

Characterization of PbSnS₃ Nanorods Prepared via an Iodine Transport Hydrothermal Method

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An iodine transport hydrothermal route has been developed to prepare PbSnS₃ nanorods at 200°C for the first time. X-ray powder diffraction and transmission electron microscopy results show the as-synthesized PbSnS₃ displays rod-like morphology with diameters of 50–60 nm and lengths of up to a few micrometers. The as-prepared PbSnS₃ nanorods is also investigated by Raman spectra. The various factors influencing the formation of the PbSnS₃ nanorods were discussed. © 2001 Academic Press

Key Words: iodine transport; PbSnS₃; nanorods; hydrothermal route.

1. INTRODUCTION

The preparation and design of semiconductor one-dimensional (1D) structure, such as nanowires (nanorods) and nanotubes has received great attention because of their potential application in mesoscopic research, the development of nanodevices, and the potential application of large surface area structures (1, 2).

Unlike the I-III-VI₂ and I-IV-V₂ ternary semiconductor, the preparation routes and properties of II-IV-VI₃ group of compounds, especially the sulfide semiconductors, are rarely described in the literatures. PbSnS₃, a member of II-IV-VI₃, is a ternary sulfide semiconductor, which has been cursorily examined (3). Its fundamental optical edge is placed at 1.05 eV, which makes it attractive for possible photovoltaic application. Kuku and Azi (4) investigated optical properties of PbSnS₃ thin films. The fundamental absorption edge is placed at 1.04 ± 0.05 eV and is forbidden in nature.

Traditionally, PbSnS₃ is prepared by direct combination of the elements (5) or by thermal annealing of mixtures of

binary sulfides (3). All the above routes are carried out in vacuum-sealed quartz ampoules in the temperatures above 600°C.

The hydrothermal process is an effective crystallization process. Our research groups have developed the hydrothermal method for the preparation of many nonoxide nanocrystals based on hydrothermal routes such as ZnS (6), CuFeS₂ (7) and SnS₂ (8). In this paper, we report preparation and properties of PbSnS₃ nanorods through iodine transport hydrothermal route. To our knowledge, the synthesis of PbSnS₃ nanorods by an iodine transport hydrothermal method has not been reported previously.

2. EXPERIMENTAL

Starting materials were analytically pure PbCl₂ (1.39 g), SnCl₄ · 5H₂O (1.75 g), thiourea (NH₂CSNH₂) (1.80 g) aqueous solution, and a small amount of iodine (I₂) (ca. 0.30 g). These charges were put into an autoclave of 50 ml capacity. The autoclave was then filled with distilled water up to 85% of the total volume. The autoclave was maintained at 200°C for 10 h and then cooled to room temperature naturally. The final product was filtered and washed with distilled water several times. After drying in vacuum at 70°C for 4 h, green powders were obtained.

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku Damax γ A X-ray diffractometer with CuK α ₁ radiation ($\lambda = 1.54056$ Å). Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. For the high-resolution transmission electron microscopy (HRTEM) observations, a JEOL-2010 transmission electron microscope was used at 200 kV. X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromated MgK α radiation as the excitation source.

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Raman spectra were recorded on SPEX-1403 spectrometer with 514.5-nm radiation from an Ar⁺ laser at room temperature.

3. RESULT AND DISCUSSION

The XRD patterns for the PbSnS₃ sample are shown in Fig. 1. All reflections can be indexed as the orthorhombic PbSnS₃ phase with cell constants $a = 8.736 \text{ \AA}$, $b = 3.776 \text{ \AA}$, $c = 13.977 \text{ \AA}$, which are consistent with the value reported in the literature (JCPDS, 25-464). No impurities such as SnS₂, PbS, PbI₂, and SnI₄ were detected.

The quality of the samples was also characterized by XPS. No obvious impurities, e.g. chloride ion or element I₂, could be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 at%).

Figure 2 shows TEM images of as-prepared PbSnS₃ nanorods. It can be seen that the as-synthesized PbSnS₃ nanorods have diameters of 50–60 nm (Figs. 2a and 2b) and 10–15 nm (Figs. 2c and 2d) and lengths of up to a few micrometers.

Figure 3 shows HRTEM image of a single PbSnS₃ nanorod with a diameter of 40 nm. The interplanar spacing is about 5.477 Å, which corresponds to the {102} plane of the orthorhombic system of PbSnS₃. This image furthermore reveals that the structure of the nanorod is a uniform orthorhombic PbSnS₃.

