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Convenient, room-temperature, amine-assisted routes to metal sulfides, selenides and tellurides†

Vincent Dusastre, Bashe Omar, Ivan P. Parkin* and Graham A. Shaw

Chemistry Department, Christopher Ingold Laboratories, University College London,
20 Gordon Street, London, UK WC1H 0AJ

The reaction of elemental powders of Ag, Pb and Hg with S, Se or Te in *n*-butylamine for 12–72 h produced crystalline metal chalcogenides ME (M = Pb or Hg; E = S, Se or Te) and Ag_2E in good yield (>90%). The reactions of Cu with Se or Te in *n*-butylamine gave crystalline $Cu_{2-x}Se$ and $Cu_{0.64}Te_{0.36}$, whilst the reaction of Cu or Ni with sulfur under similar conditions produced an amorphous material that on heating to 250–300 °C for 2 h yielded crystalline NiS and Cu_2S. Products were analysed by Fourier-transform IR, Raman spectroscopy, scanning electron microscopy with energy dispersive analysis by X-rays, powder X-ray diffraction and X-ray photoelectron spectroscopy. The elemental reactions were also investigated in *n*-hexylamine, ethane-1,2-diamine, cyclohexane and aqueous ammonia solution.

Late transition-metal and main-group metal sulfides, selenides and tellurides have a number of commercial applications in pigments, semiconductors and fluorescence devices.[1] They are traditionally made by elemental combination reactions at high temperatures for prolonged times;[2] these reactions typically produce the thermodynamic products with little control in stoichiometry or crystallinity.

Many metal chalcogenides are found in nature as minerals.[1] A wide range of techniques has been developed to synthesize metal chalcogenides with control of micro structure and particle size. These developments include Self propagating High temperature Synthesis (SHS),[3] molecular precursor reactions (involving either the thermal decomposition of compounds containing M–S or M–Se bonds[4] or H_2E as the chalcogen source[5]), and the use of templating agents that utilise restrictive environments[6] (zeolites and micelles). Much of this work has been focused on the formation of controllable nanoparticulate chalcogenides (especially PbS, PbSe, CdS and CdSe[7]). These nanoparticulates exhibit quantisation effects that have a potential use for optical signal processors and switches.[8] Such materials have been prepared using H_2E (E = S or Se) by aerosol pyrolysis decomposition at elevated temperatures,[9] arrested precipitation of micelles[10] and trapping within a polymer matrix[11] or glass.[12] Single-source molecular precursors have also proved to be successful using moderately high temperatures[13] (250 °C). Other work has shown that Solid State Metathesis (SSM) reactions can be utilised for the formation of metal chalcogenides by treating alkali-metal sulfides with metal halides.[14] Most of this work involves the use of high temperatures either from a conventional oven or, in the case of SSM and SHS reactions, from the inherent exothermicity of the reaction.

The most straightforward way of preparing metal sulfides would be the direct combination of the elements at room temperature and pressure. Rauchfuss and co-workers[15] have shown that it is possible to combine zinc and sulfur by refluxing the elements in strongly co-ordinating solvents, such as pyridine (py), to form complexes of the form $M(S_6)(py)_2$. These complexes can be thermally decomposed[15] at 500 °C to form the binary chalcogenide ZnS. Similar low-energy approaches, involving $[Cu(en)_2]^{2+}$ (en = ethane-1,2-diamine) and thiourea, have enabled essentially amorphous CuS to be made at room temperature.[16]

In a previous paper[17] we reported that the reaction of sulfur with some elemental metals in liquid ammonia at room temperature in a pressure vessel (*ca.* 7 atm) produced amorphous and crystalline metal sulfides, equations (1) and (2). The

$$\mathrm{M\ (s) + S\ (NH_3) \longrightarrow MS\ (M = Zn, Cd, Hg\ or\ Pb)} \qquad (1)$$

$$\mathrm{2Ag\ (s) + S\ (NH_3) \longrightarrow Ag_2S} \qquad (2)$$

reactions of lead and silver produced essentially crystalline metal sulfides, whilst the other reactions produced amorphous sulfides that could be crystallised by heating at 300 °C for 2 h. These reactions were facilitated by the use of liquid ammonia, which dissolved the sulfur giving coloured reactive solutions. Sulfur also dissolves in amine solutions to form a variety of different colours (red, orange, green) that change with time and cannot be accounted for on the basis of simple dissolution of the S_8 ring.[18] This led us to investigate whether these sulfur–amine solutions could also react with elemental metals.

