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An Elegant Room Temperature Procedure for the Precise Control of Composition in the Cu−S System

Prashant Kumar and R. Nagarajan*

Materials Chemistry Group, Department of Chemistry, University of Delhi, Delhi 110007, India

S Supporting Information

ABSTRACT: A general methodology for the precise control of the final product composition in the copper sulfide system has been established for the first time. Cu_2S, prepared by the dissociation of $[Cu(tu)_3]Cl$ in ethylenediamine, was subjected to controlled chemical oxidation by iodine to obtain Cu_{2-x} ($x = 0.2, 0.25, 0.88, 1.0$) at room temperature. The compositions were characterized by powder X-ray diffraction, ICP spectroscopy, Raman spectroscopy, and magnetization measurements.

The research interest in the copper−sulfur system originated with mineralogists and geologists and expanded to chemists, physicists, and material scientists due to the discovery of useful technological applications.[1] Various interesting properties exhibited by the copper sulfides, such as semiconductivity, electrodes in solar cells, fast ionic conductivity, thermo- and photoelectric transformers, high temperature thermistors, and superconductivity, fueled further interest in understanding the structure−property correlation in this structurally complex Cu−S sytem.[2−6] Copper sulfides exist in a wide range of stable and metastable compositions that include Cu_2S, $Cu_{31}S_{16}$ ($Cu_{1.96}S$), Cu_9S_5 ($Cu_{1.8}S$), Cu_7S_4 ($Cu_{1.75}S$), Cu_9S_8 ($Cu_{1.12}S$), CuS, and CuS_2.[7,8] It has been a great challenge for crystallographers to understand the structures of $Cu_{2-x}S$ phases due to the positions of the copper atoms, within the close packed sublattice of S atoms, which are not well-defined. They depend on the temperature, and at high temperatures they are unusually mobile, thus making these compositions partially ionic conductors. Due to this special status, crystallographers and theorists, considereding statistical distribution of copper atoms, with Cu_2S to be the ideal starting crystal structural model for obtaining other compositions.[9] Stoichiometric Cu_2S exhibits a monoclinic symmetry below 103.5 ± 1 °C and hexagonal symmetry above that temperature. The hexagonal phase is stable up to 436 ± 10 °C, above which it embraces the cubic symmetry. The complex phase diagram of the copper−sulfur system is dominated by $Cu_{2-x}S$ at higher temperatures and a broad homogeneity range containing phases $Cu_{1.75}S$, $Cu_{1.95}S$, and monoclinic and hexagonal forms of Cu_2S.[10] The phase relations are complicated due to the tendency to form metastable phases.

Despite the existence of numerous generalized synthetic methods available for the fabrication of metal chalcogenides in different sizes and shapes,[11−13] enough understanding toward achieving the composition control of the final products is lacking. This is of the utmost importance in the case of copper sulfides for the reasons mentioned above. Variation of the copper to sulfur ratio, tuning the pH of the medium, and use of a mixed solvent system are the major strategies followed in the solution-based synthesis to achieve the various compositions.[14−18] Also, the use of stabilizing agents and reducing agents to form a selective set of copper sulfides is known.[19,20] For example, copper(I) thiobenzoate is decomposed in the presence of dodecane, trioctyl phosphine, and tributyl phosphine as stabilizing agents to yield $Cu_{1.75}S$ and Cu_2S.[19] Jiang et al.[20] synthesized Cu_9S_8 first and transformed it to CuS and Cu_7S_4 ($Cu_{1.75}S$) with the aid of KBH_4 and $SnCl_4$, respectively. It is important to note that these were achieved under solvothermal conditions in an ammoniacal medium at 60 °C.

One of the ideal approaches to achieving the various compositions in the copper sulfides is to obtain the end member of the copper-rich sulfide, Cu_2S first, followed by the systematic introduction of holes through the controlled removal of copper from this system. Since all of the copper ions are present in the +I oxidation state in Cu_2S, either the oxidation of copper ions or their removal must preferably be carried out at room temperature without involving high temperatures, wherein the control will not be very precise. Additionally, the use of higher temperatures may introduce contaminants such as oxides at the grain boundaries.

