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Convenient, room-temperature liquid ammonia routes to metal chalcogenides †

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Reaction of sulfur, selenium or tellurium with elemental metals in liquid ammonia at room temperature in a pressure vessel produced metal chalcogenides ME (M = Ca, Sr, Ba, Eu, Yb, Ni, Zn, Cd, Hg, Sn or Pb; E = S, Se or Te), Ag_2E, solid solutions of mixed-metal chalcogenides $M_xM'_yE_z$ ($x + y = 1$, $z = 1$ or 2), and metal-mixed chalcogenides MS_xSe_y. Products showed a range of crystallite sizes from 700 Å for PbSe and Ag_2S to essentially amorphous (ZnS). Heating at 250–300 °C under vacuum for 2 h induced crystallinity in the amorphous powders. The pre- and post-heated metal chalcogenides were analysed by X-ray powder diffraction, Fourier-transform IR, Raman microscopy, scanning electron microscopy-energy dispersive analysis of X-rays, electron microprobe, X-ray photoelectron spectroscopy, elemental analysis and magnetic susceptibility studies.

The alkali metals, calcium, strontium, barium, ytterbium and europium are all known to dissolve in liquid ammonia to produce at low concentrations a blue solution and at greater concentration a metallic bronze.[1] These solutions have been the source of fascination for chemists[2] and physicists[3] alike because of their unusual behaviour attributable to the presence of metal cations and solvated electrons.[4] Sulfur will also dissolve in liquid ammonia to give green, blue and sometimes red solutions.[5] Data on these solutions have been interpreted in a variety of ways which include formation of a range of sulfur anions, cations and sulfur–nitrogen species.[6] Alkali metals react with sulfur–ammonia solutions to form metal sulfides.[7] Dissolution of selenium or tellurium in liquid ammonia to give coloured solutions is not reported, however the elements can also be made to react with alkali-metal–ammonia solutions to form a variety of metal chalcogenides.[8] Sodium–ammonia solutions can solubilise a range of predominantly main-group metals to form Zintl anions.[9]

Transition-metal chalcogenides can be made in a variety of ways, the most straightforward of which is the combination of the elements at elevated temperatures.[10] This process requires a significant energy input, is of relatively long duration and gives little control in material stoichiometry.[11] Such elemental combination reactions can also be promoted in a microwave oven where the synthesis time is significantly reduced.[12] A low-energy approach is the precipitation of metal chalcogenide from aqueous solutions of the metal cation by use of H_2E (E = S, Se or Te).[13] 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[14,15] involving thermal decomposition of a compound containing a M−S and M−Se bond, or involving H_2E as the chalcogen source,[16] have been thoroughly investigated and shown to be reliable at significantly lower temperature (200–350 °C) than those of conventional elemental syntheses. The latter approach has allowed synthesis of bulk powders and coatings. Bulk materials have also been prepared from the elements by self-propagating high-temperature synthesis[17] and from the reaction of alkali-metal sulfides and metal halides by solid-state metathesis.[18] One particularly noteworthy development has been the elemental reaction between zinc or copper with sulfur at reflux in strongly coordinating solvents such as pyridine and *N*-methylimidazole.[19] 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.[19] 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.[20]

In this paper we report the convenient one-step room-temperature preparation of both crystalline and amorphous transition- and main-group metal chalcogenides from elemental reactions in liquid ammonia.[21]

Results and Discussion

Sulfides; synthesis and characterisation

Reaction of a range of transition-metal and main-group metals with sulfur–liquid ammonia solutions [S (am)] at room temperature in a Teflon-in-glass Youngs-type pressure tube produces metal sulfides in good yield, equations (1)–(4). In these

$$\text{M (s)} + \text{S (am)} \longrightarrow \text{MS (M = Zn, Cd, Hg or Pd)} \qquad (1)$$

$$2\text{Ag (s)} + \text{S (am)} \longrightarrow Ag_2S \qquad (2)$$

$$\text{Cu (s)} + \text{S (am)} \longrightarrow Cu_{1.8}S + Cu_{7.2}S_4 + Cu_{1.96}S \qquad (3)$$

