

From 2D Framework to Quasi-1D Nanomaterial: Preparation, Characterization, and Formation Mechanism of Cu_3SnS_4 Nanorods

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Received January 8, 2002

An ion–ion reaction route under solvothermal condition at relatively low temperatures was first put forward to the preparation of tetragonal Cu_3SnS_4 nanorods, on the basis of the strategy that 2D framework structure of Cu_3SnS_4 containing layers could provide orientation for the growth of quasi-1D nanomaterials. X-ray diffraction (XRD) pattern, transmission electronic microscope (TEM) images, electronic diffraction (ED) pattern, X-ray photoelectron spectra (XPS), energy-dispersive X-ray analysis (EDXA), Mössbauer spectrum, Raman spectrum, thermal analysis (DTA and TGA), ultraviolet and visible light (UV–vis) spectrum, and photoluminescence (PL) spectrum were used to characterize the products. On the basis of a series of supplementary experiments and the result of infrared absorption spectrum (IR), a reaction mechanism was proposed: ethanol as solvent and reductant and trace water/ CH_3CSNH_2 as sulfur source and acid-making components could form 2D network through hydrogen bonds, which provided the orientation for the formation of a 2D framework structure; appropriate concentration of CH_3CSNH_2 , warming speed, reaction constant temperatures (T_{rc}), and reaction time also played important roles.

Introduction

A number of reviews have illustrated the continuing interests in new multinary chalcogenides materials.^{1–6} Sulfide-based materials can exist in many forms, such as 1-dimensional chains, 2-dimensional dense or porous sheets, and 3-dimensional open frameworks, because of the multiple local coordination geometry around a tin center and the catenation ability of sulfur, which enriches tin sulfide chemistry and is important to solid-state chemists.⁷ Especially, Cu_3SnS_4 can be thought as a type of compound by the incorporation of copper into tin sulfides units,^{7–9} which

adopts an ordered superstructure of sphalerite-type.^{7,10} Cu_3SnS_4 has a two-dimensional (2D) structure which contains $\text{Cu}(\text{I})\text{S}_4$ and SnS_4 tetrahedra in the ratio of 2:1 as building blocks to form $[\text{Cu}_2\text{SnS}_4]^{2-}$ anionic layers, shown as Figure 1A. The $[\text{Cu}_2\text{SnS}_4]^{2-}$ layers are best described as an ordered defect anti-PbO type structure (Figure 1B), which are separated by Cu^{2+} cations. Recently, Cu_3SnS_4 has attracted great attention because of its promising optical properties,^{11–13} thermal properties,¹⁴ mechanical properties^{8,12,13} as solid lubricant,¹⁵ and Mössbauer effect.¹⁶

Traditionally, multinary chalcogenides were synthesized by solid-state reaction,¹⁷ which required elevated temperature, inert atmosphere protection, and a relatively long duration. Cu_3SnS_4 could be prepared in evacuated silica ampules at ~500–600 °C, either with compressed mixture of the

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- (1) Disalvo, F. J. *Science* **1991**, *247*, 649.
- (2) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206.
- (3) Samanta, L. K.; Ghosh, D. K.; Bhar, G. C. *Phys. Status Solidi A* **1986**, *93*, K51.
- (4) Samanta, L. K.; Ghosh, D. K. *Proceedings 2nd Asia and Pacific Phys. Conference SAPPCC*; Raman Research Institute, Bangalore, India, Jan 13–17, 1986.
- (5) Chen, X.; Wada, H.; Sato, A.; Mieno, M. *J. Solid State Chem.* **1998**, *139*, 144.
- (6) Berger, L. I.; Prochukhan, V. D. *Ternary Diamond Like Semiconductors*; Consultants Bureau: New York, 1969.
- (7) Jiang, T.; Ozin, G. A. *J. Mater. Chem.* **1998**, *8*, 1099.
- (8) Kovalenker, V. A.; Evstigneeva, T. L.; Troneva, N. V. *Zap. Vseross. Mineral. O-va.* **1979**, *108*, 564 (Russian).
- (9) Liao, J. H.; Kanatzidis, M. G. *Chem. Mater.* **1993**, *5*, 1561.

- (10) *Mineralogische Tabellen*; Strunz, H., Ed.; Leipzig: Geest & Portig, 1977.
- (11) Gunter, H. M. *Neues Jahrb. Mineral., Abh.* **1960**, *94*, 1125.
- (12) Kovalenker, V. A.; Nekrasov, I. Y.; Malov, V. S. *Geol. Rudn. Mestorozhd.* **1986**, *28*, 67 (Russian).
- (13) Kalinina, T. A.; Nenashva, S. I.; Ryabeva, E. G. *Zap. Vseross. Mineral. O-va.* **1989**, *118*, 11 (Russian).
- (14) Kalinina, T. A.; Nenashva, S. N. *Zap. Vseross. Mineral. O-va.* **1986**, *115*, 455 (Russian).
- (15) Geringer, M. PCT Int. Appl. WO 96 36, 681, 1996.
- (16) Katada, M. *J. Sci. Hiroshima Univ., Ser A: Phys. Chem.* **1975**, *39*, 45.
- (17) Badding, M. E.; Disalvo, F. J. *Inorg. Chem.* **1990**, *29*, 3952.

