

Simple Synthesis of Copper and Silver Sulfides under Hydrothermal Condition

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Pure copper (II) sulfide, CuS, was successfully prepared by a simple reaction of copper and sulfur powder in water at low temperatures (≥ 60 °C), though the solid state reaction of the elements requires higher temperatures to complete the reaction. Pure Copper (I) sulfide (Cu₂S) and silver (I) sulfide (Ag₂S) were also prepared by similar reactions between the elements above 150 °C and 90 °C, respectively. Two phases (chalcocite-Q and chalcocite-low) were observed in the yielded Cu₂S. Observation with the scanning electron microscope revealed that the CuS was composed of the particles of polyhedral frameworks with dimensions of 2 - 3 μ m. Whereas the particle sizes of the as-prepared Cu₂S were similar to those of CuS, the particles had indefinite frameworks. For Ag₂S, the as-prepared particles at 90 °C were like sharp thin blades and became duller with the increasing reaction temperature.

Key words: hydrothermal condition, copper sulfide, silver sulfide

1. INTRODUCTION

Various metal sulfides can be prepared by thermal reactions of the elements in an evacuated silica tube at high temperatures. The reactions of sulfide ion sources like hydrogen sulfide gas and sodium sulfide with aqueous solutions of metal salts are also well known to give metal sulfides. Recently, some new synthetic methods of metal sulfides at low temperatures such as hydrothermal [1-5], sonochemical [6-8], and mechanochemical [9,10] techniques have been reported. In these methods, hydrothermal syntheses have been pursued especially for the preparation of nano-sized particles.

Leaf-like nanosheets of Ag₂S were synthesized in NH₃-CS₂ system by a hydrothermal route in an alcohol-water medium [1]. Micro-crystalline CuS was synthesized by the reaction between Na₂S₂O₃·5H₂O and various copper sources (CuO, CuSO₄·5H₂O and CuCl₂·2H₂O) under hydrothermal conditions (130 - 170 °C) [2]. Hollow spheres of CuS were prepared hydrothermally from CuSO₄·5H₂O and thiourea at 180 °C [3]. Sea-urchinlike nanocrystallines of NiS and Co₉S₈ were synthesized via a hydrothermal route from the thiourea and hydrated metal chloride in hydrazine hydrate solution [4]. Uniform NiS nanowhiskers were prepared via hydrothermal reaction between NiCl₂·6H₂O and Na₂S₂O₃ in the presence of surfactant C₁₇H₃₃COOK [5].

In these methods under hydrothermal conditions, metal sulfides were synthesized by using complex compounds. One of the simplest methods to form these sulfides is to use the elements as starting materials. If metal sulfides can be prepared from the elements, the formation of complex impurities can be avoided. Two studies have been reported about the syntheses from the elements under hydrothermal conditions. One was concerned with the reaction of copper and sulfur to form CuS [11]. The reaction proceeds well even at 60 °C in water. The other study was about the hydrothermal synthesis of MnS at 260 °C [12]. In this article, we report the products obtained in systems Cu-S and Ag-S.

2. EXPERIMENTAL

The powders of the metal and sulfur were weighed, ground, and introduced along with 20 mL of distilled water into a 50 mL Teflon-lined pressure vessel, which was then heated at 60 - 180 °C (at 30 °C intervals) for 1, 10 or 60 h. After heating, the pressure vessel was allowed to cool to room temperature. The precipitates were filtered and washed with distilled water several times. After drying in a desiccator for 12 h, the powder was collected for characterization.

Powder X-ray diffraction (XRD) patterns were measured with Cu-K α radiation on a RINT2000 diffractometer (Rigaku) equipped with a graphite monochromator. The morphology and particle size of the products were observed by FE-SEM images, taken with S-4500 system (Hitachi). Energy dispersive X-ray fluorescence spectrometer (EDX) was used to evaluate the compositions of the products.