Our recent research on the dissociation of the single source precursors $[Cu(tu)_3]Cl$, $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$, and $[Cu_2(tu)_6]SO_4 \cdot 4H_2O$ in ethylene glycol solvent, showed conclusively that the final product stoichiometry was greatly influenced by the anions of the starting precursor.[21] Also, the use of other copper(I)-containing single source precursors for the easy synthesis of Cu_2S described in the literature motivated us to choose $[Cu(tu)_3]Cl$ for the present study.[22−24] The greater reducing power of ethylenediamine (as compared to ethylene glycol) and its widespread use for the successful synthesis of copper sulfides, even at room temperature from their elements, prompted us to select ethylenediamine to be the solvent medium for preparing Cu_2S.[25] It was resolved to apply room temperature for the synthesis due to the stringent requirement to make stoichiometric Cu_2S.

The synthesis and characterization results of the precursor $[Cu(tu)_3]Cl$[26] are provided in the Supporting Information. The addition of ethylenediamine to the solid precursor results immediately in a black colored product with the release of heat as indicated by the temperature of the reaction flask. Vigorous stirring, over a magnetic plate, was continued for 12 h, and the product is obtained by filtration under vacuum and dried over a desiccant. The powder X-ray diffraction pattern of the reaction product is shown in Figure 1a. As Cu_2S is known to exist in monoclinic, hexagonal, and cubic symmetries, the positions of the reflections observed in the powder X-ray diffraction pattern

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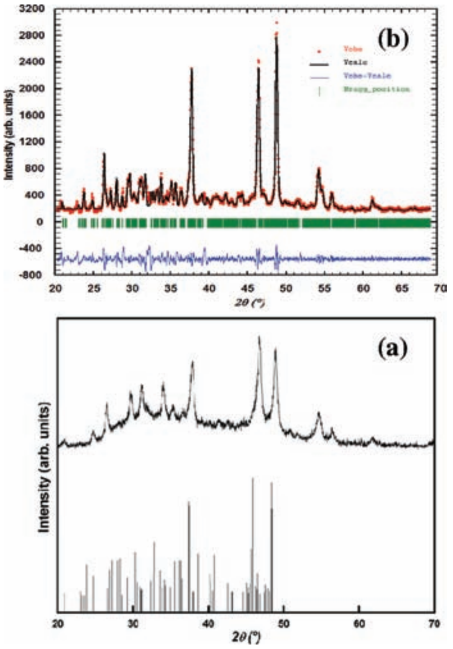


Figure 1. Powder X-ray diffraction pattern of the product obtained after the dissociation of the complex $[Cu(tu)_3]Cl$ in ethylenediamine (a) at room temperature and (b) under solvothermal conditions at 130 °C for 12 h. The line representations of JCPDS file no. 83-1462 for the monoclinic Cu_2S are shown for easy identification. LeBail fitting with the difference pattern is shown for the Cu_2S obtained under solvothermal conditions.

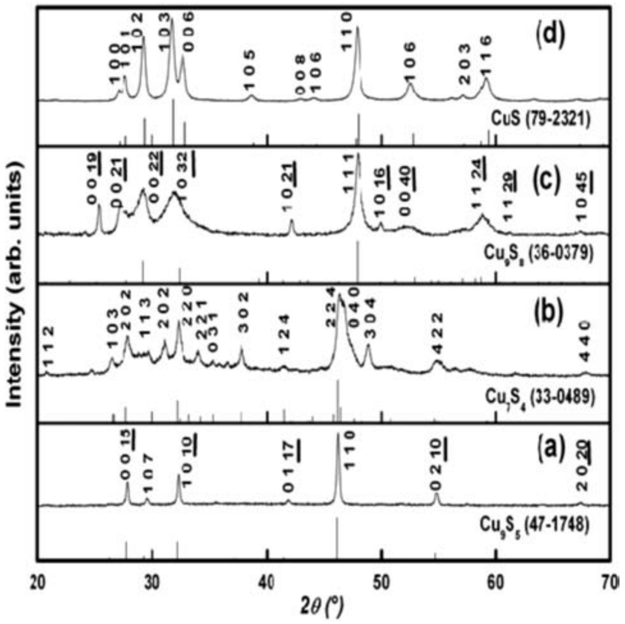
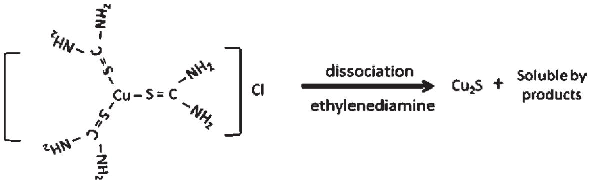


