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Synthesis of $Cu_{1.8}S$ and CuS from Copper-Thiourea Containing Precursors; Anionic (Cl^-, NO_3^-, SO_4^{2-}) Influence on the Product Stoichiometry

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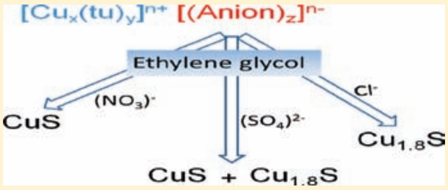
S *Supporting Information*



ABSTRACT: A novel and unique understanding pertaining to the synthesis of $Cu_{1.8}S$ and CuS in bulk was achieved from the analysis of the products of the Cu-Tu precursors, with Cl^-, NO_3^-, and SO_4^{2-} as the counteranions, in ethylene glycol. $[Cu_4(tu)_9](NO_3)_4\cdot 4H_2O$ always yielded CuS whether the dissociation was carried out in ethylene glycol in the presence of air or argon or under solvothermal conditions. $Cu_{1.8}S$ was the only product when $[Cu(tu)_3]Cl$ was dissociated in air as well as in flowing argon in ethylene glycol. A mixture of $Cu_{1.8}S$ and CuS was formed from the chloride ion containing precursor when dissociated solvothermally. $[Cu_2(tu)_6]SO_4\cdot H_2O$ yielded a mixture of CuS and $Cu_{1.8}S$ on dissociation in the presence of air and argon, as well as under solvothermal conditions. The oxidizing power of the anions Cl^-, SO_4^{2-}, and NO_3^-, present in the precursor, greatly determined the extent of formation of $Cu_{1.8}S$ and CuS. While $Cu_{1.8}S$ showed hexagonal plate like morphology, flower like morphology was observed for CuS in the SEM images. In the mixed phase, $Cu_{1.8}S$ + CuS, both these morphologies were present. $Cu_{1.8}S$ and CuS showed scattering resonances at 470 cm^{-1} and 474 cm^{-1}, respectively, in the Raman spectrum. Magnetization measurements at room temperature revealed diamagnetic behavior for $Cu_{1.8}S$ indicating the presence of +1 oxidation state for copper. Weak paramagnetic behavior was observed for CuS with χ_M value of 1.198×10^{-3} emu/mol at 300 K. Both $Cu_{1.8}S$ and CuS showed similar emission behavior in the photoluminescence spectrum with band positions centered at around 387, 390, 401, 423, and 440 nm. The origin of photoluminescence in these two copper sulfides remains elusive.

1. INTRODUCTION

Among the transition elements of group 10−12, copper is well placed in terms of the chalcophilicity, and hence the synthesis and exploration of interesting properties exhibited by them have attracted a great deal of attention. The breadth of electrical conductivity, from metallic to semiconducting to superconducting and the defect chemistry shown by the copper sulfides because of nonstoichiometry, render these materials attractive for the applications such as p-type conductors in solar cells and photovoltaic materials.[1−6] In addition, the scope of applications is expanded by the usage of CuS for catalytic and photo catalytic applications.[7,8]

Generally, copper sulfides, like any other inorganic materials, can be synthesized by various methods such as the solid state reactions, solvothermal, precipitation methods including micro emulsion approach; microwave and ultrasonic wave assisted synthesis.[5,6,8−15] Shaw and Parkin[16] reported the synthesis of copper sulfides from their elemental forms using liquid ammonia at room temperature. Recently, CuS has been synthesized using cation exchange from CdS and by the anion exchange from Cu_2O.[17,18] Gazelbash et al.[11] obtained $Cu_{1.8}S$ and CuS by varying the Cu/S ratio from 2:1 to 1:2 by the arrested precipitation method. Zhang et al.[19] formed $Cu_{1.75}S$ and CuS starting from copper to sulfur ratio of 2:1, 1:1, and 2:3. Their study concluded that excess sulfur did not affect the composition of the final product. Zhao et al.[20] described the synthesis of $Cu_{2-x}S$ (x = 1, 0.2, and 0.03) by the electro sonochemical method by varying the potential, hydrothermally by adjusting the pH, and by solvent less synthesis of drying the precipitates obtained from $CuSO_4$ and MPA (mercapto-propionic acid) in the presence of air and nitrogen atmosphere. Jiang et al.[21] used the reducing agent KBH_4 to prepare Cu_7S_4 ($Cu_{1.75}S$) from Cu_9S_8 and oxidized Cu_9S_8 to CuS with the help of $SnCl_4$ in ammonia solvent system from the precursor containing copper, thiourea, and chloride anion. They also reported the inertness of the other anions NO_3^-, ClO_4^-, CH_3COO^- on the composition and purity of Cu_9S_8.