In this paper we report the convenient preparation of amorphous and crystalline metal chalcogenides from one-step elemental reactions in *n*-butylamine.

Results and Discussion

The reactions of Ag, Pb, Cu and Hg with S, Se or Te in *n*-butylamine at room temperature for 24 h produces crystalline metal chalcogenides Ag_2E, PbE, HgE (E = S, Se or Te) and $Cu_{2-x}Se$, $Cu_{0.64}Te_{0.36}$, equations (3)–(5), in virtually quantitative

$$\mathrm{2Ag + E\ (amine) \longrightarrow Ag_2E\ (E = S, Se\ or\ Te)} \qquad (3)$$

$$\mathrm{M + E\ (amine) \longrightarrow ME\ (M = Pb\ or\ Hg;\ E = S, Se\ or\ Te)} \qquad (4)$$

$$\mathrm{(2-x)Cu + Se\ (amine) \longrightarrow Cu_{2-x}Se} \qquad (5)$$

$$\mathrm{2Cu + Te\ (amine) \longrightarrow Cu_{0.64}Te_{0.36}} \qquad (6)$$

yield (Table 1). The metal chalcogenides were characterised by Fourier-transform IR and Raman spectroscopy which showed broad absorption bands in the region from 600 to 200 cm^{-1}, depending on the sample. The vibrational spectra invariably matched those of authentic samples. No IR stretches corresponding to N–H vibrations were observed. Further, microanalysis showed negligible amounts of C, H and N (less than

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† *Non-SI units employed*: atm = 101 325 Pa, eV ≈ 1.60×10^{-19} J.

Table 1 Summary of experimental data, including reaction times, material colour, the identity of the phases comprising the reaction product before and after thermolysis at 523–573 K (as determined by X-ray powder diffraction studies) and, where possible, a comparison of the lattice parameters of these phases with those obtained from the literature. Phases in square brackets were traces (typically less than 3%)

Ratio of elements	Colour of material	Reaction time/h	Unthermolysed XRD pattern	Thermolysed XRD pattern (250–300 °C, 2)	Lattice parameters (±0.02 Å) (lit. values in parentheses)		
					a	*b*	*c*
Ag : S 2 : 1	Black	48	Ag_2S (acanthite)	Ag_2S (acanthite)	4.48 (4.46)	4.48 (4.46)	4.48 (4.46)
Ag : Se 2 : 1	Black	48	Ag_2Se (naumannite)	Ag_2Se (naumannite)	4.33 (4.33)	7.06 (7.06)	7.76 (7.76)
Ag : Te 2 : 1	Black	48	Ag_2Te (hessite), [Ag]	Ag_2Te (hessite)	8.07 (8.09)	4.47 (4.47)	8.94 (8.96)
Hg : S 1 : 1	Black	24	HgS (metacinnabar)	HgS (metacinnabar)	5.85 (5.85)	5.85 (5.85)	5.85 (5.85)
Hg : Se 1 : 1	Black	24	HgSe (tiemannite)	HgSe (tiemannite)	6.07 (6.07)	6.07 (6.07)	6.07 (6.07)
Hg : Te 1 : 1	Black	24	HgTe (coloradoite)	HgTe (coloradoite)	6.45 (6.45)	6.45 (6.45)	6.47 (6.45)
Pb : S 1 : 1	Black	48	PbS (galena), [Pb]	PbS (galena)	5.93 (5.93)	5.93 (5.93)	5.93 (5.93)
Pb : Se 1 : 1	Black	48	PbSe (clausthalite)	PbSe (clausthalite)	6.12 (6.12)	6.12 (6.12)	6.12 (6.12)
Pb : Te 1 : 1	Black	48	PbTe (altaite)	PbTe (altaite)	6.45 (6.46)	6.45 (6.46)	6.45 (6.46)
Cu : S 1 : 1	Black	24	Amorphous	Cu_2S (chalcocite) + S	—	—	—
Cu : Se 1 : 1	Black	12	$Cu_{2-x}Se$ (berzelianite)	$Cu_{2-x}Se$ (berzelianite)	5.74 (5.77)	5.74 (5.77)	5.74 (5.77)
Cu : Te 1 : 1	Black	72	$Cu_{0.64}Te_{0.36}$		5.10 (—)	5.10 (—)	4.17 (—)
			$[Cu_4Te_3]$	$Cu_{2-x}Te$ (rickardite)	—	—	—
				$Cu_{2-x}Te$ (weissite)	—	—	—
Fe : S 1 : 1	Black	60	Amorphous + Fe	Amorphous	—	—	—
Fe : Se 1 : 1	Black	60	Amorphous + Fe, Se	Amorphous	—	—	—
Fe : Te 1 : 1	Black	60	Amorphous + Fe, Te	Amorphous	—	—	—
Ni : S 1 : 1	Black	36	Amorphous + Ni	NiS (millerite)	3.43 (3.42)	3.43 (3.42)	3.43 (3.42)
Ni : Se 1 : 1	Black	36	Amorphous + Ni	Amorphous + Ni	—	—	—
Ni : Te 1 : 1	Black	36	Amorphous + Ni	Amorphous + Ni	—	—	—
Sb : S 2 : 5	Red	60	Amorphous, Sb	Amorphous, Sb			
As : S 2 : 5	Yellow	24	Amorphous	Amorphous	—	—	—