The effect of iodine on the formation of PbSnS₃ nanorods was investigated. If element iodine was not added to an autoclave, the reaction among PbCl₂, SnCl₄·5H₂O, and NH₂CSNH₂ (route 1) at 200°C after 10 h produced PbSnS₃, PbS, and SnS₂; otherwise it needed to prolong the reaction time up to 24 h to produce PbSnS₃ nanorods only (see Figs. 2c and 2d). When element iodine was added (route 2),

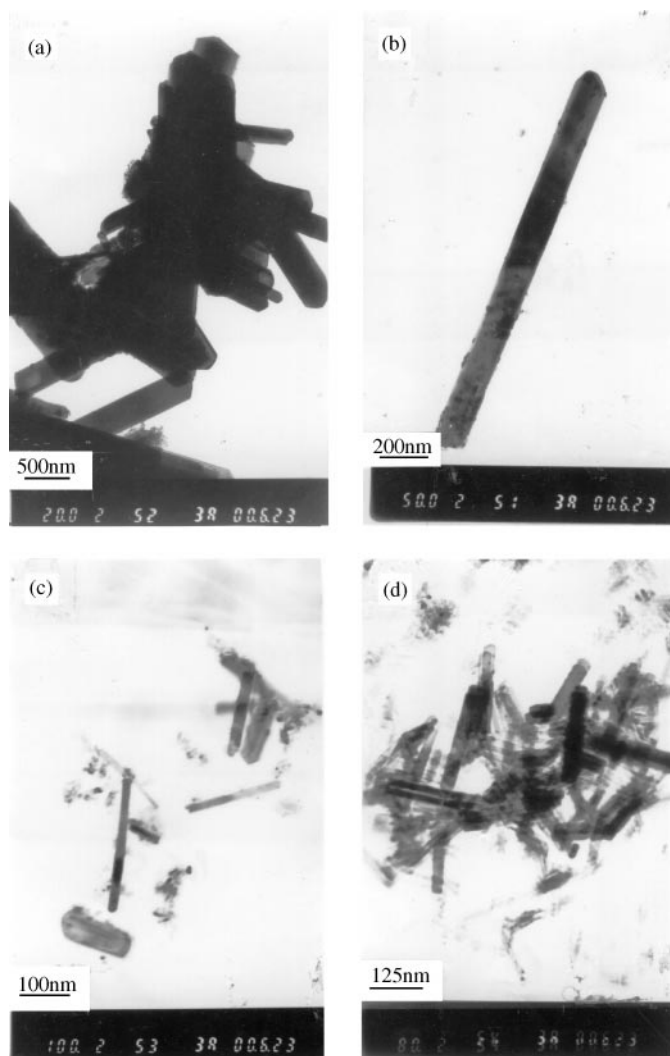


FIG. 2. TEM images of as-prepared PbSnS₃ from the two routes listed in Table 1: (a and b) Route 2; (c and d) route 1.

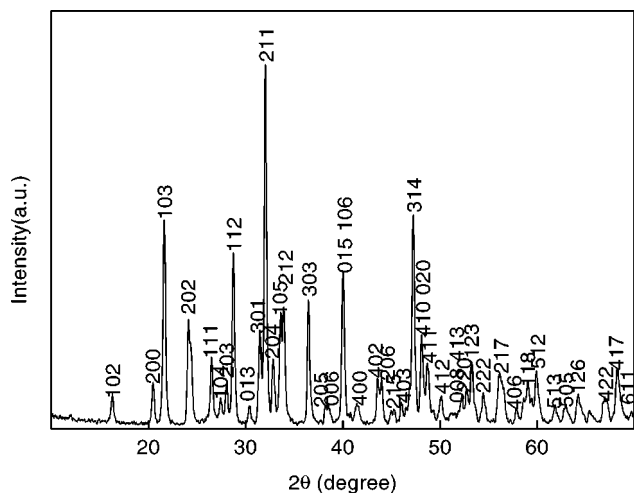


FIG. 1. XRD patterns of as-prepared PbSnS₃ from route 2 listed in Table 1.

the PbSnS₃ nanorods were synthesized at 200°C after 10 h (see Figs. 2a and 2b). Thus iodine can accelerate the reaction and change the size of PbSnS₃ nanorods. The difference of obtained PbSnS₃ nanorods are summarized in Table 1. The role of iodine in the hydrothermal process is similar to the chemical vapor transport method using iodine as a transporting agent (9), although we do not detect intermedia appearing in the iodine vapor transport such as PbI₂ or Pb₅S₂I₆ (10). So we call this method iodine transport hydrothermal method.

The effect of different sulfur sources on the formation of PbSnS₃ nanorods was also studied. Na₂S·9H₂O and (NH₄)₂S were used to replaced thiourea (NH₂CSNH₂), keeping the other reaction condition identical. The product of the reaction among PbCl₂, SnCl₄·5H₂O, Na₂S·9H₂O, and a small amount of I₂ was PbSnS₃ (poorly crystalline).

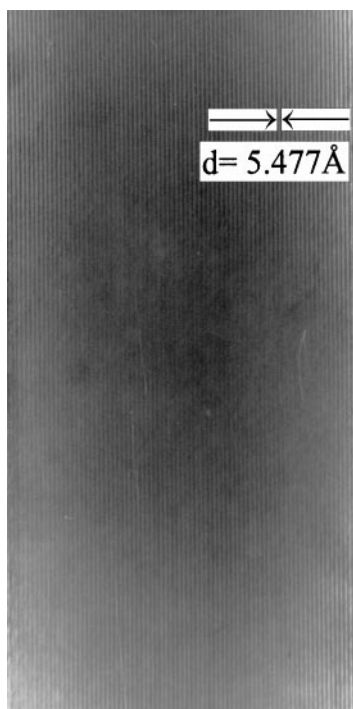


FIG. 3. HRTEM image of a PbSnS₃ nanorod.

