

Synthesis and Characterization of Ternary Chalcogenides Ag_8SnE_6 ($E = \text{S}, \text{Se}$)

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Nanocrystalline Ag_8SnS_6 and Ag_8SnSe_6 were directly synthesized by the reaction of AgNO_3 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and sulfur/selenium in a solvothermal process and 100°C for 10 h, respectively. X-ray powder diffraction patterns, X-ray photoelectron spectra, and transmission electron microscope images show that the products are the Ag_8SnS_6 and Ag_8SnSe_6 phases which are well crystallized with the average size of about 20 and 25 nm, respectively. The possible mechanism for the formation of the nanocrystals in the solvothermal process was proposed. The solvent ethylenediamine played an important role in the growth of nanocrystals. © 2000 Academic Press

Key Words: ternary chalcogenides; nanocrystalline; Ag_8SnS_6 ; Ag_8SnSe_6 ; ethylenediamine; solvothermal process.

1. INTRODUCTION

In recent years a number of papers reviewed multinary chalcogenides which illustrate the continuing interest in new multinary chalcogenides materials (1–5). The titled compounds belong to a group of compounds represented by the general formula $\text{Ag}_8\text{M}^{\text{IV}}\text{X}_6^{\text{VI}}$ ($M = \text{Si}, \text{Ge}, \text{Sn}$; $X = \text{S}, \text{Se}, \text{Te}$). Compounds of this class were reported by several authors and are of particular interest because of their promising photosensitivity as semiconductors (6), high ionic conductivity (7), and incomplete occupancy of certain cation sites, giving rise to order–disorder phenomena and phase transitions (8).

An important aspect of the recent research focus in solid-state chemistry has been the preparation of kinetically stabilized solids (9). Those are prepared at relatively low temperatures and thus are not the thermodynamically stable products appearing on high-temperature phase diagrams (10). The synthetic challenge is to develop techniques whereby there is intimate contact between the (mostly solid starting materials and sufficient thermal energy for them to react.

This desirable side would be the ability to grow crystals of the product. A common technique is using fluxes or molten salts to dissolve the reactants at intermediate temperatures (11, 12). Multinary chalcogenides containing alkali metals can be prepared by the reactive-flux method (13) at intermediate temperatures (about $600\text{--}300^\circ\text{C}$) or by the solvothermal method (2) at relatively low temperatures (about 200°C). However, the multinary chalcogenides without alkali metals are still synthesized by the traditional method at high temperatures ($> 600^\circ\text{C}$) (14), which involves the direct combination of the elements in evacuated silica tubes. To complete the reaction, high temperatures, inert atmosphere protection, and long periods of time are required, and it is difficult to obtain nanocrystalline materials under such conditions.

Recently, the solvothermal pathway, which is carried out at a relatively low temperature and does not require organometallic or toxic procurers, has been developed as a mild route to synthesis materials. Various kinds of nanocrystalline materials were obtained by such a process (15–17). We report here a solvothermal route to a ternary nanocrystalline chalcogenidometalate at a temperature as low as 100°C . To our knowledge, this is the first time that nanoscale ternary chalcogenides were prepared under so mild conditions.

2. EXPERIMENTAL

In a typical experimental procedure, the products, Ag_8SnS_6 (I) and Ag_8SnSe_6 (II), can be prepared from stoichiometric mixtures of AgNO_3 (1.919 g, 11.29 mmol), $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.319 g, 1.41 mmol), and sulfur (0.271 g, 8.44 mmol) for I or selenium (0.670 g, 8.48 mmol) for II. The mixtures, all with nominal purity greater than 99.9%, were loaded into a 100-ml Teflon liner autoclave, which was then filled with anhydrous ethylenediamine up to 90% of the total volume. The autoclave was sealed and maintained at 100°C for 10 h and then cooled to room temperature naturally. The products were filtered and washed with distilled

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water and absolute ethanol several times to remove the by-products. The precipitates were dried in vacuum at 60°C for 4 h.

The obtained products were characterized by X-ray power diffraction (XRD), using a Japan Rigaku D/max-γA X-ray diffractometer with CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). The scan rate of $0.05^\circ \text{ s}^{-1}$ was applied to record the patterns in the 2θ range of 20–60°. To examine the morphology and particle size of the products, transmission electron microscope (TEM) images were taken on a Hitachi model H-800, using an accelerating voltage of 200 kV.

