

Microwave-Assisted Elemental-Direct-Reaction Route to Nanocrystalline Copper Sulfides Cu_9S_8 and Cu_7S_4

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Non-stoichiometric copper sulfides Cu_9S_8 and Cu_7S_4 nanocrystallites were synthesized by the reaction between elements S and Cu under microwave radiation for several minutes. The products were analyzed by using XRD, TEM, XPS, ICP and PL. © 2002 Elsevier Science (USA)

Key Words: non-stoichiometry; copper sulfide; microwave; elemental-direct reaction.

1. INTRODUCTION

Transition metal chalcogenides have attracted considerable attention in recent decades due to their interesting properties (1). Among these compounds, copper sulfides are useful minerals, exhibit fast-ion conduction at high temperature. There are lots of literature which have focused on their mineralogical and technological properties (2). In addition, because of the effect of $3d$ electrons, copper–sulfur system, which has numerous stable and metastable species, is very complex. It is interesting to synthesize different species by changing the experimental conditions and most recently it is becoming a subject interest for some chemists (3).

Traditionally, copper sulfides have been synthesized by solid-state metathesis reaction (4, 5), self-propagating synthesis (6–8), the precipitation methods using sulfides (9, 10), and solvothermal reaction (3, 11). Some methods require high temperatures and long time for initiating the reaction. If gaseous H_2S is used to prepare copper sulfides, the total process is dangerous and highly toxic (12). Parkin reported a low-temperature synthesis route to copper sulfides in liquid ammonia (13). During their experiments,

several manipulations had to be carefully carried out at -77°C in thick-walled glass vessels, and all manipulations had to be conducted with care and behind a safety screen. The most straightforward way to synthesize copper sulfides is the direct combination of elements Cu and S. Unfortunately, traditional element-direct-reaction route needs high temperature and leads to powders of relatively large grain size.

Recently, microwave (MW) irradiation method which is faster, simpler and highly energy efficient has been used for the acceleration of organic chemical reactions and synthesis of inorganic materials (14–17). More importantly, the method can cause molecular-level heating, which leads to homogeneous and quick thermal reactions. Thus, MW heating has recently begun to attract the attention of chemists as a new method for preparing nanosized inorganic particles and is a very rapidly developing area of research (18, 19). Furthermore, it is easy for using MW equipment to continuously synthesize large quantities of products. This is significant for obtaining products in bulk amounts in industry (20). However, to the best of our knowledge, there is no report on the preparation of non-stoichiometric copper sulfides by using MW method.

In this paper, we report a MW assisted synthesis method for the rapid preparation of phase-pure Cu_9S_8 in ethylenediamine (en), N,N -dimethylformamide (DMF) or aqueous ammonia and Cu_7S_4 in aqueous hydrazine. Elements S and Cu were used to react under the radiation of MW for several minutes. We selected amine as the medium for two reasons. On the one hand, they act as alleviant to prevent burning of powder Cu and S under MW. On the other hand, the existence of the solvent can prevent the oxidization of copper sulfide to warrant the purity of the products. In our experiment, the property of solvents plays a key role in the synthesis of non-stoichiometric copper sulfides, whereas the power of MW and reaction time had a minor effect on the products. Photoluminescence spectra show obvious blue-shift of emission peak from their smaller size.

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2. EXPERIMENTAL SECTION

All reagents were of analytic purity and used without further purification. X-ray powder diffraction patterns were determined on a D/max-III A X-ray diffractometer equipped with a graphite mono-chromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). A scanning rate of $0.05^\circ \text{ s}^{-1}$ was applied to record the patterns in 2θ range from 25° to 65° . The TEM images were taken with a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. Powdered Cu_9S_8 and Cu_7S_4 were ultrasonically dispersed in water-ethanol mixed solvent, then a drop of the suspension was placed on a copper grid and dried in air before observation. The electronic binding energy of copper sulfides was examined by X-ray photoelectron spectroscopy (XPS) on an ESCALab MKII instrument with $\text{AlK}\alpha$ X-ray as the excitation source. 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 0.51 min^{-1} . Photoluminescence spectra were recorded using an Aminco Bowman series-2 fluorescence spectrophotometer.

