Solvent Mediated Synthesis of Metal Chalcogenides

Graham Andrew Shaw

Supervised by Dr. I. P. Parkin

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Christopher Ingold Laboratories, University College London

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Abstract

This thesis is primarily concerned with the synthesis of binary and ternary transition metal and main-group metal chalcogenides (excluding oxides) at room temperature. Bulk material was sought using both elemental combination and metathetical reactions, in either liquid ammonia or n-butylamine. In addition, solid-state metathesis reactions were employed in the synthesis of a selection of low valent transition metal chalcogenides.

Elemental combination reactions at room temperature afforded a simple, reproducible single-stage preparation of a range of transition and main-group metal chalcogenides in good yield (> 90%). Products were either highly crystalline (c) or X-ray amorphous (a) in nature. In most cases, annealing the X-ray amorphous powders at 200-250 °C for 2h was found to induce sufficient crystallinity for characterisation by X-ray powder diffraction. Both binary and ternary materials were afforded by the liquid ammonia reactions - M_S(a) (M = Cd, Hg, Ni, Sn), ZnE(a) (E = S, Se, Te), As_S(e) (E = S, Se, Te), NiE(x) (E = Se, Te), ME(a) (M = Pb, Tl, E = S, Se; M = Cd, Hg, E = Se, Te), Ag_2E(c) (E = S, Se, Te), Ti_{2-x}E(c) (E = Se, Te). AgICTe(c), Zn_0,5Cd_0,5S(a), Zn_{1-2x}S(a), M_2E_{3-2y} (M = Mg, Ca, Ba, Yb; E = S, Se, Te), Sr_2Ba_2S_{1-2x} / CdHgTe_{2-6} (E(x,y) = 1.00; x = 0.25, 0.50, 0.75), EuYbE_{2-6} (E = S, Se, Te), MS_{2+x}E_{2-y} (E(x,y) = 1.00; M = Cu, Cd), Ag_3PnS_{3-6} (Pn = As, Sb), CuAsS(c). Similar reaction schemes and conditions were carried out in n-butylamine, resulting in a more restricted range of binary materials - M_E(c) (M = Hg, Tl, Pb, E = S, Se; M = Hg, Pb, E = Te), Ag_2E(c) (E = S, Se, Te), Cu_{2-x}E(c) (E = Se, Te), Cu_2S(c) and As_2S(c). In some cases, elemental combination was obtained by annealing the solvent treated elements, yielding highly crystalline, homogeneous products - liquid ammonia: M_2E_3 (M = In, Sb, Bi; E = S, Se; Ga_2Se_3), As_2Te_3, Bi_2Te_3, InE (E = S, Se) and PbTe; n-butylamine: NiS, M_2E_3 (M = As, Sb, Bi; E = Se Te).

Solid state metathetical reactions of sodium chalcogenide (Na_2S or Na_2E where E = S, Se Te) and low valent transition metal halides MX_n (n = 1, 2) were carried out in evacuated ampoules at 300 °C for 48h. In each case, removal of the co-produced salt from the highly sintered, fused product mixture afforded crystalline binary chalcogenides (typically of a single phase) – ME_2 (M = Fe, Co, E = S, Te), NiS_{2+x}, ME (MnS, FeSe, SnSe and SnTe), M_{1+x}E (M = Fe, Co, E = S), Ni_{1+x}E (E = S, Se, Te) and Ag_2E (E = S, Se, Te). Analogous reactions were observed in liquid ammonia at room temperature, affording a range of amorphous (a) and crystalline (c) chalcogenide powders, with each exhibiting an aggregated structure of typically <50-100 nm. Average crystallite sizes of ca. 10-50 nm have been calculated for nanocrystalline materials.

Both binary and ternary materials were obtained as single phases in high yield (> 90%) - ME(c) (M = Pb, Tl; E = S, Se), PbTe(c), Ag_2E(c) (E = S, Se, Te), Ti_{2-x}Te(c), MS(a) (M = Ni, Zn, Cd, Hg), HgE(a) (E = Se, Te), Cu_{2-x}S(a), CuE(a) (E = S, Se, Te), M_2E_{3-6} (M = Ga, In; E = S, Se, Te), M_2Pn(a) (M = Fe, Co, Ni; Pn = As, Sb), M_2E_{2-6} (M = Zn, Cd; Pn = As, Sb), ABE_{2-6} (A = Cu, Ag, B = Ga, In, E = S, Se; A = Cu, B = Sb, E = S, Se, Te), Cu_{13}Sb_4S_{13}(a) and CuFeS_{2-6}.
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List of Abbreviations

Abbreviations of analytical techniques

**XRD** – X-ray powder diffraction  
**XPS** – X-ray photoelectron spectroscopy  
**SEM** – Scanning electron microscopy  
**EDXA** – Energy dispersive X-ray analysis  
\(^{119}\text{Sn NMR} – \text{Nuclear magnetic resonance (of tin nuclei with a nuclear mass of 119)}\)  
**IR** – Infra-red  
**LIF** – Laser Induced Fluorescence

Abbreviations of synthetic techniques

**SHS** – Self-propagating high temperature synthesis  
**SSM** – Solid state metathesis  
**LAM** – Liquid ammonia metathesis  
**MOCVD** – Molecular organic chemical vapour deposition

Abbreviations of units

**pm** – picometres \((10^{-12} \text{ metres})\)  
**Å** – Angstroms \((10^{-10} \text{ metres})\)  
**nm** – nanometres \((10^{-9} \text{ metres})\)  
**µm** – micrometers \((10^{-6} \text{ metres})\)  
**eV** – electronvolts

Miscellaneous

**R.T.** – room temperature
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For Esther, Lynne and all that is to follow.
Preface

A comparative study of elemental combination and metathetical procedures, utilising both liquid ammonia and n-butylamine

The following project has been largely concerned with the application of liquid ammonia as a medium in which to synthesise bulk binary and ternary materials at room temperature. Initial studies were concerned with the synthesis of the ‘chalcogenide’ class of compounds (by which reference is made to those containing sulfur, selenium and / or tellurium). Interest in these materials has arisen from both their extensive practical applications as well as the resultant bias towards the manufacture of thin films, which has left the synthesis of bulk materials a relatively open area of research. These points will be discussed more fully in sections 1.3a and 1.5.

The physical properties of liquid ammonia are well understood, as are the more fundamental reaction types which may be carried out in it (a comparison of reactions in liquid ammonia and aqueous solution is described in chapter 1.1). The fundamental aim of this project is to extend the understanding of how the properties of liquid ammonia may facilitate the synthesis of the aforementioned materials, through the use of two reaction types. These are elemental combination and solvent mediated metathesis reactions. The thesis is also concerned with two comparative studies. The first impresses a change in the reaction solvent, with a study of elemental combination reactions in other nitrogen-based solvents (notably n-butylamine, chapter 4). The second is concerned with a change in the reaction medium, with a study of metathesis reactions carried out in liquid ammonia and those done in the solid state. These studies are described in chapters 5 and 6 respectively. These fundamental aims are described in the flow diagram below (figure 1.0).

Attempts were later made to apply elemental combination in liquid ammonia to the synthesis of binary ‘pnictides’ (by which we refer to compounds classed as phosphides, arsenides and antimonides).
Figure 1.0 Fundamental Objectives of Thesis

Liquid Ammonia at Room Temperature

- Initial Reaction Types
  - Comparative Reactions
    - Fundamental Objectives
  - Elemental Combination Reactions
  - Solution Phase Metathesis Reactions

- Elemental Reactions in n-butylamine

- Solid State Metathesis Reactions
  - Comparison of N-based solvents
  - Comparison of Metathetical products
    - Extend scope of Solid State Metathesis
**Chapter 1  General Introduction**

1.1 **Liquid Ammonia as a non aqueous solvent**

1.1a **Structure of ammonia (NH₃)**

The nitrogen atom (electron configuration 1s²2s²3p³) in ammonia is sp³ hybridised. VSEPR theory therefore suggests the presence of three identical σ N-H interactions and a non bonding electron pair located upon the nitrogen (a ‘lone pair’). This would lead to a tetrahedral environment for the nitrogen, slightly distorted by the increased electrostatic repulsion that exists between the electrons of ‘lone pair-bonding pair’ interactions when compared to the electrons of ‘bonding-bonding’ pairs. This is in good agreement with studies carried out in the gas phase, which show a pyramidal structure (with respects to atomic positions) with three equivalent N-H bonds, of length 101.4pm at equilibrium, and HNH bond angles of 106°47′ (cf. 109°08′ for a perfect tetrahedron). With respects to atomic positions, this leads to a point group description for a discrete molecule of C₃v (figure 1.1). Molecular orbital theory suggests the presence of three N-H orbitals - one doubly degenerate (with 2b₁ symmetry) and another singly degenerate (with a₁).

Gaseous ammonia molecules have a large dipole moment of 4.90 x10⁻³⁰ Cm, indicative of the high electronegativity of nitrogen atoms. From this, one would expect the intermolecular interactions in both the liquid and solid state to be due to hydrogen bonding. This is indeed the case, as illustrated by comparing the N-H bond lengths of the solid and gaseous state (figure 1.1).

**Figure 1.1**

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<th>Gaseous State</th>
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<td>113 pm</td>
<td>101.4 pm</td>
</tr>
<tr>
<td>φ (angle HNH)</td>
<td>107°</td>
<td>106° 47′</td>
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</tbody>
</table>
In the solid state, ammonia has been shown to preserve its $C_{3v}$ symmetry, with the nitrogen lying on a three-fold axis of symmetry. Each nitrogen has six nearest (nitrogen) neighbours at 338 pm. Three lie on one side of a central nitrogen at angles of 118.05°, with three on the other side at angles of 71.66°. The central nitrogen is hydrogen-bonded asymmetrically with its six neighbours. Each hydrogen of the central ammonia interacts with the nitrogen atoms subtended at 118°; the N-H bond lengths being significantly longer (113 pm) than in the gas phase whilst the HNH bond angle (107°) is only slightly perturbed. It should be noted that in comparison to the remaining group 15 hydrides, ammonia molecules have a notably reduced energy of activation towards structural inversion through the unique (group 15) atom (i.e. pyramidal → trigonal planar → pyramidal).

