Room Temperature Synthesis of Metal Chalcogenides in Ethylenediamine

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Reaction of sulfur and selenium with elemental or ionic metals in liquid ethylenediamine at room temperature produced metal chalcogenides ME (M = Cu, Sn, Co^{2+}, Ni^{2+}, Mn^{2+}, or Pb^{2+}; E = S or Se), Ag_2E, M_2E_3 (M = Bi or Sb). The results showed that the products had a range of crystalline sizes from 10 to 100 nm. Some reactions produced molecular precursors. Heat treatment of these precursors at 250 °C under a N_2 atmosphere induced crystalline chalcogenides. The pre- and postheated metal chalcogenides were analyzed by X-ray diffraction (XRD). Some key compounds are analyzed by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The roles of ethylenediamine in the reaction system are also discussed in this report.

Introduction

Ethylenediamine, as a strong coordinating agent, was extensively employed in inorganic synthesis recently. Sulfur can dissolve in ethylenediamine completely and form deep green solutions.[1] Data in these solutions have been investigated, and formation of a range of sulfur anions, cations, and sulfur−nitrogen species occurred.[1] GeS_2 and CdS nanorods have been synthesized successfully via sulfur−ethylenediamine solutions.[2,3] Mecury oxide reacts with sulfur−ethylenediamine solutions to form HgS nanocrystals.[1] Dissolution of selenium in liquid ethylenediamine to give color solutions has not been reported; however, HgO and selenium in liquid ethylenediamine can react to produce HgSe crystals.[1]

Metal chalcogenide synthesis has been reported many times in the literature. The most straightforward route to transition-metal chalcogenides is the combination of the elements at high temperature.[4] This process requires a significant energy input and gives little control in particle size of products. Such elemental combination reactions can also be promoted in a microwave oven where the synthesis time is significantly reduced.[5] A low-energy approach is the precipitation of metal chalcogenides from aqueous solutions of the metal cation by use of H_2E(E = S, Se, or Te).[6] Problems with this method include the use of very toxic reagents and consistently obtaining the product with a high degree of purity. Molecular precursor methods[7−12] involving thermal decomposition of a compound containing a M−S and M−Se bond, or involving H_2E as the chalcogen source,[13] have been thoroughly investigated and need significantly lower temperatures than those of conventional elemental synthesis. The elemental reaction between zinc or copper with sulfur at reflux in strongly coordinating solvents such as pyridine and *N*-methylimidazole also has been developed.[14−16] This forms complexes of the form $M(S_6)(solv)_2$ that can be thermally decomposed at 500 °C to form a binary chalcogenide such as ZnS.[14−16] Similar low-energy approaches involving $[Cu(en)_2]^{2+}$ and thiourea have enabled essentially amorphous CuS to be made at room temperature.[17]

Parkin et al[18] reported the preparation of both crystalline and amorphous transition- and main-group metal chalcogenides from elemental reactions in liquid ammonia. Most of the products Parkin et al. obtained are amorphous, but they become crystalline after heat treatment at 300 °C. One problem with Parkin's method is the low b.p. (boiling point) of ammonia that makes raising the temperature above the b.p. impossible. This gives little chemical control over the morphology of the products.

In this paper we report a room temperature synthetic route to crystalline transition- and main-group metal chalcogenides from elemental and ionic reaction in liquid ethylenediamine. By controlling the reaction temperature, we can control the morphology of the products well.

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Experimental Section

All reagents were of 99.9% purity or better and used without further purification. Ethylenediamine has a trace of water and was used without drying. Most reactions were carried out at temperature 10 −20 °C. X-ray diffraction (XRD) patterns were determined on Japan Rigaku Dmax rA X-ray diffractometer with graphite monochromatized $CuK\alpha$ radiation ($\lambda = 1.5418$ Å). They were indexed using JCPDS cards. To obtain further information about stoichiometry of some key compounds, X-ray photoelectron spectroscopy (XPS) analysis were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using non-monochromatized Mg $K\alpha$ as the excitation source and choosing C1s (284.60eV) as the reference line. TEM images were carried out on a Hitachi model H-800 transmission electron microscopy, using an accelerating voltage of 200 kV.

