JOURNAL OF
Materials
CHEMISTRY

Preparation and phase transformation of nanocrystalline copper sulfides (Cu_9S_8, Cu_7S_4 and CuS) at low temperature

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Received 29th March 2000, Accepted 8th June 2000
Published on the Web 26th July 2000

Nanocrystallites of non-stoichiometric copper sulfides were synthesized *via* the reaction between $[Cu(NH_3)_4]^{2+}$ and thiourea in sealed autoclaves at the low temperature of 60 °C for 3 h. Thiourea played a key role in the process of Cu_9S_8 nanocrystal formation. Through adjusting the redox atmosphere, Cu_7S_4 and CuS were obtained from the freshly formed Cu_9S_8 nanocrystals. The products were characterized by means of X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS), FT-IR spectroscopy and transmission electron microscopy (TEM) techniques. The Cu : S atomic ratios for Cu_9S_8 and Cu_7S_4 were 9 : 8.08 and 7 : 4.05, respectively, analyzed by inductively coupled plasma (ICP) spectroscopy. The possible mechanism of phase transformation among copper sulfides (Cu_9S_8, CuS, and Cu_7S_4) was discussed. The optical properties of the products were also recorded by means of UV–vis absorption, and photoluminescence spectroscopy.

Introduction

Transition metal chalcogenides including sulfides, selenides and tellurides are often found in minerals and have attracted considerable attention in recent decades due to the interesting properties they possess.[1] They have a number of commercial applications in pigments, semiconductors, fluorescence devices and even superconductors.[2] Because of the effect of the 3d electrons, transition metal compounds, such as cobalt sulfides, copper sulfides, *etc.*, have many different phase compositions. It is known that copper sulfides are useful minerals, and their mineralogical and technological properties have been studied extensively.[3] The compounds exhibit fast-ion conduction at high temperature, and exist in a wide variety of compositions ranging from Cu_2S at the ‘copper rich’ side to CuS_2 at the ‘copper deficient’ side, such as CuS,[4] $Cu_{1.96}S$,[5–8] $Cu_{1.94}S$,[9] $Cu_{1.8}S$,[10,11] Cu_7S_4,[12] and Cu_2S.[13,14]

Traditionally, copper sulfides have been synthesized by solid-state reactions[15,16] and self-propagating high temperature synthesis.[17] Although CuS and $Cu_{2-x}S$ $(0.25 \geqslant x \geqslant 0.18)$ were produced *via* the above methods, high temperatures (> 500 °C) are required to initiate the reaction. If gaseous H_2S is used to prepare copper sulfides, the total process is dangerous and highly toxic.[18] Molecular precursors have also been used to obtain copper sulfides. Paul *et al.* prepared CuS by decomposing the complex $Cu(S_6)(solv)_2$ at 500 °C.[4a] Grijavala *et al.* used $[Cu(en)_2]^{2+}$ and thiourea to synthesise CuS;[4b] however, the products were amorphous. In order to obtain crystalline products, a post-treatment at relatively high temperature (250–500 °C) was necessary. Recently, Parkin and coworkers reported a low-temperature synthesis route to copper sulfides *via* Cu(s) and S(s) in liquid ammonia;[5] however, only a mixture of $Cu_{1.8}S$, $Cu_{7.2}S_4$ and $Cu_{1.96}S$ was obtained. During their experiments, several manipulations had to be carefully carried out at −77 °C in thick-walled glass vessels, and all operations had to be conducted with care and behind a safety screen.

In this paper, we report a novel solvothermal reaction for the fabrication of phase-pure Cu_9S_8, Cu_7S_4 and CuS nanocrystallites in aqueous ammonia at 60 °C. In our experiments, thiourea was used as the sulfur source, because the release of S^{2-} from thiourea in aqueous ammonia can be controlled by adjusting the pH value of the reaction system. It is concluded that this process favors the synthesis of phase-pure Cu_9S_8. Through adjusting the redox atmosphere, Cu_7S_4 and CuS were obtained from the freshly formed Cu_9S_8. In comparison with the other methods mentioned above, this route is relatively mild and non-toxic. In order to fully characterize the materials, optical absorption and photoluminescence spectra were recorded, as well as X-ray diffraction patterns and transmission electron micrographs to confirm the morphology of the Cu_9S_8, Cu_7S_4 and CuS nanocrystallites. The compositions of products were accurately analyzed using inductively coupled plasma (ICP) spectroscopy. A possible mechanism of formation for the copper sulfides is discussed.

