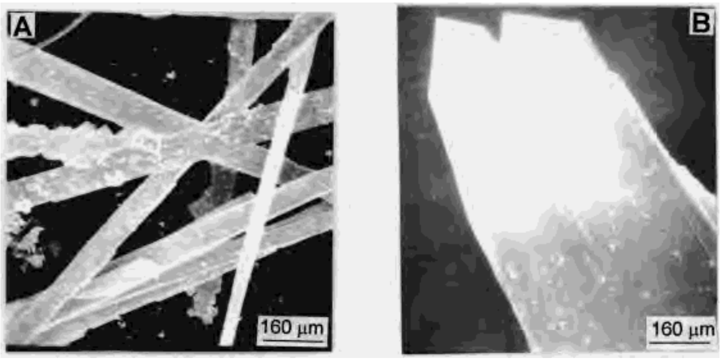

Figure 2. SEM image of SnSe single crystal prepared (A) by route I and (B) by route II.

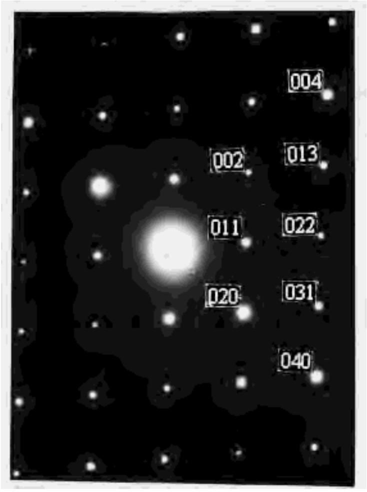

Figure 3. Electron diffraction of SnSe single crystal.

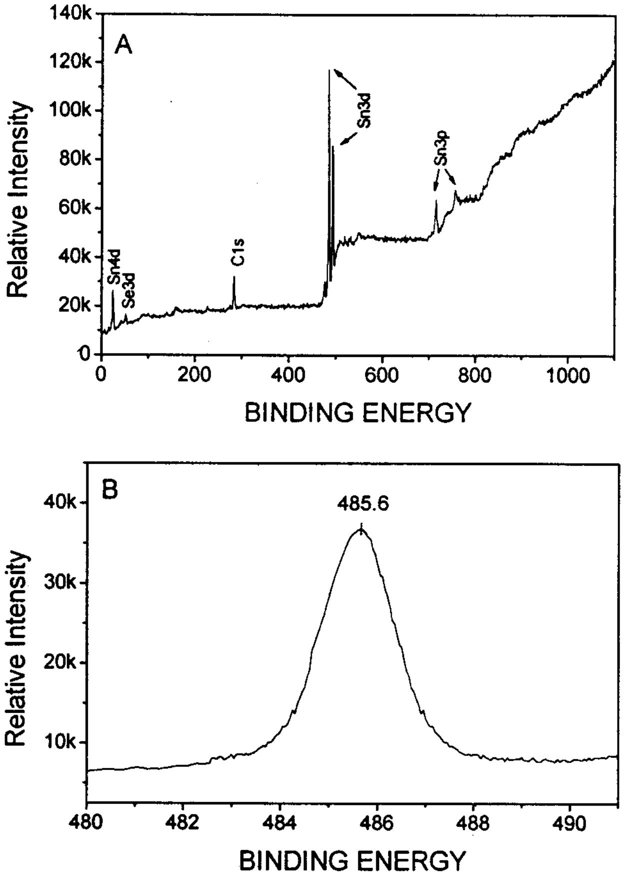

Figure 4. (A) XPS survey spectra. (B) Sn 3d core level spectrum of SnSe single crystal.

observed in SnSe.[17] Quantification of the XPS peaks gives the ratio of Sn/Se as 0.986:1, which is almost consistent with the stoichiometry of SnSe.

By comparison of the two routes to grow SnSe single crystals, it is interesting that the concentration of reactants in the system is important to the morphology of product. The product prepared from a higher concentration of reactants is rodlike, while a lower concentration brought platelike single crystals. However, no bulk single crystals but polycrystalline powders were obtained when a concentration (6.6 mmol Se and 6.6 mmol $SnCl_2$ in 40 mL of en) higher than that of route I or a concentration (2.5 mmol Se and 2.5 mmol $SnCl_2$ in 40 mL of en) lower than that of route II was tested. The result was confirmed by repeated experiments. It was speculated that the suitable concentration is favorable to the nucleation and growth of crystals. To further affirm the result, in the ethylenediamine system the same experiments were made at 140 °C for 12 h, as listed in Table 1, with the reactant concentration of route I, the reactant concentration of route II, and the reactant concentration between that of the two routes. From the XRD analyses, all of the products were orthorhombic-phase SnSe polycrystals. However, the SnSe polycrystals have different morphologies, which were studied by transmission electron microscope as shown in Figure 5. The SnSe nanocrystals obtained from the reactant concentration of route I display rodlike morphology, while the SnSe nanocrystals obtained from the reactant concentration of route II show platelike morphology. Both of the rodlike and platelike morphologies can be observed in the sample obtained from the reactant concentration between that of the two routes. From the above result, the concentration of reactants in solvent is believed to be responsible for the distinctive morphologies. In this process mass diffusion probably exerts an impact on the crystal growth. When the concentration of reactants is low, the growth of crystals has a lower orientation, so the product displays platelike morphology. Despite the earlier observation of various morphologies of crystals[18,19] and the Monte Carlo simulations of growth in two dimensions as a mathematical function of the driving potential,[20] the influential mechanics of the solvent on the morphology of crystals still remains obscure.

