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Solvent–thermal preparation of nanocrystalline tin chalcogenide

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Abstract

Nanocrystalline β-SnS_2 has been successfully prepared by the reaction between $SnCl_4$ and anhydrous Na_2S using a solvent–thermal method at 150°C, which is similar to the well-known hydrothermal process except that toluene is substituted for water. X-ray diffraction analysis indicates that the product is the β-SnS_2 phase, and no Sn–O vibrations are found in the IR spectra. Transmission electron microscopy shows that the average particle size is about 12 nm. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Tin chalcogenide (SnS_2) has interesting optical and electrical properties [1–3], and has been used widely as a semiconductor and a photoconductor [4]. Conventionally, SnS_2 is synthesized by direct combination of the elements [5], by the vapor-phase reaction of the halides with hydrogen sulfide [6–8], and by a solid-state methathesis reaction, the reaction of SnI_4 and Li_2S [9]. All the above procedures are carried out in sealed tubes and in the temperature range 400–700°C.

Chianlli and Dines [10] synthesized a number of transition metal dichalocogenides in non-aqueous solution at room temperature by the reaction between an anhydrous transition metal chloride and either lithium sulfides or ammonium hydrogen sulfide. The products had large surface areas, but were poorly crystalline or were amorphous. Schleich and co-workers [11–14] also prepared amorphous transition metal sulfides by the reaction between metal halides and organic sulfur compounds such as hexamethyldisilane (HMDST), di-*tert*-butyldisulfide (DTBDS), di-*tert*-butylsulfide (DTBS), and *tert*-butylmercaptan (TBMC) at low temperature.

The hydrothermal process is an effective crystallization process. Recently, Qian et al. [15] prepared nanocrystalline ZnS using the hydrothermal process at 150°C. However, tin chloride has been found to be very susceptible to water, so nanocrystalline β-SnS_2 cannot be synthesized by the hydrothermal method.

In this study, we successfully synthesized nanocrystalline β-SnS_2 at 150°C via a solvent–thermal process, which is similar to the well-known hydrothermal process except that toluene is substituted for water.

2. Experimental

All the manipulations were carried out in a dry-box filled with nitrogen since the reagents had been found to be very susceptible to oxidation.

Anhydrous tin tetrachloride ($SnCl_4$) was of analytical grade (Shanghai Chemistry Co.). Na_2S was prepared from stochiometric amounts of the elements in liquid ammonia under an inert atmosphere [16]. Toluene was distilled with sodium to remove water, stored over 3 Å molecular sieves, and degassed with dinitrogen prior to use.

In a typical reaction, stoichiometric amounts of $SnCl_4$ and anhydrous Na_2S were added to a Teflon-lined autoclave of 120 ml capacity. The autoclave was filled with toluene up to 75% of the total volume. At room temperature, there was no observable reaction of $SnCl_4$ with Na_2S. The autoclave was maintained at 150°C in an oven for 6–8 h, then cooled to room temperature naturally. After being washed several

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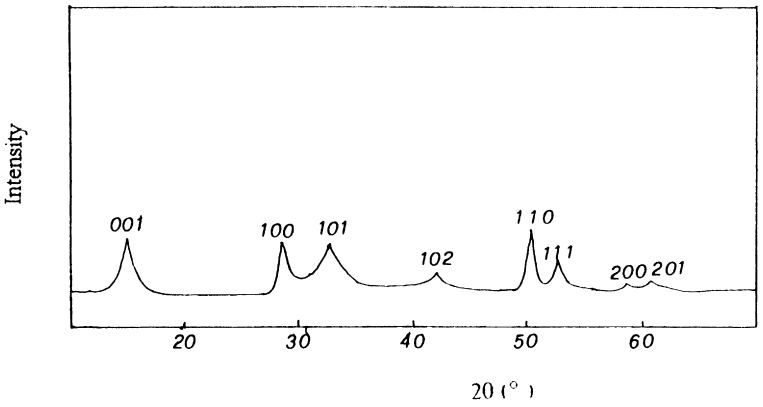

Fig. 1. XRD pattern of β-SnS_2 formed in toluene.

times with absolute ethanol to removal NaCl, a yellow powder was collected. The final product was dried at 80°C in a vacuum drier for 4 h.