Further evidence for the composition of the products as prepared was obtained by the X-ray photoelectron spectra (XPS). The XPS were collected on an ESCALAB MK II X-ray photoelectron spectrometer, using a nonmonochromatized MgK α X ray as the excitation source. The binding energies were referred to the C(1s) binding energy (248.6eV) of the carbonaceous contaminant of the samples.

3. RESULTS AND DISCUSSION

The XRD patterns of Ag $_8$ SnS $_6$ and Ag $_8$ SnSe $_6$ as prepared through the solvothermal method are shown in Figs. 1A and 1B, respectively. In each XRD pattern all the reflections can be indexed to those of the correspondent pure phases, as listed in Table 1. Both their lattice parameters are very close to the reported data (18). The TEM images in Figs. 2A and 2B show the particle sizes and the shapes of Ag $_8$ SnS $_6$ and Ag $_8$ SnSe $_6$, respectively, and the particle sizes are listed in Table 1. Small particles have extremely small dimensions and high surface energy, so it is easy for them to aggregate into secondary particles as shown in the TEM images.

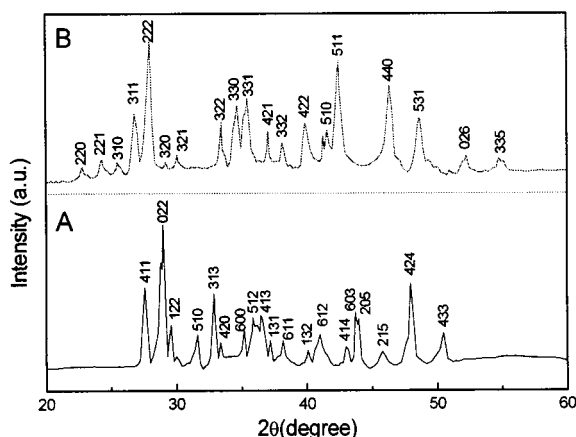


FIG. 1. XRD patterns of as-prepared products: (A) Ag $_8$ SnS $_6$ and (B) Ag $_8$ SnSe $_6$.

TABLE 1
Characterization of Products As Prepared

Compounds	Phase	Lattice parameters (\AA)		Grain size (nm)
		Calculated	Literature (16)	
Ag $_8$ SnS $_6$	Orthorhombic	$a = 15.293$, $b = 7.546$, $c = 10.715$	$a = 15.298$, $b = 7.548$, $c = 10.699$	20
Ag $_8$ SnSe $_6$	Cubic	$a = 11.05$	$a = 11.07$	25

XPS (Fig. 3) of Ag $_8$ SnS $_6$ illustrates the Sn3d core level spectrum, the observed values of the binding energies for Sn(3d $_{5/2}$) and Sn(3d $_{3/2}$) are in good agreement with the literature values (19). Besides, the Sn(3d $_{5/2}$) satellite peak characterizing Sn $^{2+}$, which is usually centered at about 485.7 eV (20), is absent in Fig. 3. Therefore, we may conclude that only Sn $^{4+}$ exists in this compound. XPS analysis also revealed the normal valence states for Ag and S atoms. The Ag core level spectrums exhibit the binding energies of 367.95 and 373.9 eV corresponding to 3d $_{5/2}$ and 3d $_{3/2}$ states, respectively, and are very similar to the observed values in Ag $_2$ S (20). The S(2p $_{3/2}$) and S(2p $_{1/2}$) binding energies, 161.9 and 162.8 eV, respectively, are very consistent with those observed in chalcopyrite CuFeS $_2$ (21). The XPS spectra of Ag $_8$ SnS $_6$ show that the Ag and Sn core level spectra have the same binding energies as that of Ag $_8$ SnS $_6$, and the Se(2p $_{3/2}$) and Se(2p $_{1/2}$) binding energies, 53.65 and 54.15 eV, respectively, are in agreement with those of Ag $_2$ Se (20).