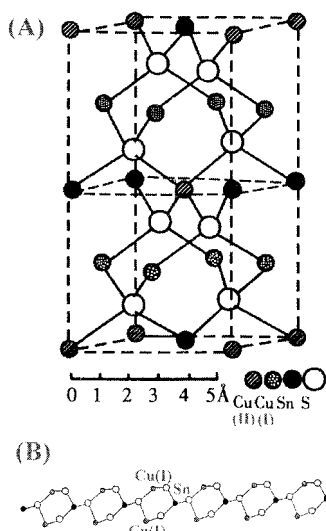


Figure 1. Schematic structure of Cu_3SnS_4 : (A) ordered superstructure of sphalerite-type; (B) fragment of the $[\text{Cu}_2\text{SnS}_4]^{2-}$ anionic layer.

components or in melts of KCl-LiCl or KCl-NaCl .¹¹ To our knowledge, no report has been published about the preparation of pure tetragonal Cu_3SnS_4 nanocrystallites at relatively low temperatures.

To prepare nanocrystalline materials at low temperatures and avoid using organometallic or toxic precursors, a solvothermal technique was developed.^{18–20} Recently, our group synthesized Ag_3SnS_6 and Cu_2SnS_3 nanocrystallites in ethylenediamine at relatively low temperatures ($\geq 100^\circ\text{C}$).^{21,22} However, the as-desired syntheses of nanomaterials are the goal and challenge of both materials scientists and inorganic synthesis researchers at all times. Thus, how to prepare quasi-1D nanomaterials with 2D framework structure as a type of as-desired synthesis has been of interest. Here, we chose a new ion-ion reaction route, which was absolutely different from the elemental reaction routes by the previous research,^{20,23,24} to first synthesize pure tetragonal Cu_3SnS_4 nanorods in ethanol at lower temperature ($\sim 80\text{--}190^\circ\text{C}$). The 2D framework structure of as-obtained products could form on the basis of a 2D network array of reactants via this route, which provided a way to grow quasi-1D nanomaterials. Moreover, under such conditions, we avoided using a toxic solvent, such as ethylenediamine, and obtained products with as-desired morphologies, on which the optical and electronic properties of materials were dependent. On the basis of a series of supplementary experiments and the result of the infrared absorption spectrum (IR), a formation mechanism of Cu_3SnS_4 nanorods was proposed.

- (18) Xie, Y.; Qian, Y. T.; Wang, W. Z.; Zhang, S. Y.; Zhang, Y. H. *Science* **1996**, 272, 1926.
 (19) Xie, Y.; Qian, Y. T.; Wang, W. Z.; Liu, X. M.; Zhang, Y. H. *Appl. Phys. Lett.* **1996**, 69, 334.
 (20) Hu, J. Q.; Lu, Q. Y.; Tang, K. B.; Qian, Y. T.; Zhou, G. E.; Liu, X. M. *Chem. Commun.* **1999**, 1093.
 (21) Li, B.; Xie, Y.; Huang, J. X.; Su, H. L.; Qian, Y. T. *J. Solid State Chem.* **2000**, 149, 338.
 (22) Li, B.; Xie, Y.; Huang, J. X.; Qian, Y. T. *J. Solid State Chem.* **2000**, 153, 170.
 (23) Jiang, Y.; Wu, Y.; Mo, X.; Yu, W. C.; Xie, Y.; Qian, Y. T. *Inorg. Chem.* **2000**, 39, 2964.
 (24) Lu, Q. Y.; Hu, J. Q.; Tang, K. B.; Qian, Y. T.; Zhou, G. E.; Liu, X. M. *Inorg. Chem.* **2000**, 39, 1606.

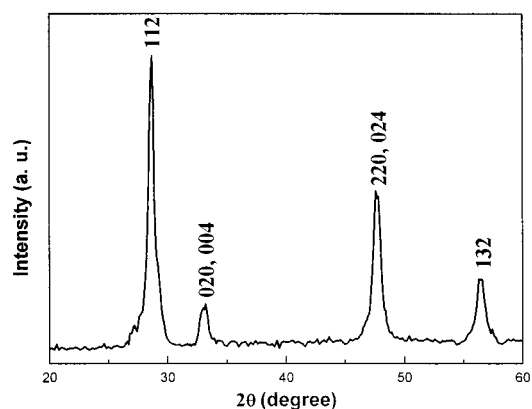


Figure 2. XRD pattern of tetragonal Cu_3SnS_4 nanorods.

Experimental Section

Analytical grade solvent and reagents were purchased from Shanghai Chemistry Co. Ltd.

The compound Cu_3SnS_4 was synthesized from stoichiometric mixtures of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1.089 g, 6.39 mmol), $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (0.754 g, 2.15 mmol), and CH_3CSNH_2 (0.657 g, 8.75 mmol). The mixtures were loaded into a 100-mL Teflon-lined autoclave, which was then filled with absolute ethanol up to 90% of the total volume. The autoclave was sealed, warmed at a speed of $1^\circ\text{C}/\text{min}$, and maintained at $\sim 80\text{--}190^\circ\text{C}$ (reaction constant temperature: T_{rc}) for $\sim 12\text{--}24$ h, and it was then cooled to room temperature naturally. The precipitate was filtered off, washed with absolute ethanol and distilled water for several times, and then dried in a vacuum at 60°C for 4 h.