In the solvothermal process, the solvent plays an important role in the formation of the products. Ethylenediamine was selected as a solvent because it is strongly basic and can be a bidentate ligand, which may serve as a molecular template in control of the crystals growth.[21] We speculate that elemental

---

(18) Wald, F. V. *Sol. Energy Mater.* **1991**, *23*, 175.
(19) Vicsek, T. *Fractal Growth Phenomena*; World Scientific: Singapore, 1989.
(20) Satio, Y.; Ueta, T. *Phys. Rev. A: Gen. Phys.* **1989**, *40*, 3408.

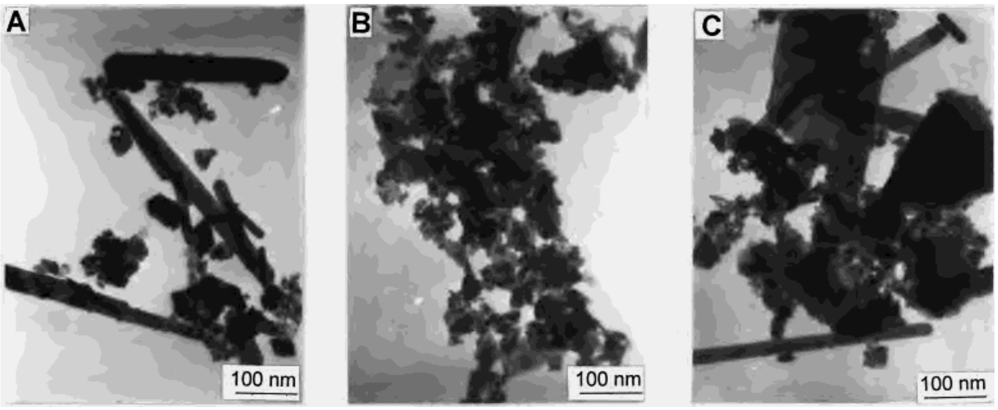

Figure 5. TEM images of SnSe nanocrystals obtained from the reactant concentration (A) of route I, (B) of route II, and (C) between that of the two routes.

selenium is activated by a nucleophilic attack of the amine to form Se^{2-} in the solvothermal process, which may be similar to the way that the sulfur is activated by amine or hydroxide.[22] The following phenomenon supports this speculation. At room temperature, elemental selenium is soluble in ethylenediamine, which is supported by the fact that the solution color changed from opaque to dark-brown and that the selenium powder disappeared soon after it was added to ethylenediamine. To improve the understanding of the influence of solvent, we substituted ethylenediamine with diethylamine, pyridine, and benzene, as listed in Table 1. When pyridine or benzene was selected as the solvent and the reaction was kept at 180 °C for 12 h, XRD analysis showed that the obtained samples were not orthorhombic-phase SnSe but hexagonal-phase $SnSe_2$. In this process, the selenium cannot be activated by pyridine or benzene, both of which are of mild basicity. The selenium was reduced by the Sn^{2+}, while the Sn^{2+} is oxidized to Sn^{4+}. When in the diethylamine system, a strong base such as ethylenediamine but without double N-chelation, orthorhombic-phase SnSe polycrystals were obtained. However, in the case of diethylamine used as solvent, to get pure product the reaction temperature and time must be no less than 180 °C for 36 h, and no bulk single crystals were obtained even if the reaction were kept at 180 °C for times as long as 7−12 days. Furthermore, no matter how the concentration of reactants was changed, only polycrystalline powders were obtained. Experiments show that ethylenediamine is an excellent solvent to prepare SnSe single crystals.

In summary, we have succeeded in synthesizing SnSe bulk single crystals with rodlike and platelike morphology using a relatively simple solvothermal method. The solvent plays an important role in the formation of the products in the solvothermal process. Different morphologies of single crystals can be conveniently obtained under controlled conditions. This method can be easily controlled and is expected to be applicable for the preparation of other single crystals. By use of this method, single crystals of copper selenide with hexagonal platelike morphology and silver selenide with spherical morphology have been prepared in ethylenediamine system. However, growth of inorganic bulk single crystals by this technique needs further study.

Acknowledgment. Financial support from the Chinese National Foundation of Natural Sciences through the National Outstanding Youth Fund is gratefully acknowledged.

IC990964V

---

(21) Morris, R. E.; Weigel, S. J. *Chem. Soc. Rev.* **1997**, *26*, 309.
(22) Jiang, T.; Ozin, G. A.; Bedard, R. L. *Adv. Mater.* **1994**, *11*, 860.