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Synthesis of SnSe in Various Alkaline Media under Mild Conditions

C. Wang,* Y. D. Li,* G. H. Zhang, J. Zhuang, and G. Q. Shen

Department of Chemistry, Tsinghua University, Beijing, 100084, P. R. China

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The synthesis of SnSe was systematically investigated in various alkaline media and at various temperatures with $SnCl_2 \cdot 2H_2O$ and selenium as source materials. The basicity of the alkaline media and the reaction temperature are two key factors considered in our process. The synthesis of SnSe in sodium hydroxide solution and aqueous ammonia is limited to a narrow temperature range, while the synthesis in hydrazine hydrate and ethylenediamine proceeds over a wider range. The final products were characterized by X-ray diffraction pattern (XRD), energy dispersive X-ray (EDX), and transmission electron microscopy (TEM). TEM results showed a variation of crystal morphology of SnSe obtained in different media. Two simple chemical mechanisms for the formation of SnSe are presented.

Introduction

Compared with high-temperature pathways, low-temperature synthetic techniques involving, for example, sol−gels,[1] hydrothermal and solvothermal processes,[2,3] molecular precursors,[4] and so on can provide materials with metastable structures, low-temperature phases, or stable phases in the form of fine particles, upon which many industrial and technological applications might be realized. Application of these techniques toward materials synthesis has been and will remain among the most vigorous research areas in materials chemistry.

Solution routes to inorganic materials, particular in aqueous media, possess some of the above-mentioned desired characteristics. Solution techniques show a high degree of compositional control inherent in the synthesis of multielement inorganic materials.[2] Organic solvents provide an alternative to aqueous solutions as reaction media. Although dissolution of inorganic source materials is usually poor in them, the unique environment (for example, viscosity, absence of water, and so on) they offer is often beneficial for preparing novel materials. We have prepared some metal chalcogenides with different morphologies[5] in pyridine and ethylenediamine.[6] In this work, we study the effect of media on the synthesis of metal selenides in order to optimize the experimental conditions.

Tin mono- and diselenide have attracted the attention of many researchers because of their high absorption coefficients, which are useful for optoelectronic applications. Additionally, tin selenide has great potential for use as a memory switching device.[7] As a direct semiconductor with band gap 1.0 eV, tin monoselenide is an orthorhombic solid with unit parameters $a = 11.496$ Å, $b = 4.151$ Å, and $c = 4.444$ Å. This orthorhombic structure transforms to a tetragonal structure at high temperature below the melting point (860 °C).

Traditionally, tin monoselenide can be synthesized through elemental combination at high temperature or precipitated from aqueous solutions. But these procedures require either high-energy input or toxic reagents such as H_2Se. Pramanik et al. proposed a method to deposit many metal selenides thin films, including SnSe, in concentrated alkaline solutions using $SeSO_3^{2-}$ as the selenium precursor.[8] The pyrolysis of organometallic molecular precursors has been demonstrated to be useful in forming II−VI[9−11] and III−V[12,13] semiconductors. Powders and thin layers of SnSe can be also obtained from this method.[14,15] In this paper, we describe our systematic investigation of the synthesis of tin monoselenide in several alkaline media. We found that the basic capacity, oxidation−reduction potential, and coordination ability of the media, as well as the reaction temperature, play complex roles in controlling the reaction product and its crystal morphology and grain size. Compared with previous reported methods using high-temperature or toxic reagents, our approaches are milder or less complicated and might be enlarged.

Experimental Section

(1) In Sodium Hydroxide Solution. After addition of 1.4 g of $SnCl_2 \cdot 2H_2O$ (about 6×10^{-3} mol) to 50 mL of distilled water, NaOH was added until a transparent solution was observed. The concentration of OH^- was estimated to be 1.8 mol/L based on the amount of NaOH added. The solution was transferred to a 70 mL stainless Teflon lined autoclave, and then 0.24 g of selenium (about 3×10^{-3}mol) was added. The autoclave was sealed and heated at various temperatures.

(2) In Aqueous Ammonia and Ethylenediamine. A total of 1.4 g of $SnCl_2 \cdot 2H_2O$ and 0.24 g of selenium were added to 50 mL of aqueous ammonia (mass percentage: 25−28%) or ethylenediamine, which were

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* To whom correspondence should be addressed.