Reactions of Cu, Sn, Mn^{2+}, Ni^{2+}, and Co^{2+} with Sulfur in Liquid Ethylenediamine. The same general reaction scale and procedure was adopted for all the reactions exemplified here for CuS.

Powder copper metal (0.32 g, 0.005 mol) and sulfur (0.24 g, 0.075 mol) were added to liquid ethylenediamine (10 mL) in a vessel at room temperature and magnetically stirred for about 12 h. The mixture changed to a dark green/black color and finally to green with a black precipitate. The precipitate was collected by filtering the solution and then washed with water and ethanol. Then the sample obtained was heated until dry at 70 °C. The sample was analyzed by XRD. XPS and TEM analyses were also carried out to obtain further information.
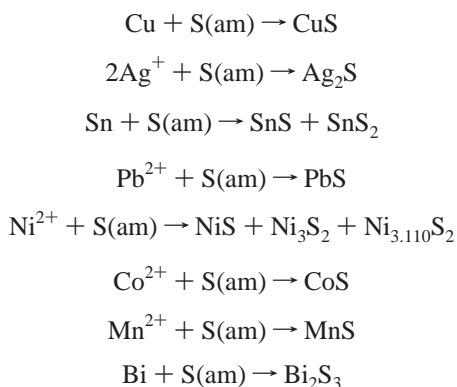
Reactions of Bi and Sb with Sulfur or Selenium in Liquid Ethylenediamine. The same general reaction conditions and scale were used like the Cu case except that the reactants ratio M(M = Bi,Sb): E(E = S,Se) was 2:3.

Reactions of Ag^+ and Pb^{2+} with Sulfur in Liquid Ethylenediamine. The same reaction conditions and scale were used as detailed above for Cu except that in the silver reaction a Ag:S ratio of 2:1 was employed. In both cases the products formed were crystalline as assessed by X-ray diffraction and did not require heating for characterization. The samples obtained were analyzed by XPS and TEM means.

Reactions of Selenium with Metals in Liquid Ethylenediamine. The same reaction scale and conditions were employed as described above for CuS reactions. The products were analyzed by XRD. Some of the products were precursors that have many unknown peaks. After heat treatment at 250 °C at N_2 atmosphere, crystalline chalcogenides were produced.

Results and Discussion

Sulfides: Synthesis and Characterization. Reactions of a range of transition- and main-group metals elements or cations with sulfur−liquid ethylenediamine solutions [S(am)] at room temperature in a vessel produced metal sulfides in good yield. We selected the following typical metal elements or ions to investigate, and equations are listed as following:
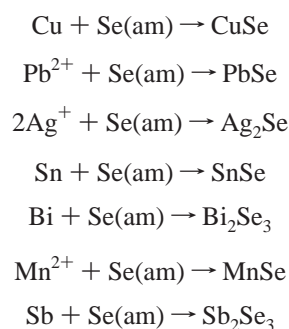
$$Cu + S(am) \rightarrow CuS$$

$$2Ag^+ + S(am) \rightarrow Ag_2S$$

$$Sn + S(am) \rightarrow SnS + SnS_2$$

$$Pb^{2+} + S(am) \rightarrow PbS$$

$$Ni^{2+} + S(am) \rightarrow NiS + Ni_3S_2 + Ni_{3.110}S_2$$

$$Co^{2+} + S(am) \rightarrow CoS$$

$$Mn^{2+} + S(am) \rightarrow MnS$$

$$Bi + S(am) \rightarrow Bi_2S_3$$

Reactions of Pb^{2+} and Ag^+ with sulfur−ethylenediamine solutions produced pure crystalline sulfides Ag_2S and PbS which