$$\text{Sn (s)} + \text{S (am)} \longrightarrow SnS + SnS_2 \qquad (4)$$

reactions the sulfur dissolved in the liquid ammonia to give a variety of colours including blue, red and green. The metal in some of the reactions (Zn, Cd) seemingly dissolves in the sulfur–ammonia solution and precipitates as the metal sulfide. In others the disappearance of the metal coincided with the formation of a new solid. After removal of the ammonia the colour expected of the metal sulfide was invariably seen. Examination of the powder by optical microscopy revealed a homogeneous solid (except in the tin reaction).

Reaction of silver and lead with S (am) produced crystalline Ag_2S and PbS which indexed with literature cell parameters[22] (Table 1). These materials had crystallite sizes in the range 500–800 Å based on the Scherrer equation.[23] All of the other reactions between sulfur and metals in liquid ammonia produced a featureless powder X-ray diffraction (XRD) pattern, indicating that the elements had reacted but had not formed a crystalline sulfide.

Scanning electron microscopy (SEM) analysis of all the sulfide powders revealed agglomerates of particles of typical size 2–5 µm. Energy-dispersive analysis by X-rays (EDAX) revealed

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

Table 1 X-Ray powder diffraction data from the reaction of chalcogenides and metals in liquid ammonia. Phases in square brackets represent less than 5–10% of the sample

Ratio of elements	Colour of material	Reaction product(s) (identified by XRD)	Products after heating at 573 K for 2 h (by XRD)
Ni : S 1 : 1	Black	X-Ray amorphous + Ni	$NiS_{1.03}$ + [NiS millerite]
Ni : S 3 : 2	Black	X-Ray amorphous + Ni	Ni_3S_2 (heazlewoodite) + [Ni]
Ni : Se 1 : 1	Black	X-Ray amorphous + Ni	$NiSe_2$ + NiSe
Ni : Te 1 : 1	Black	X-Ray amorphous + Ni + Te	Ni + Te + [$NiTe_2$ melonite]
Cu : S 1 : 1	Black	X-Ray amorphous	$Cu_{1.8}S$ (digenite) + $Cu_{7.2}S_4$ + $Cu_{1.96}S$
Cu : Se 1 : 1	Black	$Cu_{2-x}Se$ (berzelianite) + [CuSe, klockmannite]	$Cu_{2-x}Se$ (berzelianite)
Cu : Te 1 : 1	Black	$Cu_{2.74}Te_2$ + CuTe + $Cu_{2-x}Te$ (rickardite)	$Cu_{2.74}Te_2$ + CuTe + $Cu_{2-x}Te$ (rickardite)
Ag : S 2 : 1	Black	Ag_2S (acanthite)	Ag_2S (acanthite)
Ag : Se 2 : 1	Black	Ag_2Se (naumannite)	Ag_2Se (naumannite)
Ag : Te 2 : 1	Silver	Ag_2Te (hessite) + [Ag_7Te_4 stuetzite]	Ag_2Te (hessite) + [Ag_7Te_4 stuetzite]
Zn : S 1 : 1	White	X-Ray amorphous	ZnS (wurtzite)
Zn : Se 1 : 1	Red	X-Ray amorphous	ZnSe (stilleite)
Zn : Te 1 : 1	White	X-Ray amorphous	ZnTe
Cd : S 1 : 1	Yellow	X-Ray amorphous	CdS (greenockite)
Cd : Se 1 : 1	Red	X-Ray amorphous	CdSe (cadmoselite)
Cd : Te 1 : 1	Black	CdTe	CdTe
Hg : S 1 : 1	Red-black	X-Ray amorphous	HgS (cinnabar) + HgS (metacinnabar)
Hg : Se 1 : 1	Black	HgSe (tiemannite)	HgSe (tiemannite)
Hg : Te 1 : 1	Black	HgTe (coloradoite)	HgTe (coloradoite)
Sn : S 1 : 1	Black	X-Ray amorphous	SnS (herzenbergite)
Sn : S 1 : 1	Black	X-Ray amorphous + Sn	SnS (herzenbergite)
Pb : S 1 : 1	Black	PbS (galena)	PbS (galena)
Pb : Se 1 : 1	Black	PbSe (clausthalite)	PbSe (clausthalite)
Pb : Te 1 : 1	Black	Pb + Te	PbTe (altaite)