0.3%), thus indicating that amine is not bound up in the product. Scanning electron microscopy (SEM) revealed small irregularly shaped aggregates (typically of size 3–8 μm), whilst energy dispersive analysis by X-rays (EDAX) commonly showed only the metal and chalcogenide to be present and in the expected elemental ratios across many surface spots (of width 1 μm). In some samples (Table 1) small regions of unreacted metal were observed (<5%). The X-ray photoelectron spectra of the solid from the reaction of silver and tellurium in *n*-butylamine showed the elements with a stoichiometry of $Ag_2Te_{1.03(5)}$. The binding energy values of 367.6 eV for Ag $3d_{\frac{5}{2}}$ and 571.8 eV for Te $3d_{\frac{5}{2}}$ are consistent with the formation of silver telluride (Ag_2Te).[19]

The X-ray powder diffraction (XRD) patterns of the products produced from the reaction of Ag, Pb and Hg with chalcogens in *n*-butylamine are summarised in Table 1. These showed the formation of crystalline metal chalcogenide powders that indexed well and gave cell parameters identical to those in the literature.[20] Crystallite sizes determined by the Scherrer equation[21] were of the order of 300–700 Å. In all of these reactions a single-phase metal chalcogenide product was obtained with the exception of the reactions of Ag with Te and Pb with S where a small trace of unchanged Pb and Ag (*ca.* 2%) was detected. On thermolysis of these powders the trace of metal disappears from the XRD pattern, presumably because of either reaction with a small amount of X-ray amorphous chalcogen or by incorporation within the metal chalcogenide phase.

Treatment of copper with sulfur in *n*-butylamine produced a black X-ray amorphous material that on thermolysis produced crystalline Cu_2S (as assessed by powder X-ray diffraction). Reaction of selenium and tellurium with copper in *n*-butylamine also produced black crystalline solids, $Cu_{2-x}Se$ (berzelianite) (Fig. 1) and predominantly copper telluride $Cu_{0.64}Te_{0.36}$ (with a trace of Cu_4Te_3). It should be noted that the elemental ratio of the starting materials for the copper reactions was 1 : 1 and that the preferred products were effectively 2 : 1. The excess of chalcogenide in the reaction was removed by washing with CS_2. Combination of the elements in the 2 : 1 ratio also produces 'Cu_2E' but without the need of CS_2 washing.