Feng et al.[22] prepared CuS by the sulfurization of $Cu_{2-x}S$. The effect of sulfurization agent on polyamide and polyethylene also resulted in different compositions in copper sulfides.[23] Kundu et al.[24] evidenced the formation of chalcocite (Cu_2S), roxbyite (Cu_7S_4), and covellite (CuS) films by changing the sulfurization time over Cu. Synthesis of different compositions of copper sulfides, in the solution phase, has been achieved using a variety of solvents.[25] Utilizing the corrosion principles, CuS has also been prepared in water containing ammonia.[26] There exists plenty of literature on the controlled fabrication of microstructures and morphologies of CuS.

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The factors responsible for the synthesis of nonstoichiometric compositions of $Cu_{2-x}S$ are not clearly understood because of either the multiple solvent systems used in their synthesis or the absence of a clear-cut mechanism explaining their formation. One of the synthetic challenges for the copper sulfides in solution phase synthesis is to understand the factors contributing to the final stoichiometry of the bulk products. For transition metal or p-block chalcogenides synthesis, the single source precursor approach offers an ideal alternative because of the ease of application, prevention of evolution of toxic gases, formation of high quality products under relatively milder reaction conditions and naturally has attracted the constant attention of many researchers. The conditions benefit when the single source precursor is air stable, and the procedure followed for the synthesis is one pot and single step. Therefore, our obvious choice was centered on single source precursor complexes containing copper and sulfur. Ethylene glycol was chosen to be the medium in which the dissociation of the complexes was performed as this is a widely employed solvent system, in which the reactions can be understood to a greater extent. Also, ethylene glycol provides an effective convective heat transfer medium and maintains a reducing atmosphere and thereby protects the products from oxygen contamination. Single source precursors of the formula, $[Cu(tu)_3]Cl$, $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$, and $[Cu_2(tu)_6]SO_4 \cdot H_2O$ have been isolated in pure form which are air stable.[27,28] In the present study, analysis of the dissociated products of these precursors in ethylene glycol in air (open) and closed (solvothermal) conditions and under flowing argon (inert atmosphere) were studied with the purpose of understanding the role of the anions as well as the other factors responsible for the final copper sulfide stoichiometry in bulk.

2. EXPERIMENTAL SECTION

The complexes containing copper, thiourea, and the anions Cl^-, NO_3^-, and SO_4^{2-} were prepared according to the published procedures and characterized by spectroscopy techniques and thermal analysis.[27,28] For the synthesis $CuCl_2 \cdot 2H_2O$ (Spectrochem 99%), Cu $(NO_3)_2 \cdot 3H_2O$ (Kemphasol 99+%), $CuSO_4 \cdot 5H_2O$ (SISCO, 99%), and thiourea (SRL, 99%) were used. Dissociation of the 1 g of each of the precursors was carried out in three different ways in ethylene glycol which is of analytical grade (AR). When the precursors were refluxed in ethylene glycol (30 mL) for 1 h in the presence of air, the preparations were referred as open system dissociation. If the air is replaced with flowing Ar, then the preparations were referred as inert atmosphere. Solvothermal dissociations were carried out in 100 mL capacity Parr autoclaves filled with 40 mL of ethylene glycol and 1 g of the precursors followed by heating in a controlled oven at 150 °C for 4 h and therefore mentioned as closed system. After the reactions, the product was filtered and washed several times with CS_2, ethanol, and d. d. water. These washed products were dried naturally at room temperature.