In the liquid phase, X-ray diffraction studies have shown that each ammonia molecule has an average co-ordination sphere of eleven.

1.1b Solvent properties of liquid ammonia and aqueous solutions

The physical and chemical behaviours of liquid ammonia show strong similarities with that of water since both are highly associated species, exhibiting extensive hydrogen bonding. As a result, both $\text{H}_2\text{O}$ and $\text{NH}_3$ show anomalous properties when compared with the other hydrides of their respective periodic groups. A comparison of some common physical constants for liquid ammonia ($\text{NH}_3$), phosphine ($\text{PH}_3$), water ($\text{H}_2\text{O}$) and hydrogen sulfide ($\text{H}_2\text{S}$) is represented in table 1.1. Such anomalous properties include high melting / boiling points, heat capacity, dielectric constants and latent heats of fusion / vaporisation. They are both unique in their behaviour as protonic solvents, whereby each molecule can react with a proton to yield a cation that behaves as a Bronsted acid in the parent solvent. This is exemplified by the ‘auto-ionisation’ of both solvents (equations 1.1 and 1.2).

\begin{align*}
\text{2 NH}_3(l) & = [\text{NH}_4]^+(\text{am}) + [\text{NH}_2]^-(\text{am}) & (1.1) \\
\text{2 H}_2\text{O}(l) & = [\text{H}_3\text{O}]^+(\text{aq}) + [\text{OH}]^-(\text{aq}) & (1.2)
\end{align*}

In addition, both water and liquid ammonia are ionising solvents as well as excellent electrolytic solvents. However, the extremely low electrical conductivity of liquid ammonia in comparison with water shows that its degree of ionisation in accordance with equation 1.1 is even less than for water.
Table 1.1 Selected physical constants for NH₃, H₂O, H₂S and PH₃

<table>
<thead>
<tr>
<th>Physical Constants</th>
<th>Liquid Ammonia¹</th>
<th>Water²</th>
<th>Phosphine³</th>
<th>Hydrogen Sulfide⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.D.M. μ (debyes, D)</td>
<td>1.47</td>
<td>1.85</td>
<td>0.58</td>
<td>0.97</td>
</tr>
<tr>
<td>Dielectric Constant (εᵣ)</td>
<td>εₑ₂₅ = 22.40</td>
<td>εₑ₂₅ = 78.54</td>
<td>εₑ₋₇₈ = 2.50</td>
<td>εₑ₋₇₈ = 9.05</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>-77.70</td>
<td>0.00</td>
<td>-133.80</td>
<td>-85.49</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>-33.35</td>
<td>100.00</td>
<td>-87.40</td>
<td>-60.70</td>
</tr>
<tr>
<td>ΔHₜₙₒ (Kjmol⁻¹)</td>
<td>5.654</td>
<td>6.008</td>
<td>-</td>
<td>2.376</td>
</tr>
<tr>
<td>ΔHᵥₚ (Kjmol⁻¹)</td>
<td>23.350</td>
<td>40.878</td>
<td>-</td>
<td>18.673</td>
</tr>
</tbody>
</table>

Legend: E.D.M: Electric Dipole Moment (μ) of molecules in gas phase (± 0.01 D)

Dielectric Constant (εᵣ) taken at temperature T (°C). Data above normal boiling point obtained at the vapour pressure of the liquid at T.
Pᵥₑ (°C): Temperature required to obtain a vapour pressure (Pᵥₑ) equivalent to 100 mm Hg
ΔHₜₙₒ: Latent heat of fusion
ΔHᵥₚ: Latent heat of vaporisation

It should be noted that owing to a lower dielectric constant (εₑₑ ≈ 22; εₑₐq ≈ 82)⁴, liquid ammonia is better suited than water to dissolve compounds with a higher degree of covalency. Indeed, it is the subtle differences in properties that have stimulated much research into liquid ammonia solutions.⁶ A selection of the more fundamental differences is described below.

Liquid ammonia dissolves a range of metals without reaction (group 1, Sr, Ba, Eu, Yb). The dissolution of the alkali metals was first published by Weyl in 1864.⁷ Since then, this property has shown to have many important organic and inorganic synthetic applications. These solutions are amongst the best homogeneous reducing agents. Such reactions include the reductions of elements, chemical bonds, salts and covalent compounds.⁸ Generally, the reductions are independent of the metal used, unless the solubilities of the reaction products influence the course of the reaction (the amides of lithium and sodium are highly insoluble, unlike potassium amide). Certain reactions become allowed in metallo-ammonia solutions,
since the reagents have a longer ‘life expectancy’ (a more detailed description of these solutions is dealt with later, in section 1.2c; p. 16). This is typified by the unique reduction of sodium nitrite ($\text{N}_2\text{O}_3$) to sodium nitroxylate ($\text{N}_2\text{O}_4$) by sodium in liquid ammonia - equation 1.3.

$$2\text{NaNO}_3(\text{am}) + 2\text{Na}(\text{am}) \rightarrow \text{Na}_4\text{N}_2\text{O}_4$$  (1.3)

It may be said that the controlled stepwise reduction of materials by metallo-ammonia solutions has found dominance in organic, rather than inorganic synthesis. An example is given (equations 1.4, 1.5) for the preparation of some useful organo-pnictide precursors ($\text{Pn} = \text{Sb}, \text{Bi}$).

$$(\text{C}_6\text{H}_5)_2\text{Pn-I(ani)} + \text{Na}(\text{am}) \rightarrow (\text{C}_6\text{H}_5)_2\text{Pn}(\text{am}) + \text{NaI(s)}$$  (1.4)

$$(\text{C}_6\text{H}_5)_2\text{Pn}^- (\text{am}) + \text{Na}(\text{am}) \rightarrow (\text{C}_6\text{H}_5)_2\text{PnNa}(\text{am}) + \text{NaI(s)}$$  (1.5)

Where reactions between the solvent and solvated species are undesired, the target product yield may be increased upon using liquid ammonia rather than water. An important application of this in organic chemistry is the preparation of germane from Mg$_2$Ge. In aqueous solution the reaction with HBr yields germane in 20 % yield. The non aqueous analogy ($\text{NH}_3/\text{NH}_4\text{Br}$) results in an increase in yield to 80 %.

The temperature range at which ammonia is a liquid (-78°C to -33°C) enables the preparation of certain materials that are thermodynamically unstable at higher temperatures. As an example of this one may look at the effect of temperature ($T$) upon the reaction between ammonium chloride and potassium nitrate in liquid ammonia (equation 1.6) and water (equation 1.7).

$$\text{NH}_4\text{Cl}(\text{am}) + \text{KNO}_2(\text{am}) \rightarrow \text{NH}_4\text{NO}_2(\text{s}) + \text{KCl}(\text{am}) \quad -78 \, ^\circ\text{C} \leq T \leq -33 \, ^\circ\text{C}$$  (1.6)

$$\text{NH}_4\text{Cl}(\text{aq}) + \text{KNO}_2(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + \text{KCl}(\text{aq}) \quad T \geq 0 \, ^\circ\text{C}$$  (1.7)

If one considers the driving force to the equilibria of many ionic solution reactions as being the formation of insoluble salts, then the differences in solubility of species can lead to
marked differences in reaction pathways when comparing aqueous and liquid ammonia solutions. A good example of these is described by equations 1.8 and 1.9 if one considers that BaBr$_2$ is the least soluble of the species in liquid ammonia whereas in water, AgBr is the most insoluble material.\(^1\)

\[
\text{Ba(NO}_3\text{)}_2\text{(am)} + 2\text{AgBr(am)} \rightarrow 2\text{AgNO}_3\text{(am)} + \text{BaBr}_2\text{(s)} \quad \text{Solvent is NH}_3\text{(l)} \quad (1.8)
\]

\[
2\text{AgNO}_3\text{(aq)} + \text{BaBr}_2\text{(aq)} \rightarrow \text{Ba(NO}_3\text{)}_2\text{(aq)} + 2\text{AgBr(s)} \quad \text{Solvent is H}_2\text{O(l)} \quad (1.9)
\]

1.1c General reaction types in liquid ammonia

Solvolysis

Dissolution of ionic solids in liquid ammonia resembles that of water since both solvent molecules have strong dipoles with electron lone pair(s) on the unique atom.\(^1\)\(^2\) Therefore, dissolution will occur if the lattice energy of the solid is less than the solvation energy, to which the cation-dipole forces being the major contributor. Owing to their similar sizes, a first co-ordination sphere of six solvent molecules around each cation is common for both liquid ammonia and water. These ion-dipole electrostatic interactions commonly result in the formation of ammoniates (cf. salt hydrates).\(^1\)\(^0\) The ionic nature of these interactions (typical of salts of groups 1 and 2) result in the ammoniates exerting a dissociation vapour pressure of ammonia, and so may be completely removed more easily than the analogous hydrates by facile heating under vacuum.\(^1\)\(^1\) As with the nature of cations in aqueous solutions, those with a larger charge to radius ratio (typically a formal oxidation state greater than +II) interact more strongly with the solvating ammonia molecules, creating extensive distortion of the ligand charge cloud. This increasing covalent character may lead to the ammoniate acting as a Bronsted acid, thereby leading to ammonolysis (cf. hydrolysis; equations 1.10, 1.11).\(^1\)\(^2\)

\[
[M\text{(NH}_3\text{)}_6\text{]}^{3+} + \text{NH}_3 = [\text{NH}_4]^+ + [M\text{(NH}_3\text{)}_5\text{(NH}_2\text{)}]\text{]}^{2+} \quad \text{‘Ammonolysis’} \quad (1.10)
\]

\[
[M\text{(H}_2\text{O)}_6\text{]}^{3+} + \text{H}_2\text{O} = [\text{H}_3\text{O}]^+ + [M\text{(H}_2\text{O)}_5\text{(OH)}]\text{]}^{2+} \quad \text{‘Hydrolysis’} \quad (1.11)
\]

