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Solvent-Mediated Room Temperature Synthesis of Highly Crystalline Cu_9S_5 ($Cu_{1.8}S$), CuSe, PbS, and PbSe from Their Elements

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Supporting Information

ABSTRACT: Highly crystalline Cu_9S_5 ($Cu_{1.8}S$), CuSe, PbS, and PbSe are obtained by reacting the elements in 2-mercaptoethanol as the solvent for 24 h at room temperature. The elemental reactions of copper and lead with sulfur in ethylene glycol were successful, yielding CuS and PbS, respectively. Metal sulfide formation was not observed using dimercaptoethane.

Metal chalcogenides represent an important class of inorganic materials exhibiting a broad range of interesting optical, electronic, and magnetic properties and thereby have attracted the attention of researchers from various disciplines.[1−4] Superionic conductivity, photovoltaic ability, gas-sensing properties, and solar-energy harvestation are properties of metal chalcogenides, among many, that are worth mentioning. There has been a great demand for simplified synthetic procedures for bulk preparations, as well as the fabrication of these materials in various sizes and shapes, as evidenced from the large number of research publications.[5−7]

Metal and chalcogen are the basic reactant requirements for the synthesis of metal chalcogenides, and on the basis of this perspective, reactions utilizing the appropriate elements can be considered the most straightforward and convenient approach. It will be further more beneficial if the reactions can be conducted at room temperature, yielding crystalline products. The first report on the successful demonstration of the room temperature synthesis of metal chalcogenides from their elements was presented by Parkin and co-workers using liquid ammonia.[8a,b] Parkin's group[8c] further showed the successful use of *n*-butylamine for these reactions. Li et al.[9] employed ethylenediamine to synthesize metal chalcogenides using metal salts as well as metal powders with chalcogen (sulfur/selenium) powders.

The philosophy behind the success of these elemental combination reactions originated from the extensive work of Rauchfuss and co-workers,[10] who reported the complex formation between metal and sulfur powders in the presence of donor solvents such as pyridine (C_5H_5N), 4-(dimethylamino)pyridine [$(CH_3)_2NC_5H_4N$], *N*-methylimidazole ($CH_3C_3H_3N_2$), and tetramethylethylenediamine [$(CH_3)_2NCH_2CH_2N(CH_3)_2$], which upon thermolysis yielded metal sulfides. Further, they could isolate metal polysulfide complexes of manganese, iron, nickel, and magnesium only after several days of reaction.[10] From these reports, it is clear that some amines promote complex formation in elemental combination reactions, while few others produce metal chalcogenides at room temperature. Though the room temperature elemental combination reaction appears to be simple, the intricate chemistry governing the metal chalcogenide formation is yet to be fully understood. The solvent systems for the elemental combination reactions explored until now are mainly based on amines due to the dissolution of sulfur in most of the amines, producing reactive sulfide species.[11a,b] Recently, Ozin and co-workers[11c] have revealed that the sulfur−amine solutions, commonly referred as the "black box" precursor in metal sulfide synthesis, in fact exist as alkylammonium−polyammonium polysulfide. The fact that water (H_2O), THF [$(CH_2)_4O$], acetone [$(CH_3)_2CO$], dichloromethane (CH_2Cl_2), carbon disulfide (CS_2), and cyclohexane (C_6H_{12}) were unsuccessful for metal chalcogenide synthesis at room temperature[8] justifies the exploration of alternate solvents that can facilitate the formation of crystalline metal chalcogenides at room temperature.

The development of a novel synthetic strategy for metal chalcogenides is one of the major focus of our research group.[12] Despite the widespread use of molecular precursors (coordination complexes) consisting of metal−sulfur and metal−selenium bonds for the synthesis of metal sulfides and metal selenides,[13] the use of a sulfur-containing solvent for direct elemental combination reactions for their synthesis at room temperature is lacking. The ability of a mercapto (HS−) functionality to bind with highly chalcophilic metals has been successfully utilized in the synthesis of metal nanoparticles,[14] and therefore a simple thiol, 2-mercaptoethanol, was investigated for the elemental combination reactions at room temperature.

Elemental reactions of metal powders (copper and lead) with sulfur and selenium powders were carried out independently in 2-mercaptoethanol as the solvent, and the products were characterized. Details of synthetic conditions and characterizations are provided in the Supporting Information (SI).