Experimental

Thiourea (NH_2CSNH_2, Tu) (A.R) was selected as the sulfur source to control the slow release of S^{2-} ions, and aqueous ammonia ($NH_3 \cdot H_2O$, the concentration of NH_3 is *ca.* 28%) as the solvent and the Cu^{2+} complexing agent; all of these were purchased from Shanghai Chemistry Co. Ltd. Other chemicals were all analytical grade and pretreated before use.

Preparation of nanocrystalline copper sulfides

The procedure included three steps. First, 10 ml 0.4 mol dm^{-3} $CuCl_2$ was mixed with 20 ml aqueous ammonia solution, resulting in the formation of a blue solution of copper ammonia complex. Second, 10 ml 1.0 mol dm^{-3} thiourea solution was titrated into the mixture at 0.5 ml min^{-1} with continuous stirring, whereupon the solution turned grayish and a precipitate was formed. Third, the mixed solution was sealed in an autoclave to heat at 60 °C for 3 h in order to crystallize the product. After being left to cool to room temperature, the precipitate was filtered off, and then washed several times with dilute HCl solution and distilled water. The final products were dried *in vacuo* at 25 °C for 2 h. Phase transformation took place *via* the addition of oxidant or reducing agent to the Cu_9S_8 systems.

Appropriate amounts of the freshly produced Cu_9S_8 and KBH_4 were introduced into a Teflon-lined autoclave. The autoclave was filled with aqueous ammonia up to 75% of the total volume, maintained at 60 °C for 3 h, and then allowed to

DOI: 10.1039/b002486o

cool to room temperature. The post-treatment of the precipitate was the same as for Cu_9S_8. The preparation of CuS was analogous to that for Cu_7S_4, except that $SnCl_4$ was used to substitute for KBH_4.

Characterization

The three samples were characterized as follows. The XRD analysis was carried out with a Japan Rigaku D/max-γ rotation anode X-ray diffractometer, using Ni-filtered Cu-Kα radiation at 25 °C. A scanning rate of 0.05° s^{-1} was applied to record the patterns in the 2θ range 10–70°. The reflection data were collected at 25 °C. The TEM images were taken with a Hitachi H-800 transmission electron microscope at an acceleration voltage of 200 kV. Powdered Cu_9S_8, or Cu_7S_4, or CuS was ultrasonically dispersed in absolute ethanol, then one droplet of solution was absorbed on a copper grid for measurement. Infrared analyses of these samples were conducted on a Magna IR-750FT spectrometer in the range 400 to 4000 cm^{-1} at 25 °C using the KBr wafer technique. The electronic binding energy of the copper sulfides was examined by X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII instrument with Mg-Kα ($h\nu = 1253.6$ eV) radiation as the exciting source with an energy resolution of 1.0 eV. The compositions of copper sulfides were measured *via* measuring the concentrations of copper ions remaining in supernatant solutions using inductively coupled plasma (ICP) spectroscopy with a Seiko Electronics SPD 1200A ICP emission analyzer with a pump flow of 1.85 ml min^{-1} and a flow rate of the auxiliary gas (Ar 99.99%) of 0.5 l min^{-1}. The UV–vis absorption spectra were recorded using a Schimadzu UV-240 spectrophotometer, and the photoluminescence (PL) spectra were recorded using a Hitachi 850-fluorescence spectrophotometer.