The phase composition and structure of the final products were examined from powder X-ray diffraction patterns using a Bruker D8 Discover X-ray diffractometer, with Cu $K\alpha_1$ radiation (λ = 1.5405 Å) with a scan rate of 1.2 s/step and step size 0.02° at 298 K. Raman spectra of the samples, in compact form, were collected using a Renishaw spectrophotometer equipped with a microscope having laser wavelength of 514 nm. Photoluminescence (PL) measurements were performed on a Horiba Jobin Yvon Fluorolog 3 Spectrofluorometer at room temperature. The morphology of the final products was observed using scanning electron microscopy (SEM) using a FESEM, FEI Quanta 200F microscope. Magnetic measurements were carried out at 300 K using a Vibrating Sample Magnetometer (Microsense EV9). The FT-IR spectrum was recorded using Perkin-Elmer 2000 Fourier-Transform infrared spectrometer in the range 400−4000 cm^{-1} using KBr disks. Thermogravimetric (TG) analysis was carried out using Shimadzu simultaneous TG/DTA thermal analyzer (DTG-60). The samples were heated at the rate of 10 °C/min.

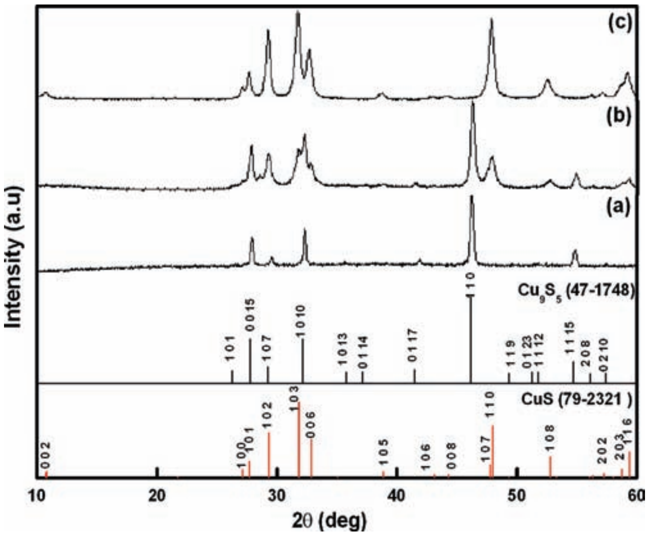

Figure 1. Powder X-ray diffraction patterns of the dissociated products from the complexes $[Cu(tu)_3]Cl$, $[Cu_2(tu)_6]SO_4 \cdot H_2O$, and $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$ in ethylene glycol in air. JCPDS reference patterns of CuS and $Cu_{1.8}S$ are also provided.

3. RESULTS AND DISCUSSION

The single source precursors containing copper ion, thiourea and the anions (Cl^-, NO_3^-, and SO_4^{2-}) were characterized by the elemental analysis, IR and Raman spectroscopy techniques. The number of water molecules was determined from the TG analysis of the precursors. The characterization details are presented in the Supporting Information, Table S1, Figures S1−S6 which confirmed the compositions of the precursors.

Thiourea played a dual role, being able to complex effectively with the copper ion as well as the source of sulfur.[27−29] During the dissociation of copper-thiourea precursors, generation of S^{2-} ions can be justified according the following equations.

$$2HOCH_2CH_2OH \rightarrow 2CH_3CHO + 2H_2O$$

$$NH_2CSNH_2 + H_2O \rightarrow H_2S + CO_2 + NH_3$$

Figure 1 represents the powder X-ray diffraction pattern of the dissociated products from the precursors $[Cu(tu)_3]Cl$, $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$, and $[Cu_2(tu)_6]SO_4 \cdot H_2O$ in ethylene glycol in air for 1 h. $Cu_{1.8}S$ was the single crystalline product when the single source precursor had Cl^- as the anion (Figure 1a). All the diffraction peaks in the pattern could be indexed in rhombohedral symmetry with lattice constants of a = 3.925 Å and c = 48.13 Å which are in good agreement with those reported in the literature (JCPDS file no. 47-1748). The product was a mixture of CuS and $Cu_{1.8}S$ from the complex that contained the sulfate anion (Figure 1b), and hexagonal CuS was formed from the nitrate ion containing copper-thiourea complex (Figure 1c. All the reflections of the hexagonal CuS were indexed with lattice constants of a = 3.772 Å; c = 16.32 Å, matching very well with the reported values (JCPDS file no.79-2321). Similar products were obtained even when the atmosphere of dissociation was changed