2.1. Preparation of Cu_9S_8

Powder Cu (5 mmol) and S (5 mmol) were mixed with en (5 mL), DMF (5 mL) or aqueous ammonia solution (25%, 5 mL). Then the mixture was put into a MW oven (Spectra 900 W), one-third output power of the MW was used to irradiate the mixture for 2 min. At room temperature, the precipitate was filtered off, and washed three times with distilled water, ethyl alcohol and CS_2 , then dried with

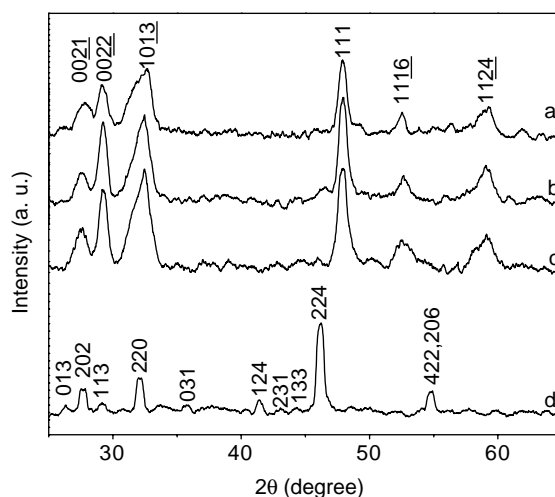


FIG. 1. XRD patterns of the products: (a) Cu_9S_8 obtained in en; (b) Cu_9S_8 obtained in DMF; (c) Cu_9S_8 obtained in aqueous ammonia and (d) Cu_7S_4 obtained in aqueous hydrazine.

anhydrous diethyl ether. The products produced from en, DMF and aqueous ammonia solution were labeled as Sample 1, 2 and 3, respectively.

2.2. Preparation of Cu_7S_4

The procedure is the same as that in the preparation of Cu_9S_8 , the only difference being that the solvent was changed into aqueous hydrazine. The product was labeled as Sample 4.

3. RESULTS AND DISCUSSION

3.1. XRD Study of the Products

The results of the powder XRD patterns of Samples 1–4 are shown in Figs. 1a–d, respectively. They perfectly match

TABLE 1
Diffraction Peaks Index in PDF of Different Phase Cu_7S_4 and in XRD Pattern of the As-Prepared Cu_7S_4

References (PDF Number)									
23-958 (Roxbyite)		22-250 (Anilite)		24-61 (Digenite)		33-489 (Anilite)		Experiment	
d (Å)	Int	d (Å)	Int	d (Å)	Int	d (Å)	Int	d (Å)	Int
3.35	55	3.32	18			3.34	10	3.34	14
		3.20	55	3.22	40	3.22	40	3.22	38
3.00	45					3.08	3	3.06	20
		2.77	65	2.79	68	2.78	55	2.79	41
2.54	35	2.54	30			2.54	25	2.55	17
2.18	10	2.16	40			2.17	35	2.17	23
2.12	10	2.13	15			2.14	6	2.14	10
2.02	10	2.05	5			2.06	20	2.06	18
1.94	100	1.96	100	1.97	100	1.96	100	1.97	100
1.68	40	1.68	35	1.68	14	1.68	15	1.68	26

TABLE 2
Diffraction Peaks Index in PDF Number 36-379 and in XRD Patterns of As-Prepared Cu₉S₈

PDF Number 36-379		Sample 1		Sample 2		Sample 3	
<i>d</i> (Å)	Int	<i>d</i> (Å)	Int	<i>d</i> (Å)	Int	<i>d</i> (Å)	Int
3.22	8	3.21	35	3.23	20	3.21	28
3.06	55	3.07	49	3.06	52	3.05	71
2.77	35	2.77	60	2.80	53	2.79	41
1.90	100	1.90	100	1.90	100	1.90	100
1.73	15	1.74	33	1.73	20	1.74	23
1.57	15	1.57	39	1.57	21	1.56	21

with the diffraction patterns of Cu₉S₈ with cell constant $a = 3.800 \text{ \AA}$, $c = 67.269 \text{ \AA}$ (JCPDS files No. 36-379, Table 2, Samples 1–3) and Cu₇S₄ with cell constant $a = 7.9065 \text{ \AA}$, $b = 7.8223 \text{ \AA}$, $c = 11.078 \text{ \AA}$ (JCPDS files No. 33-489, Table 1, Sample 4). The sizes of particles for Samples 1–4 calculated from the half-width of diffraction peaks using the Scherrer formula are 20.6, 27.5, 27.5 and 32.7 nm, respectively. It should be noted that the elemental ratio of the starting materials for the reactions was 1:1. The excess powder S could be easily removed by CS₂. We did not do any post-treatment to remove powder Cu. However, there are not diffraction peaks of powder Cu, which would be intensive even if there were a little Cu due to its high crystallinity, in the PXRD patterns. This indicates that the yield is very high using this method.