Results and discussion

The phase-transformation reactions of different copper sulfides are listed in Table 1. Here, the phase-pure copper sulfides were obtained under different conditions. CuS was obtained after adding $SnCl_4$ oxidant into the Cu_9S_8 aqueous ammonia system, while the addition of a reducing reagent (KBH_4) led to the production of Cu_7S_4. The anionic effects of SO_4^{2-}, ClO_4^-, Cl^- and NO_3^- on the products in reaction A (Table 1) were investigated, and it was found that they had no influence on the composition and purity of Cu_9S_8.

The XRD patterns for Cu_7S_4 (a), Cu_9S_8 (b), and CuS (c) are shown in Fig. 1; all their reflection peaks were indexed. The cell parameters and particle sizes of products after refinement are listed in Table 2. The cell parameters calculated were close to those in the JCPDS files. The average sizes of particles for CuS, Cu_9S_8, and Cu_7S_4 were calculated by using the Scherrer formula.[19] The results are in good agreement with the observations from TEM images (Fig. 2). All the reflection peaks were used to calculate the cell parameters in each XRD pattern. Note that the pattern of Cu_9S_8 nanocrystals is very similar to that of CuS, but the cell parameters and reflection indices are different. The reflection intensities of Cu_9S_8 and Cu_7S_4 are in agreement with their powder patterns, whilst for CuS, the (103) reflection peak weakens and the (110) peak strengthens, which corresponds to the (111) reflection peak of Cu_9S_8. This change probably results from the structure of Cu_9S_8, since CuS is obtained from hexagonal Cu_9S_8. The Cu_7S_4 obtained in our work is hexagonal, rather than orthorhombic as reported by Koto and Morimoto.[12] According to the literature,[20] hexagonal Cu_7S_4 is the metastable form of digenite. The structure Cu_xS ($1.96 \geqslant x \geqslant 1.86$) transforms to digenite between 50 and 70 °C. In our experiments, the temperature of the reaction systems is 60 °C, which is favorable for the formation of the metastable hexagonal structure of Cu_7S_4.

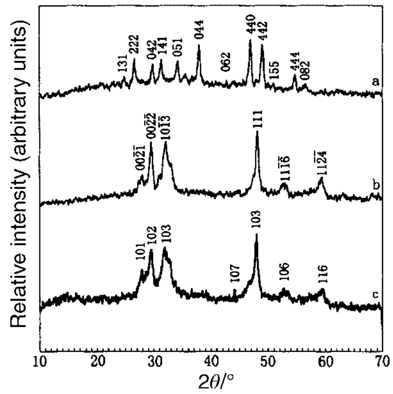

Fig. 1 XRD patterns of nanocrystalline copper sulfides: (a) Cu_7S_4, (b) Cu_9S_8, (c) CuS.

TEM images for the products are shown in Fig. 2. The morphologies of as-prepared products were different. The spherical Cu_7S_4 nanocrystallites (a) and sheet-like Cu_9S_8 nanocrystallites (b) are shown, with diameters of *ca.* 24 and 27 nm, respectively, while CuS crystals are needle-like fibers of size 26 nm × 110 nm, as shown in (c).

The IR spectra of the samples do not show any characteristic thiourea N–H peaks, indicating that thiourea is at most weakly bonded to the surface of copper sulfides and can readily be removed by washing with distilled water.

From X-ray photoelectron spectra (XPS), the binding energy values are 931.9 eV for Cu2p in Cu_9S_8 and 932.1 eV for Cu2p in Cu_7S_4, and are 933.5 eV for Cu(II)2p in CuS and 932.5 eV for Cu(I)2p in Cu_2S.[21] From the relationship between the Cu2p and S2p peak areas of phase-pure Cu_9S_8, and Cu_7S_4, the quantification of peaks gives the atomic ratios of Cu to S as 9 : 8.40, and 7 : 4.48, respectively. The Cu : S atomic ratio was also examined by a chemical analysis method.[22] The samples were dissolved in 3.0 mol dm^{-3} HNO_3 aqueous solution and the post-treated solution was subjected to ICP measurement. The Cu : S atomic ratios for Cu_9S_8, Cu_7S_4, and CuS are 9 : 8.08, 7 : 4.05, and 1 : 1.03, respectively.