3. RESULTS AND DISCUSSION

3.1 Cu-S system

The XRD patterns of the products obtained by the reactions of copper and sulfur (Cu : S = x : 1, $x = 1 \sim 2$) under a hydrothermal condition (180 °C for 10 h) are shown in Fig. 1. When x was 1, a single phase of CuS was obtained as described below. With the increase of x , the peak intensities of the phase Cu_{7,2}S₄ [13] increased. Almost pure phase of Cu_{7,2}S₄ was obtained at $x = 1.7$. However, the completely pure phase of Cu_{7,2}S₄ was not obtained and unknown peaks were observed at $2\theta = 29.3^\circ$ and 41.5° . Further increase of x induced the formation of Cu₆₂S₃₂. At $x = 2$, pure Cu₂S was obtained as a mixture of two forms (see below). In this system, five phases, CuS, Cu_{7,2}S₄, Cu₆₂S₃₂, Cu₂S (chalcocite-Q), and Cu₂S (chalcocite-low), were observed, CuS and Cu₂S being obtained as pure compounds.

As we reported before [11], pure CuS can be prepared in water by a stoichiometric reaction of sulfur and copper (Cu : S = 0.01 mol : 0.01 mol) for 10 h at the

temperature as low as 60 °C (yield > 95% based on copper). This temperature for a complete reaction is much lower than the solid state reaction without water: Although the reaction of elemental copper and sulfur to form CuS starts at ~ 46 °C, higher temperatures (>165 °C) are required to complete the reaction [14]. Under hydrothermal condition, water provides a medium to continuously transport solid sulfur (m.p. ~120 °C) to the reactant copper surface, thereby avoiding passivation and completing the solid-state reaction at low temperatures. The color of the product of the reaction in water is deep blue, similar to the color of authentic CuS (covellite). The energy dispersive X-ray (EDX) analysis of the sample obtained by the reaction at 180 °C for 10 h gave the result that the sample contained only copper and sulfur at the average Cu/S atomic ratio 1.01(11), confirming the stoichiometry of CuS. Figure 2 shows the XRD profiles of the products. Observed diffraction peaks of all products, except for the sample obtained at 60 °C for 1 h, coincided with those of CuS (JCPDS Card No. 06-0464) with a hexagonal unit cell, and no impurity peaks were observed. The XRD pattern of the sample obtained at 60 °C for 1 h showed the presence of elemental sulfur and Cu₂O. The peaks of these phases disappeared after longer reaction time as shown in Fig. 2 (f) and (g). The diffraction profiles in Fig. 2 clearly indicate that the crystallinity of the products increases with temperature and/or longer reaction time; however, no increase in crystallization was observed between the reaction period of 10 and 60 h at 180 °C.

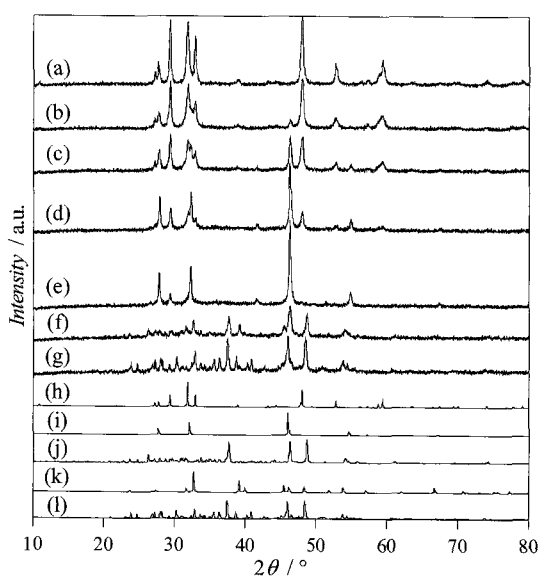


Fig. 1 The XRD patterns of the products of Cu : S = x : 1, obtained at 180 °C for 10 h; x = (a) 1, (b) 1.1, (c) 1.3, (d) 1.5, (e) 1.7, (f) 1.9, and (g) 2. (h) CuS (ICSD No. 67581), (i) Cu_{7.2}S₄ (ICSD No. 20211), (j) Cu₆₂S₃₂ (ICSD No. 100334), (k) chalcocite-Q Cu₂S (ICSD No. 16550), and (l) chalcocite-low Cu₂S (ICSD No. 100333).