indexed according to the literature.[19] XPS spectra show that the ratio of metal element to sulfur element is close to stoichiometry of the compounds. All of the materials obtained had crystalline sizes in the range of 10−100 nm on the basis of the Scherrer equation.[20] TEM images also attest this. Reaction of Co^{2+} with S(am) produced a kind of molecular precursor without CoS and unreacted reactant $CoCl_2$. After heating at 250 °C under a N_2 atmosphere for 0.5 h, crystalline CoS is obtained. Reaction of Mn^{2+} and S(am) produced some α-MnS and molecular precursor, and heat treatment at 250 °C under a N_2 atmosphere induced crystalline α-MnS. Reaction of copper with S(am) produced large amounts of crystalline CuS and a little of the molecular precursor. After heat treatment at 250 °C under N_2 atmosphere for 0.5 h, we obtained pure crystalline CuS. Quantification of the peaks from the XPS spectra gives the ratio of Cu to S near to 1:1. Reaction of Ni^{2+} or tin with S(am) produced inhomogeneous products. In the tin case, most of the tin remained unreacted and little of sulfide was obtained at temperatures of 10−20 °C. When the reaction temperature was raised to 150−160 °C, the products obtained were mostly SnS, SnS_2, and a little unreacted tin (less than 5%). In the Ni^{2+} reaction the XRD pattern showed that NiS, Ni_3S_2, $Ni_{3.110}S_2$, and molecular precursors are present. Heating the nickel and tin products at 250 °C under a N_2 atmosphere for 0.5 h formed SnS, NiS, Ni_3S_2, and $Ni_{3.110}S_2$. SnS_2 is thermally unstable,[21] so the products after heating made up of only SnS.

Reaction of antimony with sulfur−ethylenediamine solutions under the same conditions as above was also investigated. The reaction products are related to the reaction time. The reaction solutions changed to dark green to black, and if the reaction time extended over 8 h, the solutions changed to dark yellow without any precipitate left. But if we controlled the reaction time and the ratio of Sb to S, we can obtain Sb_2S_3(XRD pattern determined this). In this case, we propose an explanation as follows:

$$Sb + S(am) \rightarrow Sb_2S_3$$

$$Sb_2S_3 + S_2^- \rightarrow [SbS_4]^{2-}$$
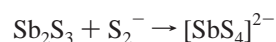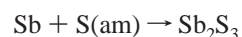
Selenides: Synthesis and Characterization. Reactions of selenium with various transition- and main-group metals in liquid ethylenediamine were investigated. Equations were listed as follows:

$$Cu + Se(am) \rightarrow CuSe$$

$$Pb^{2+} + Se(am) \rightarrow PbSe$$

$$2Ag^+ + Se(am) \rightarrow Ag_2Se$$

$$Sn + Se(am) \rightarrow SnSe$$

$$Bi + Se(am) \rightarrow Bi_2Se_3$$

$$Mn^{2+} + Se(am) \rightarrow MnSe$$

$$Sb + Se(am) \rightarrow Sb_2Se_3$$

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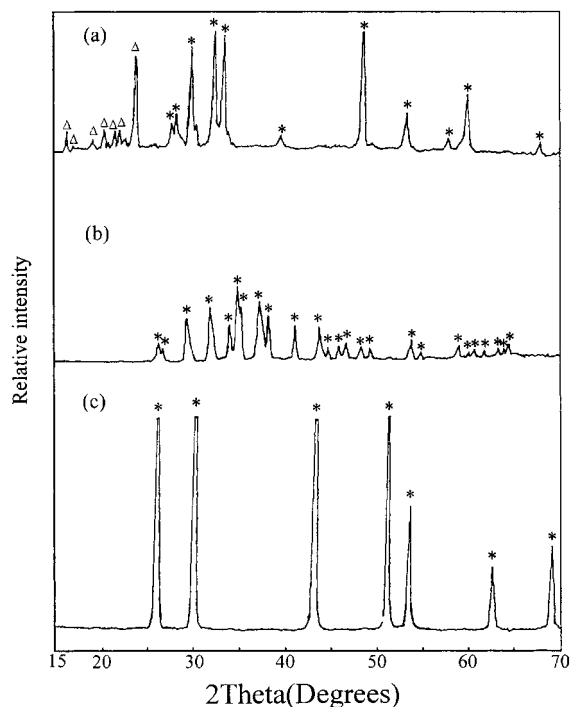
Figure 1. X-ray diffraction (XRD) patterns of selected sulfide samples. (a) XRD pattern of CuS sample: ($\triangle$) peaks of molecular precursor; (*) peaks of CuS crystal. (b) XRD pattern of Ag$_2$S sample: (*) peaks of Ag$_2$S crystal. (c) XRD pattern of PbS sample: (*) peaks of PbS crystal.
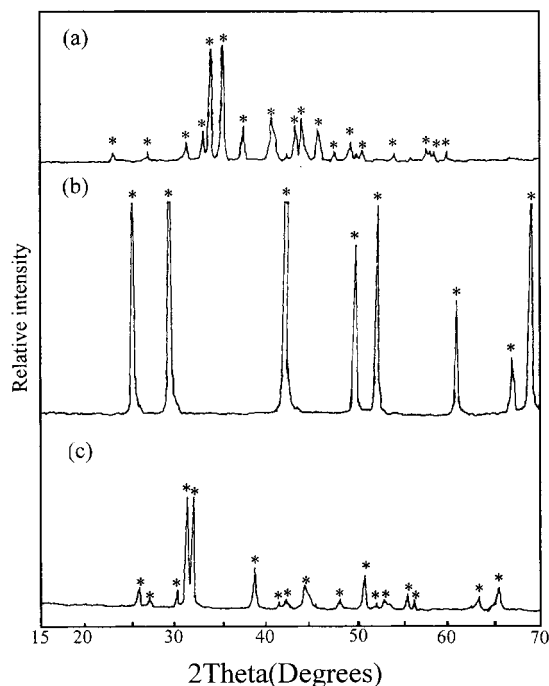