The analogy continues in the presence of added base (OH$^-$ or NH$_2^-$) whereby solvolysis continues in a ‘stepwise’ fashion, resulting in the formation of consecutively reduced metal complexes (ultimately to the formation of metal amides which, due to their polymeric
nature, will precipitate). In addition, amphoterism occurs for both solvent species with the addition of excess base, generating amido metallates (analogous to oxo-metallates). Complete ammonolysis occurs with some of the covalent halides (notably that of Group 14, equation 1.12).

\[
\text{SiCl}_4 + 8\text{NH}_3 \rightarrow \text{Si(NH}_2)_4 + 4\text{NH}_4\text{Cl} \quad (1.12)
\]

Note: At \(0 \, ^\circ \text{C} \leq T \leq 100 \, ^\circ \text{C}\):

\[
\text{Si(NH}_3)_4 \rightarrow \text{SiNH(NH}_2) + \text{NH}_3
\]

**Acid-Base reactions**

Liquid ammonia is a more basic solvent than water. Strong acids are thus reduced in acidity to that of the ammonium ion (analogous to aqueous solutions). However, acids that are weak in aqueous solution have enhanced acidity in ammonia due to their ability to protonate the ammonia molecule. Thus hydrogen sulfide becomes ammonium hydrogen sulfide. As mentioned previously, metal ions as well as covalent metal and non-metal halides can also produce the ammonium ion by solvolysis. In contrast there are few bases in ammonia. Only alkali metal amides show any appreciable basicity (of which only potassium amide is appreciably soluble). Alkali metal hydroxides show very little basicity due to their insolubility. The amide ion will form only from strong bases (equations 1.13, 1.14).

\[
\text{KH} + \text{NH}_3 \rightarrow \text{KNH}_2 + \text{H}_2 \quad (1.13)
\]

\[
\text{Na}_2\text{O} + \text{NH}_3 \rightarrow \text{NaNH}_2 + \text{NaOH} \quad (1.14)
\]

**Redox**

Only oxidising agents that can oxidize ammonia can be used in redox reactions, and so this type of reaction is more limited than for non-aqueous solutions. However, it must be remembered that the large overvoltage (\(ca. 1\) V) that ammonia can exhibit through solvated electrons can enable the synthesis of metal compounds of unusually low oxidation states. This is exemplified by equation 1.15.

\[
K_{(am)} + K_4[M(\text{CN})_4]_{(am)} \rightarrow K_4[M(\text{CN})_4]_{(am)} \quad (M = \text{Ni, Pd})
\]

\[
M^{II} \rightarrow M^0
\]
The majority of synthetic reactions in liquid ammonia solutions that cannot be classified as either acid-base or redox are metathetical, where the driving force of the reaction is the insolubility of one or more of the products. Simple substitution reactions for the \([\text{M(NH}_3]_6\)^{2+} cation in liquid ammonia occur more readily than than the \([\text{M(OH}_2]_3\)^{2+} cation in aqueous solution. This is due, in part, to both the difficulty in obtaining high ligand concentrations as well as the lower solubilities in liquid ammonia, resulting in intermediate precipitation.\(^\text{18}\) This is exemplified by the treatment of metal (II) salts with ammonium chloride, whereby the amines of the metal (II) chlorides precipitate preferentially to the chlorometallates (equations 1.16, 1.17)\(^\text{18}\)

\[
\begin{align*}
\text{[Co(NH}_3]_6^{2+}} \text{(am)} + \text{excess Cl}^- \text{(am)} & \rightarrow \text{[Co(NH}_3]_6\text{Cl}_2} \text{(s)} \quad (1.16) \\
\text{[Co(OH}_2]_3^{2+}} \text{(aq)} + \text{excess Cl}^- \text{(aq)} & \rightarrow \text{[CoCl}_6]^{2-} \text{(aq)} + 6 \text{H}_2\text{O} \text{(l)} \quad (1.17)
\end{align*}
\]

Anionic species must be either precipitated directly or formed by ammonolysis (such as with covalent halides with readily polarisable anions), as shown in equations 1.18 and 1.19.\(^\text{18}\)

\[
\begin{align*}
\text{[Ti(NH}_3]_4\text{Br}_2}\text{Br} + 7\text{CsCN} & \rightarrow \text{Cs}_4\text{[Ti(CN)}_3]_1 \downarrow + 3\text{CsBr} + 4\text{NH}_3 \quad (1.18) \\
\text{[Co(NH}_3]_6\text{(SCN)}_2} + 2\text{KCN} & \rightarrow \text{Co(CN)}_2.x\text{NH}_3 + \text{excess KCN} \rightarrow \text{[Co(CN)}_3]^{2+} \quad (1.19)
\end{align*}
\]

Many metathetical preparations are not paralleled in either aqueous or other common solvents. The greater basicity and reduced tendency towards solvolysis of liquid ammonia enables the synthesis of salts containing ligands that would be protonated by water (such as \text{NH}_2^-, \text{PH}_2^-, \text{O}_2^2- and \text{C:CH}).\(^\text{15}\)
1.2 Chemistry of some N-based solutions

Rauchfauss et al. have reported the isolation from strongly coordinating nitrogen based solvents (such as TMEDA) of a variety of species of general formula $\text{MS}_6(\text{solv})_2$, where the metal is divalent cadmium or zinc. They observed the formation of the common metal sulfides (ZnS and CdS) upon heating the solid products to 500 °C. This has fuelled some research into the formation of other metal chalcogenides from other nitrogen based solvents. From our perspective, we have researched syntheses in both liquid ammonia and n-butylamine. The behaviour of sulfur upon its dissolution in these solvents is discussed below.

1.2a Chemistry of sulfur–ammonia solutions

Sulfur is known to dissolve in liquid ammonia within a few hours to form highly coloured solutions (blue / green at RT; red at low temperature). The solvated species have absorption maxima at 295 nm, 450 nm and 580 nm, which vary very little with concentration at -35 °C. The solutions are fairly strong electrolytes ($\sigma \approx 1$ unit charge for every 5 or 6 sulfur atoms). This is unique with respects to the dissolution of sulfur in organic solvents (such as $\text{CS}_2$), whereby solvation as either a ring or chain results in colourless, non-conducting solutions. Upon evaporation of ammonia, all sulfur is retrieved as crystalline modifications of the $\text{S}_8$ ring.

The characterisation of the solvated species in sulfur-ammonia solutions has been, and still continues to be, the focus of much speculation. Kerovorton's study of 0.1M solutions of sulfur in ammonia at room temperature, under pressure, showed absorption maxima at 440 nm and 585 nm (and a broad band at 610 nm after time), with no e.s.r. signal. In conjunction with electrochemical studies, he concluded that the dissolution of sulfur in liquid ammonia at room temperature afforded the chromophores $\text{S}_2\text{NH}_3$ (red) and $\text{SNH}_3$ (blue), and so may be represented by equation 1.20

$$6\text{S} + 2\text{NH}_3 = 3[\text{S}_2\text{NH}_3]^2 + 6\text{H}^+ + 2\text{N}_2$$ (1.20)

Conversely, on the basis of one electrochemical study, Guiraud suggested that sulfur dissolves in liquid ammonia to afford dinitrogen and hydrogen sulfide (equation 1.21).

$$3\text{S} + 2\text{NH}_3 = 3\text{H}_2\text{S} + \text{N}_2$$ (1.21)
The identity of the solvated species has also been suggested from synthetic uses of sulfur-ammonia solutions in organic chemistry. Notable examples include the reaction with 4-chloronitrobenzene, affording 4-nitrobenzene-thiosulphonamide (O₂NC₆H₄SSNH₂). This suggests the presence of such ions as [H₂NS]⁻ and [H₂NS₂]⁻. Also, the reaction of gaseous ammonia with sulfur in hexamethyl phosphoric triamide (HMPT) affords [S₄N]⁻ which Chivers suggested was responsible for the blue colouration in sulfur-ammonia solutions.

Meyer reported a Raman spectrum of sulfur dissolved in liquid ammonia and suggested the existence of [S₃]⁻, [S₄]⁻ and [S₅N]⁻. Civers confirmed the existence of [S₃]⁻ and [S₅N]⁻ by matching solution and solid state vibrational frequencies using Raman and UV/vis spectroscopy. He suggested that Kerovorton did not observe an e.s.r. spectrum due to dimerisation of the [S₃]⁻ radical at high concentrations (equation 1.22).

Chivers then proposed a mechanism for the dissolution of sulfur in liquid ammonia based upon a redox disproportionation process. The nucleophilic attack of sulfur by [NH₂]⁻ affords [S₈NH₂]⁻ which would then disproportionate to give [S₅N]⁻ and H₂S, and subsequently [S₅N]⁻ and ammonium polysulfide. Bernard described these equilibria by equations 1.22 and 1.23.

\[
\begin{align*}
2[S₃]⁻ &= [S₅]⁻ \quad (1.22) \\
10S + 4NH₃ &= [S₅N]⁻ + [S₄]⁻ + 3[NH₂]⁻ \quad (1.23)
\end{align*}
\]

However, subsequent Raman detection of the [S₃N]⁻ anion as well as the observation of large amounts of sulfur present in the zero oxidation state upon the addition of sodamide, showed these equations to be oversimplified.

Prestel tried to quantify these species by monitoring the changes to the sulfur-ammonia system by continuous light irradiation (using UV/vis and Raman spectroscopies) as well as upon addition of silver salts. He proposed that the main species present were [S₅N]⁻ (37%), [S₄N]⁻ (4%) and [S₅N]⁻ (6%), in addition to various ammonium polysulfides.