Figure 2. Powder X-ray diffraction pattern of (a) Cu_9S_5, (b) Cu_7S_4, (c) Cu_9S_8, and (d) CuS obtained from the reaction of Cu_2S with 0.20, 0.25, 0.88, and 1 mol of iodine solution in acetonitrile for 2 days at 25 °C.

matched closely with the monoclinic Cu_2S (see JCPDS file no. 83-1462). But, the intensities of the reflections were not matching, as reported in the JCPDS file, probably due to the partially disordered nature of the Cu_2S obtained by this procedure. As the monoclinic is a lower symmetry, compared to hexagonal, the presence of these two might be masking the intensities of the reflections. Generally, noisy powder X-ray diffraction patterns for Cu_2S are reported in the literature.[27,28] The reflections in the 2θ range of 20−40° are well-defined in the product after the solvothermal treatment at 130 °C for 12 h. The LeBail fitting procedure of the powder X-ray diffraction pattern (Figure 1b) converged well in monoclinic symmetry with lattice constants of $a = 15.131(2)$, $b = 11.843(1)$, and $c = 13.502(2)$ Å and $\beta = 115.90\ (6)°$. The details of the fitting procedure are provided in the Supporting Information. Also, the Cu/S ratio, as analyzed by the inductively coupled plasma (ICP) spectroscopy, came out to be 2:1.04.

It is important to recognize that copper sulfide formation is extremely difficult, with CuCl and thiourea as the reactants, in an ethylenediamine medium, due to the formation of a quite stable complex between CuCl and ethylenediamine. This complex has been observed to undergo dissociation under hydrothermal conditions at 170 °C.[29] In our study, this situation does not arise, since a single source precursor, in which the copper to sulfur bond existed before the dissociation, is used. This facilitated the copper sulfide formation at room temperature itself. The formation of crystalline Cu_2S, by the dissociation of the precursor, is believed to be assisted by the mechanical energy supplied in the form of vigorous stirring. This explanation is further supported by the fact that mechanochemical syntheses, from the elements, exist as an alternate synthetic strategy to make crystalline metal chalcogenides due to their soft character.[30] The reaction between the precursor and ethylenediamine is represented as follows:



The standard chemical oxidation procedure using the iodine solutions in acetonitrile has been applied to control the composition of the final product.[31] A total of 0.0710 g (0.2 mol of I) of freshly sublimed iodine in acetonitrile is added to 0.2 g of highly crystalline Cu_2S, and the reaction is carried out under constant stirring in flowing argon. A slight excess of iodine is used, as the reaction is performed for 24−48 h. Highly colored iodine becomes colorless after the reaction. The product, after the reaction, is $Cu_{1.8}S$, as evidenced from its powder X-ray diffraction pattern (Figure 2a) in which the positions and intensities of the peaks match closely with the hexagonal Cu_9S_5 (JCPDS file no. 47-1748). When 0.2 g of Cu_2S was treated with 0.080 g (0.25 mol of I) for 48 h, orthorhombic anilite, Cu_7S_4, is obtained, as validated by its powder X-ray diffraction pattern (Figure 2b). Along similar lines, Cu_9S_8 and CuS are obtained after reacting Cu_2S with 0.3124 g (0.88 mol of I) and 0.3550 g (1 mol of I) of iodine in acetonitrile for 48 h respectively (Figure 2c,d). The oxidation reaction of Cu_2S with iodine in acetonitrile can be expressed by the following equation:

$$Cu_2S + x/2I_2 \rightarrow Cu_{2-x}S + xCuI$$

CuI, formed in the reaction, gets dissolved in acetonitrile and repeated washing is done to make sure it is not present with the copper sulfide.