X-ray diffraction (XRD) pattern was carried out on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized high-intensity $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The transmission electron microscopy (TEM) images, electronic diffraction (ED) pattern, and energy-dispersive X-ray analysis (EDXA) were taken on a Hitachi Model H-800 instrument with a tungsten filament, using an accelerating voltage of 200 kV. The X-ray photoelectron spectra (XPS) were collected on an ESCALab MKII X-ray photoelectron spectrometer, using nonmonochromatized $\text{Mg K}\alpha$ X-ray as the excitation source. The Raman spectrum was performed at room temperature with a LABRAM-HR Confocal Laser MicroRaman Spectrometer. The Mössbauer spectrum was recorded on a MS-500 spectrometer using a constant accelerated drive at room temperature and a $^{119}\text{Sn}/\text{BaSnO}_3$ source. The thermal analysis (DTA and TGA) was taken on a Shimadzu TA-50 thermal analyzer; the sample was heated from room temperature to 600°C at a rate of $10^\circ\text{C}/\text{min}$ in a steady flow of dry N_2 gas. An FT-IR spectrum of the solvent was obtained with a Magna IR-750FT spectrometer in the range $500\text{--}2750 \text{ cm}^{-1}$ at room temperature, with the sample in a KBr disk. The ultraviolet and visible light (UV-vis) spectrum and photoluminescence (PL) spectrum were recorded on a JGNA Specord 200 PC UV-vis spectrophotometer and Hitachi 850 fluorescence spectrophotometer, respectively.

Results and Discussion

Phase and Morphology of the Products. The XRD pattern of as-prepared Cu_3SnS_4 through the solvothermal method is shown in Figure 2. All the reflection peaks can be indexed to tetragonal Cu_3SnS_4 phase with lattice parameters $a = 5.448 \pm 0.003 \text{ \AA}$, $c = 10.760 \pm 0.006 \text{ \AA}$, which are in agreement with the reported data of $a = 5.445 \text{ \AA}$, $c =$

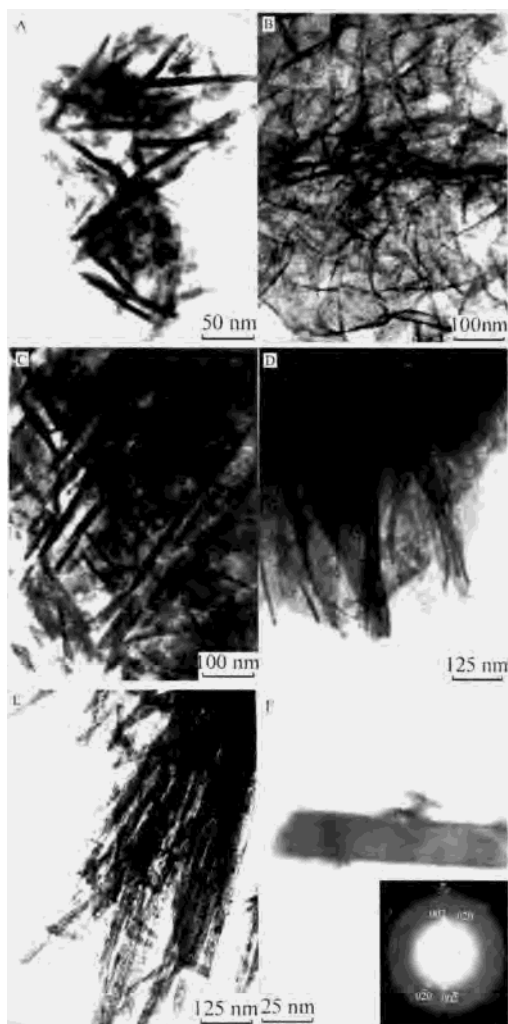


Figure 3. TEM images of samples obtained by (A) 80 °C for 12 h; (B) 120 °C for 12 h; (C) 190 °C for 12 h; (D) 190 °C for 24 h; (E) 190 °C for 24 h with excessive CH_3CSNH_2 as reactant; (F) ED pattern of nanorod in sample E.

10.75 Å for Cu_3SnS_4 (JCPDS Card Files, 33-501). No characteristic peak was observed for the other impurities such as CuS , SnS_2 , or S.

The TEM images in Figure 3 show that the as-prepared products are some nanorods with nanoparticles. The size of the nanorods is $\sim 200\text{--}1000$ nm in length and $\sim 8\text{--}25$ nm in diameter on average, which is determined by the concentration of CH_3CSNH_2 , reaction constant temperatures (T_{rc}), and reaction time. ED pattern (Figure 2F) of the as-prepared Cu_3SnS_4 nanorods in sample E shows they are tetragonal single crystals. EDXA analysis of the as-prepared Cu_3SnS_4 nanorods indicates that they are made up of Cu, Sn, and S, which gives a ratio of Cu/Sn/S in the products (0.76:0.26:1). It is very consistent to the stoichiometry of Cu_3SnS_4 within the error of 1.5%.