Pure Cu₂S was obtained by heating copper and sulfur (Cu : S = 0.01 mol : 0.005 mol) in water at 180 °C for 10 h and 60 h, and at 150 °C for 60 h. The yield of Cu₂S was above 95% based on copper, which confirmed the reaction was essentially stoichiometric. Figure 3 shows the XRD patterns of the product obtained by the reaction

at 180 °C for 10 h. Two phases of Cu₂S, chalcocite-Q and chalcocite-low, are detected in the product. Though pure Cu₂S was obtained, no single phase products were obtained in this study. Milder conditions, for example, even at 60 °C for 1 h, gave Cu₂S as the main product, but Cu_{7.2}S₄, Cu₆₂S₃₂, and Cu₂O were observed as impurities. The complete reaction to yield pure Cu₂S needs higher temperature and/or longer reaction time compared with the synthesis of pure CuS described above. The difference can be explained as follows. In the initial stage of the reaction, inhomogeneity of the distribution of sulfur and copper induces the formation of intermediate sulfides Cu_{7.2}S₄ and Cu₆₂S₃₂ as observed in the XRD pattern. Once the intermediate sulfides are formed, the reaction of copper with them is necessary to form Cu₂S, and it requires longer reaction time or higher temperatures since their reactivity is lower than that of sulfur.

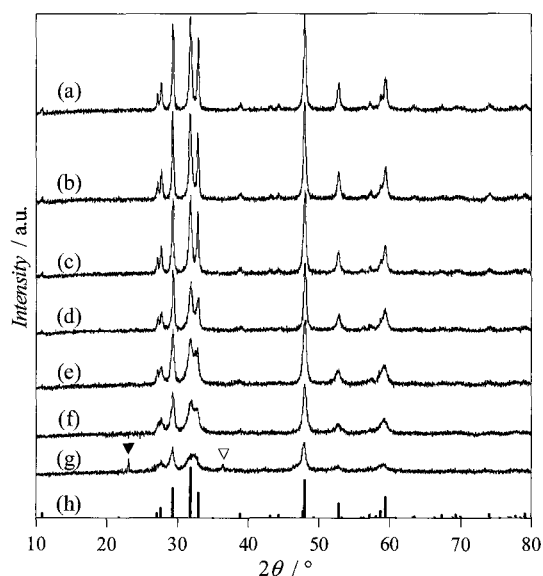


Fig. 2 The XRD patterns of the products obtained at (a) 180 °C for 60 h, (b) 180 °C for 10 h, (c) 150 °C for 10 h, (d) 120 °C for 10 h, (e) 90 °C for 10 h, (f) 60 °C for 10 h, and (g) 60 °C for 1 h. (h) Reported pattern of CuS (JCPDS Card No. 06-0464). Open inverted triangle and filled inverted triangle show the main peaks of Cu₂O (JCPDS Card No. 05-0667) and S (JCPDS Card No. 08-0247), respectively.

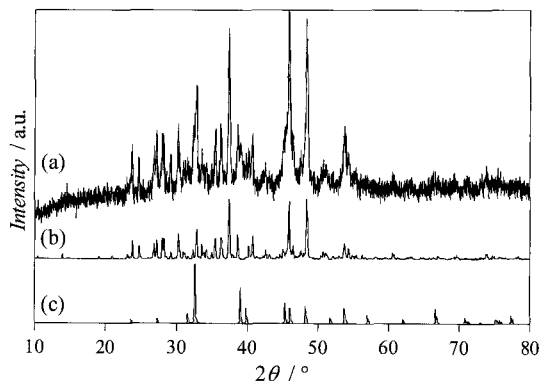


Fig. 3 The XRD patterns of the products obtained at (a) 180 °C for 10 h. (b) chalcocite-low Cu₂S (ICSD No. 100333) and (c) chalcocite-Q Cu₂S (ICSD No. 16550).

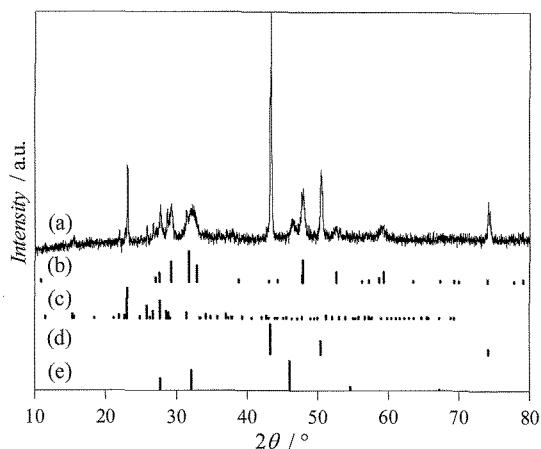


Fig. 4 The XRD patterns of the products obtained at (a) 60 °C for 1 h in argon atmosphere using oxygen-free water. (b) CuS (JCPDS Card No. 06-0464), (c) S (JCPDS Card No. 08-0247), (d) Cu (JCPDS Card No. 04-0836), and (e) $\text{Cu}_{7.2}\text{S}_4$ (JCPDS Card No. 24-0061).