The Raman spectrum of the prepared copper sulfides endorsed the results from the powder X-ray diffraction studies, showing the shifting of the bands to higher wave numbers, as one moves from Cu_2S to CuS, confirming earlier reports (Figure 3).[32]

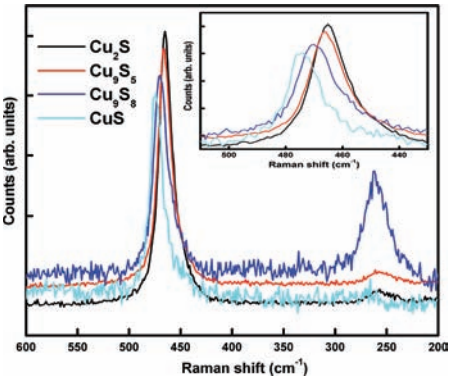


Figure 3. Raman spectra of Cu_2S, Cu_9S_5, Cu_9S_8, and CuS.

Highly intense peaks at 465, 466, 470, and 474 cm^{-1} are observed along with the weaker ones at 257, 259, 262, and 266 cm^{-1} for Cu_2S, Cu_9S_5, Cu_9S_8, and CuS, respectively.

It is very important to note that Cu_2S is PL inactive, and it shows diamagnetic behavior at room temperature (Figure S4). Very interesting magnetic characteristics are observed for Cu_9S_5, Cu_9S_8, and CuS samples. On moving from Cu_2S to CuS through $Cu_{1.8}S$ and Cu_9S_8, the magnetic character goes through a transition from diamagnetic to paramagnetic, with Cu_9S_8 showing a mixed diamagnetic and paramagnetic nature in the magnetic hysteresis loop. A significant paramagnetic nature, prevalent in the magnetic field between 0 and 2000 Oe with a weak molar susceptibility of $\chi_M = 1.08 \times 10^{-4}$ emu/mol, is observed for Cu_9S_8. CuS shows a very clear paramagnetic hysteresis loop with the $\chi_M = 1.198 \times 10^{-3}$ emu/mol. CuS is a special hexagonal crystalline structure, consisting of layers of planar CuS_3 triangles, containing Cu^{2+} and S^{2-} ions, surrounded (above and below) by CuS_4 tetrahedral arrangements of Cu^+ and $S_2{}^{2-}$ ions.[33,34] The presence of a mixed diamagnetic and paramagnetic character of Cu_9S_8 proves that the ratio of the tricoordinated Cu^{2+} to the tetrahedral coordinated Cu^+ decisively determines the overall magnetic behavior of the copper sulfides.

In conclusion, a simple and very effective approach has been described for the synthesis of copper sulfides in which the composition is precisely controlled. The superiority of this approach lies in the fact that all of the reactions are conducted simply at room temperature. In addition, this paves the way for the preparation of other nonstoichiometric compositions known in the Cu−S phase diagram as well as in other copper-based chalcogenides.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Magnetization measurements at room temperature of the prepared copper sulfides and the LeBail fitting details of the powder X-ray diffraction pattern of the monoclinic Cu_2S. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: rnagarajan@chemistry.du.ac.in.

Notes

Scope of the reactionThough this study has been concentrated to copper sulfides, a similar approach can effectively be applied for composition control in other metal sulfides.

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REFERENCES

(1) Chakrabarti, D. J.; Laughlin, D. E. *Bull. Alloy Phase Diagrams* **1983**, *4*, 254–271.

(2) Wu, Y.; Wadia, C.; Ma, W.; Sadtler, B.; Alivisatos, A. P. *Nanotechnolgy* **2008**, *8*, 2551–2555.

(3) Sakamoto, T.; Sunamura, H.; Kawaura, H.; Hasegawa, T.; Nakayama, T.; Aono, M. *Appl. Phys. Lett.* **2003**, *82*, 3032–3034.

(4) Okamoto, K; Kawai, S. *Jpn. J. Appl. Phys.* **1973**, *12*, 1030–1038.

(5) Liang, W.; Whangbo, M.-H. *Solid State Commun.* **1993**, *85*, 405–408.

(6) Lou, Y. B.; Samia, A. C. S.; Cowen, J.; Banger, K.; Chen, X. B.; Lee, H.; Burda, C. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1091–1095.

(7) Goble, R. J. *Can. Mineral.* **1985**, *23*, 61–76.

(8) Mumme, W. G.; Sparrow, G. J.; Walker, G. S. *Mineral Mag.* **1988**, *52*, 323–330.

(9) Lukashev, P.; Lambrecht, W. R. L.; Kotani, T.; Schilfgaarde, M. *Phys. Rev. B* **2007**, *76* (195202), 1–14.