X-ray Photoelectron Spectrum (XPS). The quality and composition of the samples are characterized by XPS. The XPS survey spectra show that no obvious impurities, for example, chloride ions, elemental tin, or sulfur, can be detected in the samples, indicating that the level of impurities is lower than the resolution limit of XPS (1 at. %). The

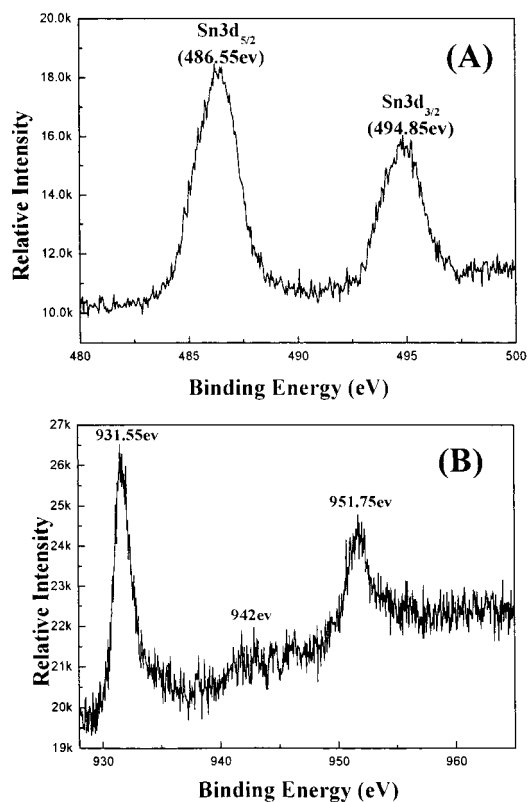


Figure 4. XPS spectra of samples: (A) Sn 3d core level spectrum; (B) Cu 2p core level spectrum.

binding energies obtained in the XPS analysis are corrected for specimen charging by referencing the C1s to 284.60 eV.

The Sn 3d core level spectrum (Figure 4A) of Cu_3SnS_4 illustrates 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.²⁵ Besides, the Sn $3d_{5/2}$ satellite peak characterizing Sn^{2+} , which is usually centered at about 485.7 eV,²⁶ is absent in Figure 4A. Therefore, we can conclude that the Sn element existing in compound Cu_3SnS_4 is all at IV value state. The Cu 2p core level spectrum (Figure 4B) illustrates that the observed values of the binding energies for Cu $2p_{3/2}$ and Cu $2p_{1/2}$ are in agreement with the literature values of bulk for Cu^+ .²⁷ Besides, the Cu $2p_{3/2}$ satellite peaks characterizing Cu^{2+} , which are usually centered at about 942 eV,²⁸ are also found in Figure 4B. It indicates there are Cu^+ and Cu^{2+} in Cu_3SnS_4 . XPS analysis also reveals the normal valence states for S atoms. The S $2p_{3/2}$ and S $2p_{1/2}$ binding energies of Cu_3SnS_4 , 161.9 and 162.8 eV, respectively, are very consistent with those observed in chalcopyrite CuFeS_2 .²⁹ So, the XPS analysis shows the normal valence states for Cu_3SnS_4 are $\text{Cu}^+_2\text{Cu}^{2+}\text{Sn}^{4+}\text{S}^{2-}_4$, which agree with the literature report.⁸

(25) Ettema, A. R. H. F.; Hass, C. *J. Phys.: Condens. Matter* **1993**, *5*, 3817.

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

(27) Llanos, J.; Buljan, A.; Mujica, C.; Ramirez, R. *J. Alloys Compd.* **1996**, *234*, 40.

(28) Partain, L. D.; Schneider, R. A.; Donaghey, L. F.; Meleod, P. S. *J. Appl. Phys.* **1985**, *57*, 5056.

(29) Nakai, I.; Sugitani, Y.; Nagashima, K.; Niwa, Y. *J. Inorg. Nucl. Chem.* **1978**, *40*, 789.

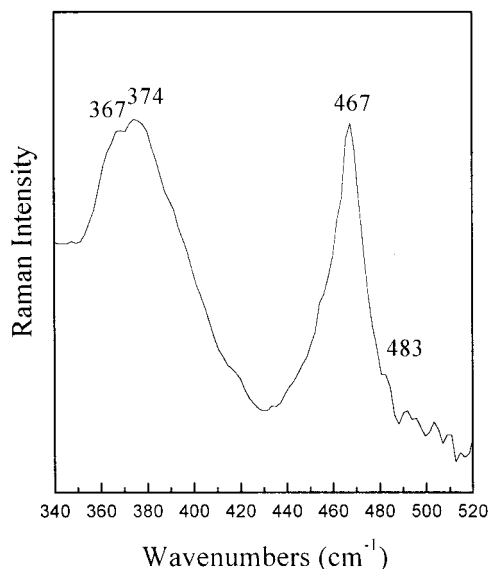


Figure 5. Raman spectrum of samples.

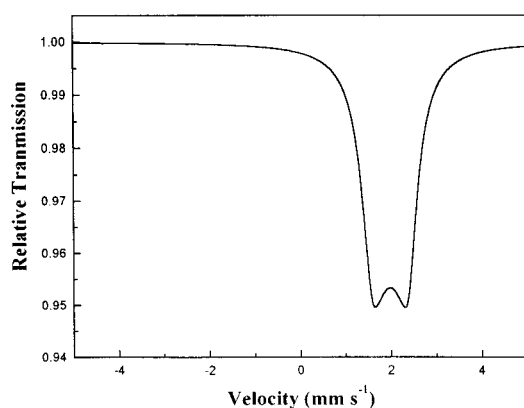


Figure 6. ^{119}Sn Mössbauer spectrum of samples.