Lepoutre et al. rebuked these values, suggesting that the sulfur-ammonia solution had not been left for a sufficient length of time to fully equalibriate, proposing a time of up to 1000 hours. He proposed a series of equilibria that rely upon the existence of both...
$S_2NH_3$ and $[S_2NH_3]^{2-}$. These are represented in figure 1.2.

**Figure 1.2** Equalibria associated with Lepoutre’s proposed dissolution of sulfur in liquid ammonia

\[
\begin{align*}
\text{S}_8 + \text{NH}_3 & \quad \rightarrow \quad \text{S}_8\text{NH}_3 \\
\text{S}_8\text{NH}_3 & \quad \rightarrow \quad [\text{S}_6]^{2-} + [S_2\text{NH}_3]^{2+} \\
\text{S}_2\text{NH}_3 + \text{NH}_3 & \quad \rightarrow \quad 3[\text{NH}_4]^+ + [S_2\text{N}]^- = [S_2\text{NH}_3]^{2+} + 3\text{NH}_3 \\
\text{NH}_3 + S_8\text{NH}_3 & \quad = 4S_2\text{NH}_3 \\
S_2\text{NH}_3 + \text{NH}_3 & \quad = \text{SNH}_3 + [S_3\text{N}] \\
\text{S}_2\text{NH}_3 + \text{NH}_3 & \quad = 2\text{SNH}_3 \\
5S_2\text{NH}_3 & \quad = \text{NH}_3 + [\text{NH}_4]^+ + [S_4\text{N}]^+ + [\text{S}_6]^{2-} \\
\end{align*}
\]

Also,

$S_8 + [\text{NH}_2]^- = [S_8\text{NH}_2]^-$

Without question, some of the anionic species proposed have been unequivocally detected, such as $[S_3\text{N}]^-$, $[S_4\text{N}]^-$ and $[S_6]$.\textsuperscript{2} In general, the sulfur-ammonia system may be described as a solution containing a complex and interdependant series of equilibria, established between anionic / neutral sulfur-nitrogen rings and polysulfur anions.\textsuperscript{32-33} However, to enable more accurate analysis requires either new techniques or improvements in the existing techniques. As with the previous studies on this subject, in the absence of irrevocable quantified results any proposed series of equilibria are speculative. Analysis has relied heavily upon UV/vis and Raman spectroscopies which are restricted, even as qualitative tools, by the very nature of the absorption maxima (broad and of varying intensity).

With interest to this ongoing saga, attention is drawn to more recently, Woollins \textit{et al.}, who have analysed the solvated species produced upon dissolution of a variety of sulfur-nitrogen compounds in liquid ammonia by $^{14}$N NMR. Interestingly, they observe that the dissolution of a wide range of sulfur-nitrogen species gives rise, unequivocally,
to $[S_N^3]$ as the major species and, in some cases, $[S_{N^3}]^-$, They have gone on to suggest the presence of $[S^2_N]^2$, $[S_N^2]^-$ and $[S_N^1]^-$, at low levels in equilibrium with the $[S_N^3]^-$ anion (based upon previously reported chemical shift values for the nitrogen in sulfur diimides). \cite{34}

The work by Dubois, Lelicur, Lepoutre\cite{32,33} into the simple dissolution of sulfur show the major species present to be $S_{N^3}$, $[S_n]^2$ and $S_{N}^-$. The general reaction scheme is illustrated in an abridged format below:

\begin{align*}
\text{generally} : & S_N \rightarrow S_{N^3} = S_{n}^{2-} \{0 < n < 7\} \\
\text{In detail (simplified)} \quad \text{Note the } \textit{in situ} \text{ abundance of hydrogen sulfide.} \\
S_N + NH_3 &= S_{N^3}^- + H_2S \\
S_{N^3}^- + NH_3 + S &= S_{N^3}^- + S_{N^-}^- + H_2S \\
S_{N^-}^- + 2NH_3 + 2S &= S_{N^3}^- + H_2S \\
S_{N^-}^- + 2NH_3 + 3S &= S_{N^3}^- + H_2S \\
H_2S + (n-1)S &= S_n^{2-}
\end{align*}

Dubois \textit{et al.} have postulated that the formation of the least massive polyanions (such as the $S^2^-$ species - the main anionic constituent of the sulfides prepared can only be formed from the above reaction scheme by \textit{in situ} reactions that result in a favourable shift in the polyanionic equilibria. They suggest that three mechanistic routes should be considered:

(A) Reaction of $H_2S$ with $NH_3$

\begin{align*}
H_2S + NH_3 &= (NH_4)^+ HS^- \quad \text{at pH} < 5.8 \quad \text{(acidic solution)} \\
(NH_4)^+ HS^- + NH_3 &= 2(NH_4)^+ + S^{2-} \quad \text{at pH} \geq 5.8 \quad \text{(acidic or neutral solutions)}
\end{align*}

The plausibility of this mechanism is two fold. First, there is a high $\textit{in situ}$ concentration of $H_2S$ on dissolution of sulfur in liquid ammonia. Secondly, the
solvation of an electron may lead either directly to the reduction of HS\(^-\) (or indeed H\(_2\)S) to S\(^{2-}\) or to the formation of an amide which, if in sufficient concentration, will raise the pH above 5.8.

(B) Reaction between S-N rings and S-polyanions in the presence of the amide anion

(C) Dissociation of the polyanions – this is described in figure 1.3

Figure 1.3 Dissociation of sulfur polyanions in liquid ammonia

\[
\begin{align*}
[S_6]^{2+} &= 2[S_3]^- \\
\downarrow \uparrow & \quad \downarrow \uparrow \\
\downarrow \uparrow & \quad \downarrow \uparrow \\
2[S_3]^{2-} &= [S_4]^{2-} + [S_2]^{2-} \\
\uparrow & \quad \downarrow \\
[S_3]^{2-} + S^{2-} &= 2[S_2]^{2-}
\end{align*}
\]

On dissolution of sulfur, the initial concentrations of all the polyanions with n < 6 is very small. Since there is no net transfer of charge during dissociation, this mechanism is independent of the solvent used and its pH. However, the above two pathways (A and B) will favour the formation of the lower order polyanions, whether by direct formation of the polyanions themselves, or by creating a favourable shift in the above equilibria (such as the removal from solution of S\(_4^{2-}\) and increase in the concentration of S\(_2^{2-}\)).

We could surmise, therefore, that the solvent can act as a "carrier" of electrons from the metal to the hydrogen sulfide via the formation of NH\(_2^-\), which also acts as the base required to enable the full reduction of this sulfide species. This reduction is facilitated by the oxidation of the amide by sulfur-nitrogen anionic rings. The formation of the S\(^{2-}\) anion is further assisted by favourable shifts in the dissociative equilibria for the polyanions.

Whether or not the above equilibria are responsible mechanistically in the formation of
metal sulfides from their respective elements, they are fundamental in the necessity for these reaction to be carried out in anhydrous, anaerobic conditions. In the presence of NH$_3$/H$_2$S, S$_3$N$_3^-$ can be very readily oxidised to a solid, thereby driving the equilibria towards the removal of sulfur from solution (equations 1.24 and 1.25).

$$S_3N_3^- + [O] = S_4N_4^-$$ (1.24)
$$S_4N_4^- + NH_3 \rightarrow \{S_3N_3^- + SN_2^{2-} + 3 H^+\} \rightarrow S_4N_4.NH_3 \text{ (solid)}$$ (1.25)

Coincidentally, small amounts of water can also greatly restrict the extent of any mechanism arising from solvated sulfur species (equations 6a and 6b), by reducing the concentrations of both HS$^-$ from mechanism A and S$_2^{2-}$ from mechanism B.

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$ (1.26)
$$OH^- + HS^- + S_3^{2-} \rightarrow 2S_2^{2-} + H_2O$$ (1.27)

Red selenium has a very restricted solubility in liquid ammonia. Both black selenium and tellurium (black or grey) are insoluble in liquid ammonia.

### 1.2b Chalcohalides as an ‘in situ’ source of chalcogen

The formation of ‘in situ’ chalcogen may be of considerable synthetic value when considering elemental combination reactions at room temperature. The use of chalcohalides as a suitable precursor in liquid ammonia is considered here – that is, those compounds containing both a chalcogen (S, Se or Te) and a halide (F, Cl or Br). Chalcohalides undergo rapid solvolysis in liquid ammonia, resulting in the formation of the co-produced salt (ammonium halide). A selection of these reactions is given in table 1.2.
Table 1.2 Reaction products of ammonolysis of some chalcohalides

<table>
<thead>
<tr>
<th>Oxidation State of Chalcogen</th>
<th>Halide used (X = Cl, Br)</th>
<th>Reaction Products (NH₄X not shown)</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ I</td>
<td>S₂Cl₂</td>
<td>S₄N₄ + S</td>
</tr>
<tr>
<td>+ I</td>
<td>Se₂X₂</td>
<td>Se₂NX</td>
</tr>
<tr>
<td>+ II</td>
<td>TeCl₂</td>
<td>Te + N₂</td>
</tr>
<tr>
<td>+ II</td>
<td>F₃CSCI</td>
<td>F₃CS(NH₂)</td>
</tr>
<tr>
<td>+ IV</td>
<td>SCl₄</td>
<td>S₄N₄</td>
</tr>
<tr>
<td>+ IV</td>
<td>SeX₄</td>
<td>Se₄N₄ + N₂</td>
</tr>
<tr>
<td>+ IV</td>
<td>TeX₄</td>
<td>Te₄N₄</td>
</tr>
<tr>
<td>+ IV</td>
<td>SOCl₂</td>
<td>NH₄[N(SONH₂)₂]</td>
</tr>
<tr>
<td>+ IV</td>
<td>Ph₃SeCl₂</td>
<td>Ph₃Se</td>
</tr>
<tr>
<td>+ VI</td>
<td>SOF₄</td>
<td>NH₄[SO(N)F₂]</td>
</tr>
<tr>
<td>+ VI</td>
<td>SO₂F₂</td>
<td>SO₂(NH₂)₂</td>
</tr>
<tr>
<td>+ VI</td>
<td>SO₃Cl₂</td>
<td>SO₄(NH₂)₂</td>
</tr>
<tr>
<td>+ VI</td>
<td>S₂O₅F₂</td>
<td>NH₄SO₂F + NH₄SO₃F</td>
</tr>
<tr>
<td>+ VI</td>
<td>S₂O₅Cl₂</td>
<td>SO₂(NH₂)₂ + NH₄[N(SO₂NH₂)₂]</td>
</tr>
</tbody>
</table>

From the table it is clear that whilst the fluorides of sulfur only achieve partial ammonolysis, complete solvolysis in liquid ammonia is observed for the chloride analogues (with the exception of disulfur dichloride, which undergoes disproportionation; equation 1.28).³⁵

6S₂Cl₂ + 16NH₃ → S₄N₄ + 8S + 12NH₄Cl  \hspace{1cm} (1.28)

All the common oxidation states of sulfur undergo some degree of ammonolysis, whether it be a single product (thionyl chloride to sulphamide) or a mixture (sulfuryl chloride is converted to both sulphamide and ammonium imidosulphamide) – refer to Table 1.2.