the presence of only metal and sulfur with virtually uniform composition over many surface scans. Electron-microprobe analysis showed excellent agreement with the empirical formula for the sulfides (Zn, Pb) however it did show in some cases a trace of metal in the powder (typically 1% or less). Microanalysis of the metal sulfides showed trace levels of nitrogen and hydrogen (typically less than 0.4%). Infrared and Raman analyses were consistent with the formation of metal sulfides with vibrations between 600 and 250 cm^{-1}.[24] In IR analyses of the Group IIB metals very weak bands at 3200 and 1450 cm^{-1} were observed, due to a N–H vibration. The X-ray photoelectron spectrum of ZnS shows the presence of metal and sulfur with little associated carbon and nitrogen. The binding-energy values of 1022.1 eV for the Zn $2p_{\frac{3}{2}}$ and 161.6 eV for the S 2p are similar to the previously reported values for ZnS (zinc Auger parameter observed at 2011.4 eV, ZnS 2011.3 eV; sulfur binding energy for ZnS 161.7 eV).[25] The X-ray photoelectron spectrum suggests an elemental ratio of 1.00 Zn to 1.08 S. No elemental Zn or S were observed in the spectrum, only values expected for Zn^{2+} and S^{2-}.[24]

Heating the X-ray amorphous powders at 250–300 °C for 2 h *in vacuo* induces crystallinity and enables the materials to be characterised by X-ray powder diffraction as the binary sulfide (Table 1). This showed a single phase of metal sulfide for M = Zn and Cd, predominantly α-HgS with a trace of β-HgS and a mixture of phases for copper ($Cu_{1.8}S$, $Cu_{7.2}S_4$ and $Cu_{1.96}S$). The IR and Raman analysis of thermolysed powders showed the expected vibrations and did not show weak NH bands.[24] The SEM/EDAX analysis of the thermolysed powders showed in general a homogeneous solid of uniform composition.

Reaction of the early transition metals (Ti, Zr, V, Cr, Nb or W) with sulfur–ammonia solutions did not produce a sulfide. The product from the reaction was inhomogeneous and consisted of the unreacted metal powder and sulfur. This was confirmed by X-ray powder diffraction which showed the patterns for the elements and SEM/EDAX which showed two distinct phases for the elements. Heating the powder from these reactions at 250–300 °C *in vacuo* did not produce a binary sulfide.

Reaction of Ni or Sn with S (am) produced an inhomogeneous product. In the tin case three separate phases were observed by Raman microscopy, one gold coloured (SnS_2, *ca.* 35%), one black (SnS, *ca.* 60%) and a minor amount of a grey phase (unreacted Sn, *ca.* 5%). The gold and black phases had the anticipated Raman signatures for SnS_2 and SnS.[26] The XRD pattern of this sample showed just tin metal. Tin-119 NMR spectroscopy confirmed the presence of two separate tin nuclear environments with chemical shift values of δ 6871 and 7220. In the nickel reaction the XRD pattern showed only nickel to be present; EDAX showed the nickel to be a minor product (*ca.* 5%), with the rest of the material consisting of a homogeneous nickel sulfide with approximate ratios of the elements of 1 : 1. Heating the nickel and tin products to 250–300 °C induced crystallinity and formed SnS and $NiS_{1.03}$ [with a minor amount (5–10%) of NiS]. In the tin case the formation of purely SnS is consistent with the known thermal instability of SnS_2.[27]