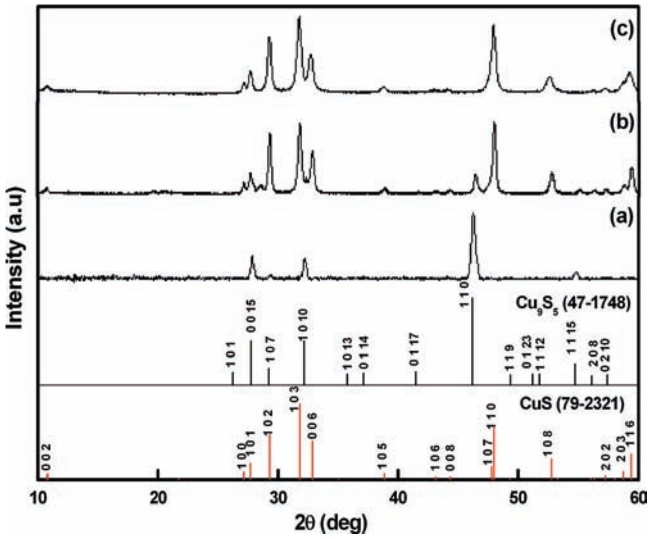

Figure 2. Powder X-ray patterns of the products obtained after the dissociation of complexes $[Cu(tu)_3]Cl$, $[Cu_2(tu)_6]SO_4 \cdot H_2O$, and $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$ in ethylene glycol in inert atmosphere. JCPDS reference patterns of CuS and $Cu_{1.8}S$ are also provided.

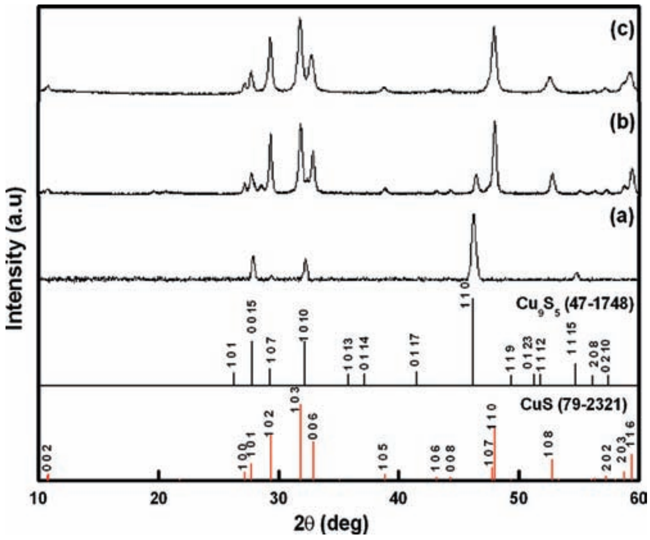

Figure 3. Powder X-ray patterns of the products obtained after the dissociation of complexes $[Cu(tu)_3]Cl$, $[Cu_2(tu)_6]SO_4 \cdot H_2O$, and $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$ under solvothermal conditions using ethylene glycol. JCPDS reference patterns of CuS and $Cu_{1.8}S$ are also provided.