Raman Spectrum. Figure 5 shows the Raman spectrum of Cu_3SnS_4 . The mode at 367 and 374 cm^{-1} of Cu_3SnS_4 can be assigned to Sn–S stretching vibration by analogy to other tin sulfide complexes.^{30–32} The vibrations at 483 and 467 cm^{-1} are assignable to $\gamma_{(S-S)_{\text{sym}}}$ and $\gamma_{(S-S)_{\text{asym}}}$, respectively. The results indicate that $[\text{SnS}_4]^{4-}$ actually exists in the as-obtained products.

Mössbauer Spectrum. ^{119}Sn Mössbauer spectroscopy (Figure 6), a powerful experiment technique for the identification and characterization of the Sn local environment and formal oxidation state, shows the presence of tetrahedral $[\text{SnS}_4]^{4-}$ anions in this material. The isomer shift ($\delta = 1.98 \text{ mm}\cdot\text{s}^{-1}$) and quadrupole splitting ($\Delta E_{\text{q}} = 0.72 \text{ mm}\cdot\text{s}^{-1}$) parameters are very similar to all compounds containing Sn^{4+} and characteristic of tetrahedral Sn^{4+} centers.³³ The appearance of quadrupole splitting in the spectrum suggests that the local lattice symmetry of the Sn^{4+} center is relatively low, which is attributed to binding of the copper centers which lowers the tetrahedral symmetry. The spectrum also

(30) Schiwy, W.; Pohl, S.; Krebs, B. *Z. Anorg. Allg. Chem.* **1973**, *402*, 77.

(31) Krebs, B.; Pohl, S.; Schiwy, W. *Z. Anorg. Allg. Chem.* **1972**, *393*, 241.

(32) Krebs, B.; Schiwy, W. *Z. Anorg. Allg. Chem.* **1973**, *393*, 63.

(33) Lippens, P. E. *Phys. Rev. B* **1999**, *60*, 4576.

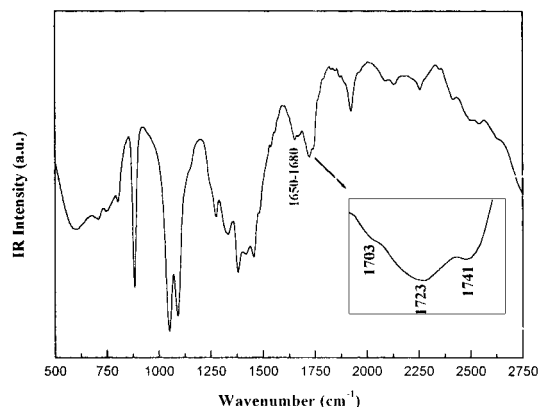


Figure 7. Infrared absorption spectrum (IR) of solvent after reaction.

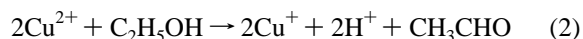
reveals two slightly different Sn environments, suggesting at least two different binding modes for SnS_4 . Those results further confirm the existence of $[\text{Sn}(\text{IV})\text{S}_4]^{4-}$.

Formation Mechanism of Tetragonal Cu_3SnS_4 Phase.

In the solvothermal process, ethanol is an important solvent. It is known that tin chloride ($\text{SnCl}_4\cdot 5\text{H}_2\text{O}$) and thioacetamide can easily dissolve in ethanol; ethanol and water are always mutually soluble. So during the experimental process, tin ions (Sn^{4+}) and sulfur source thioacetamide were homogeneously dispersed in the mutually soluble solvent of ethanol and trace water from hydrated tin chloride. Thus, thioacetamide would react with trace water to produce H_2S slowly, shown by eq 1.³⁴



It was obvious that the reaction system was weakly acidic and effectively deferred the formation of binary copper and tin chalcogenides. Besides, the produced NH_3 could easily be combined with Cu^{2+} to form a relatively stable complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$, which also held back the formation of copper chalcogenides. So, tin ions could react with S^{2-} first to provide monomeric species $[\text{SnS}_4]^{4-}$.² Synchronously, Cu^{2+} ions were reduced to Cu^+ , as eq 2 showed.^{34,35} Subsequently, copper ions (Cu^+ and Cu^{2+}) reacted with $[\text{SnS}_4]^{4-}$ to form tetragonal Cu_3SnS_4 nanocrystallites.



Infrared Absorption Spectrum (IR). The transformation of the solvent ethanol is identified by the result of infrared absorption spectrum (IR) (Figure 7). The absorption peaks at 1650–1680, 1703, and 1723 cm^{-1} are C=S stretching vibration, N–H bending vibration of non-hydrolyzing CH_3CSNH_2 , C=O stretching vibration of produced CH_3COOH by hydrolysis, and C–H bending vibration of $-\text{CH}_3$, respectively. It is obvious that the absorption peak at 1741 cm^{-1} corresponds to C=O stretching vibration of aldehyde, which is produced by the oxidization of ethanol.

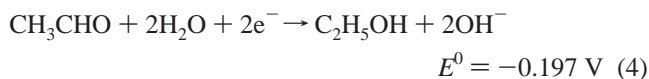
(34) McMurry, J. *Organic Chemistry*, 3rd ed.; Brooks/Cole Publishing Company: Pacific Grove, CA, 1992.

(35) *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill Book Company: New York, 1972.