Reactions of calcium, strontium, barium, ytterbium and europium with sulfur–ammonia solutions under the same conditions as those outlined for the non-soluble metals were also investigated. The metal dissolved in the ammonia to form a blue, and then bronze, solution characteristic of an increasing concentration of solvated electrons.[28] The sulfur reacted with this solution to form a light purple or brown precipitate, with the solution colour fading to colourless through the loss of the solvated electron. Evaporation of the ammonia produced a further change in colour of the precipitate to the red-brown of the binary metal sulfide, suggesting a loss of complexed ammonia molecules. This powder was amorphous to X-rays and also partly contaminated with traces of the metal (up to 5%, as determined by optical microscopy). Work-up of this material in air can be problematic as the metal fragments tend to be pyrophoric. The EDAX and IR analyses were consistent with the formation of the binary sulfide. Heating the powders at 300 °C for 2 h was sufficient to induce crystallinity and so allow characterisation by XRD.[28] The binary sulfides, with stoichiometry MS, of calcium, strontium, barium, ytterbium and europium were synthesized. Dissolution of these metals in liquid ammonia but without the addition of sulfur resulted in the formation, after 18–24 h, of the metal(II) amides; the general stoichiometry $M(NH_2)_2$ for each of these white precipitates was confirmed by microanalysis and the existence of strong N–H stretching frequencies in each of the samples (at 3200 and 1450 cm^{-1}).

Binary selenides and tellurides; synthesis and characterisation

Reaction of selenium and tellurium with various transition- and main-group elements in liquid ammonia were investigated [Table 1, equations (5)–(12)] [minor phases (*ca.* 5–10%) in

$$\mathrm{M + E \longrightarrow ME\ (M = Zn,\ Cd\ or\ Hg,\ E = Se\ or\ Te,\ and\ M = Pb,\ E = Se)} \qquad (5)$$

$$\mathrm{Pb + Te \longrightarrow Pb + Te \xrightarrow{523\ K,\ 2\ h} PbTe} \qquad (6)$$

$$\mathrm{Cu + Se \longrightarrow Cu_{2-x}Se} + \mathit{CuSe} \qquad (7)$$

$$\mathrm{Cu + Te \longrightarrow Cu_{2-x}Te + Cu_{2.72}Te_2 + CuTe} \qquad (8)$$

$$\mathrm{Ag + Se \longrightarrow Ag_2Se} \qquad (9)$$

$$\mathrm{Ag + Te \longrightarrow Ag_2Te} + \mathit{Ag_7Te_4} \qquad (10)$$

$$\mathrm{Ni + Se \longrightarrow NiSe_2 + NiSe} \qquad (11)$$

$$\mathrm{Ni + Te \longrightarrow NiTe_2} \qquad (12)$$

italics]. No colour appeared in the ammonia solution in any of these reactions, unlike the reaction of sulfur. Product work-up and analysis were identical to the cases described for sulfur above. In some cases the selenide products were amorphous (*e.g.* ZnSe, CdSe, NiSe) and required gentle heating (250–300 °C for 2 h) in order to form a crystalline material. All of the tellurides were crystalline prior to heating except that of nickel. The amorphous powders were confirmed as metal selenides and tellurides by SEM/EDAX, microprobe, XPS and IR analysis and not a mixture of the individual elements. All reactions formed binary compounds prior to heating, except lead and tellurium which showed by XRD and EDAX the presence of the unreacted elements [equation (6)].

The silver and lead selenides were crystalline prior to heating as had been the case observed for sulfur. The selenides of copper and mercury also formed crystalline products directly from the reaction in liquid ammonia, yet they formed amorphous sulfides. Only cadmium and zinc showed amorphous products prior to heating when treated with either sulfur or selenium. Only nickel formed amorphous products when treated with any of the three chalcogens. The metals that produced a single-phased selenide or telluride were from Group IIB, as well as lead; this trend was also seen for the formation of the sulfides. Silver reacted to give a single-phase selenide (as with the sulfide), but two phases formed when treated with tellurium. The heating changed the initial product composition in three reactions. The trace CuSe phase [equation (7)] disappeared and only berzelianite ($Cu_{2-x}Se$) was observed. A trace of AgTe was formed on heating the product of equation (10). Heating also promoted the reaction between lead and tellurium to form PbTe.