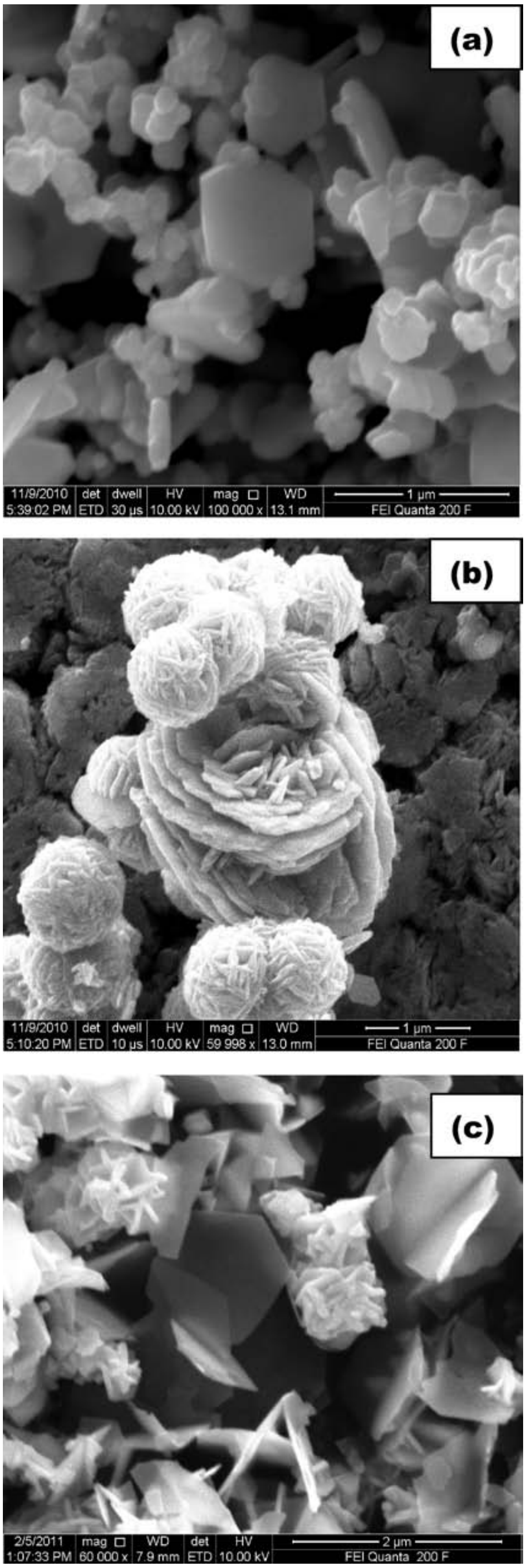

Figure 4. Scanning electron micrograph of (**a**) $Cu_{1.8}S$, (**b**) CuS, and (**c**) $Cu_{1.8}S$ + CuS.

to flowing argon (Figure 2a−c).The powder X-ray diffraction patterns of the slovothermally dissociated products from the three precursors are presented in Figure 3a,b,c, from which, one can identify a mixture of $Cu_{1.8}S$ and CuS from both the chloride and the sulfate ions containing precursors, where a pure hexagonal form of CuS was obtained from the precursor containing nitrate anion. SEM images of pure $Cu_{1.8}S$, CuS and mixed phase (CuS+$Cu_{1.8}S$) are reproduced in Figure 4. Hexagonal plate-like morphology was exhibited by $Cu_{1.8}S$, and a flower-like morphology was obtained for CuS (Figure 4 a,b). In the SEM image of the mixed product CuS + $Cu_{1.8}S$, the presence of flower like morphology along with hexagonal plates were observed Figure 4c.

To clarify whether the duration of the reaction has an effect on the final stoichiometry, $[Cu(tu)_3]Cl$ was refluxed for 4 h in ethylene glycol which resulted again in crystalline $Cu_{1.8}S$ (Supporting Information, Figure S7 a). To determine whether the