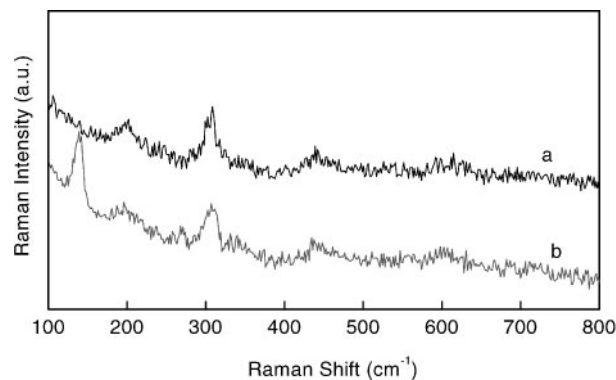
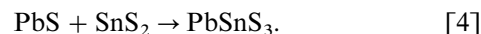
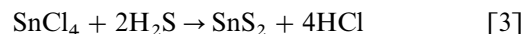
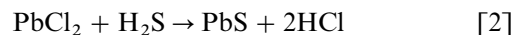
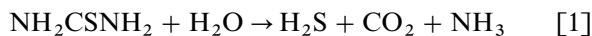


FIG. 4. Raman spectra of the as-prepared PbSnS₃ at room temperature. (a) PbSnS₃ obtained from route 1; (b) PbSnS₃ from route 2.

Supported by the above result, the whole reaction can be represented by the following equations:



The possible reason is that a reaction between the aqueous solution of SnCl₄·5H₂O and Na₂S·9H₂O immediately occurred at room temperature, yielding amorphous SnS₂ (8), which reacts with PbS and produces PbSnS₃ (poorly crystalline). The reaction among PbCl₂, SnCl₄·5H₂O, (NH₄)₂S, and a small amount of I₂ produced only PbS, because the reaction between SnCl₄·5H₂O and (NH₄)₂S did not occur (8).

The influence of reaction temperature on the formation PbSnS₃ nanorods was also studied. If the reaction temperature was lower than 190°C, the products were PbS and SnS₂. It was found that an optimum condition for the formation PbSnS₃ nanorods was the reaction among PbCl₂, SnCl₄·5H₂O, (NH₄)₂CS, and a small amount of I₂ at 200°C for 10 h.

Figure 4 shows the Raman spectrum of as-prepared PbSnS₃ at room temperature. As far as we know, this spectrum of PbSnS₃ has not reported before in the literature. The Raman spectrum of the PbSnS₃ shows a complex behavior with two modes, which can be assigned to the vibrational modes of PbS and SnS₂. This behavior is very similar to SnS_{2-x}Se_x (11) and NiS_{2-x}Se_x (12), which can be assigned to the vibrational modes of SnS₂ and SnSe₂ and NiS₂ and NiSe₂, respectively. The frequencies of 309 and 625 cm⁻¹ correspond to A_{1g} mode and second-order effects of SnS₂ (13,14), respectively. According to Ref. (15) we assign the line at 442 cm⁻¹ to the vibrational mode of PbS. The frequency of 201 cm⁻¹ may correspond to the E_g mode

TABLE 1
The Comparison of Obtained PbSnS₃ Nanorods from Two Routes

Route	Time (h)	Temperature (°C)	Length (μm)	Diameter (nm)	Morphology	Product
1	24	200	0.2	10–15	See Figs. 2c and 2d	PbSnS ₃
1	10	200				PbSnS ₃ , ^a PbS, SnS ₂
2	10	200	2	50–60	See Figs. 2a and 2b	PbSnS ₃
2	4	200				PbSnS ₃ , PbS, ^a SnS ₂ ^a

Note. Route 1, the reaction among PbCl₂, SnCl₄, and (NH₂)₂CS; route 2, the reaction among PbCl₂, SnCl₄, and (NH₂)₂CS and a small amount of I₂.
^aTrace in product.

of SnS₂ (14) or the first-order phonon mode of PbS (15). However, this mode could not be observed in SnS₂ nanocrystalline (8). The peak in the Raman spectrum at 143 cm⁻¹, observed which we observed only in the Raman spectrum of 50–60 nm PbSnS₃ nanorods (Fig. 3b), has not been assigned.

4. CONCLUSIONS

An iodine transport hydrothermal method has been developed and PbSnS₃ nanorods have been synthesized by using this method at 200°C. The as-synthesized PbSnS₃ nanorods have diameters of 50–60 nm and lengths of up to a few micrometers. The vibrating property of as-synthesized PbSnS₃ nanorods was studied by Raman spectra at room temperature. The effect of various factors on the formation of the PbSnS₃ nanorods was discussed.

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