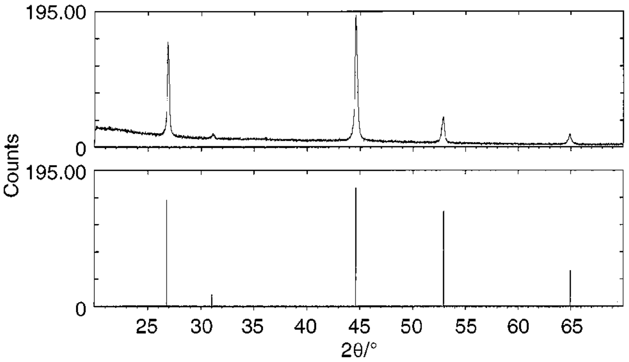

Fig. 1 The XRD pattern (top) obtained for the reaction product of copper with selenium ($Cu_{2-x}Se$). The data base standard for $Cu_{2-x}Se$ (berzelianite) is shown below

The reaction of Fe, Sb or Ni with S, Se or Te in *n*-butylamine at room temperature did produce a slight colour change to the solid. However, both X-ray powder diffraction studies and EDAX analysis of the material showed the presence of the unchanged elements. Only in the case of Ni with sulfur, heating the material at 250–300 °C for 2 h showed the formation of a crystalline chalcogenide (NiS, millerite), although the thermolysed product of the iron reaction showed no unreacted elements. Arsenic reacted with sulfur in *n*-butylamine to afford a yellow solid that was amorphous to X-rays even after heating at 823 K for 2 h. The EDAX analysis showed the correct ratios of arsenic to sulfur, *i.e.* the major product from the reaction (>90%) was arsenic sulfide (As_2S_3). Similar analysis showed that the reaction between antimony and sulfur produced a red solid on the surface of unreacted antimony, whose elemental composition suggests the formation of Sb_2S_3. In both the reactions of As and Sb the initial starting material ratios were 2 : 5 and not 2 : 3, indicating a preference for the lower-oxidation-state sulfides of these elements; the excess of unreacted sulfur was removed from the product by trituration with CS_2. No reaction was observed between Sn or Cd with sulfur in *n*-butylamine even after refluxing the solutions both conventionally (12 h) and by microwave irradiation (2 h).

Reactions were also investigated between Ag, Pb and Hg with the chalcogens at room temperature in a variety of solvents. Although these proceeded in *n*-hexylamine, the reactions were significantly slower (requiring about 1 week to go to completion). The same crystalline phases were observed as for the *n*-butylamine reactions. The use of cyclohexane or ethane-1,2-diamine as a solvent did not promote formation of a crystalline metal sulfide, even after 14 d. Use of aqueous ammonia as solvent for the reaction of Pb and S did facilitate the formation of crystalline PbS within 48 h. However, the product was also contaminated with significant quantities of metal oxide and unchanged metal (*ca.* 75% in total, as determined by EDAX). There was no observed reaction between sulfur and Hg (or Ag) in aqueous ammonia after 48 h.

Sulfur reacts with aliphatic primary and secondary amines to form coloured solutions that have been attributed to the stepwise nucleophilic attack of the S_8 rings by the amine, resulting in first the formation of *N*,*N'*-polythiobisamines (with the *in situ* release of H_2S), and then the progressive attack of the aliphatic amine by hydrogen sulfide to yield amine polysulfides.[18] These new sulfur–amine species coexist and are uniquely coloured, but contain long straight chains of sulfur that are inherently less stable than the original S_8 rings. Hodgson *et al.*[18] suggested that these species would therefore undergo subsequent homolytic scission to form sulfur-based radicals, thereby achieving a degree of resonance stability. It is possible that these radicals are involved in the reaction with the elemental metals. Selenium and tellurium are insoluble in *n*-butylamine yet, as stated above, also react with elemental Ag, Cu, Pb and Hg. Consequently, the amine solvent may play a role in activating the metal or chalcogenide surface, effectively allowing good contact between the elements. In any case, the reactions of selenium and tellurium appear to be solid-state reactions, although the presence of a solvated species of extremely low concentration cannot be ruled out. The time taken for complete reaction (Table 1) suggests that the rate of elemental solid-state diffusion is excellent (especially since a crystalline material is produced). It might be expected that the rates of reaction of sulfur with Ag or Hg would be faster than for selenium and tellurium, since the sulfur fully dissolves in the amine. However, competitive reactions between either of these elements and sulfur/selenium in *n*-butylamine resulted in the preferential formation of Ag_2Se (>95%) and HgSe (>95% as determined by EDAX/XRD). It was found difficult to form solid solutions of the form MS_xSe_y.