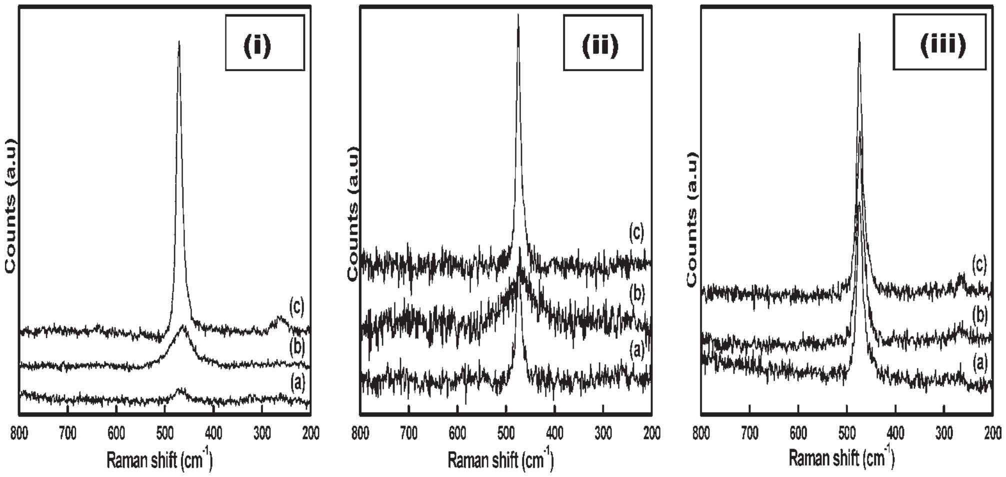

Figure 5. Raman spectrum of the dissociated products from **(i)** $[Cu(tu)_3]Cl$, **(ii)**$[Cu_2(tu)_6]SO_4 \cdot H_2O$, **(iii)** $[Cu_4(tu)_9]$ $(NO_3)_4 \cdot 4H_2O$. (a), (b), and (c) in each spectrum denotes the dissociation of the precursor in EG in air, solvothermal, and EG in flowing Ar, respectively.

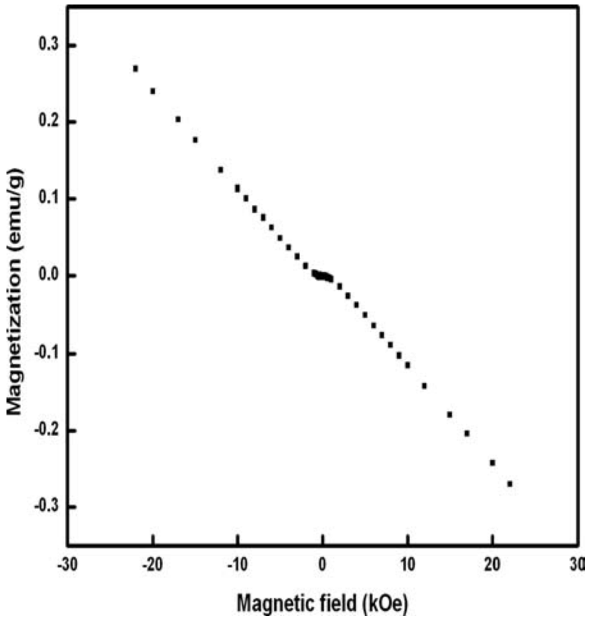

Figure 6. Plot of magnetization versus applied field of $Cu_{1.8}S$ at 300 K.

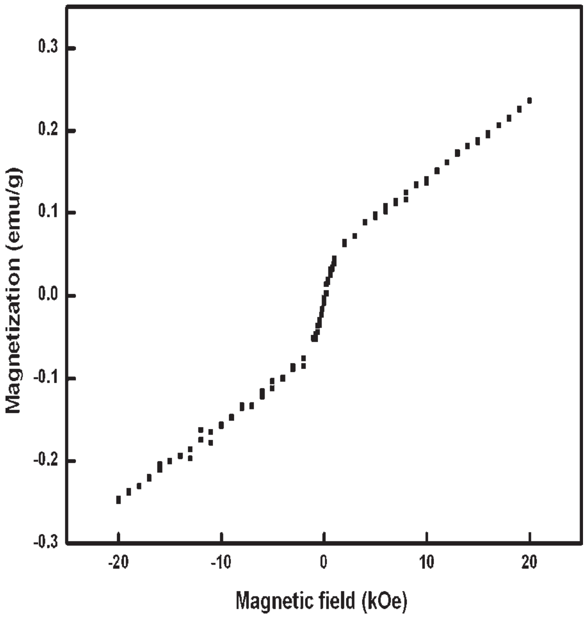

Figure 7. Plot of magnetization versus applied field of CuS at 300 K.

autogenously generated pressure had an effect on the phase transformation of $Cu_{1.8}S$, $Cu_{1.8}S$ (obtained after refluxing for an hour from $[Cu(tu)_3]Cl$) was treated solvothermally for 12 h at 150 °C. After the reaction, the product contained only $Cu_{1.8}S$ (Supporting Information, Figure S7 b) suggesting the absence of any phase transformation. To verify the effect of the ratio of copper to thiourea (sulfur source) on the final stoichiometry, one mole of $CuCl_2 \cdot 2H_2O$ and five moles of thiourea were mixed and dissociated in ethylene glycol for 1 h, yielding again in $Cu_{1.8}S$ (Supporting Information, Figure S8). All these results pointed out that neither the time of dissociation nor the pressure did alter the final stoichiometry of $Cu_{1.8}S$. Even, excess sulfur did not result in a change of the composition of the final product. But, a commonality in all these trials is the presence of chloride ion in the starting precursor or in the copper salt. Therefore, one can rationalize that $Cu_{1.8}S$ would be the only product from copper chlorides and thiourea and $[Cu(tu)_3]Cl$ could possibly be the intermediate formed in the previous reports whenever the product obtained was $Cu_{1.8}S$ in ethylene glycol starting from CuCl. A careful examination of the literature reports that in produced copper rich sulfides, for example, $Cu_{1.75}S$ or $Cu_{1.93}S$, the starting copper source had chloride anion.[30,21]