Figure 2. X-ray diffraction (XRD) patterns of the selected selenide samples. (a) XRD pattern of Ag$_2$Se sample: (*) peaks of Ag$_2$S crystal. (b) XRD pattern of PbSe sample: (*) peaks of PbSe crystal. (c) XRD pattern of SnSe sample: (*) peaks of SnSe crystal.

Product workup and analysis were identical to the cases described for sulfur above. Unlike the reaction of copper metal with S(am) which produced the most crystalline CuS, reaction of copper metal with selenium in liquid en produced almost all molecular precursor. The silver and lead selenides were crystalline prior to heating as had been the cases observed for sulfur. Reactions of bismuth metal with sulfur or selenium in liquid

ethylenediamine both produced molecular precursors without crystalline Bi$_2$S$_3$ or Bi$_2$Se$_3$ prior to heating. Unlike the sulfur reactions, tin metal reactions with selenium produced SnSe and a little unreacted tin (less than 5%) at temperatures of 150−160 °C, however the products were almost all of unreacted tin at temperatures of 10−20 °C. Reactions of Mn^{2+} with selenium-(am) produce molecular precursor without the MnSe phase, unlike the reaction of Mn^{2+} with sulfur in liquid ethylenediamine. Since the dissolution of selenium in liquid ethylenediamine is different from that of sulfur, from the reaction of Sb with selenium we obtained crystalline Sb$_2$Se$_3$, which differs from the sulfur reaction.

Scope of the Reaction. The reactions are all of redox type with the metal element being oxidized. The nature of the oxidizing agent in the solution has yet to be investigated. Sulfur−ammonia solutions have been shown to contain various sulfur imides (e.g., S$_7$NH) as well as sulfur−nitrogen anions sulfur polyanions (S$_6^{2-}$, S$_4^-$, S$_4$N$^-$, S$_7$NH).[22] Analogy to sulfur ammonia solutions, sulfur−ethylenediamine solutions are reported to contain above anions, including S^{2-}.[1]

These anions could be responsible for the redox chemistry. The ethylenediamine solution acts not only to produce the active sulfur species in solution but could also play a role in activating the metal surface and in electron transfer in the reacting system. It is known that some metals such as mercury will react with sulfur at room temperature.[23] The reaction is, however, largely surface limited and for most metals slow. This may be, in part, due to a passive surface oxide coating. The ethylenediamine may act to remove this coating and so facilitate contact between the metal and the dissolved sulfur, thereby promoting the reaction. Another important factor that should be noted is that ethylenediamine is a strong coordinating agent. Many metallic elements or cations can coordinate with en to form fairly stable complexes. The K_{sp} of MS is also a significant factor affecting the formation of MS.

$$[M(en)_2]^{2+} + S^{2-} \rightarrow MS + 2en \qquad (*)$$
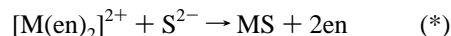
There is competition between the formation of [M(en)$_2$] and the formation of MS precipitate. The stability constant of complex (β_2) and the K_{sp} together decide the reaction direction and yield of MS.