Optimum conditions for preparing the nanocrystals were at 100°C for 10 h in the autoclave. Lower temperatures or shorter times lead to incomplete reaction with decreased

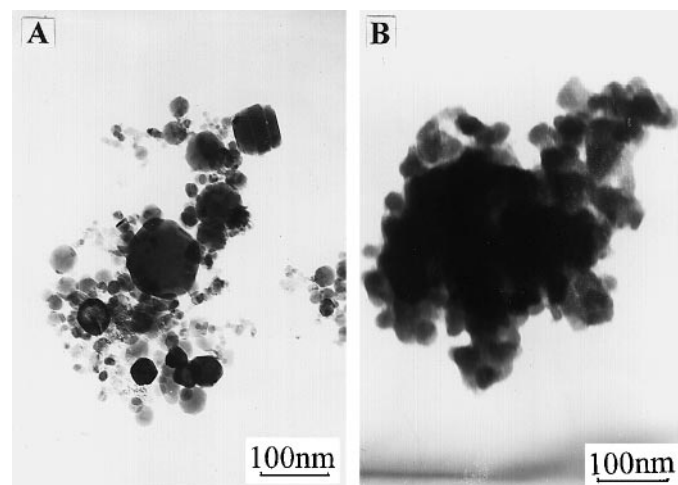


FIG. 2. TEM images of as-prepared products: (A) Ag $_8$ SnS $_6$ and (B) Ag $_8$ SnSe $_6$.

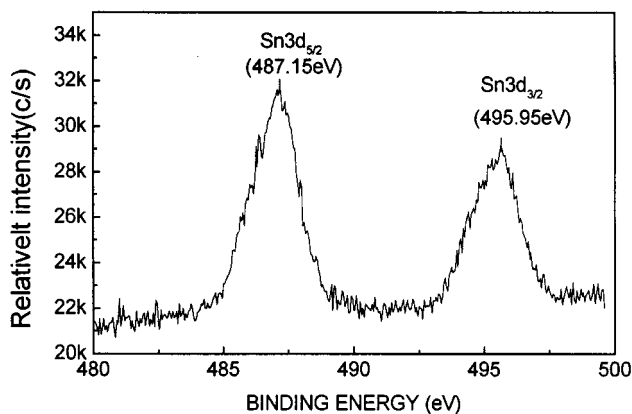


FIG. 3. Sn(3d) core level XPS spectrum of Ag_8SnS_6 .

yield and crystallinity. When the temperature was lower than 80°C , the reaction cannot be initiated. On the other hand, the resultant grains were bigger under higher reaction temperatures or longer times. When the reaction was carried out at 180°C for 15 h, the grain size increased to 100 nm. In general, the grain size varied with the reaction temperature and time.

In the solvothermal process, the solvent plays an important role in the formation of the titled compound nanocrystals. Ethylenediamine was selected as the solvent due to its special properties, such as strong polarity and strong chelation, which are important to the reaction. Ethylenediamine can easily chelate the Ag^+ and form a stable complex $[\text{Ag}(\text{en})_n]^+$ ($K = 10^{7.7}$), which effectively defers the formation of binary silver chalcogenides. So the binary tin chalcogenides formed first, but this kind of chalcogenides have little solubilization in ethylenediamine and provide monomeric species SnE_4^{4-} ($E = \text{S}, \text{Se}$) which readily condense to afford oligomeric anions $\text{Sn}_m\text{E}_n^{(2n-m)-}$ in which individual SnE_4 tetrahedral are linked through shared chalcogen atoms (2). With the increased temperature and pressure, the stable complex decomposes to Ag^+ and forms the product with the oligomeric anions. The contrast experiments were done using other solvents such as benzene, ethanol, or diethylamine. The results showed that no titled compounds but the mixture of silver sulfide and tin sulfide obtained in those cases, which were detected by XRD. On the other hand, being a strongly polar solvent and an absorber to release the excess heat produced in the reaction, ethylenediamine can greatly enhance solubility, diffusion, and crystallization but still provide reaction conditions mild enough to leave molecular-building blocks to participate in the following formation of the solid-state phase. The success of ethylenediamine when employed as a solvent proved that it is an optimum solvent.

4. CONCLUSIONS

In conclusion, solvothermal synthesis of ternary chalcogenidometals is not only feasible and interesting but also a promising alternative to the traditional techniques usually employed in this synthetic chemistry. Solvothermal synthesis can prepare structurally and functionally unique compounds not accessible otherwise. The obvious extensions of this work are the use of different reactants and solvents in an attempt to produce other nanocrystalline ternary chalcogenidometals. Through this method, some other ternary chalcogenides, such as Cu_2SnS_3 and Cu_2SnSe_4 , also have been prepared, which will be reported furthermore.

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