Supplementary Experiments. Is the formation of Cu_3SnS_4 carried out through the ionic intermediate $[\text{SnS}_4]^{4-}$ or the solid solution intermediate tin sulfides? Here, solid solution mechanism means the route such as $\text{CuS} + \text{Cu}_2\text{S} + \text{SnS}_2 \rightarrow \text{Cu}_3\text{SnS}_4$. In our previous research,³⁶ it was found that tin sulfides could be obtained with tin sources and CH_3CSNH_2 as reactant, under the same condition as that in present paper. If the formation of Cu_3SnS_4 were carried out through the solid solution intermediate of tin sulfides, both Cu_3SnS_4 and tin sulfides would be obtained with excessive tin sources and CH_3CSNH_2 in our present experiments. However, when excessive tin sources and CH_3CSNH_2 were added into the described reaction systems, no tin sulfides were found in the products. This result may further confirm that the products were formed through the ionic intermediate $[\text{SnS}_4]^{4-}$,² rather than tin sulfides. In addition, in our previous research,^{28,29} the results of Raman spectrum and Mössbauer spectrum were in agreement with the present result.

The transformation of copper ions in the reaction system was compared with some supplementary experiments: Cu_3SnS_4 failed to be obtained from CuCl with SnCl_4 and CH_3CSNH_2 , because Cu^+ ions could not be oxidized to Cu^{2+} in these reaction systems because Cu^+ and Cu^{2+} ions were both necessary for the formation of Cu_3SnS_4 . It indicated eq 2 was reasonable to some extent.

Moreover, the oxidation–reduction potentials of Cu^{2+} and $\text{C}_2\text{H}_5\text{OH}$ show the possibility of eq 2:³⁵

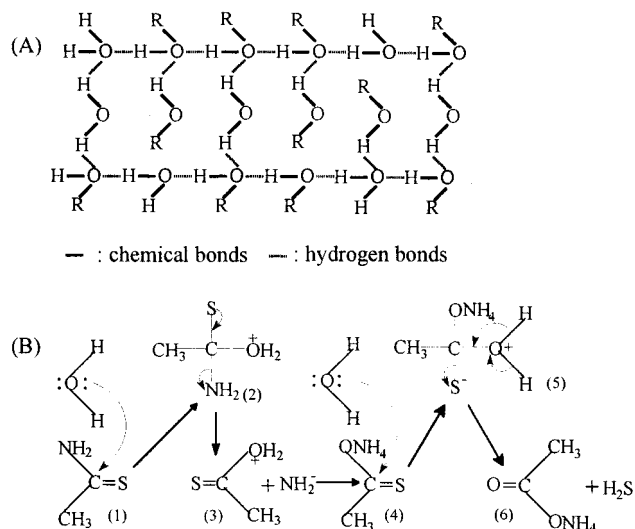


To investigate the influence of different solvents on the formation of Cu_3SnS_4 , we substituted ethanol with ethylenediamine or benzene, respectively, and kept other reaction conditions constant. When ethylenediamine was used, the reaction systems were alkaline and could not hold back the formation of copper and tin chalcogenides, and thus, the product was copper and tin sulfides, not the as-desired products. When benzene was used, trace water and the solvent could not dissolve mutually. Therefore, the produced H_2S and reagents dissolved in benzene were in a heterogeneous system, which was unfavorable for the formation of the products. Besides, the failure to obtain the products in other solvents showed the reducibility of ethanol to the reaction system was crucial.

The experiment with anhydrous SnCl_4 as reactant was carried out via the same route when other reaction conditions were kept constant. It was found that copper sulfide and tin sulfide rather than Cu_3SnS_4 were obtained, which indicated that trace water was important for the formation of Cu_3SnS_4 .

The lack of side products upon characterization was further supported by the experimental result that the reaction yield was all the same and no side product was found when adding

Scheme 1. (A) Chain Arrangement of Hydrogen Bonds; (B) Hydrolysis Mechanism of CH_3CSNH_2



extensive copper or tin source into reaction system. It indicated that the reaction was clean.

Formation Mechanism of Nanorods. The oriented growth of nanocrystalline Cu_3SnS_4 may be due to the array way of trace water and ethanol in the system and appropriate reaction temperature. At appropriate temperature (for example, 80°C), the water molecules surrounded by ethanol molecules could go away from tin chlorides and array on chains with ethanol molecules to form 2D network, because of the hydrogen bonds between them,^{34,37} shown as Scheme 1A. The 2D network arrangement of ethanol and trace water was preferential to the epitaxial growth of crystalline Cu_3SnS_4 , because ethanol and trace water participated in the formation reaction of Cu_3SnS_4 . So, the chains of hydrogen bonds between trace water and ethanol molecules were thought to provide orientation to form the two-dimensional structure of $[\text{Cu}_2\text{SnS}_4]^{2-}$ anionic layers,^{7,10} which were separated by Cu^{2+} cations. This is probably the reason Cu_3SnS_4 cannot be prepared in other reaction systems.²² This 2D framework structure was composed of some 1D units, which obviously could provide orientation to obtain quasi-1D nanomaterials, Cu_3SnS_4 nanorods.

To investigate the influence of ethanol on the formation of nanorods, we substituted ethanol with *n*-hexyl alcohol or aldehyde, and no Cu_3SnS_4 nanorods could be obtained, probably because the chains of hydrogen bonds could not form in higher alcohols³⁴ and aldehyde.