Previously[17] we reported the reactivity between elemental metals and chalcogenides in liquid ammonia. Similar results are obtained here, with comparable phases being observed but for two notable exceptions. First, when conducted in ammonia the reaction of sulfur with mercury gave an amorphous powder identified as a mixture of cinnabar and metacinnabar (after heating to 250 °C for 2 h). Yet a single crystalline phase of HgS (metacinnabar) was produced in *n*-butylamine. Secondly, reactions of copper with Se and Te in *n*-butylamine produced predominantly single-phase materials, whilst in liquid ammonia a mixture of phases was observed that included significant amounts of CuTe and CuSe. Elemental reactions in liquid ammonia have a greater scope in that Zn, Cd and Sn all react to form amorphous chalcogenides (with crystalline materials being obtained on heating these powders at 250–300 °C for 2 h). In *n*-butylamine no reaction was observed for these elements, even at reflux, except in the case of Zn and S where the formation of 5–10% amorphous ZnS was observed on the surface of the zinc after 1 week. In the cases where a reaction did occur in *n*-butylamine at room temperature the phases of the metal chalcogenides observed were invariably the same as the most common mineral forms of these species. The materials formed with copper and silver were formally M^I d^{10}, with Hg^{II} d^{10}, and with Pb^{II} $d^{10}s^2$. This is in line with the known preferred oxidation states of these elements in metal chalcogenides.[1]

Much current research on metal chalcogenide synthesis has been devoted to the preparation of nanoparticulate materials.[6–12] These can be roughly divided into two main areas: synthesis from the gas phase,[9] invariably by the use of molecular precursors, and synthesis from solution either *via* autoclave or refluxing solvents.[12] Both of these methods employ the use of toxic H_2E as the chalcogenide source. These syntheses do produce chalcogenides of high quality, often with very precise and controlled particle sizes, and distributions that are usually stabilised in some polymer matrix,[11] micelle[10] or framework structure. The elemental reactions studied here are arguably more straightforward than many of these new methods, in that they do not require elevated temperatures, special reaction vessels, precursor synthesis or the use of H_2E. Amine-promoted elemental reactions do as yet have little control over the materials crystallinity, the products from the reactions being either amorphous (Cu_2S) or very crystalline (PbSe) with seemingly nothing in between. Significant differences in the reactivity are observed between the chalcogens and metallic elements in ammonia and *n*-butylamine solutions. This is as yet unexplained, as too is the reason why the reactions occur more slowly in *n*-hexylamine and not at all in cyclohexane. It is known that some chalcophilic elements will react on contact with chalcogens in the absence of a solvent at room temperature. In our hands the products from the reaction of mercury with sulfur (cinnabar and metacinnabar) were not crystalline, and the reaction stops after an initial period leaving only partly coated reacting particles. In order to test the rate of solid-state reaction, discs of silver metal and elemental sulfur were pressed together. The silver disc was seen gradually to darken with the formation of crystalline acanthite (Ag_2S). The reaction progressed from the elemental boundary into the silver disc to a depth of 0.5–1 mm after a month. It is probable that in a stirred *n*-butylamine solution the formed metal chalcogenides are cleaned from the surface of the reacting elements, effectively regenerating clean surfaces for subsequent reaction. Perhaps liquid ammonia at room temperature (7 atm) is more aggressive at removing partly formed metal chalcogenide from the surface of a metal than is *n*-butylamine, and thus it can promote elemental reactions between a wider range of elements.

Conclusion

The reactions between some elemental metals (Ag, Cu, Hg and Pb) and the chalcogens in *n*-butylamine for 12–60 h produce single-phase crystalline metal chalcogenides in good yield. The reactions are easy to perform, do not require any precursor synthesis or the use of H_2E (E = S, Se or Te) and afford perhaps the simplest means of preparing a selected range of main-group and late transition-metal chalcogenides. The reactions with Se and Te seem to proceed *via* a solid-state reaction, possibly with the *n*-butylamine solvent helping to remove partly reacted material and encouraging fresh surfaces for the reaction.

