

Synthesis of Nanocrystalline CuMS_2 ($M = \text{In}$ or Ga) through a Solvothermal Process

Qingyi Lu, Junqing Hu, Kaibin Tang,* Yitai Qian,*
Guien Zhou, and Xianming Liu

Structure Research Laboratory and Department of Chemistry,
University of Science and Technology of China,
Hefei, Anhui 230026, P. R. China

Received September 22, 1999

Introduction

CuMS_2 sulfides are tetrahedrally coordinated semiconductors and possess the uniaxial chalcopyrite structure.^{1,2} Among them, CuInS_2 is a good candidate for photovoltaic applications because its band gap (about 1.53 eV at room temperature) matches well the solar spectrum,³ and CuGaS_2 is a promising material for the production of light-emitting devices in the green light region because of its wide and direct energy gap (about 2.49 eV at room temperature).⁴

The usual method for CuInS_2 and CuGaS_2 crystallites is solid-state reaction, which needs high temperature to overcome the energy barrier.⁵ The traditional homogeneous precipitation method used to prepare CuInS_2 and CuGaS_2 requires post-annealing at high temperature (about 800 °C) to obtain crystalline products.⁶ Christopher et al. synthesized polycrystalline chalcopyrite CuInS_2 by microwave irradiation.⁷ Recent efforts to develop new methods for chalcopyrites have focused on using organometallic precursors as reactants.⁸ This method is very useful for synthesizing target products at low temperature; however, the toxicity and the difficulty of the preparation of the organometallic precursors limit its utility.

A solvothermal process, as a mild synthetic method, has been used for the preparation of many binary sulfides and some III–V semiconductors.^{9–11} In this Note, we developed this method for the direct production of CuMS_2 ($M = \text{In}$ or Ga) nanocrystallites with commercial CuCl , In or Ga , and S powders as reagents. The synthetic reaction was carried out in an autoclave under solvothermal conditions at 200 °C. In order to explore the reaction mechanism, we chose different synthetic reaction systems to investigate various solvents, reaction reagents, and synthetic temperatures systematically.

* To whom correspondence should be addressed.

- (1) Bodnar, I. V.; Smirnova, G. F.; Karoza, A. G.; Chernyakova, A. P. *Phys. Status Solidi B* **1990**, *158*, 469.
- (2) Hsu, H. J.; Yang, M. H.; Tang, R. S.; Hsu, T. M.; Hwang, H. L. *J. Cryst. Growth* **1984**, *70*, 427.
- (3) Thiel, F. A. *J. Electrochem. Soc.* **1982**, *129*, 1570.
- (4) Oishi, K.; Kobayashi, S.; Ohta, S.-i.; Tsuboi, N.; Kaneko, F. *J. Cryst. Growth* **1997**, *177*, 88.
- (5) Honeyman, W. N.; Wilkinson, K. H. *J. Phys. D: Appl. Phys.* **1971**, *4*, 1182.
- (6) Yasusada, U.; Takashi, S.; Youhei, H.; Hideki, M. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1993**, *61*, 1206.
- (7) Landry, C. C.; Barron, A. R. *Science* **1993**, *260*, 1653.
- (8) Hepp, A. F.; Andras, M. T.; Bailey, S. G.; Duraj, S. A. *Adv. Mater. Opt. Electron.* **1992**, *1*, 99.
- (9) Trentler, T. J.; Hickman, K. M.; Goel, S. C.; Viano, A. M.; Gibbons, P. C.; Buhro, W. E. *Science* **1995**, *270*, 1791.
- (10) Li, Y.; Duan, X.; Liao, H.; Qian, Y. *Chem. Mater.* **1998**, *10*, 2301.
- (11) Wang, W.; Geng, Y.; Qian, Y.; Ji, M.; Liu, X. *Adv. Mater.* **1998**, *10*, 1479.

Experimental Section

In a typical process, appropriate amounts of analytical grade CuCl , In or Ga , and an excess of S powders were put into an autoclave of 50 mL capacity, and then the autoclave was filled with solvent such as benzene or distilled water up to 90% of the total volume. Neither shaking nor stirring was needed during the experimental process. Thereafter sealed, the autoclave was kept at 200 °C for 12 h and then cooled to room temperature. The precipitate was washed with dilute acid, distilled water, and absolute ethanol, in that order, and dried in a vacuum at 50 °C for 4 h to obtain the final product.