Influence Factors. The concentration of CH_3CSNH_2 , warming speed, reaction constant temperatures (T_{rc}), and reaction time were found to play essential roles in the formation of Cu_3SnS_4 nanorods.

Too low reaction constant temperature (T_{rc}) or short reaction time led to incomplete reaction with decreased yield and crystallinity. For example, when the temperatures were lower than 80°C (closed to boiling point of ethanol), the reactions could not be initiated, because water molecules

(36) Su, H. L.; Xie, Y.; Xiong, Y. J.; Gao, P.; Qian, Y. T. *J. Solid State Chem.* **2001**, *161*, 190.

(37) Akhmetov, N. S. *General and Inorganic Chemistry*; Mir Publishers: Moscow, 1983.

were combined with tin chlorides, which was not in favor for hydrolytic reaction of thioacetamide and epitaxial growth of crystalline tin sulfides. It indicated that the complete reaction needed enough energy.

When the reaction constant temperatures (T_{rc}) were at 80 °C, the as-prepared product was some Cu_3SnS_4 nanoparticles with a few nanorods (Figure 3A). With the increase of reaction constant temperatures (T_{rc}), the content ratio of nanorods in as-prepared products and the size of nanorods increased (Figure 3A–C). This result may be due to the effect of the $[\text{Cu}_2\text{SnS}_4]^{2-}$ anionic layers and rapid crystal growth: When the reaction constant temperature (T_{rc}) was relatively high (for example 190 °C), the Cu_3SnS_4 phase with 2D orientation could be produced during the warming process, because the warming speed was relatively low and there was enough time to react based on the chains of hydrogen bonds at low temperature (~ 80 – 120 °C). It was reported that the relation of crystal growth velocity and temperature was consistent with the equation $V_g = Ae^{-C/RT}$ (V_g : growth velocity; A , C : constant; R : gas constant).^{38,39} It is obvious that the Cu_3SnS_4 crystallites, which formed during the warming process, grew relatively rapidly at higher temperature and were in nonequilibrium state. Finally, these crystallites had large surface energy and usually epitaxially grew along some apex angles or edges to column-, needle-, and rodlike crystals, and so forth.^{38,39} Therefore, relatively high reaction constant temperature (T_{rc} : 190 °C) led to Cu_3SnS_4 nanorods of high yield.

However, the Cu_3SnS_4 nanorods were unstable at too high temperatures (for example, 280 °C) and could be converted into Cu_3SnS_4 nanoparticles. When the temperature went higher (for example, 500 °C), the as-prepared Cu_3SnS_4 would decompose to CuS and SnS, which were identified by XRD analysis. This result was consistent with the previous report.⁴⁰ It indicated that Cu_3SnS_4 nanorods were the as-desired product at medium temperatures (~ 80 – 190 °C).

It was also found that with the increase of reaction time, the content ratio of nanorods in as-prepared products and the size of nanorods increased. Therefore, the optimum condition for preparing Cu_3SnS_4 nanorods is at 190 °C for 24 h (Figure 3D).

It was found that the concentration of CH_3CSNH_2 was crucial to the formation of Cu_3SnS_4 nanorods. When the concentration of CH_3CSNH_2 was higher (for example, 0.985 g of CH_3CSNH_2), the content ratio of nanorods in as-prepared products increased (Figure 3E). This is probably due to the hydrolysis mechanism of CH_3CSNH_2 , shown as Scheme 1B. The hydrolysis of CH_3CSNH_2 needs two water molecules which array on the chains in Scheme 1A. It makes $\text{CH}_3\text{-CSNH}_2$ molecules absorb on the chains, which acts in the role of surface modifier in forming Cu_3SnS_4 nanorods. Thus, the high concentration of CH_3CSNH_2 was helpful to the formation of Cu_3SnS_4 nanorods.

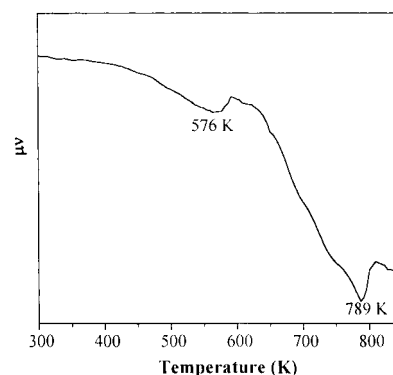


Figure 8. DTA curve of sample E during thermal analysis.

Low warming speed also plays an important role in the formation of Cu_3SnS_4 nanorods. The experiment was carried out via the same route at 190 °C for 24 h without warming process. The as-prepared product was some nanoparticles of the mixture of Cu_3SnS_4 , CuS, and SnS_2 . This is probably due to the fact that hydrogen bonds cannot form stably at high temperature. It indicated the effect of chains of hydrogen bonds on the formation of Cu_3SnS_4 nanorods to some extent.

Taking one with another, the medium reaction constant temperatures (T_{rc} : 190 °C), long reaction time (for example, 24 h), high concentration of CH_3CSNH_2 (for example, 0.985 g), and low warming speed (for example, 1 °C/min) were advantageous for the formation of Cu_3SnS_4 nanorods. It also identified the mechanism that the 2D network $[\text{Cu}_2\text{SnS}_4]^{2-}$ arrangement of ethanol and trace water provided orientation to form 2D framework of anionic layers and led to quasi-1D Cu_3SnS_4 nanomaterial.