In the case of the formation of Cu_9S_8, the reaction and its possible reaction mechanism may be described as follows:

$$SC(NH_2)_2 + OH^- \rightarrow OC(NH_2)_2 + SH^- \qquad (1)$$

$$SH^- + OH^- \rightarrow S^{2-} + H_2O \qquad (2)$$

$$9[Cu(NH_3)_4]^{2+} + 8SC(NH_2)_2 + 8OH^- + 10e^- \rightarrow$$
$$Cu_9S_8 + 36NH_3 + 8OC(NH_2)_2 + 4H_2 \qquad (3)$$

In the process of forming Cu_9S_8, S^{2-} ions are released from thiourea through hydrolysis in aqueous ammonia [eqn. (1), (2)]. The concentration of S^{2-} ions is a crucial factor for

Table 1 The reaction parameters of phase transformation for the synthesis of copper sulfides[a]

Reaction	Precursors	Solvent	Molar ratio Cu : S : NH_3	Product
A	Cu^{2+} + Tu	Aqueous ammonia	1 : 2.5 : 36	Cu_9S_8
B	$Cu_9S_8 + SnCl_4$	Aqueous ammonia	1 : 2.5 : 36	CuS
C	$Cu_9S_8 + KBH_4$	Aqueous ammonia	1 : 2.5 : 36	Cu_7S_4

[a] All the reactions were performed at 60 °C for 3 h.

Table 2 The cell parameters and particle size of copper sulfides

Product	Cell parameters/Å Calculated	Cell parameters/Å Theoretical	Crystal system	JCPDS	Size/nm
CuS	$a = 3.643 \pm 0.034$ $c = 16.128 \pm 0.083$	$a = 3.792$ $c = 16.344$	Hexagonal	No. 6-464	26.8
Cu_9S_8	$a = 3.781 \pm 0.048$ $c = 67.11 \pm 0.095$	$a = 3.800$ $c = 67.269$	Hexagonal	No. 36-379	27.4
Cu_7S_4	$a = 15.423 \pm 0.056$ $c = 13.272 \pm 0.045$	$a = 15.475$ $c = 13.356$	Hexagonal	No. 23-958	25.3

forming non-stoichiometric copper sulfides, which is similar to the reaction mechanism for Co_3S_4.[23] We also used other sulfur sources, such as CS_2, Na_2S, $Na_2S_2O_3$ and $Et_2NCSSNa$, to substitute for thiourea, but no Cu_9S_8 was obtained. This fact shows that thiourea is a good sulfur source for the synthesis of Cu_9S_8. This process can be controlled *via* adjustment of the concentration of OH^- ions with 4.0 mol dm^{-3} NaOH solution, thus affecting the concentration of S^{2-} in the reaction system and the nucleation of copper sulfide crystallites. Perea[24] also reported that the formation of copper sulfide (djurleite) $Cu_{1.934}S$ from native copper (Cu^0) under anoxic (reducing) conditions was enhanced by the availability of dissolved H_2S in the groundwater (pH > 7.8), showing that the concentration of S^{2-} does affect the composition of copper sulfides.

Through adjustment of the redox atmosphere, phase transformations between the different forms of copper sulfide took place. In reaction B (Table 1), CuS was obtained by adding $SnCl_4$ oxidant to the Cu_9S_8 + aqueous ammonia system, corresponding to eqn. (4). The SnS by-product was removed by dissolution in dilute HCl.

$$Cu_9S_8 + SnCl_4 + 2S^{2-} \rightarrow 9CuS + SnS + 4Cl^- \qquad (4)$$

When the reducing reagent KBH_4 was added to the Cu_9S_8 + aqueous ammonia system, Cu_7S_4 was precipitated. Here, KBH_4 was selected to reduce Cu_9S_8 to Cu_7S_4, since the pH value and temperature of the reaction system determines its hydrolysis rate. In the reducing process, the solution (pH 10) delayed the hydrolysis of KBH_4 and its reducing ability decreased so that no Cu_2S was obtained in the end. The reaction took place as shown in eqn. (5).

$$\begin{aligned} &7Cu_9S_8 + 40KBH_4 + 120H_2O \rightarrow 9Cu_7S_4 + 20K_2S \\ &+ 40B(OH)_3 + 140H_2 \qquad (5) \end{aligned}$$

From eqn. (4) and (5), phase-pure copper sulfides can be obtained from Cu_9S_8 *via* adjustment of the redox atmosphere.