The X-ray power diffraction (XRD) pattern was recorded using a Japan Rigaku Damax γA X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Transmission electron microscopy (TEM) images were obtained with use of a Hitachi H-800 transmission electron microscope. The IR spectra were obtained using a Shimadzu IR-440 spectrometer at room temperature.

3. Results and discussion

A typical XRD pattern for the sample is shown in Fig. 1. All the peaks could be indexed as the hexagonal β-SnS_2 phase with cell constants $a = 3.65$ Å, $c = 5.90$ Å, which is consistent with the literature [17]. The crystal size of the sample was about 12 nm, which was calculated from the half-width of the diffraction peaks using the Debye–Schererr formula.

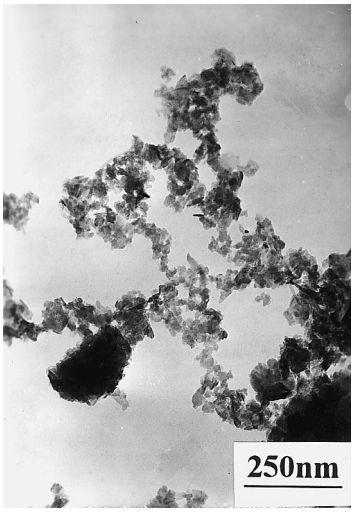

Fig. 2. TEM image of β-SnS_2 formed in toluene.

Fig. 2 shows a TEM micrograph of the β-SnS_2 particles, which shows the particles to consist of uniform, spherical crystallites. One can see that the morphology is homogeneous and the average size is about 12 nm, which is consistent with that deduced from the XRD pattern.

The solvent–thermal reaction process can be described as follows. It may be a liquid–solid reaction, as $SnCl_4$ is soluble in toluene.

$$SnCl_4 + 2Na_2S \rightarrow SnS_2 + 4NaCl$$

The reaction of $SnCl_4$ with Na_2S involves no redox chemistry; the oxidative states of the metal atoms in the reactants do not differ from those of the corresponding metal atoms in the products.

In the preparation of nanocrystalline β-SnS_2 through the solvent–thermal procedure, several factors such as temperature, reaction time and solvent were considered. Toluene was chosen due to its appropriate boiling point. Furthermore, toluene is a weakly polar organic solvent that should prevent the immediate reaction of Na_2S with $SnCl_4$ at room temperature, which is beneficial in controlling the reaction and in forming crystalline tin sulfide. In the solvent–thermal process, the optimum conditions for preparing β-SnS_2 were 150°C for 6–8 h. If the temperature was lower than 100°C or the time was shorter than 4 h, the yield of β-SnS_2 was lower and the as-prepared β-SnS_2 was of low quality. In the reaction process, we used specially treated toluene in the rigorous absence of oxygen and water, which may prevent the oxidation of $SnCl_4$ and Na_2S. The IR spectra of the final product also indicated that there were no tin oxides, because no Sn–O vibrations was detected in the range 500–720 cm^{-1} [18]. The NaCl byproduct could be removed by washing with absolute ethanol.

We also used tetrahydrofuran (THF) as the solvent. As we slowly added Na_2S to the THF solution of $SnCl_4$ at room temperature in a dry-box, a reaction immediately occurred, yielding a yellow solid. XRD indicated that the product was

amorphous. Even if the product were treated under similar conditions to those of the toluene–thermal process, the SnS_2 was still poorly crystalline. The reason is that THF is a polar solvent, so $SnCl_4$ and Na_2S can dissolve in it and can react with each other to form an amorphous product immediately, which is not beneficial in forming cystalline SnS_2.

4. Conclusion

In this paper, we have described the preparation of β-SnS_2 through the reaction of $SnCl_4$ with Na_2S via a solvent–thermal process at 150°C, which is similar to the well-known hydrothermal process except that toluene is substituted for water. The process is simple and easy to control. XRD indicates that the final product is β-SnS_2, and no Sn–O vibrations are found in the IR spectra. TEM images show that the average particle size is about 12 nm. The byproduct can easily be removed using absolute ethanol.

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