In terms of the halides of selenium and tellurium in the lower oxidation states,
diselenium dihalides undergo partial ammonolysis whereas tellurium (II) chloride oxidizes ammonia (even at temperatures as low as -50 °C; equation 1.29)\textsuperscript{35}

\[ 3\text{TeCl}_2 + 8\text{NH}_3 \rightarrow 3\text{Te} + \text{N}_2 + 6\text{NH}_4\text{Cl} \]  
(1.29)

The simple chlorides and bromides of high (+IV) oxidation state chalcogens (S, Se, Te) undergo complete ammonolysis to yield the nitrides \( \text{S}_4\text{N}_4 \), \( \text{SeN} \), \( \text{Se}_3\text{N}_4 \), \( \text{Te}_4\text{N}_4 \) and \( \text{Te}_3\text{N}_4 \) (equation 1.30).\textsuperscript{35} It should be noted that \( \text{S}_4\text{N}_4 \), \( \text{Se}_4\text{N}_4 \), \( \text{Te}_4\text{N}_4 \), and \( \text{Te}_3\text{N}_4 \) are all highly explosive solids.\textsuperscript{35}

\[ 3\text{TeBr}_4 + 16\text{NH}_3 \rightarrow \text{Te}_3\text{N}_4 + 12\text{NH}_4\text{Br} \]  
(1.30)

Although the extent of ammonolysis varies with the chalcohalide, this preferential solvent reaction and the resultant formation of amines, imides or nitrides, renders these precursors of little value as an \textit{in situ} source of the chalcogen.

**1.2c Chemistry of metallo-ammonia solutions**

On dissolution of certain metals in liquid ammonia (Group Ia, Ca, Sr, Ba, Eu, Yb) a deep blue solution forms. Jolly\textsuperscript{36} has noted several key observations pertaining to the nature of these metallo-ammonia solutions. The metals involved have very negative reduction potentials. The solutions are excellent electrical conductors, being similar to electrolytic solutions at low metal concentrations and approach metallic behaviour at high concentrations. Conductance measurements show that the ‘negative ion’ is the same for all solvated metals. All the solutions have equivalent light absorptions at the same dilute concentrations and are paramagnetic. They are blue when dilute and bronze when concentrated; a result of the increasing conductivity of the solution.

These observations are a result of the solvation of the electrons formed from the dissolution of the metal to its associated cation.\textsuperscript{37} The stabilisation of the ‘solvated electron’ is due, in part, to the greater stability of the N-H bonds in liquid ammonia relative to the O-H bonds in water, which leads to ammonia having a reduced tendency to react with solvated species. Consequently, ammonolysis is much less extensive than hydrolysis (re: section 1.1c). However, the theory of Ogg\textsuperscript{38} suggests that a free
ammoniated electron is not acceptable on thermodynamic grounds and that the electrons are quantised in cavities they produce in the solvent. These cavities (of similar size to discrete ammonia molecules) would account for the reduced density of the metallo-ammonia solutions, resembling familiar types of electron traps in molecular crystals.\textsuperscript{39} The electrons are thereby believed to become “trapped” within a cage of ammonia molecules, the structure of which absorbs part of the visible electromagnetic spectrum.\textsuperscript{37}

The stabilisation of the solvated electrons, has enabled these solutions to be used as reducing agents in both organic and inorganic chemistry, enabling the preparation of compounds of low oxidation states (re: section 1.1b). Metallo-ammonia solutions are stable for long time periods (> 24 h) in the absence of catalytic impurities such as platinum black or iron (III) oxide.\textsuperscript{\textdagger} Removal of the ammonia leaves alkali metals unchanged and alkali earth metals as metal ammoniates (M\textsubscript{6}NH\textsubscript{4}).\textsuperscript{40} This stability has been attributed to the low electrode potentials of the metals against ammonia (compared to water) in addition to the comparatively low auto-ionisation constant of the solvent (K = 10\textsuperscript{-24} at 25 °C).\textsuperscript{41} It is here that liquid ammonia makes a dramatic departure from the properties of aqueous solution. Whilst in water, the strongest reducing agents reduce H\textsuperscript{+} ions to H\textsubscript{2}, this tendency is low in liquid ammonia. Therefore reduction is characteristic of the direct addition of an electron to an atom or ion, forming a cation and solvated electron. This is typified by the preparation of Na\textsubscript{2}S (equations 1.31 and 1.32).

\begin{align*}
S\textsubscript{(am)} + 2\text{Na}^+\textsubscript{(am)} + 2e^-\textsubscript{(am)} &\rightarrow S^{2-}\textsubscript{(am)} + 2\text{Na}^+\textsubscript{(am)} \\
S\textsubscript{(aq)} + 2\text{Na}^+\textsubscript{(aq)} + 2e^-\textsubscript{(aq)} &\rightarrow S\textsubscript{(aq)} + 2\text{Na}^+\textsubscript{(aq)} + 2\text{OH}^-\textsubscript{(aq)} + \text{H}_2\textsubscript{(g)}
\end{align*} \textsuperscript{(1.31) (1.32)}

It may be said that, unlike most ionic solvents, the free energy diagram for the dissolution of a metal in ammonia exhibits a significant activation barrier in the reaction coordinate for the conversion of solvated electrons / metal cation to the ground state products. The consequence of this is that these very reactive species are relatively long lived. However, when considering these species one cannot ignore the ultimate thermodynamic response to what are ultimately metastable products (typified by the reaction of sodium below and facilitated by the presence of the aforementioned catalysts):

27
\[ \text{Na}(s) + \text{NH}_3(l) \rightarrow \text{Na}^+(am) + e^-(am) \]
\[ \text{NH}_3(l) + e^-(am) \rightarrow \text{NH}_2^-(am) \quad + \quad 0.5 \text{H}_2(g) \]
\[ \text{Na}^+(am) + \text{NH}_2^-(am) \rightarrow \text{NaNH}_2(l) \]

Dissolution of the metal is driven, in part, by the electronic stability of the cations that are formed:

\[ \text{Na}(s) + \text{NH}_3(l) \rightarrow \text{Na}^+(am) + e^-(am) \]
\[ \text{Mg}(s) + \text{NH}_3(l) \rightarrow \text{Mg}^{2+}(am) + 2e^-(am) \]

Both metal cations have the stable electronic configurations \([\text{Ne}]2s^22p^6\) associated with a full p-valence orbital.

Similarly, Eu and Yb both form divalent cations, through the loss of their 6S\(^2\) electrons, thereby obtaining the kinetic stability of either a half filled valence 4f subshell (Eu\(^{II}\) : \([\text{Xe}]4f^7\)) or a full 4f subshell (Yb\(^{II}\) : \([\text{Xe}]4f^{14}\)).

### 1.2d Chemistry of sulfur-amine solutions

Whilst alkali metals generate solvated electrons upon dissolution in amines of low molecular weight (notable methylamine and ethylamine), they do not exhibit such behaviour in n-butylamine.\(^{36}\) However, 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 \textit{in situ} release of H\(_2\)S), and then the progressive attack of the aliphatic amine by hydrogen sulfide to yield amine polysulfides.\(^{42}\) These new sulfur-amine species co-exist 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.\(^{42}\) 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 may provide a mechanistic route for the reaction of sulfur with elemental metals. Ternary amines do not exhibit the same behaviour. Hodgson \textit{et al.} also observed that the extent of reaction with the S\(_8\) rings was a simple coordination phenomena resulting in the formation of a R\(_3\)N-S\(_8\) moiety. The N-S bond is effectively
polarised such that the nitrogen lone pair resides mainly in an orbital with a high degree of 3p character. This electronic transition from the nitrogen to the sulfur results in fluorescence, thereby making the sulfur appear “more yellow” than in the absence of tert-butylamine. Selenium and tellurium are insoluble in n-butylamine. No formal chemistry has been researched pertaining to the synthesis of bulk metal chalcogenides in n-butylamine from direct combination of the elements.
1.3 Synthetic routes to metal chalcogenides

1.3.1 Bulk materials

In terms of discussing the possible synthetic routes to metal chalcogenides, one must first address whether a bulk material or thin film is required. Various established syntheses exist for the synthesis of bulk materials. The Group 16 hydrides have been widely used in the precipitation of aqueous cations from solution, as well as in reaction with metal oxides, to yield a variety of single phased metal chalcogenides. Traditional routes (elemental combination reactions) employ elevated temperatures (ca. 800 - 1400 °C), long processing times (ca. 3-7 days) and offer little control over material stoichiometry. Research into improving this technique has lead to the development of self-propagating high temperature synthesis (SHS) and solid state metathesis (SSM) reactions, described in detail below.