The progress of the reaction in 2-mercaptoethanol is best illustrated between copper and sulfur because they are distinctly colored and the reaction can be monitored by just observing the color of the product in the reaction flask. The color of the suspension changed to black within a few hours of stirring, indicating the initiation and propagation of the reaction (Figure S1 in the SI). The powder X-ray diffraction (PXRD) pattern of the product (Figure 1a), from the reaction of copper and sulfur (in a 1:1 mole ratio) in 2-mercaptoethanol after 24 h, contained reflections whose positions and intensities match closely with

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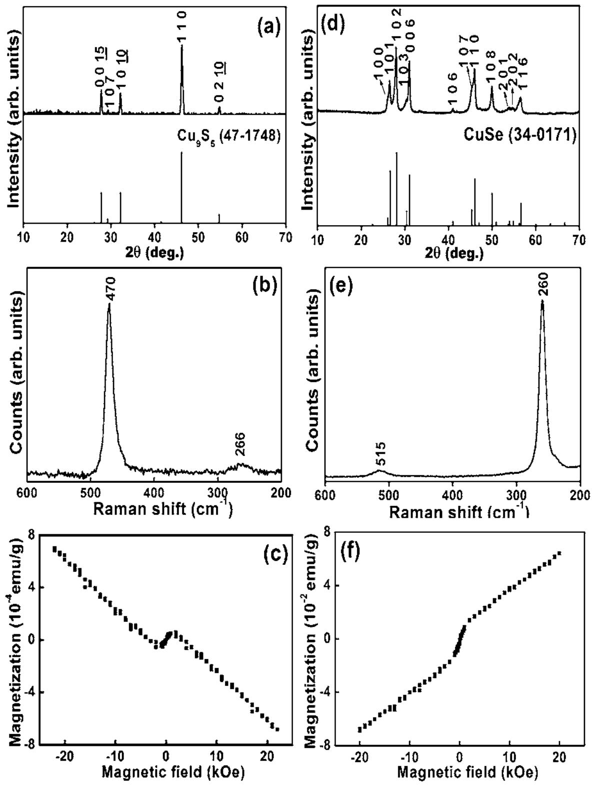

Figure 1. (a) PXRD pattern, (b) Raman spectra, and (c) $M-H$ plot of the product from the reaction of copper and sulfur powders in 2-mercaptoethanol at room temperature for 24 h. (d) PXRD pattern, (e) Raman spectra, and (f) $M-H$ plot of the product from the reaction of copper and selenium powders in 2-mercaptoethanol at room temperature for 24 h. JCPDS patterns are provided for reference.

$Cu_9S_5(Cu_{1.8}S)$ (JCPDS file no. 47-1748). The peaks can very well be indexed in rhombohedral symmetry with a = 3.951 Å and c = 48.13 Å. The presence of the S−S stretching mode at 470 cm^{-1} (Figure 1b) in the Raman spectrum strongly suggested the product to be $Cu_9S_5(Cu_{1.8}S)$.[12,15] The room temperature diamagnetic character also supported the product to be copper sulfide, in which the copper existed in the 1+ oxidation state (Figure 1c).[12b,16] Hexagonal CuSe resulted from the reaction of copper and selenium powders (in a 1:1 mole ratio), as endorsed by the peak positions and intensities in its PXRD pattern (JCPDS file no. 34-0171; Figure 1d). The peaks were indexable, taking a = 3.939 Å and c = 17.25 Å as the lattice constants. A natural question arises as to whether sulfur would also be present in the lattice with selenium when a sulfur-containing solvent is used for the synthesis of metal selenides. This is particularly applicable to copper metal because a continuous solid solution, $CuS_{1-x}Se_x$ has been reported.[17]

Ishii et al.[18] employed Raman spectroscopy as the pivotal tool to study the solid solution $CuS_{1-x}Se_x$ in which the progressive disappearance of the S−S stretching mode at around 460 cm^{-1} with the emergence of the Se−Se stretching mode positioned at around 270 cm^{-1} was reported to occur as the selenium content increased. The absence of the S−S stretching mode (at 470 cm^{-1}), together with the presence of a band at 258 cm^{-1} (due to Se−Se stretching), confirmed the formation of CuSe without sulfur in the lattice (Figure 1e). Energy-dispersive X-ray (EDX) analysis [of its scanning electron microscopy (SEM) image] also confirmed the ratio of copper to selenium to be very close to unity (Figure S2 in the SI). The characteristic paramagnetic behavior of CuSe[16] was observed at room temperature with χ_g of 4.02 × 10^{-6} emu/g (Figure 1f). The use of 2-mercaptoethanol for the room temperature elemental combination reactions was extended to lead, a nontransition metal. The PXRD pattern of the product from the reaction of lead and sulfur powders (in a 1:1 mole ratio) clearly indicated the formation of highly crystalline cubic PbS (JCPDS file no. 78-1901), with the observed reflections being indexable with a = 5.931 Å (Figure 2a). The cubic symmetry of PbS was also supported by the presence of the fundamental Raman band at 135 cm^{-1} and the first overtone at 270 cm^{-1} (Figure 2b).[15] An increased cubic unit cell of a = 6.105 Å was observed for PbSe from its PXRD pattern (Figure 2c), matching closely with JCPDS file no. 78-1902.