3.2. TEM Images for the Products

The morphology of Samples 1–4 are determined by TEM and accordingly shown in Figs. 2a–d. We can see that Sample 1 consists of particles with 20 nm diameter (Fig. 2a). Sample 2 consists of dispersed rectangular particles with an average width of 30 nm (Fig. 2b). Sample 3 consists of sheet-like particles (Fig. 2c). Sample 4 is strongly aggregated due to the higher surface energy.

3.3. ICP of the Products

The ratio of Cu:S of samples was examined by ICP. The samples were dissolved in 3.0 mol dm⁻³ HNO₃ aqueous solution and the post-treated solution was subjected to ICP measurement. The Cu:S atomic ratios are 9:7.97, 9:8.02, 9:7.96 and 7:3.99 for Samples 1–4, respectively.

3.4. XPS of the Products

Figs. 3a–d show the XPS of Samples 1–4, respectively. The binding energy values for Cu_{2p_{3/2}} are 932 eV in Cu₉S₈ and 933 eV in Cu₇S₄. The survey indicated that the product were pretty pure. Quantification of peaks gave a ratio of Cu to S as 9:8.4, 9:8.1, 9:8.3 and 7:4.3 for Samples 1–4, respectively. This ratio is similar to the results of ICP, which conformed that the products are Cu₉S₈ and Cu₇S₄, as indexed by the XRD patterns.

3.5. The PL Spectra of the Products

Fig. 4 shows the luminescence spectra of copper sulfides. From the excitation spectra of Samples 1–4 (shown in Figs. 4a₁–d₁, respectively), we can see that the maximum excitation wavelength of Sample 1–3 is 318, 319 and 320 nm, respectively and that of Sample 4 is 233 nm.

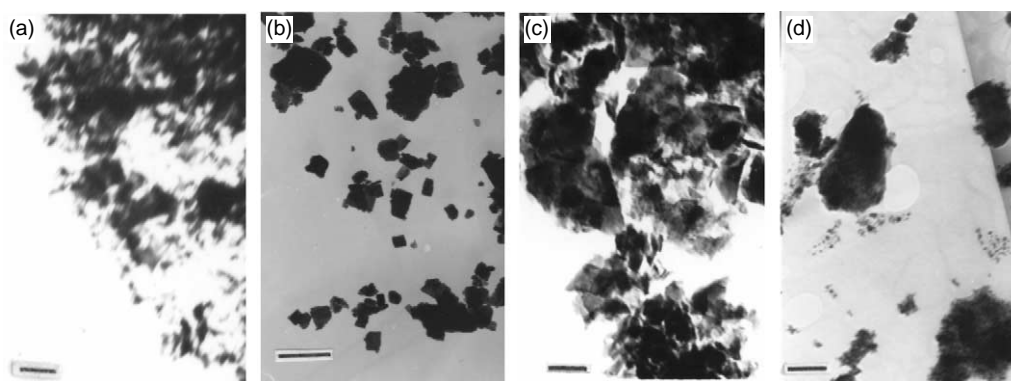


FIG. 2. TEM images of Cu₉S₈ obtained in (a) en; (b) DMF; (c) aqueous ammonia; and TEM micrograph of Cu₇S₄ (d) obtained in aqueous hydrazine (bar equal to 100 nm).