(10) Blachnik, R.; Muller, A. *Thermochim. Acta* **2000**, *362*, 31–52.

(11) Wang, W.; Zhuang, J.; Peng, Q.; Li, Y. *Nature* **2005**, *437*, 121–124.

(12) Du, X.-S.; Mo, M.; Zheng, R.; Lim, S.-H.; Meng, Y.; Mai, Y.-W. *Cryst. Growth Des.* **2008**, *8*, 2032–2035.

(13) Choi, S.-H.; An, K.; Kim, E.-G.; Yu, J. H.; Kim, J. H.; Hyeon, T. *Adv. Funct. Mater.* **2009**, *19*, 1645–1649.

(14) Zhang, H.; Zhang, Y.; Yu, J.; Yang, D. *J. Phys. Chem. C* **2008**, *112*, 13390–13394.

(15) Zhao, Y.; Pan, H.; Lou, Y.; Qiu, X.; Zhu, J.; Burda, C. *J. Am. Chem. Soc.* **2009**, *131*, 4253–4261.

(16) Gorai, S.; Ganguli, D.; Chaudhuri, S. *Mater. Sci. Eng. B* **2005**, *116*, 221–225.

(17) Gorai, S.; Ganguli, D.; Chaudhuri, S. *Cryst. Growth Des.* **2005**, *5*, 875–877.

(18) Zheng, X.; Hu, Q. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *94*, 805–812.

(19) Lim, W. P.; Wong, T. W.; Ang, S. L.; Low, H. Y.; Chin, W. S. *Chem. Mater.* **2006**, *18*, 6170–6177.

(20) Jiang, X.; Xie, Y.; Lu, J.; He, W.; Zhu, L.; Qian, Y. *J. Mater. Chem.* **2000**, *10*, 2193–2196.

(21) Kumar, P.; Gusain, M.; Nagarajan, R. *Inorg. Chem.* **2011**, *50*, 3065–3070.

(22) Larsen, T. H.; Sigman, M.; Ghezelbach, A.; Doty, R. C.; Korgel, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 5638–5639.

(23) Sigman, M. B., Jr.; Ghezelbach, A.; Hanrath, T.; Saunders, A. E.; Lee, F.; Korgel, B. A. *J. Am. Chem. Soc.* **2003**, *125*, 16050–16057.

(24) Chen, L.; Chen, Y.-B.; Wu, L.-M. *J. Am. Chem. Soc.* **2004**, *126*, 16334–16335.

(25) (a) Dusastre, V.; Omar, B.; Parkin, I. P.; Shaw, G. A. *J. Chem. Soc., Dalton Trans.* **1997**, 3505–3508. (b) Li, Y.; Wang, Z.; Ding, Y. *Inorg. Chem.* **1999**, *38*, 4737–4740.

(26) Bombicz, P.; Mutikainen, L.; Krunks, M.; Leskela, T.; Madarasz, J.; Niinisto, L. *Inorg. Chim. Acta* **2004**, *357*, 513–525.

(27) Chen, Y.-B.; Chen, L.; Wu, L.-M. *Chem.—Eur. J.* **2008**, *14*, 11069–11079.

(28) Qin, A.-M.; Fang, Y.-P.; Ou, H.-D.; Liu, H.-Q.; Su, C.-Y. *Cryst. Growth Des.* **2005**, *5*, 855–860.

(29) Lu, Q.; Gao, F.; Zhao, D. *Nano Lett.* **2002**, *2*, 725–728.

(30) Godočíková, E.; Baláž, P.; Gock, E.; Choi, W. S.; Kim, B. S. *Powder Technol.* **2006**, *167*, 147–152.

(31) Murphy, D. W.; Cros., D.; Salvo, F. J. D.; Waszcak, J. V. *Inorg. Chem.* **1977**, *16*, 3027–3031.

(32) Isac, L. A.; Dutta, A.; Enesca, I. A.; Nanu, M. *J. Phys.: Conf. Ser.* **2007**, *61*, 477–481.

(33) Okamato, K.; Kawai, S.; Kiriyama, R. *Jpn. J. Appl. Phys.* **1969**, *8*, 718–724.

(34) Nozaki, H.; Shibata, K.; Ohhashi, N. *J. Solid State Chem.* **1991**, *91*, 306–311.