1.3.1a Self-propagating High Temperature Synthesis

SHS (or ‘combustion synthesis’) is any processing technique that utilises highly exothermic reactions to obtain a sustainable combustion wave. Following initiation of a region of the reaction mixture (typically by either a high temperature flame or resistively heated wire), sufficient heat is generated to either vapourise or liquefy most of the reagents and products. Consequently, solid state diffusion is no longer rate limiting and the rate of reaction greatly exceeds the rate of heat dissipation. The reaction becomes self-propagating, thereby greatly reducing processing time and applied energy when compared to conventional sintering. High reaction temperatures may also expel volatile impurities. SHS can be broadly categorised into three main reaction types described below.

1. Elemental reactions – e.g. Ti + C + Ni + Al → TiC + NiAl
2. Thermite reactions – e.g. 3TiO₂ + 4Al + 3C → 3TiC + 2Al₂O₃
3. Metathesis reactions – e.g. Ti₂O₃ + 2AlN → 2TiN + Al₂O₃

SHS has been widely employed in the synthesis of a variety of ceramics, including borides, carbides, nitrides, oxides, intermetallics and composite materials (and have been
extensively reviewed\textsuperscript{31}). However, although SHS appears simple and cost effective, it is problematic to reduce the highly porous nature of the products (typically 50%) without either the application of external means, or by reverting to consolidation of powdered products by conventional multi-stage methods.\textsuperscript{32} High porosity can result from the outgassing of impurities or from pores present in the reagents (the short reaction times result in little time for sintering).\textsuperscript{33} In addition, higher reaction temperatures typically result in larger volume changes, which make densification difficult.\textsuperscript{32} Preheating of reagents is often employed to increase reaction temperature to a point where a liquid phase forms, facilitating densification.\textsuperscript{34,35} However, since most ceramics have notably higher densities in the solid state, significant porosity may still arise upon solidification, in which case the temperature must be maintained above the ductile-brittle transition temperature.\textsuperscript{35} High reaction rates also variation in the sintering conditions and so the control of microstructure (specifically grain size and density). In the case of a purely solid state reaction, reagent particle size becomes critical to the reaction temperature, thereby giving some degree of control over reaction conditions.\textsuperscript{36} It has been observed that increasing the particle size results in a decreasing combustion wave velocity and a 'broadening of the combustion wave.' These changes of conditions may result in a change in the reaction products. Much research is being carried out into the control of reaction rate through particle size, addition of diluents and reaction preheating, in conjunction with the thermodynamic modelling of the SHS process. Ultimately, ways are sought to simultaneously synthesise and densify SHS materials.

The addition of diluents (in the form of either the desired product or as non-reactive species) increases the thermal mass of the system and lowers the combustion temperature, thereby lowering both the reaction rate\textsuperscript{37} and the velocity of the propagation wave.\textsuperscript{38} These principles have been successfully applied to the synthesis of chromium substituted magnesium-zinc ferrite $\text{Mg}_{0.5}\text{Zn}_{0.3}\text{Fe}_2\text{Cr}_x\text{O}_4$ ($0 \leq x \leq 1.5$) by Parkin \textit{et al.}\textsuperscript{39} (equation 1.33). They have not only shown that SHS can be used to form complex materials with tight control on stoichiometry, but also that the application of a 1.1T magnetic field to such reactions influences the microstructure and magnetic properties of the final material.
Fe + 0.5MgO + 0.5ZnO + 0.35Fe₂O₃ + 0.15Cr₂O₃ + 0.375NaClO₄ → Mg₀.₅Zn₀.₅Fe₁.₇Cr₃O₄
+ 0.375NaCl (1.33)

However, for such SHS reactions to become self-sustaining, the calculated adiabatic reaction temperature must be in excess of 1525 °C. These typically high reaction temperatures limit the application of SHS in the synthesis of metal chalcogenides, whether due to product decomposition or undesirable changes in either phase or state. Yi and Moore⁴¹ write that 'success has been largely restricted to the synthesis of high temperature transition metal dichalcogenides M₀S₂, NbS₂, WSe₂, and TaSe₂.' A limitation on the maximum reaction temperature may, however, be achieved by the application of specific solid state metathesis reactions. Any further references made to SSM reactions in this thesis will imply the reactions between alkali metal chalcogenides and metal halides.

1.3.1b Solid State Metathesis

Although SSM may be considered a sub-section of SHS, the metathetical exchange of two or more species during a reaction can, in principle, be carried out in the solid, liquid or gaseous phase. Metathesis reactions thereby have, at first site, a wider scope for synthetic applications. SSM reactions initiate at relatively low temperatures and are extremely rapid (typically 1-5 s). Also, they are frequently self-propagating and sometimes explosive (total heat of formation of the product mixture is typically 100-200 kcal/mol). Some reaction temperatures exceed 1000 °C, the propagation wave can be observed as intense colour flashes and the emission of clouds of volatile material is typical. Unlike many precursor reactions, these by-products are highly ionic in character and so may be easily removed from the markedly less ionic / covalent metal sulfide (to < 0.01 %) simply by trituration with a suitable solvent (water, THF or methanol), although some of the products are solvent sensitive. It is the formation and subsequent melting of this co-produced salt that ultimately gives control of the reaction temperature. The molten salt constitutes the propagation wave of the majority of such reactions, the maximum reaction temperature thereby being restricted to its melting point. Choice of the co-produced salt formed therefore gives a degree of control over the temperature obtained by the reaction. This
liquid phase also results in densification of the product, resulting in a dark fused mass of highly sintered products and by-products.

The use of SSM reactions to form metal chalcogenides has largely focused on the synthesis of metal oxides and sulfides. The reaction of anhydrous metal chlorides with lithium oxide or sodium sulfide has yielded a range of transition metal, lanthanide, actinide and main-group metal chalcogenides. In order to allow propagation of the reaction, such reactions can either be initiated thermally (inside a sealed ampoule), by a heated filament, by mechanical grinding (notably for solids with low melting points), or by simple addition of the reagents at room temperature (notably highly volatile, liquid reagents). The table below shows the binary metal chalcogenides (sulfides, selenides, tellurides) synthesised by this process (as reported for the 1996 Chemical Society Review):

<table>
<thead>
<tr>
<th>MS₂</th>
<th>M = Ti, Zr, Hf, V, Nb, Ta, Mo, W, Ni as well as MoSe₂, WSe₂, WTe₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ME</td>
<td>M = Zn, Hg, Te; E = S, Se, Te as well as MoS, MoTe</td>
</tr>
<tr>
<td>Others</td>
<td>Mo₃Te₄</td>
</tr>
</tbody>
</table>

One of the most active areas of this research (R.B.Kaner *et al.*) has been focused on the formation of layered dichalcogenide materials (MS₂ where M = Mo, W). Mechanistic evaluation has in part evolved from their synthesis of a range of metal mixed chalcogenides (equation 1.34) and mixed metal disulfides (equation 1.35) have also been formed from analogous reactions:

\[
x \text{MoCl}_5 + y \text{WCl}_6 + \text{Na}_2\text{S} \rightarrow \text{Mo}_x\text{W}_y\text{S}_2 + \text{NaCl} \quad (1.34)
\]

\[
\text{MoCl}_5 + \text{Na}_2\text{S}_x\text{Se}_y \rightarrow \text{MoS}_p\text{Se}_q + \text{NaCl} \quad \text{where } p > x \text{ and } q < y \quad (1.35)
\]

From equation 1.35 one can see that filament-initiated SSM synthesis of metal mixed dichalcogenides (MoSₓSeᵧ) result in a product whose stoichiometry does not reflect that of the starting materials. Kaner suggests that the high energy released in the propagation wave allow a significantly greater mobility of the more volatile sulfur, and so higher sulfur content in the reaction product relative to the selenium. Conversely, the relative low
volatility (and so mobility) of the intermediate tellurium species results in an
inhomogeneous tellurium concentration throughout the reaction mixture. Consequently,
they were unable to form the analogous MoTe_2 and WTe_2 materials by filament-initiated
SSM reactions. Repeating the aforementioned reactions with alkali-metal mixed
dichalcogenide (Na_xS_x, Na_xSe_x) precursors again showed the aforementioned influence
of reaction temperature upon product stoichiometry. Kaner suggests this selective
enrichment of the more volatile chalcogen to be indicative of elemental intermediates in the
reaction mechanism.

It is not uncommon for SSM reactions themselves to form mixed products - reactions of
lanthanide halides with sodium sulfide have, in some cases, formed both binary (Ln_xS_x) and
ternary products (NaLnS_y). Interestingly, it is reported that these reactions have also
been hampered somewhat by oxygen contamination from the air or the vessel walls.

Interestingly, many studies have been carried out for making ceramic materials with
improved mechanical properties. The metal oxides should be monodispersed,
stoichiometric, homogeneous, dense and consist of spherical particles. Matijevic has
produced a variety of materials as monodispersed spheres or polyhedra by ageing metal
salts at high temperature, or by heating dilute solutions of metal chlorides in either urea or
formamide. More recently, hydrolytic condensation of metal alkoxides, followed by
calcination, has produced submicrometer sized spheres of such materials as amorphous
SiO_2, ZrO_2, Ta_2O_5, TiO_2, Sr-Ta-doped TiO_2, SnO_2 and crystalline ZnO. Gulliver and co­
workers have extended the methodology to include the formation of SnO_2 (≤ 250 nm
diameter) and ZnSnO_3 powders, the former being of use as gas sensors.

This metathetical route has been extended in recent years with the synthesis of binary main­
group and ternary transition-main-group metal compounds, pnictide materials have been
shown to be equally accessible to this technique as chalcogenides. These reaction-types
may also be carried out in either uncoordinating (e.g. toluene) or coordinating solvents
(e.g. diglyme), whether in solution or with the presence of a solution-solid interface.
Chapter 6 of this thesis refers to the synthetic study of some binary and ternary
chalcogenide materials in liquid ammonia.
1.3.2 Thin film material synthesis

The continuing progress into thin film syntheses has been largely fuelled by the requirements of the optical and electronics industry, with developments in technological devices demanding thin films (< 5μm) of sufficiently high purity, homogeneity and uniformity of structure. Although the research reported in this thesis is solely based upon bulk materials, by mentioning some key synthetic procedures relating to thin films this thesis also deals with related chemistry as well as some key properties of the compounds concerned.