The product phases were determined by X-ray powder diffraction (XRD) studies, using a Japan Rigaku $D_{\text{max}} \gamma\text{A}$ X-ray diffractometer with graphite-monochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The elemental analysis of the products was done by traditional chemical analysis combined with PE-1100B atomic absorption spectrophotometry (AAS). The grain size and morphology of the final product were investigated by transmission electron microscopy (TEM), carried out on a Hitachi (model H-800) transmission electron microscope.

Results

Figure 1 shows the XRD pattern of the sample CuInS_2 prepared in distilled water. All of the peaks can be indexed as the tetragonal copper indium disulfide. After refinement, the lattice parameters $a = 5.53 \text{ \AA}$, $c = 11.13 \text{ \AA}$ are consistent with the literature values ($a = 5.523 \text{ \AA}$, $c = 11.141 \text{ \AA}$; JCPDS card, No. 27-159). No characteristic peaks of impurity phases such as copper sulfides and indium are observed. The average particle size of the sample, estimated by the Scherrer equation, is 15 nm. By substituting Ga for In under similar conditions, we also synthesized nanocrystalline CuGaS_2 , confirmed by XRD studies. Further evidence for the formation of CuInS_2 is the elemental analysis result, $\text{Cu}_{1.00}\text{In}_{1.04}\text{S}_{2.02}$, which reveals the stoichiometric relations between Cu , In , and S . The morphologies of the prepared CuMS_2 are studied by transmission electron microscopy. The TEM image of CuInS_2 nanocrystallites prepared in distilled water is given in Figure 2a. From this figure, we can see that the CuInS_2 nanocrystallites consist of uniform particles. The size of the particles is in the range 5–15 nm, which is consistent with the XRD result. The TEM image of CuGaS_2 prepared under similar conditions is shown in Figure 2b, which reveals that the average size of the spherical CuGaS_2 particles is 35 nm.

The disproportionation of S has been well-documented.^{12,13} Previous literature reported that the reaction between sulfur and alkali metal carbonates or transition metal chlorides under solvothermal conditions could be interpreted as the redox disproportionation of sulfur leading to the formation of reduced species and oxidized species of sulfur which might cause metal to be oxidized.^{13,14} In our experiments, the disproportionation of S was used to prepare CuInS_2 crystallites with CuCl , In , and S as reactants and XRD studies revealed that CuInS_2 crystallites were produced successfully in many solvents such as benzene, toluene, pyridine, and ethylenediamine. The fact that CuInS_2 crystallites were produced in inert solvent benzene indicated that the synthetic reaction could occur without the participation of solvent as a reactant. To simplify the synthetic path, we chose benzene as the solvothermal synthetic solvent to investigate the

- (12) Gobeltz, N.; Demortier, A.; Lelieur, J. P. *Inorg. Chem.* **1998**, *37*, 136.
- (13) Sheldrick, W. S.; Wachhold, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 206.
- (14) Lu, Q.; Hu, J.; Tang, K.; Qian, Y.; Liu, X.; Zhou, G. *J. Solid State Chem.* **1999**, *146*, 484.

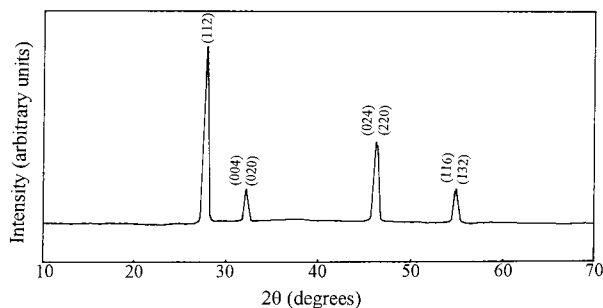


Figure 1. XRD pattern of the sample CuInS_2 prepared in distilled water.