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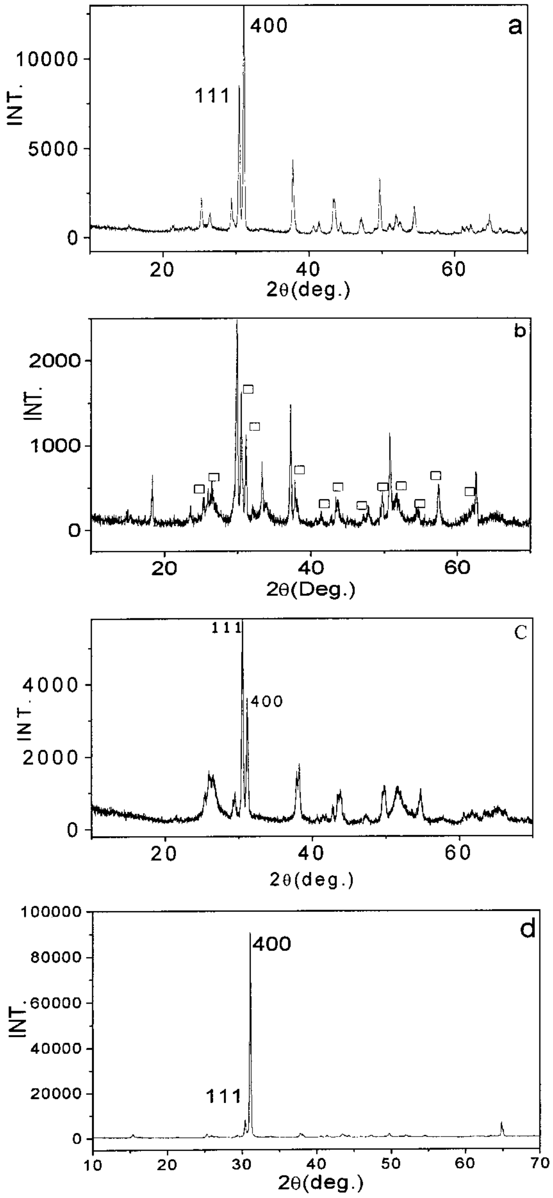

Figure 1. X-ray diffraction pattern (XRD) of the products prepared in (a) 1.8 mol/L sodium hydroxide solution at 100 °C for 48 h, (b) aqueous ammonia (m/m, 25−28%) at 100 °C for 48 h (□, the phase of SnSe), (c) hydrazine hydrate (v/v > 50%) at 100 °C for 48 h, (d) ethylenediamine at 170 °C for 24 h.

also contained in autoclaves. Heating procedures similar to that in (1) were applied.

(3) In Hydrazine Hydrate. Addition of 0.7 g of $SnCl_2 \cdot 2H_2O$ (about 3×10^{-3}mol) to 50 mL of hydrazine (volume ratio is a little larger than 50%) formed a light-yellow precipitate. Then 0.24 g of selenium (about 3×10^{-3} mol) was added. The mixture was transferred to a 70 mL Teflon lined stainless autoclave. A heat treatment similar to the above was applied.

After heat treatment, the obtained products were filtered, washed with distilled water several times, and then desiccated at 60 °C under vacuum. The as-prepared products were characterized by X-ray diffraction (XRD) using a Rigaku D/max γ A X-ray diffractometer with Cu Kα ($\gamma = 1.5418$ Å) incident radiation. The morphology and particle sizes were observed from transmission electron microscopy (TEM) (Hitachi 800).

Results and Discussion

Some experimental conditions and results are summarized in Table 1. Figure 1 shows that high-purity crystalline SnSe could be obtained in 1.8 mol/L sodium hydroxide solution heated at 100 °C for 48 h. But the relative intensities of each peak is not too consistent with that of the JCPDS card file (no. 14-159), where (111) is the strongest lattice plane and (400) ranks second. Here, we observe converse intensities for these two lattice planes, which indicate that preferred orientations might occurred along (400) or some other lattice planes. A mixture of SnO and SnSe, as shown in Figure 1b, was obtained in aqueous ammonia under the same conditions. After treatment in diluted HCl solution (0.1−0.3 mol/L), the mixture yields phase-pure SnSe with an X-ray diffraction pattern analogous to that of Figure 1c. As this pattern indicates, less variation of relative intensities of peaks could be observed compared with that in parts a and d of Figure 1. A significant variation of intensity between (400) and other lattice planes can be seen for SnSe obtained in ethylenediamine at 170 °C for 24 h (Figure 1d). Transmission electron microscopy (TEM) results reflect the variation of intensity. Parts a and b of Figure 2 illustrate the irregular morphology of SnSe and correspond to parts a and c of Figure 1, respectively. The former consists of spherical and short rodlike particles with sizes up to several micrometers. The latter is comprised of spherical particles with smaller grain size than that obtained in sodium hydroxide solution. The crystals of SnSe obtained in ethylenediamine at 170 °C are much larger than those obtained in NaOH, NH_3, and hydrazine. 1D single crystals with length up to 10 μm and width of about several hundred nanometers could be observed under TEM. Energy dispersive X-ray analysis (EDXA) gives a ratio of Se to Sn in these products in the range of 1.10:1.00 to 1.00:1.00, though there is a little inconsistency among the results, which are very close to the stoichiometry of SnSe.