Thermal Stability of Cu_3SnS_4 Nanorods. The solid sample E is studied by thermal analysis. No weight loss is found in the TGA curve, and there are two endothermic peaks at 303 and 516 °C in the DTA curve (Figure 8). The products after thermal analysis from room temperature to 303 and 516 °C are studied by XRD and TEM, respectively. It is found that the Cu_3SnS_4 nanorods can be transformed into Cu_3SnS_4 nanoparticles at 303 °C and the as-prepared Cu_3SnS_4 decomposes to CuS and SnS at 516 °C, which agrees with the reported results in references.⁴⁰ It identifies that the described results of experiments at ~ 280 – 500 °C are reasonable. Certainly, because of the influence of solvent pressure at high temperatures, the conversion temperature in our experimental solution is a little lower than that in thermal analysis of solid samples.

The endothermic peak at 303 °C indicates that the transformation from nanorods to nanoparticles needs energy and the nanorods is more stable than the nanoparticles. It is found that the peak area increases with the increase of nanorod size. This is due to the higher surface energy of small-size nanorods, which makes them more unstable and easier to transform into nanoparticles.

Optical Properties. The optical absorption property of Cu_3SnS_4 nanorods in sample E is investigated with room temperature UV–vis spectroscopy (Figure 9). The Cu_3SnS_4 nanorods possess well defined, sharp optical absorption associated with the band gap transition at 3.84 eV. The very

(38) Gilman, J. J. *The Art and Science of Growing Crystals*; John Wiley and Sons Inc.: New York, 1963.

(39) Hartman, P. *Crystal Growth: An introduction*; North-Holland Publishing Company: Amsterdam, 1973.

(40) Gunter, H. M. *Neues Jahrb. Mineral., Abh.* **1982**, *144*, 291.

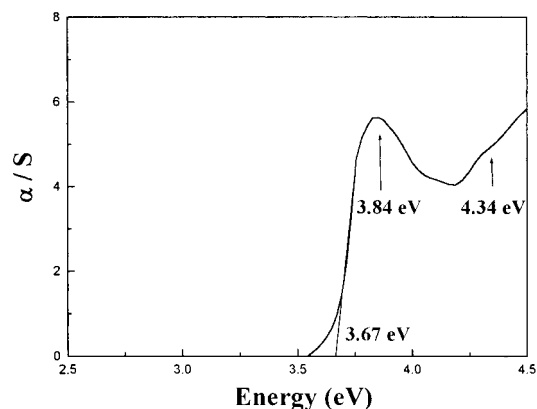


Figure 9. UV-vis spectrum of sample E.

sharp electronic transition suggests that its band gap may possibly be direct. In addition, the band gap at 3.84 eV is similar to that of ZnS semiconductors.⁴¹

Figure 10 is the PL excitation spectrum of the Cu_3SnS_4 nanorods in sample E. Under PL excitation at 264 nm, the Cu_3SnS_4 nanorods emit blue light as 319 nm (corresponding to 3.89 eV). The closeness of the emission peaks to the absorption onset of the semiconductor indicates that this emission comes from the interband electron-hole recombination. To be corrected with notations, it is necessary to note that the interband transition may actually involve electronic levels in close vicinity to the bottom of the lowest empty band and the top of the highest occupied band, as is the case for CdSe.^{42–44}

Conclusion

In summary, an ion-ion reaction route through an ethanol thermal process at $\sim 80\text{--}190\text{ }^\circ\text{C}$ for $\sim 12\text{--}24\text{ h}$ was first

(41) *Introduction to Solid State Physics*; Kittel, C., Ed.; Wiley: New York, 1986.

(42) Efros, A. L.; Rosen, M.; Kuno, M.; Nirmal, M.; Norris, D. J.; Bawendi, M. *Phys. Rev. B* **1996**, *54*, 4843.

(43) Nirmal, M.; Norris, D. J.; Huro, M.; Bawendi, M. G.; Efros, A.; Rosen, M. *Phys. Rev. Lett.* **1995**, *75*, 3728.

(44) Norris, D. J.; Bawendi, M. G. *J. Chem. Phys.* **1995**, *103*, 5260.

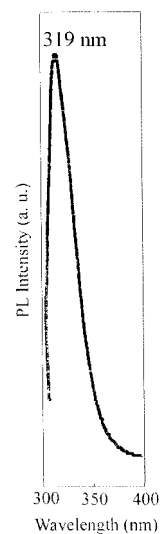


Figure 10. Photoluminescence spectrum of sample E.

put forward to the preparation of tetragonal Cu_3SnS_4 nanorods, on the basis of the strategy that a 2D framework structure of Cu_3SnS_4 containing $[\infty^2\text{Cu}_2\text{SnS}_4]^{2-}$ layers could provide orientation for the growth of quasi-1D nanomaterials. It was found that ethanol as solvent and reductant and trace water/ CH_3CSNH_2 as sulfur source and acid-making components could form 2D network through hydrogen bonds, which provided orientation for the formation of 2D framework structure; appropriate concentration of CH_3CSNH_2 , warming speed, reaction constant temperatures (T_{rc}), and reaction time also played important roles. With extensive studies, this solvothermal technique was expected to be useful for synthesis of quasi-1D nanomaterials of other multinary metal chalcogenides with 2D framework structure.

Acknowledgment. Financial support from the National Natural Science Foundation of China and Chinese Ministry of Education is gratefully acknowledged.

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