1.3.2a Electrodeposition

Electro-deposition of compound semiconductors has been shown to be useful in the construction of thin films, and so offers 'a potentially low cost step in the manufacture of photo-voltaic cells' (writes Stephen Dennison™). Research has focused on the deposition of IIb-VI materials, in particular CdXe films for n-CdS/p-CdTe solar cells. Two major issues exist concerning the electrodeposition process. The electrochemical control of dopant and poisoning (impurities) species present in the electrolyte, and the electrochemical control of the overall semiconductor stoichiometry (including the understanding of the mechanisms of the deposition reactions).

The effects of dopant and impurity species have been investigated in some detail, both in terms of the correlation between the solution concentration and the resultant concentration in the electrodeposited material,™ as well as in terms of the parameters required for photovoltaic devices.™

With respects to the electrochemical control of deposition, Kröger™ proposed a model whereby the stoichiometry of the semiconductors is determined by the dynamic equilibrium existing between the solution and the depositing solid phase(s). This instantaneous equilibrium could be measured as a Nernstian potential (the quasi-rest potential, or QRP), and so control of the bulk composition of the semiconductor could be obtained by careful control of the QRP of the deposit with respect to the solution. He showed, experimentally, that increasing the QRP to more positive potentials resulted in a change from n- to p-type conduction in the CdTe deposit. However, using the QRP as a means of controlling the
composition of the depositing semiconductor may have serious physical restraints due to the time required for the collapse of the diffusion layer at the electrode / electrolyte interface. Indeed, Stephen Dennison (working on Cl\textsuperscript{-} doped CdTe deposition onto a tin doped indium oxide / CdS substrate, from solutions of CdSO\textsubscript{4} and HTeO\textsubscript{2}\textsuperscript{-}) has shown experimentally that the QRP is not a significant parameter in the control of photovoltaic, structural and morphological properties of high quality CdTe films. Instead, by confirming the existence of the hitherto theoretical constant potential for perfect CdTe stoichiometry, his work favours the model which allows the surface stoichiometry of the electrochemical deposition to be predicted based purely upon the kinetics of the system. However, one cannot refute the model of QRP since the experimental analysis of QRP decay may be swamped by the distribution in resistance across the surface of the doped substrate and, to a lesser degree, across the depositing film itself. Analysis of the QRP therefore requires either an electrode system of lower resistance whose hydrodynamics are better understood, or one whose characteristic variation in potential across the deposition surface is fully mapped.

1.3.2b Chemical Baths

A novel application of metathesis reactions is found in the use of chemical baths to lay down thin films of synthesised material \textit{in situ}.\textsuperscript{80} For example, SnS films may be prepared by sequential immersion of a cleaned substrate in first cold (18-25 °C) solution of either Na\textsubscript{2}S or (NH\textsubscript{4})\textsubscript{2}S, and then in hot (80-90°C) SnCl\textsubscript{2} solution of the same concentration.\textsuperscript{81} Variation in the pH of the aqueous solution gives a degree of control over the crystallinity of the deposited films, and thereby can be used to alter optical band gap considerably (2.04 eV to 1.08 eV). It was also found that annealing at modest temperatures (285 °C) led to both an increase in the conductivity (by an order of magnitude) and a change in the conductivity type (from p- to n-type). However, it was also noted that long term annealing led to extensive disproportionation of the SnS films. This technique may also be employed to dope thin films with ions stable in aqueous media (e.g. Cu\textsuperscript{2+}), with concentrations up to unity.\textsuperscript{82}
This technique also proved to be very versatile in the manufacture of certain electronic components, a few of which are described here.\(^1\)

(1) n-p heterojunctions can be produced either by controlled long-term annealing (n-SnS\(_2\) / p-SnS) or by chemical deposition (n-CdO / p-SnS) - a CdO thin film serves as a transparent window electrode, thereby providing a superior heterojunction with respects to photovoltaics.

(2) n-p homojunctions may be created by short-term annealing followed by another chemical deposition over the annealed film.

(3) acid resistant coatings of controlled thickness can be formed by controlled long-term annealing at elevated temperatures (at T > 400 °C SnS films are transformed to SnO and SnO\(_2\)).

1.3.2c Molecular Organic Chemical Vapour Deposition (MOCVD)

MOCVD is a general term to describe the growth of thin films upon a substrate (epitaxial or non-epitaxial), resulting from the decomposition of volatile organometallic precursors from the gas phase. MOCVD has developed into many forms from research into the construction of optical and electronic devices from binary semiconducting compounds (notably of groups 12-16 and 13-15).\(^3\) MOCVD technology can allow highly accurate creation of complex structures involving the controlled growth of ‘ultra-thin’ layers (< 1 micron). Scope for synthetic research is extensive, with the technology extensively allowing new routes to both ternary and more complex semiconducting materials.

Commercial success has developed towards 13-15 semiconducting films due to some inherent disadvantages in 12-16 compounds.\(^3\)

1. Self-compensation effects can result from the greater ionicity of 12-16 compounds, limiting the reproducability of both conduction type and carrier concentration.
2. The majority of 12-16 compounds undergo polytypism within the temperatures of the MOCVD regime, forming both cubic and hexagonal crystal modifications. Consequently, defects can develop during the growth of thin films.

3. Significant differences in volatility of the group 12 and 16 elements make it very difficult to grow bulk 12-16 single crystals. However, 12-16 layers can usually be grown on substrates of single 13-15 crystals so long as there is little mismatch between the lattice parameters (e.g. the mismatch of the ZnSe-GaAs pair is only about 0.25 %). Thus hetero-epitaxal growth of 12-16 compounds on 13-15 crystals is possible without any defects arising from the 'hetero' nature of the two superimposed materials.

The use of simple metal alkyls and chalcogen hydrides as precursors (conventional MOCVD) has notable drawbacks, including the highly pyrophoric nature of metal alkyls and high toxicity of pressurised hydride gases. In addition, since metal alkyls are highly hydrophilic and readily oxidised, exclusion of all traces of air and water is required to avoid alkoxide formation (and so oxygen contamination of the final product). Both morphology and stoichiometry of the growing layers may be adversely affected by pre-reaction of the metal alkyl and chalcogen source. Atmospheric pressure conditions also tend to promote such pre-reaction (especially when reactive precursors are employed). Relatively high growth temperatures (ca. 250-750 °C) may promote inherent defects in the product. Finally, to compensate for differences in the volatility and thermal reactivity of the two precursors, it is usual to create a large imbalance in the molar ratios of the precursors. Consequently, an excess of precursor is wasted.

The development of various low pressure MOCVD techniques, such as molecular beam epitaxy (MBE), allows the volatilisation of less volatile precursors whilst reducing pre-reaction and allowing a lower growth temperature (typically 250 °C). However, growth rate is dramatically reduced, leaving APCVD (atmospheric pressure CVD) a more suitable technique for the mass production of semiconductor layers. The basic MOCVD technique can also be modified to facilitate the deposition of 12-16 materials. This includes photo-assisted MOCVD, whereby photo-catalytic surface reactions allow the deposition of the desired material at reduced temperatures (the exact mechanism for this process has yet to be understood).
1.3.2d Single molecular precursor approach to MOCVD

This involves the use of a single organometallic molecule as the source for all the elements required for the target compound in the desired stoichiometry. Developments into single molecule precursors may provide solutions to some the problems facing 12-16 materials, as well as developing the synthesis of 13-15 materials:

1. Coordination number of the metal centre is controlled through aggregation or adduct formation, thereby decreasing the sensitivity of the precursor to air and moisture.
2. The use of a single type of precursor molecule limits pre-reaction.
3. The use of highly toxic chalcogen hydrides is excluded.
4. Design of the precursor results in low growth temperatures through control over both the mode of decomposition and decomposition temperature.
5. Product stoichiometry is well defined by controlling the elemental ratios in the precursor.
6. The resulting layers may have improved electrical properties due to the purification of the organic moiety during the preparation of the adduct.
7. Vapour pressure of metal alkyls is reduced, eliminating the need for cooling bubblers.

Chalcogenato complexes of Zn or Cd are the simplest single molecule precursors for decomposition to 12-16 material. However, they form polymeric structures with a tetrahedral metal centre and so are practically involatile. This property differs from the chemistry of 13-15 complexes, which predominantly form tetrahedral dimers with restricted volatility. Modifications of their physical properties is thus required.

Some steps towards improving physical properties

One can modify the properties of the thiolates by forming adducts. Steigerwald and co-workers have successfully used depe (1,2-bis[diethylphosphino]ethane) adducts of phenyl and tertiary butylchalcogens to form the dimers $[M(ER_2)(depe)]_2$, where $M = Zn, Cd, Hg$ and $E = S, Se, Te$. However, they found that adduct formation does not solve the problem of the involatility of chalcogenato complexes. Chalcogenide ligands of considerable steric hindrance have been used to limit polymerisation and so reduce the molecular weight of the resulting complexes. Whilst
there has been some success in depositing thin films of zinc and cadmium sulfides and selenides, these types of precursors contaminate the films with carbon (steric bulk is generally achieved by the incorporation of carbon based ligands). They are also restricted to low pressure MOCVD techniques.