Experimental

All reagents were of 99.9% purity or better from Aldrich Chemical Co. and used without further purification. Manipulations and weighings were carried out in air. Reactions were carried out in 40 cm^3 sample tubes. X-Ray powder diffraction patterns were determined on a Siemens D5000 transmission powder diffractometer using germanium-monochromated Cu-Kα_1 radiation ($\lambda = 1.504$ Å); SEM/EDAX was performed on a JEOL JSM820 microscope equipped with a Kevex Quantum detector Delta 4 and a Hitachi S-570 scanning electron microscope. Electron probe analysis were conducted on a JEOL EMA using polished samples and compared to metal and sulfur standards. X-Ray photoelectron spectra were recorded with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic Al-Kα radiation at a pass energy of 20 eV. Scans were acquired with steps of 50 meV. A flood gun was used to control charging and the binding energies were referenced to an adventitious C 1s peak at 284.8 eV. Infrared spectra were recorded on Nicolet 205 spectrometer using KBr pressed discs, Raman spectra on a Dilor XY spectrometer [the 514.53 nm line of an argon laser (50 mW) was the excitation source; slit width 300 μm]. Magnetic moment measurements were made on a Johnson Matthey balance. Powder X-ray diffraction patterns were indexed using TREOR or METRIC-LS programmes, and referenced against an external data base.[19]

Reactions of Hg, Ag and Pb with sulfur, selenium and tellurium in *n*-butylamine

The same general reaction scale and procedure was adopted for all the reactions exemplified here for PbS.

Powdered lead metal (0.612 g, 3.06 mmol) and sulfur (0.098 g, 3.06 mmol) were added to *n*-butylamine (20 cm^3) at room temperature. The vessel was stoppered and the mixture magnetically stirred for 48 h. The sulfur dissolved in the *n*-butylamine to give a red solution which reacted with the powdered lead to produce a black solid. The lead was not observed to dissolve into the amine solution but did become used up during the course of the reaction. The black solid was collected by decanting off the amine, and washed with acetone (20 cm^3) and CS_2 (2 × 20 cm^3). Yield of PbS 0.659 g, 2.74 mmol (90%).

All the chalcogenides of Hg, Ag and Pb were analysed by X-ray powder diffraction (Table 1), Fourier-transform IR and Raman spectroscopy, SEM/EDAX and magnetic moment measurements. The metal sulfides typically showed a strong absorption band at 450–300 cm^{-1} in the IR and Raman spectra corresponding to an M–S stretch. The chalcogenide powders of Hg and Pb were diamagnetic. Microanalysis: for Ag_2Se, C, 0.29; H, 0.15; N, 0.08; for PbTe, C, 0.27; H, 0.10; N, 0.02%.

Reaction of Cu, Sb, As, Fe, Ni, Cu and Zn with S, Se and Te in *n*-butylamine

The same general reaction scale and procedure was adopted as outlined above for PbS and summarised in Table 1. Reaction of Cu with S produced an amorphous black material, whilst with Se and tellurium crystalline $Cu_{2-x}Se$ and $Cu_{0.64}Te_{0.36}$ were produced. The reactions of As and Sb with S in *n*-butylamine produced yellow and red solids respectively which were collected by decanting off the solvent, triturating with CS_2 (40 cm^3) and filtering. The materials were both X-ray amorphous before and after thermolysis (523–823 K, 2 h). Reaction of iron and nickel with S, Se and Te in *n*-butylamine produced black powders that were X-ray amorphous before and after thermolysis, with the exception of Ni with S which after thermolysis showed crystalline NiS (millerite). Reaction of Zn with S in *n*-butylamine did produce a small amount of white solid after 7 d, which was identified by EDAX as ZnS. This reaction only went, at best, to a 10% yield.

Attempts at encouraging reaction between S and Sn or Cd by refluxing (12 h) the *n*-butylamine by conventional means, as well as microwave irradiation (2 h), failed to produce an identifiable sulfide product. Reactions between S with Ag or Pb in *n*-hexylamine did proceed to form the metal chalcogenide but over 7 d.

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