Scope of the reaction

The reaction of sulfur–ammonia solutions with metals seems to be limited to the chalcophilic late transition- and main-group metals. A dividing line in reactivity is observed at cobalt. The later elements Ni, Cu, Ag, Zn, Cd, Hg, Sn and Pb all react with sulfur–ammonia solutions at room temperature to form metal sulfides, whereas the earlier metals and Au do not. The reactions that work are those of soft metals (as defined in Pearson terms). The reactions are all of the redox type with the metal being oxidised in most cases to the II oxidation state or, in the case of Cu and Ag, to the I state with small traces of M^{II}. The nature of the oxidising agent in the solution has yet to be quantified. Sulfur–ammonia solutions have been shown to contain various sulfur imides (*e.g.* S_7NH) as well as sulfur–nitrogen anions and sulfur polyanions (S_6^{2-}, S_4^-, S_4N^-, S_7NH).[6] One or more of these could be responsible for the redox chemistry. The ammonia acts not only to produce the active sulfur species in solution but could also play a role in activating the metal surface. It is known that some metals will react with sulfur at room temperature, for example mercury.[29] The reaction is however largely surface limited and for most metals slow. This may be, in part, due to a passivating surface oxide coating. The ammonia may act to remove this coating and so facilitate contact between the metal and the dissolved sulfur, thereby promoting the reaction. It should be noted that all the above reactions are unsuccessful in a variety of common solvents (water, acetone, CS_2, CH_2Cl_2, toluene, hexane and tetrahydrofuran), thus strongly suggesting that the ammonia plays a crucial mechanistic role. The sulfide formed tends to be the most thermodynamically stable.[30] Alteration of the metal to sulfur ratios was investigated to try and form other sulfide phases. In these cases it was found that when an excess of sulfur was used to try and form a phase such as ZnS_2, AgS or CuS unreacted sulfur was obtained after the reaction and only ZnS, Ag_2S and Cu_xS_y (*i.e.* a mixed-state material) were observed. If insufficient sulfur was used then unreacted metal was observed. The one exception to this trend was the reaction between nickel and sulfur, where a 3 : 2 ratio of Ni : S produced Ni_3S_2 (heazlewoodite). The reactions were found to require different lengths of time to go to completion. In some cases they were completed in 2 h at room temperature (as assessed by the lack of metal left in the reaction vessel), whereas others required up to 5 d at room temperature. If a reaction was stopped prior to completion and inspected by SEM/EDAX an intimate mixture of metal sulfide, unreacted metal and free sulfur was observed.

The metal selenide and telluride reactions were different to the sulfur–ammonia solutions in that none of the elements seemed to dissolve in the ammonia during the course of the reaction. The reaction rate generally increased from sulfur to selenium to tellurium. Attempts at altering the product stoichiometry by using an excess of selenium or tellurium (or excess of metal) did not have a bearing on the product formed. The product stoichiometry was as expected for the most thermodynamically stable binary material, and the excess of element was found unreacted.

The particle size of the metal did have an effect on the rate of reaction, with powders reacting faster than discrete pieces. However, the predominant influence on rate appears to be the degree of softness of the metal, as defined in Pearson's terms, since this has a direct bearing on the chalcophilicity of the metal. This trend can be seen clearly in the relative reaction times, with sulfur, of the 3d elements of Groups 10–12: nickel (*ca.* 60 h), copper (*ca.* 36 h), zinc (*ca.* 12 h).

The heat treatment used to induce crystallinity in the amorphous powders is less than the temperature required to combine the individual elements. Indeed, comparative reactions of the elemental powders under similar heat treatment (250–300 °C for 2 h) did not produce a metal chalcogenide in the majority of cases, and in the instances where it did occur (ZnS, CdS) the product was less crystalline than the ammonia-treated powders. This may be due to the better mixing of the particles, with the sulfur effectively coating the metal surface (and so increasing the contact area), or due to the removal of the passivating oxide layer from the surface of the metal by the ammonia. This potential 'cleaning effect' of the ammonia is borne out by the reaction between lead and tellurium; the elements reacted only when heated to 250–300 °C, yet without treatment in ammonia the reagents failed to react.