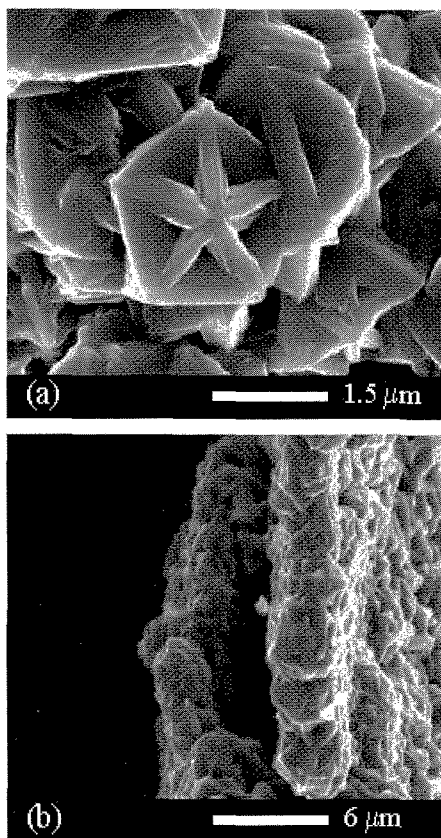


Fig. 5 The SEM images of CuS obtained at 180 °C for 10 h: (a) 2 - 3 μm polyhedral microcrystals and (b) layer-structures consisting of these particles.

As described above, sulfur reacts with copper at 60 °C to form CuS or Cu_2S as the major product depending on the starting ratios of the elements, with trace amounts of Cu_2O and S. The presence of Cu_2O in the product suggests that in the initial stage of the reaction, the reaction of the copper surface with sulfur competes with the reaction with oxygen. The oxygen-free reaction in water at 60 °C for 1 h, where copper and sulfur (1:1

molar ratio) were reacted in oxygen-free water under an argon atmosphere, resulted in the products that contain no XRD-detectable Cu_2O (see Fig. 4). However, Cu, S, and $\text{Cu}_{7.2}\text{S}_4$ were present as impurities. Thus, impurities of the reaction in the oxygen-free condition are similar to those observed in the product obtained in the condition with oxygen except for Cu_2O . It should be noted that even in the presence of oxygen, Cu_2O is not observed in the reaction at 60 °C for 10 h. This indicates that passive oxide layer can be broken gradually by sulfur in water [15].

3.2 Particle shapes and sizes

The sizes and shapes of CuS and Cu_2S particles were investigated by scanning electronic microscopy (SEM). The SEM images of CuS and Cu_2S , which were both obtained by the reaction at 180 °C for 10 h, are shown in Fig. 5 and Fig. 6. The particle sizes of CuS and Cu_2S were similar and the dimensions are of 2–3 μm . Particles of both compounds have similar edged polyhedral shapes but those of Cu_2S are less sharp. The aggregation of the particles form layers in both of the compounds (Fig. 5 (b) and Fig. 6 (b)).