CuS was obtained earlier from the reaction of $Cu(NO_3)_2 \cdot 3H_2O$ and thiourea in ethanol/water mixed solvent systems or by reacting $Cu(NO_3)_2 \cdot 0.3H_2O$ with elemental sulfur in ethylene glycol.[31] However, the ultrasonic waves assisted reaction of $Cu(NO_3)_2 \cdot 3H_2O$ with elemental sulfur yielded Cu_7S_4 nanoparticles in presence of 1-decanethiol[32] and not in ethylene glycol solvent system. Using $CuSO_4 \cdot 5H_2O$, both CuS and Cu_2S were prepared using $Na_2S_2O_3$ solution and with dimethylsulfoxide (DMSO), respectively.[33,34]

From all these results, it is conclusive that the anion of the precursors participates in the redox chemistry leading to the formation of $Cu_{1.8}S$ and CuS. The variation in the product stoichiometry from copper rich sulfides (Cu_2S, $Cu_{1.8}S$) to lower copper compositions (CuS) can be reasoned out by stating that

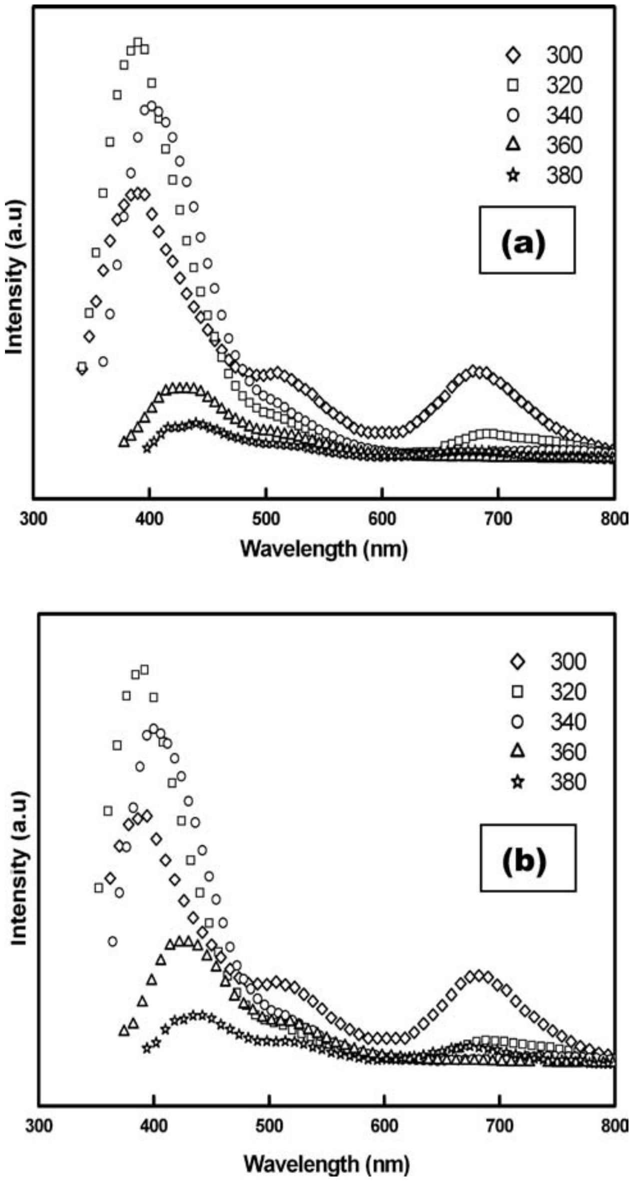

Figure 8. Room temperature photoluminescence spectra of (**a**) $Cu_{1.8}S$ and (**b**) CuS.