$$K* = [MS][en]^2/[S^{2-}][M(en)_2] = 1/K_{sp}\beta_2$$

We can take Cu, Ag$^+$, for example, to discuss.

$$Cu \xrightarrow{en} Cu^{2+} + 2e$$

$$Cu^{2+} + 2en \rightarrow [Cu(en)_2]^{2+}$$
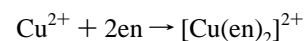
$$K^*_{Cu} = 1/K_{sp}\beta_2 = 1.7 \times 10^{15}$$

In analogy to Cu case:

$$K^*_{Ag} = 1/K_{sp}\beta_2 = 3.2 \times 10^{41}$$

From the above computations, we could predict that the formation of Ag$_2$S is easier than that of CuS. Experiments show that reaction of Ag$^+$ with S(am) produced all Ag$_2$S but Cu reaction produced CuS and some molecular precursor. In the

(22) Belton, P.; Parkin, I. P.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1989**, 511.

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reaction of M or M^{2+} with S(am), en may also act as a buffering medium. It is also known that some metal cations such as Cu^{2+} can easily react with S^{2-} to form the CuS precipitate. But the CuS particle size is large and particle agglomeration is clearly observed. We have compared the products of the Cu reaction with the Cu^{2+} reaction and found that although the rate of the former reaction is slower than the latter one, the morphology of the former products is better than that of the latter ones. So en also plays an important role in chemical control during synthesis. As to the molecular precursor, we propose the complex structure $M(S_6)(en)_2$ may be formed analogous to the $M(S_6)(solv)_2$ structure reported in the literature.[14−16] $M(S_6)(en)_2$ thermally decomposes at 250 °C under N_2 atmosphere to form a binary chalcogenide MS.

Among the metal sulfides we have synthesized, CdS, PbSe, and PbS are one-dimensional in structure (TEM images show this). In the literature,[3] we have proposed the following self-assembly mechanism via complex intermediates:

$$[M(en)_2]^{2+} + S^{2-} \rightarrow MS + 2en$$
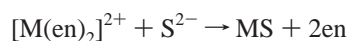
$[M(en)_2]^{2+}$ complex plays an important role as an intermediate to form MS nanorods or nanowire. In our experiment to prepare to PbSe nanowire, we added reducing agents like KBH_4, NaH, and NaH_2PO_2 to the reaction system and we found that these reducing agents played the same roles in this reaction system. They promoted the formation of PbSe phase and elevated the rate of reaction but had no effect on the formation of nanowire. PbSe nanowire structure is also formed via complex intermediate $[Pb(en)_2]^{2+}$ as we have discussed in CdS case[3]:

$$[Pb(en)_2]^{2+} Se^{2-} \rightarrow PbSe + 2en$$
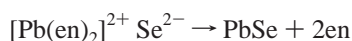
The metal selenide reactions differed from the sulfur−ethylenediamine solutions in that elemental selenium seemed to dissolve little in the ethylenediamine during the course of the reaction. The products of the reactions ME(E = S, Se) were affected not only by the K_{sp}, β_2 of $[M(en)_2]^{2+}$ but also by the concentration of active E^{2-}. For example, K_{sp}(CuS), 1×10^{-36}, is larger than K_{sp}(CuSe), 1×10^{-49}. However, XRD patterns showed that sulfur reactions produced mostly CuS and some molecular precursor, while the selenium reaction produced essentially all molecular precursor (Figures 1 and 2). The low concentration of active Se^{2-} in the selenium system may explain this phenomenon.

Conclusions

Sulfur and selenium in en react with some elemental or ionic metals at room temperature to form crystalline chalcogenides. Some of the reactions produced molecular precursor, and so heat treatment at 250 °C under a N_2 atmosphere was needed to form crystalline chalcogenides. Chemical control of synthesis in liquid ethylenediamine can be realized by adjusting the reaction temperature. Ethylenediamine plays an important role in electron transfer in redox reactions and formation of binary chalcogenides nanorods or nanocrystalls. The dissolution of chalcogen in ethylenediamine also affects the formation of chalcogenides.