Table 1. Some Experimental Conditions and Results

alkaline media	favorable reaction temp[a] (°C)	crystal morphology	yields[b] (%)
1.8 mol/L NaOH	100−130	rodlike	70−90
NH_3 (m/m, 25−28%)	100−130	spherical	80−95
N_2H_4 (v/v > 50%)	70−170	spherical	>95
$NH_2CH_2CH_2NH_2$	100−170	rodlike	>95

[a] When the systems were heated to 70, 100, 130, and 170 °C, the corresponding time could be 72, 48, 36, and 24 h. [b] The outputs of the products were calculated mainly on the basis of the input selenium.

Formation of SnSe in these reaction systems is based, we believe, on an ion−ion combination pathway. But two kinds of chemical mechanisms are involved. These can be exemplified by the following equations:

$$2Sn^{2+} + N_2H_4 + 2Se + 4OH^- \rightarrow 2SnSe + N_2\uparrow + 4H_2O \quad (1)$$

$$2Sn^{2+} + Se \rightarrow SnSe + Sn^{4+} \quad (2)$$

An alkaline medium is a requirement for the synthesis of SnSe under these mild reaction conditions. Attempts to synthesize SnSe under acidic conditions, in less basic solvents such as pyridine and in nonpolar solvents such as benzene, have all failed. As we mentioned before, selenium does not react in these alkaline media by a simple reduction process.[16] In the presence of a reductive atmosphere (here, hydrazine hydrate or the Sn^{2+} ion) and a precipitant (here, also Sn^{2+}), the alkaline media favors the disproportionation of selenium and ensures that the processes proceed by an ion−ion combination pathway. The difference in forming SnSe between hydrazine and the other media is the

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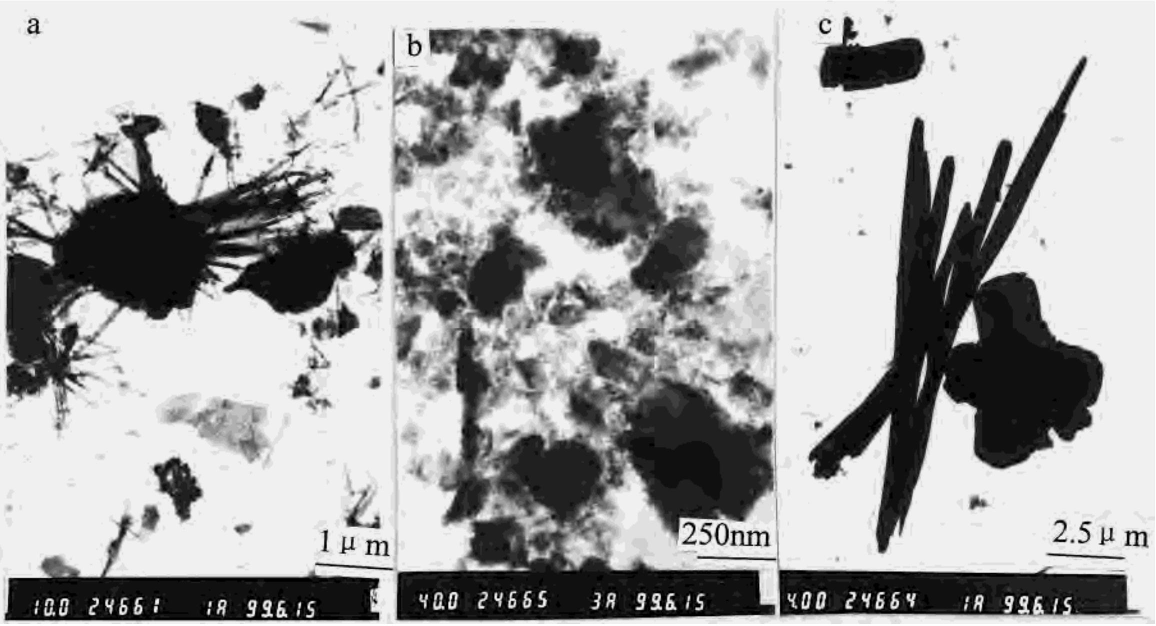