the former is preferred under relatively more reducing environment generated during dissociation than the latter. The extent of reducing atmosphere has a direct influence on the higher copper ratio in the final copper sulfide. The oxidizing power of the anion increases from Cl^- to SO_4^{2-} to NO_3^- with the corresponding end products $Cu_{1.8}S$, CuS + $Cu_{1.8}S$, and CuS. Also, from the assessment of the thermal stability of Cl^- SO_4^{2-} and NO_3^- containing precursors in the solid state, it was quite evident that the chloride and sulfate ions containing precursors were more stable to heat as compared to the nitrate ion containing complex in which the removal of anion precedes the decomposition of thiourea with increasing temperature (Supporting Information, Figure S4−S6).

Raman spectroscopy, being an ideal tool to probe the local site symmetry and hence the overall symmetry, is employed to characterize $Cu_{1.8}S$ and CuS. It is noteworthy that $Cu_{1.8}S$ possesses rhombohedral symmetry and CuS embraces hexagonal symmetry. Raman shift observed for $Cu_{1.8}S$ was 470 cm^{-1}, while for CuS it was 474 cm^{-1} which has been previously associated with the covellite system (Figure 5).[35] However, in the case of $Cu_{1.8}S$ + CuS, the observed shift was centered at 473 cm^{-1} (Figure 5).

Magnetization measurements at room temperature were carried out to elucidate the valence of copper ion in $Cu_{1.8}S$ and CuS. While $Cu_{1.8}S$ showed diamagnetic behavior signifying the +1 oxidation state of copper with $3d^{10}$ configuration (Figure 6), weak paramagnetism, with a χ_M value of 1.198×10^{-3} emu/mol, was observed for CuS, matching well with earlier reports (Figure 7).[36]

The copper rich $Cu_{1.8}S$ and CuS was further characterized by the photoluminescence spectroscopy at room temperature (Figure 8). Both $Cu_{1.8}S$ and CuS showed an identical emission behavior as shown in Figure 8a,b. When $Cu_{1.8}S$ were excited at λ = 300 nm, 320 nm, 340 nm, 360 and 380 nm, the respective emissions at 387 nm, 390 nm, 403 nm, 425 and 440 nm were observed for $Cu_{1.8}S$. For CuS, the corresponding emissions occurred at 388 nm, 390 nm, 401 nm, 423 and 440 nm. The photoluminescence behavior of CuS has not yet been well understood and always has been explained on the basis of morphology affecting the electronic transition.[6,21] The existence of two crystallographically different sulfur sites in CuS has led to the description of bonding as $(Cu^{1+})_3S_2^{2-}S^-$ or $(Cu^{1+})_3S_2^-S^{2-}$.[37] The common factor in both CuS and $Cu_{1.8}S$ is the presence of Cu^+, and the essential distinction is the presence of the $(S-S)^{2-}$ linkage in CuS and S^{2-} in $Cu_{1.8}S$. Electronic hoping among the electronic transition states of $3d^{10}$ could possibly be held responsible for the same behavior. The origin of the photoluminescence in copper sulfides of various stoichiometries has not yet been understood well, and hopefully the results of the present study would strengthen the need.

4. CONCLUSIONS

The present investigation had resulted in important conclusions that the anions of the precursor play a critical and decisive role on the formation of the $Cu_{1.8}S$ and CuS when dissociated in ethylene glycol. Monophasic rhomboheral $Cu_{1.8}S$ was obtained from the $[Cu(tu)_3]Cl$, and pure hexagonal CuS was the product of dissociation from $[Cu_4(tu)_9](NO_3)_4 \cdot 4H_2O$. A mixture of $Cu_{1.8}S$ and CuS was obtained from the precursor containing the sulfate anion, $[Cu_2(tu)_6]SO_4 \cdot H_2O$. The atmosphere of dissociation did not alter the results significantly indicating its abstention in the redox chemistry. Also, the autogenously developed pressure by the ethylene glycol was not found to greatly influence the final product compositions. All these results will be quite advantageous and significant for designing precursors to synthesize binary and ternary metal sulfides containing metals of variable oxidation states.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Further details are given in Table S1 and Figures S1−S8. This material is available free of charge via the Internet at http://pubs.acs.org.

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