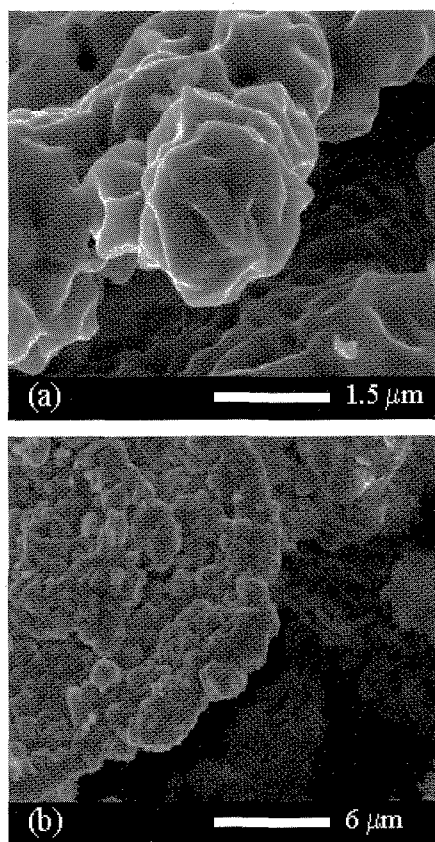


Fig. 6 The SEM images of Cu_2S obtained at 180 °C for 10 h: (a) 2 - 3 μm unclear polyhedral microcrystals and (b) layer-structures consisting of these particles.

3.3 Ag_2S

The reactions of Ag and S (Ag : S = 0.01 mol : 0.005 mol) were studied in the heating conditions at 60 – 240 °C (at 30 °C intervals) for 1 or 10 h. Single-phase products of Ag_2S were obtained in the conditions above 90 °C for 1 h or 60 °C for 10 h. The XRD patterns of

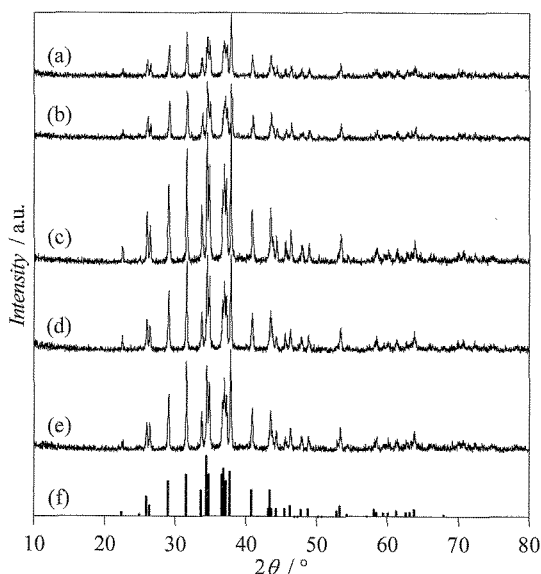


Fig. 7 The XRD patterns of the products obtained at (a) 240 °C, (b) 180 °C, (c) 150 °C, (d) 120 °C, and (e) 90 °C for 10 h. (f) Ag_2S (JCPDS Card No. 14-0072).

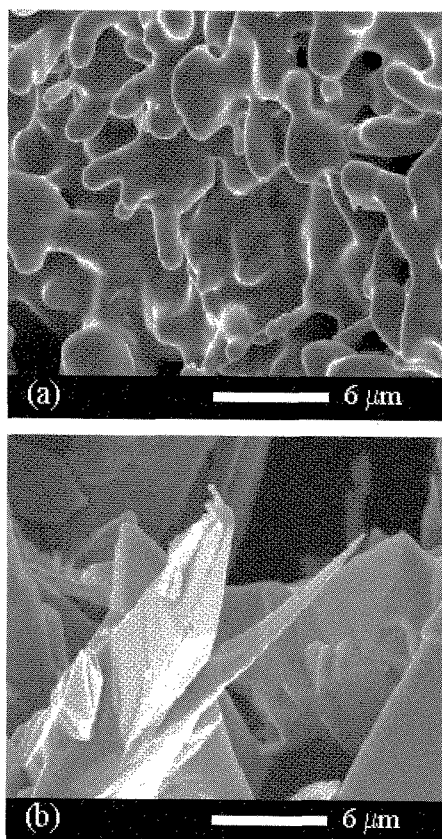


Fig. 8 The SEM images of Ag_2S obtained at (a) 240 °C for 10 h and (b) 90 °C for 10 h.

the products obtained for 10 h are shown in Fig. 7. The bulk of the products had high plasticity like clays. The plasticity was disappeared by increasing the ratio of sulfur in the starting mixture. In the reaction at lower temperatures, unreacted silver was detected in addition to Ag_2S . SEM images of as-prepared samples are shown

in Fig. 8. The Ag_2S obtained at 90 °C contains particles like sharp thin blades while the particles become duller with the increasing reaction temperature.

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