Figure 2. Transmission electron microscopy (TEM) of the products prepared in (a) 1.8 mol/L sodium hydroxide solution at 100 °C for 48 h, (b) hydrazine hydrate (v/v > 50%) at 100 °C for 48 h, (c) ethylenediamine at 170 °C for 24 h.

result of variation in the nature of the media. When the medium is hydrazine hydrate, it also plays the role of a reductant, as can be seen clearly from the oxidation−reduction potentials of hydrazine hydrate and Sn^{2+}:

$$HSnO_2^- + H_2O + 3OH^- - 2e \rightarrow Sn(OH)_6 \qquad E° = -0.96\ V \tag{3}$$

$$N_2H_4 + 4OH^- - 4e \rightarrow N_2 + 4H_2O \qquad E° = -1.15\ V \tag{4}$$

In the other media, Sn^{2+} itself acts as both reductant and precipitant. These mechanisms are supported by the mole ratios of source materials added. In the case of hydrazine hydrate, an equal ratio of $SnCl_2$ to selenium can satisfy the transformation of source materials to final product. But in the other cases, an excess of Sn^{2+} is necessary; the mole ratio of $SnCl_2$ to selenium must be larger than 2. Otherwise, red selenium dispersed homogeneously in the media can be observed, which is an indication that the transformation from selenium to SnSe is incomplete.[16]

When the four reaction systems are heated to 70 °C, the SnSe product can be obtained only in the hydrazine hydrate. This supports our speculation of the chemical mechanism for forming SnSe. The reason that the reactions in the other media could not be initiated at this low temperature might be explained as follows. The formation of complexes by Sn^{2+} and OH^- or N-containing ligands (NH_3 or $NH_2CH_2CH_2NH_2$) decreases the concentration of free Sn^{2+} and therefore decreases its reductive ability of Sn^{2+}, rendering it incapable of reducing selenium. When heated at a higher temperature, the complexes are destroyed, more free Sn^{2+} is released, and the synthesis of SnSe becomes feasible.

It should be pointed out that when the reaction temperature for the sodium hydroxide and aqueous ammonia systems was elevated to be as high as 170 °C, no product was produced. We also noticed that SnSe would decompose in these two strong alkaline solutions at this high temperature.

Besides its above-mentioned role, temperature also has some effect on crystal morphology and grain size. It inevitably causes the growth of grain size. In ethylenediamine, when the temperature was increased from 100 to 170 °C, the length of the rods increased to several micrometers compared with several hundred nanometers when heated at 100 °C. To ensure that the reaction went to completion when the autoclaves were heated to 70, 100, 130, and 170 °C, the corresponding heating time was set to 72, 48, 36, and 24 h, respectively.

The variation of crystal morphology in the different media is another important experimental phenomenon. To our knowledge, the chemical and physical mechanisms still remain elusive, even though many researchers have attributed this variation to many factors.[17,18] In our process, factors such as the nature of the crystal structure, the coordination chemistry, reaction temperature, and heating time might be involved.

We tried to extend this synthesis procedure to tin diselenide by substituting $SnCl_4 \cdot 5H_2O$ in hydrazine hydrate for $SnCl_2 \cdot 2H_2O$. But only nanocrystalline SnO_2 could be obtained at 130 °C.

Conclusion

The synthesis of SnSe could be easily effected under mild experimental conditions in several alkaline media. The basicity of the media and the reaction temperature are two key factors that determine the feasibility of the reaction and morphology of the final product. The $SnCl_2$ itself acts both as reductant and as precipitant in media other than hydrazine hydrate, where it acts only as precipitant and where the medium serves as reductant. At high temperature (e.g., 170 °C), sodium hydroxide and aqueous ammonia are not suitable for the synthesis of SnSe because it decomposes under these strong basic solutions. Various crystalline morphologies were observed under TEM.

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