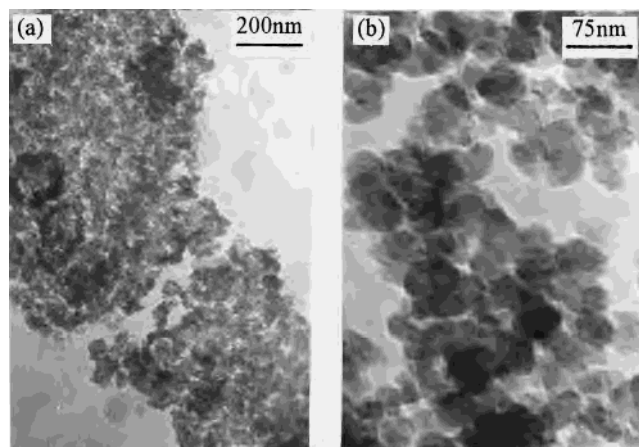
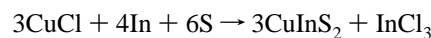


Figure 2. (a) TEM image of the sample CuInS_2 prepared in distilled water. (b) TEM image of the sample CuGaS_2 prepared in distilled water.

reaction mechanism. Since under our experimental conditions $\text{CuCl} + \text{S}$ could produce copper sulfide, one might envisage a multistep process in which copper sulfide was formed as an intermediate compound. But under our experimental conditions, the reaction between copper sulfide, In, and S did not form CuInS_2 crystallites. However, due to the low activity of copper sulfide compared with the newly produced copper sulfide, it might be too early to confirm that CuInS_2 was synthesized not through the formation of copper sulfide. In view of this reason, we designed a benzene-solvothermal process by using Cu, In, and S as reactants because $\text{Cu} + \text{S}$ under our experimental conditions could also yield copper sulfide. Nevertheless, we still failed to obtain CuInS_2 crystallites by this method. Moreover, although the reaction temperature was high enough to melt In (melting point: 157°C), $\text{In} + \text{S}$ did not produce indium sulfide under our experimental conditions. All of these results excluded the possibility of copper sulfide or indium sulfide as an intermediate compound. On the basis of these results, we proposed a one-step disproportionation mechanism: in the system of CuCl , In, and S, the disproportionation reaction of $\text{CuCl} + \text{S}$ induced the oxidization of In to give CuInS_2 crystallites directly. The possible reaction equation was de-

scribed as follows:



The evidence that after the synthetic reaction indium ion was detected in the solution further supported this synthetic mechanism.

Although CuInS_2 crystallites could be obtained in many solvents, the action between solvent and S affected the product's morphologies greatly, which could not be neglected. In inactive solvents such as benzene and toluene, the solubility of sulfur increased with reaction temperature.¹⁵ The homogeneous dissolution of S might have something to do with the final spherical morphologies of CuInS_2 particles. TEM results indicated that CuInS_2 crystallites prepared in benzene or toluene consisted of spherical particles with an average size of 20 or 25 nm, respectively. In donor solvent pyridine, the lone pair electrons on the nitrogen atom would activate sulfur molecules and might promote the synthetic reaction.^{16,17} TEM observation confirmed that under pyridine-thermal conditions the produced CuInS_2 consisted of nonuniform particles with relatively large size. In strongly coordinating solvent ethylenediamine (en), CuInS_2 crystallites were produced in irregular form with a relatively large axis ratio, which might be due to the formation of polysulfides in en and the chelation of en.^{10,18,19}

According to XRD studies, to make the synthetic reaction occur, the reaction temperature should be no less than 150°C . Higher temperature was beneficial to the product's crystallinity and particle growth. The optimal reactive temperature range for CuInS_2 nanopowders with high crystallinity was about $180\text{--}250^\circ\text{C}$. We chose 200°C as the final reaction temperature for about 10 nm CuInS_2 crystallites.

Conclusion

In this Note, we reported a solvothermal process for the synthesis of nanocrystalline CuInS_2 and CuGaS_2 at 200°C . To explore the reaction mechanism, different synthetic reaction systems such as various solvents, reactants, and synthetic temperatures were investigated, and a one-step disproportionation reaction mechanism was proposed. Although extensive studies are needed, we believe in principle that this simple method has potential applications in fabricating other ternary or quaternary chalcogenide compounds.

Acknowledgment. This work is supported by Chinese National Natural Science Research Foundation.

IC9911365

- (15) Li, J.; Chen, Z.; Lam K.; Mulley, S.; Proserpio, D. M. *Inorg. Chem.* **1997**, *36*, 684.
- (16) Verma, A. K.; Rauchfuss, T. B.; Wilson S. R. *Inorg. Chem.* **1995**, *34*, 3072.
- (17) Ramli, E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 4043.
- (18) Daly, F. P.; Brown, C. W. *J. Phys. Chem.* **1976**, *80*, 480.
- (19) Dubois, P.; Lelieur, J. P.; Lepoutre, G. *Inorg. Chem.* **1988**, *27*, 3032.