The optical properties of the products can be described as follows. Fig. 3a shows the absorption spectra of the samples. The samples of Cu_9S_8 (curve 1) and Cu_7S_4 (curve 2) have absorption peaks in the range 400–700 nm, which are assigned to the optical transition of the first excitonic state,[25] whilst CuS has no absorption in the wavelength range studied (curve 3). In contrast to the absorption spectra, the photoluminescence spectra (Fig. 3b) of the copper sulfides show emissions at 440 nm for Cu_7S_4 and 443 nm for Cu_9S_8, suggesting a near band-edge emission. CuS has no emission in the range 400–800 nm, consistent with literature reports.[26] The fluorescence bands of Cu_7S_4 and Cu_9S_8 are indicative of typical inhomogeneous broadening.[27] In this case, the structures of Cu_9S_8 and Cu_7S_4 can be considered as containing domain-like structures, with both copper-rich and copper-poor regions,[11] which may result in the hetero-structure and new photochemical properties emerging.

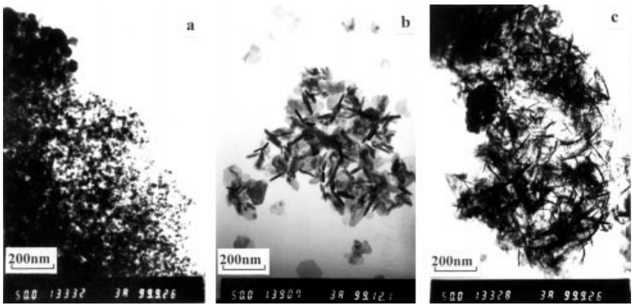

Fig. 2 TEM images of the nanoparticles of (a) Cu_7S_4 and (b) Cu_9S_8, and (c) CuS nanofibres.

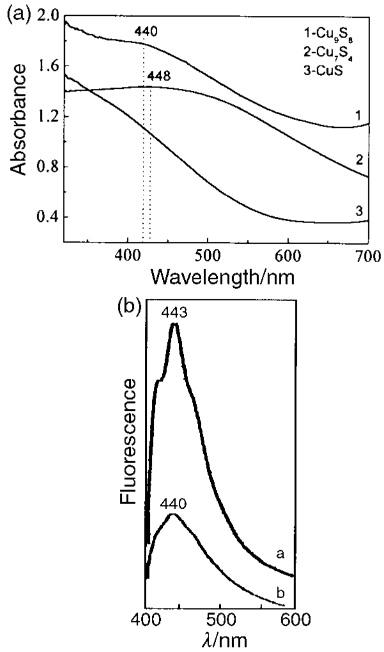

Fig. 3 (a) The UV absorption spectra for (1) Cu_9S_8, (2) Cu_7S_4, and (3) CuS. (b) The PL spectra for Cu_7S_4 (curve a) and Cu_9S_8 (curve b).

Summary

The phase-pure copper sulfides Cu_9S_8 and Cu_7S_4 were synthesized *via* the controlled release of S^{2-} ions from thiourea at the low temperature of 60 °C. TEM images confirmed the morphologies of the resulting copper sulfides. The Cu : S atomic ratios for Cu_9S_8 and Cu_7S_4 were 9 : 8.08 and 7 : 4.05, respectively, as determined by ICP spectroscopy. A possible phase-transformation mechanism between the copper sulfides has been proposed. This is significant for the synthesis of phase-pure nonstoichiometric copper sulfides.