The reactions to form metal chalcogenides from elemental reactions in liquid ammonia are truly low-temperature pathways. Indeed, they are at significantly lower temperature than solid-state metathesis[17] and self-propagating high-temperature synthesis.[18] In some ways they are more straightforward than the molecular precursor routes to metal sulfides and selenides which require the synthesis of materials with an inbuilt

'Achilles heel' for decomposition. In such reagents the decomposition temperature is often in excess of 200 °C.[14–16] The ammonia reactions have some correlations with hydrothermal synthesis methods in that the reagents are held under pressure (7 atm for ammonia at room temperature), however they are at much lower temperatures than typical hydrothermal syntheses (140–220 °C). The ammonia-promoted metal chalcogenide reactions are similar to the work of Rauchfuss and co-workers[19] where the elements are made to react at the reflux temperature of a strongly co-ordinating solvent.

Solid solutions

Attempts at forming solid solutions of metal mixed chalcogenides $MS_{0.5}Se_{0.5}$ (where M = Cu, Zn or Cd) were successful, probably because the binary selenide and sulfide commonly have the same crystalline modification. The 2 : 1 : 1 stoichiometric mix of cadmium : sulfur : selenium has a diffraction pattern that is intermediate between that of CdS and CdSe. The ternary product was a single-phased material. Therefore, an exact stoichiometry was calculated directly from a comparative study of the lattice parameters obtained from the product's XRD spectra using Vegards law, with those obtained from data base spectra for CdS and CdSe. The values obtained for the product were $a = 4.23$ (CdS, 4.14; CdSe, 4.29 Å) and $c = 6.90$ (CdS, 6.71; CdSe, 7.01 Å). This showed the product to be $CdS_{0.38}Se_{0.62}$. Chalcogenide solid solutions were only observed by XRD in the samples that had been heated at 250–300 °C; the unheated materials were X-ray amorphous. Also, all samples showed agglomerates of particles, typically of size 2–8 μm before and after heating.

Attempts at forming solid solutions of mixed-metal sulfides were also investigated. In the majority of cases, where insoluble metals were used, solid solutions were difficult to form under the conditions employed. The EDAX analysis of the surface showed variations in the elemental composition, and although the powder XRD showed broadened peaks, the lines due to individual sulfides were observed. This indicates that although some metal doping has occurred in the corresponding sulfide lattice, phase segregation has occurred (most probably as the individual metal sulfides adopt a different space group). Attempts were made to form ZnCdS and ZnCuS. Calculations carried out on the heated sample of ZnCdS, in the same manner as for $CdS_{0.38}Se_{0.62}$, showed a single-phased ternary material to be $Zn_{0.45}Cd_{0.55}S$: $a = 3.97$ (CdS, 4.14; ZnS, 3.82 Å) and $c = 6.47$ (CdS, 6.71; ZnS, 6.26 Å). However, in the case of ZnCuS the EDAX (as well as the XRD pattern for the thermolysed sample) showed the product to be an intimate mixture of ZnS (sphalerite) and Cu_8S_5 (geerite). Studies were also conducted into the formation of Cd_xHg_yE [E = S, Se or Te; $(x + y) = 1$ where $x = 0.25$, 0.50 and 0.75]. Electron-probe studies showed uniform aggregates of variable elemental composition across the sample's surface; typically the metal content would vary by *ca.* 10%, with occasional regions of binary sulfides.

Soluble metals were employed in the formation of two types of mixed-metal sulfide: MM^*S_2 and Sr_xBa_yS ($x + y = 1$, where $x = 0.25$, 0.5 or 0.75). The strontium barium sulfides were analysed in exactly the same way as for the binary sulfides, their stoichiometries being confirmed using Vegards law. The analysis of the MM^*S_2 compounds relied upon EDAX and electron-probe studies, since heating the reaction product in excess of 550 °C failed to induce sufficient crystallinity for successful XRD analysis. The syntheses of these compounds were successfully extended to include all three chalcogenides, the results of which are shown in equations (13)–(15) (ammonia, room temperature).