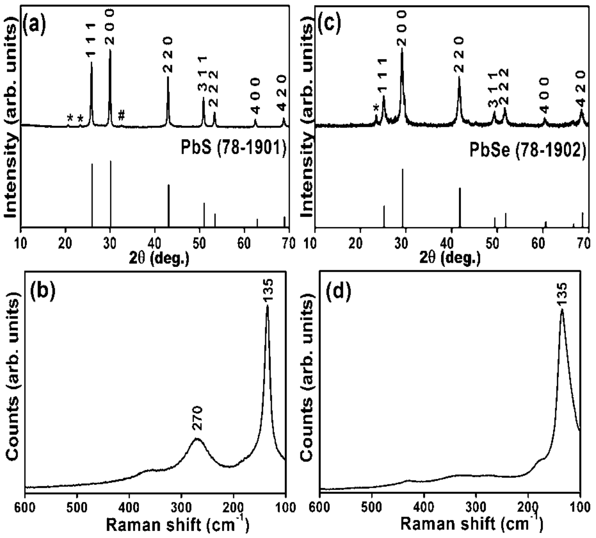

Figure 2. PXRD pattern and Raman spectra (a and b) of the product from the reaction of lead and sulfur powders in 2-mercaptoethanol at room temperature for 24 h. PXRD pattern and Raman spectra (c and d) of the product from the reaction of lead and selenium powders in 2-mercaptoethanol at room temperature for 24 h. (The * in parts a and c denote reflections due to unreacted sulfur and selenium, respectively. # denotes reflections due to lead.) JCPDS patterns are provided for reference.

To verify whether a simple mechanochemical reaction (due to the vigorous stirring) might be promoting the copper sulfide formation (in which the solvent remains as a mute spectator), copper and sulfur powders (in a 1:1 mole ratio) were suspended in 2-mercaptoethanol at room temperature without stirring. Black colored product indicated the formation of copper sulfide as revealed in its PXRD pattern (Figure S3 in the SI). The broadness of the observed reflections in the PXRD pattern suggested nanosized crystallites (with average size of 6 nm as estimated by Schreer analysis). SEM analysis showed agglomeration of nano crystallites (Figure S3 in the SI). This observation provided evidence that the metal chalcogenides are indeed formed from the concerted chemical reaction between the metal and chalcogen in 2-mercaptoethanol, whose crystallinity is further improved by the mechanical stirring. Varying the copper-to-sulfur ratio (2:1 or 1:2) yielded $Cu_9S_5(Cu_{1.8}S)$ as the sole crystalline product, suggesting that the final product stoichiometry was not governed by the ratio of the reactants.

Additionally, dimercaptoethane and ethylene glycol were also examined as solvents for these reactions. While CuS could be identified as the product after 24 h of reaction in ethylene glycol, copper sulfide formation was not observed in dimercaptoethane (Figure S4 in the SI). The reaction of lead powder with sulfur powder in ethylene glycol also yielded PbS (with unreacted lead and sulfur) as deduced from its PXRD pattern (Figure S4 in the SI). The reaction of selenium powder with copper powder in ethylene glycol indicated few reflections due to CuSe in its PXRD pattern (Figure S5 in the SI).

Copper (in powder form), having the native oxide layer, is known to chemisorb multilayers of thiols.[19] The preparation of copper thiolates (containing aliphatic groups) has been reported to be unsuccessful in most cases, and those prepared in situ had very short lifetimes in solution.[20,21] The fact that the reactions in dimercaptoethane did not yield copper sulfide and the reactions in 2-mercaptoethanol and ethylene glycol produced crystalline copper and lead sulfides at room temperature reinforces the existence of intriguing chemistry involved in these reactions. Further investigations, such as the detection of the real driving force for this redox reaction, isolating the intermediates (generated if any) are required to ascertain the plausible mechanism behind the formation of metal chalcogenides using these solvents. Efforts in this direction are in progress.

Scope of the Reaction. This work has provided a new direction for synthetic chemists and elucidating the mechanism of these reactions will be of fundamental importance.

***Caution!** Because thiols are toxic having stench, the reactions must be conducted in the fume hood and in sealed flasks.*

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Digital photograph of the progress of the reaction between copper and sulfur in 2-mercaptoethanol at room temperature, SEM-EDX analysis of CuSe, PXRD pattern of the product from the unstirred reaction of copper and sulfur powders in 2-mercaptoethanol and its SEM image, and PXRD patterns of the product from the reaction of copper with sulfur, lead with sulfur, and copper with selenium in ethylene glycol. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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