Acknowledgements

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

References

1 S. M. Stuczynski, Y. U. Know and M. L. Steigerwald, *J. Organomet. Chem.*, 1993, **449**, 167.

2 N. N. Greenwood and E. A. Earnshaw, *Chemistry of the Elements*, Pergamon, Oxford, 1990, p. 1403; M. Farnsworth and C. Kline, *Zinc Chemicals, Their Properties and Applications*, International Lead and Zinc Research Organisation, New York, 1968; G. Nickless, *Inorganic Chemistry of Sulfur*, Elsevier, London, 1968, p. 670.

3 M. T. S. Nair and P. K. Nair, *Semicond. Sci. Technol.*, 1989, **4**, 191; J. C. W. Folmer and F. Jellinek, *J. Less-Common Met.*, 1980, **76**, 153; J. C. W. Folmer, Thesis, University of Groningen, The Netherlands, 1981.

4 (*a*) P. P. Paul, T. B. Rauchfuss and S. R. Wilson, *J. Am. Chem. Soc.*, 1993, **115**, 3316; (*b*) H. Grijavala, M. Inoue, S. Buggavarapu and P. Calvert, *J. Mater. Chem.*, 1996, **6**, 1157.

5 G. Henshaw, I. P. Parkin and G. A. Shaw, *J. Chem. Soc., Dalton Trans.*, 1997, 231.

6 S. Djurle, *Acta. Chem. Scand.*, 1958, **12**, 1415.

7 E. H. Roseboom, *Am. Mineral.*, 1962, **47**, 1181.

8 N. Morimoto, *Mineral. J.*, 1962, **3**, 338.

9 T. Evans, *Science*, 1979, **203**, 356.

10 Y. Xie, P. Yan and Y. T Qian, *Chem. Lett.*, 1999, **7**, 655.

11 S. Kashida and K. Yamamoto, *J. Phys. Condens. Matter*, 1991, **3**, 6559.

12 K. Koto and N. Morimoto, *Acta Crystallogr., Sect. B*, 1972, **26**, 915.

13 R. A. Scott, *Structure (London)*, 1995, **3**, 981; C. R. Andrew and J. Sanders-Loehr, *Acc. Chem. Res.*, 1996, **29**, 365; M. Dachraoui and J. Vedel, *Sol. Cells*, 1985, **15**, 319; M. Dachraoui and J. Vedel, *Sol. Cells*, 1987, **22**, 187.

14 H. T. Evans, Jr., *Nature (London) Phys. Sci.*, 1971, **232**, 69.

15 R. J. Coustal, *Chim. Phys.*, 1958, **238**, 277.

16 I. P. Parkin, *Chem. Soc. Rev.*, 1996, **25**, 199.

17 H. C. Yi and J. J. Moore, *J. Mater. Sci.*, 1990, **25**, 1159; D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1; T. Ohtani, M. Motoki, K. Koh and K. Ohshima, *Mater. Res. Bull.*, 1995, **30**, 1495.

18 H. C. Metcalf, J. E. Williams and J. F. Caskta, *Modern Chemistry*, Holt Rinehart and Winston, New York, 1982, p. 54.

19 C. N. J. Wagner and E. N. Aqua, *Adv. X-Ray Anal.*, 1964, **7**, 46.

20 P. Cavallotti and G. Salvago, *Electrochim. Met.*, 1969, **4**, 181.

21 C. D. Wagner, W. W. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, USA, 1979.

22 *Handbook of Analytical Chemistry (in Japanese)*, Maruzen, Tokyo, 1991, p. 280; *The Analytical Chemistry of Sulfur and Its Compounds, Part 1*, ed. J. H. Karchmer, Wiley, New York, 1970.

23 F. C. Eze and C. E. Okeke, *Mater. Chem. Phys.*, 1997, **47**, 31.

24 N. M. Perea, *Mater. Res. Soc. Symp. Proc.*, 1997, **465**, 1153.

25 H. Weller, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 41.

26 A. V. Isarov and J. Chrysochoos, *Langmuir*, 1997, **13**, 3142.

27 A. Eychmüller, A. Hässelbarth, L. Katsikas and H. Weller, *Ber. Bunsen-Ges. Phys. Chem.*, 1991, **95**, 79.