$$M + M^* + E \longrightarrow MM^*E_2 \text{ (M = Sr; M* = Mg, Ca or Ba; E = S, Se or Te)} \quad (13)$$

$$Eu + Yb + E \longrightarrow EuYbE_2 \text{ (E = S, Se or Te)} \quad (14)$$

$$Sr + Yb + S \longrightarrow SrYbS_2 \quad (15)$$

Conclusion

Sulfur–, selenium– and tellurium–ammonia solutions react with some elemental metals at room temperature, to afford a low-temperature pathway to amorphous and crystalline binary metal chalcogenides. The ease of reaction is dependent on the metal, being favoured by late transition- and main-group metals. The reactions occur by direct combination of the elements, using a medium in which the elements need not be soluble. The metal chalcogenides produced are of good purity. Crystallinity can be induced in the X-ray amorphous materials by gentle heating at 250–300 °C for 2 h, whilst for the most part unaltering the product composition. A variety of ternary solid solutions can also be produced, with respect to both mixed-metal and mixed-chalcogenide materials.

Experimental

All reagents were of 99.9% purity or better (Aldrich Chemical Co.) and used without further purification. Ammonia was from BOC and used without drying. Manipulations and weighings were carried out in a dinitrogen- or argon-filled glove-box. Reactions were carried out in thick walled (3–4 mm) Schlenk tubes (sealed by a large rota-flow tap) which were surrounded by safety netting. 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). They were indexed using TREOR or METRIC-LS programs (lattice parameters matched to better than 0.02 Å).[31] The SEM/EDAX measurements were made on a JEOL JSM820 microscope, equipped with a Kevex Quantum Delta 4 detector, and a Hitachi SEM S-570. Electron-probe analyses were conducted on a JEOL EMA using polished samples and compared to metal and sulfur standards. The XPS measurements were performed with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatised 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 referred to an adventitious carbon 1s peak at 284.8 eV. Infrared spectra were recorded on a 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. The ^{119}Sn NMR spectra were obtained within the expected chemical shift range for binary tin sulfides at room temperature (δ 7600–6300) for two different spin rates (10 and 13 kHz), using a Bruker 300 MHz spectrometer. The sample was referenced against $C(SnMe_3)_4$, the chemical shift of which was taken to be δ 48.2.

CAUTION: liquid ammonia generates a pressure of about 7 atm at room temperature. Care should be exercised in its use in thick walled glass vessels. All reactions should be conducted behind a safety screen with blast-proof netting around the reaction vessel.

Reactions

Of Ni, Cu, Zn, Cd, Hg and Sn with sulfur in liquid ammonia. The same general reaction scale and procedure was adopted for all the reactions exemplified here for ZnS.

Powdered zinc metal (0.200 g, 3.06 mmol) and sulfur (0.098 g, 3.06 mmol) were added to liquid ammonia (10 cm^3) in a Teflon-in-glass sealable thick walled Schlenk tube at −77 °C. The system was sealed, allowed to warm to room temperature and magnetically stirred for about 15 h. The mixture changed to a dark blue to green and finally to colourless with a pale yellow precipitate. Within 1 h of warming to room temperature all the sulfur had dissolved. The zinc metal could initially be seen but had all been consumed within 6–10 h. The precipitate was collected by cooling the solution back to −77 °C and allowing the ammonia to evaporate under a stream of nitrogen. The precipitate was dried *in vacuo* at room temperature for 10 min. The off-white solid was collected and analysed (yield 0.275 mmol, 0.268 g, 90%). Part of the material was heated at 250–300 °C for 2 h. The unheated and heated materials were analysed by microanalysis, X-ray powder diffraction (Table 1), Fourier-transform and Raman spectroscopy, SEM/EDAX, magnetic moment measurements and X-ray photoelectron spectroscopy.