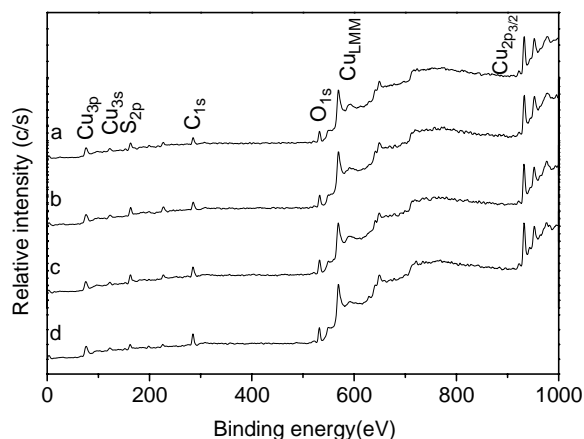


FIG. 3. XPS of the products: (a) Cu₉S₈ obtained in en; (b) Cu₉S₈ obtained in DMF; (c) Cu₉S₈ obtained in aqueous ammonia and (d) Cu₇S₄ obtained in aqueous hydrazine.

Figures 4a₂–d₂ show emissions at 419, 430 and 430 nm for Samples 1–3, respectively ($\lambda_{\text{excitation}} = 320$ nm), and 383 nm for Sample 4 ($\lambda_{\text{excitation}} = 233$ nm). The obvious blue-shift of emission peak for Sample 1 arises from its smaller size, which is in accordance with the calculated result from the XRD.

To study the function of amine, we also used other reagents as medium, such as water, acetone and alcohol, as solvents, but no copper sulfides were found. The copper sulfides powder was only deposited in amine. The formation mechanism of copper sulfides under MW irradiation is not entirely understood, but we can point out that in all

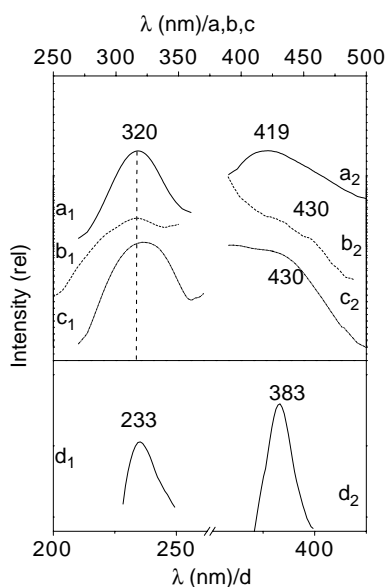


FIG. 4. Excitation (1) and emission (2) spectra of Cu₉S₈ and Cu₇S₄ prepared by MW irradiation. The solvents were: en (a₁, a₂), DMF (b₁, b₂), aqueous ammonia (c₁, c₂), and aqueous hydrazine (d₁, d₂), respectively.

these reactions the character of the solvent is important. As suggested by Parkin (5), sulfur reacts with amine to form unstable sulfur–amine species, which would subsequently undergo homolytic scission to form sulfur-based radicals. These radicals are suggested to be involved in the reaction with the elemental metals. Thus, amine solvent plays a role in activating the metal or S surface, effectively allowing good contact between the elements. In our experiments, both the particle size and phase of product are influenced by the property of the amine. Products obtained in en, DMF or aqueous ammonia is Cu₉S₈, but that obtained in aqueous hydrazine is Cu₇S₄. This is probably due to the strong reductivity of aqueous hydrazine. Moreover, the particle size of Cu₉S₈ obtained in en is the smallest. The reason is not completely clear now, but it is reported that on the solid surface of Cu, Cu loses 2e and becomes Cu²⁺, then complexes with en to form [Cu(en)₂]²⁺ under solvothermal condition (21). In fact, we also observed the formation of a blue solution of [Cu(en)₂]²⁺ when powder Cu reacts with en under MW irradiation. The formation of small particle may be due to the slow release of Cu²⁺ from [Cu(en)₂]²⁺.

4. CONCLUSION

A microwave-assisted synthesis method for the rapid preparation of phase-pure Cu₉S₈ in en, DMF or aqueous ammonia and Cu₇S₄ in aqueous hydrazine by reaction between elements S and Cu has been used. The amine solvents play a key role in the formation of copper sulfides. Aqueous hydrazine with strong reductivity is in favor of forming copper-rich Cu₇S₄. The particle size of Cu₉S₈ obtained in en is the smallest. This method is simple, energy efficient and shortens the reaction time. Furthermore, it is easy for using microwave equipment to continuously synthesize large quantities of products, which is significant for obtaining copper sulfides in bulk amounts in industry.

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