The metal sulfides typically showed a strong absorption band at 450–300 cm^{-1} in the IR and Raman spectra corresponding to a M−S stretch (weak bands at 3200 and 1450 cm^{-1} were also observed in the unheated samples).[24] All the metal sulfide powders were diamagnetic. X-Ray photoelectron spectroscopy revealed a zinc Auger parameter of 2011.4 eV (ZnS, 2011.3; ZnO, 2.0098 eV) and a binding energy for the sulfur 2p of 161.6 eV (S in ZnS 161.7 eV).[25] Microanalysis for ZnS: C, 0.2; H, 0.0; N, 0.15; S, 32.6 (32.8%). Standardised electron-probe analysis gave 66.2 Zn (calc. 66.5) and 33.8% S (calc. 33.5%). The ^{119}Sn NMR spectra confirmed the presence of two separate tin nuclear environments with chemical shift values of δ 6871 and 7220, corresponding to tin(II) and tin(IV). Standardised EDAX analysis of all the metal sulfides were typically within 1% of the expected elemental ratios for sulfur and metal.

Of Ag and Pb with sulfur in liquid ammonia. The same reaction conditions and scale were used as detailed above for Zn except that in the silver reaction a Ag : S ratio of 2 : 1 was employed. In both the lead and silver reactions the product formed was crystalline as assessed by X-ray powder diffraction and did not require heating for characterisation. Analysis for Ag_2S: C, 0.05; H, 0.1; N, 0.3%. Standardised electron-probe analysis for PbS: 86.5 Pb (calc. 86.6) and 13.5% S (calc. 13.4%).

Of selenium and tellurium with metals in liquid ammonia. The same reaction scale and conditions were employed as described above for the zinc–sulfur reactions. The reactions typically required 48–52 h to go to completion and during this time no colour was evident in the liquid ammonia. The starting materials, however, were transformed into a black powder and after *ca.* 24 h no trace of the metals was observed. No precipitation from the solution was seen. The ammonia was evaporated by passing N_2 at −77 °C and the products analysed by XRD (Table 1), SEM/EDAX, electron microprobe, Fourier-transform IR and XPS. Some of the products were amorphous to X-rays (Table 1), and so were heated to 250–300 °C *in vacuo* for 2 h in order to induce sufficient crystallinity for analysis. XPS data: HgTe, Te $d_{\frac{5}{2}}$ 572.4 eV and tellurium MNN Auger peak at 491.7 eV; for Ag_2Te, Te $d_{\frac{5}{2}}$ 572.5 eV and Auger tellurium MNN at 491.7 eV; for CdSe, Cd $3d_{\frac{5}{2}}$ Auger parameter at 786.7 eV, Se 3d at 53.7 eV.[25,32] Infrared and Raman analysis showed broad bands at *ca.* 350–180 cm^{-1} for the selenides and 250–160 cm^{-1} for the tellurides.[24]

Of calcium, strontium, barium, europium and ytterbium with sulfur, selenium and tellurium in liquid ammonia. The same reaction scale and procedure were adopted as above except that the metal was dissolved in the ammonia first to yield a blue or bronze solution before addition of the chalcogen. Over a period of 2 h the ammonia solution faded and a purple or brown precipitate formed. The materials were worked up as above and analysed by X-ray powder diffraction, IR spectroscopy and SEM/EDAX.

Of strontium and barium and liquid ammonia. Dissolution of strontium or barium in liquid ammonia (10 cm^3) at −77 °C in a Teflon-in-glass pressure tube followed by warming to room temperature produced a deep bronze solution. The bronze colour faded to blue and after 20 h to colourless with a white precipitate. Cooling of the solution to −40 °C followed by evaporation of the ammonia with a nitrogen stream produced a white solid which analysed as $M(NH_2)_2$ [$Sr(NH_2)_2$, 23.7% N (calc. 23.71%); $Ba(NH_2)_2$, 8.1% N (calc. 8.35%)]. IR: 3200 and 1450 cm^{-1}.

Formation of solid solutions between metals and chalcogens in liquid ammonia

The same general procedure and reaction scale was used to attempt to form solid solutions except that either two metals or two chalcogenides were added to the ammonia in a predetermined ratio (typically 50 : 50 for mixed metals). Product work-up and analysis were as before. The samples required heating at 250–300 °C for 2 h to induce crystallinity.

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