Bulky silicon based precursors of the type M[Esi(SiCH$_3$)$_3$]$_2$ have found success with M = Zn, Cd, Hg and E = S, Se, Te.$^92$

The use of non carbon based ligands may result in unforeseen modifications to the bulk semiconducting properties. For example, thiophosphinate complexes may be used to synthesis cadmium sulfide, which exhibits n-type conduction due to non-stoichiometry. Any unforeseen phosphorus doping, however, would result in a highly compensated semi-insulating material.$^93$

The polytypism and variety of accessible stoichiometries exhibited by 13-15 materials pose more of a problem for MOCVD than the 12-16 materials (many phases of M$_x$E$_y$ are known from x:y = 2:1 to 2:3). Their preparation by MOCVD has largely been done by the single molecule precursor approach, due to the greater control over product stoichiometry that this process offers. To this extent, progress has largely mirrored that outlined for 12-16 materials.$^93$ Interestingly, advances in indium thiolate chemistry has led research towards ternary 11-13-15 semiconductors (notably CuInE$_2$ where E = S, Se).$^94$

Adducts of zinc and cadmium alkyls have also been used as precursors for the growth of wide band-gap (12-16) semiconductors. The dioxan, thioxan, triethylamine and triazine adducts of dimethyl zinc inhibit pre-reaction in the growth of ZnSe.$^95$ Thin films of CdSe and CdS have been grown from dimethyl cadmium adducts.$^96$ The triethylamine adduct of Me$_2$Zn have been used both in the deposition of zinc chalcogenides and the p-type doping of 13-15 materials with zinc.$^97$

Although total dissociative vapourisation is common for organometallic adducts (Me$_3$In is a tetramer in the solid state, but a monomer in the gas phase), there is a marked difference to which each adduct inhibits pre-reaction with chalcogen hydrides.$^83$ It has been suggested that pre-reactions proceed via association of the precursors, and so an adduct formed from a stronger Lewis base is likely to undergo the pre-reaction with the hydride.$^83, 97$ This Lewis
base may also trap highly reactive intermediates formed during alkyl decomposition, preventing oligomerisation extending to the formation of solid materials in the reactor.\textsuperscript{83, 98}

Other semiconducting films obtained by the single molecule precursor approach include the synthesis of binary 14-16 materials, a selection of which are mentioned below:
Cheng \textit{et al.} have developed volatile CVD precursors to group 14-16 semiconductors in the form of pyridineselenolate complexes of both tin and lead - Sn(2-SeNC\textsubscript{3}H\textsubscript{4})\textsubscript{2}, Sn(2-SeNC\textsubscript{3}H\textsubscript{4})\textsubscript{4}, Pb(2-SeNC\textsubscript{3}H\textsubscript{4})\textsubscript{2} and Pb(3-Me\textsubscript{3}Si-2-SeNC\textsubscript{3}H\textsubscript{4})\textsubscript{2}.\textsuperscript{99} They report that these complexes (prepared by either metathesis or insertion of the metal into the Se-Se bond of sipyriciyl diselenide) sublime intact, but decompose at elevated temperatures to yield MSe (M = Sn, Pb) and SnSe\textsubscript{2}. However, the pyridineselenolate ligand cannot stabilize Pb (IV), yielding the divalent precursor.

1.4 Nanoparticulate semiconducting materials

Nanoparticulate semiconducting particles (‘quantum dots’) represent an intermediate state of matter between individual molecules and bulk materials, exhibiting unique electronic, optical, catalytic and transport properties.\textsuperscript{100} These have been attributed to both size quantisation effects (electronic properties) and to the increased ratio of surface to bulk atoms (physical properties) as the crystallite size approaches 2-20 nm.\textsuperscript{101}

Notably, the electronic absorption of the nanoparticulate exceeds that expected for the bulk material from which it originates.\textsuperscript{102} The electronic structure of the semiconducting material can no longer be described as continuous bands of an extended lattice, but rather as having distinct molecular characterisatics in terms of discrete (bonding / anti-bonding) energy levels.\textsuperscript{102}

1.4.1 Electronic structure

This effect arises from the ‘quantum confinement’ of weakly bound excitons (electron-hole pairs) in a semiconductor where the particle size is less than the Bohr diameter (B\textsubscript{d}) of that exciton.\textsuperscript{103} That is to say, within a particular particle size range (<B\textsubscript{d}) for a given semiconductor, electrons within the bulk material become 3-dimensionally confined within
a near spherical particle. The resultant solutions for the Schroedinger equation show that for a single, quantum confined electron the particle behaves more like an atom, with discrete electronic states becoming available whose transitions are greater than the normal band-gap of the bulk material. These new electronic transitions of the semiconductor now resemble those of atomic spectroscopy with the new energy levels being analogous to the orbitals of atoms (such nanoparticles are often referred to as 'super-atoms').

It has proven more difficult to explain the crucially important luminescent properties (for which such materials are often sought). Conceptual ideas are based on passivated quantum confined semiconductors being luminescent at frequencies close to the 'band gap' of the nanoparticle (i.e. emission via direct recombination of electron-hole pairs from atomic-like energy levels). Conversely, bulk semiconductors are seen to emit at different frequencies from the band edge since recombination of charge carriers can occur via discrete sub-levels (energy traps) in the band-gap arising through crystal / surface defects.

1.4.2 General Applications

Interesting properties associated with size quantisation include non-linear optical behaviour and unusual fluorescence, as well as photocatalysis. Specifically, the quantum size effects exhibited by certain nanoparticulate chalcogenides (notably PbS, PbSe, CdS and CdSe) can be applied to optical signal processors and switches (re: L. Buis), as well as erasable optical data storage (re: E. Corcoran). Nanoparticles of metal borides, carbides, oxides and nitrides, as well as elemental semiconductors (Ge, Si) and magnetic metals (Fe, Co), have been extensively studied for their electronic / magnetic properties.

The synthesis of highly luminescent, nearly monodispersed nanocrystallites (particularly with respect to oxide particles) has largely benefited the processing of quantum dots into optoelectronic devices. However, the high degree of control now obtained over the dimensions of nanoparticles, and the resultant implications of 'band gap engineering,' have led to a more recent expansion in the range of devices being sought. This has further been facilitated by the reproducibility in the synthesis, as well as the easy manipulation of organically capped nanocrystals. Such developments include 'tuneable devices' such as diodes and lasers.
Both Colvin et al. and Dabbousi et al. have utilised recent developments in the synthesis and characterisation of direct-gap semiconducting nanocrystals, and of electroluminescent polymers, to construct hybrid organic-inorganic electroluminescence devices, thereby realising the electroluminescence from nanoparticulate CdSe.

1.4.3 Synthetic design

In terms of a quantitative understanding of semiconducting materials subjected to quantum-confinement, it is vital to obtain 'a high concentration of monodisperse particles evenly distributed within a suitable medium with chemically well-controlled surfaces,' writes David Cole-Hamilton. He further explains the necessity of narrow particle size distributions to obtain pure colours in luminescence (apparent if one considers that the band gap of \( \text{Cd}_3 \text{P}_2 \) changes from 0.5 eV to more than 4 eV on reducing the particle size from 3 nm to 1.5 nm). The syntheses of stable binary nanoparticulates within the desired size range for quantum confinement (2-10 nm for CdS) include sol-gels, zeolites, micelles, polymer films, solutions of single molecule precursors and colloidal suspensions.

Optimising the optoelectronic properties of nanoparticulates require the material to be highly luminescent, ideally with monodispersed crystallites. The presence of large size distributions, surface defects (such as from elemental volatilisation), or deep traps in the electronic structure tends towards an unfavourable increase in emission frequencies. For this same reason, doping with oxygen is avoided and so anaerobic, non-aqueous reaction conditions have become generally preferred.

Replacing a capping ligand of CdSe with another semiconductor (CdS) has lead to increases in both efficiency and lifetime of the electroluminescence, since the inorganic capping material is more resistant to photo-oxidation. Self-luminescence of the matrix at high voltages can result in favourable increases in electroluminescence of the device.

Although laser illumination of some nanoparticulate solutions lead to further particle growth and increased crystallinity, synthetic routes by restricted growth or colloidal methods tend to be low temperature and so both suffer from a general lack of crystallinity. Amorphous colloids tend to be air sensitive and unstable at elevated
temperatures. Consequently, annealing such nanoparticulates is difficult without aggregation.\textsuperscript{107}

1.4.4 Colloidal synthesis

A range of techniques has been developed to control the precipitation of a desired product from solution, such that the desired particle growth is stopped in a reproducible way after nucleation. Effective synthesis of quantum dots can be achieved if they are of sufficiently low solubility to avoid Ostwald ripening (the dissolution and recrystallisation of less stable (smaller) crystals on to larger ones).\textsuperscript{107} Control of nucleation kinetics can be achieved through prudent selection of solvent, temperature, pH and passivating agent.\textsuperscript{107, 111} Highly monodispersed materials are achieved by combining fast nucleation with slow particle growth, and so each step must be controlled independently. This has been facilitated by the use of low dielectric solvents or copolymers to increase colloidal stability of these crystals.\textsuperscript{107, 111} However, these synthetic approaches do have notable drawbacks. Some important semiconductors cannot be easily synthesised by colloidal methods (notably CdSe, GaAs, InP and InAs). The methodologies tend to be low temperature processes and so often result in poorly crystalline or amorphous colloidal particles that are unstable towards subsequent annealing without agglomeration.\textsuperscript{107}

A low temperature route has been developed by Kauzlarich \textit{et al.}, based upon the solution phase metathetical reaction of solvated SiCl\textsubscript{4} and KSi (Zintyl salt). The reactions were carried out in either glyme, diglyme or THF at reflux,\textsuperscript{112} with these coordinating solvents giving kinetic stability by capping the nano-sized clusters.

\textgamma-Irradiation of precursors has been widely employed in the low temperature synthesis of nanocrystalline metals, alloys and metal oxides, as well as silver / polyacrylamide nanocomposites.\textsuperscript{113} D.Hayes \textit{et al.}\textsuperscript{113} have used \textgamma-irradiation of thiol solutions (3-mercato-1,2-propanediol) containing cadmium ions to obtain colloids of nanocrystalline CdS. This methodology has been extended by Qian \textit{et al.} to afford bulk nanocrystalline CdS using different sulfur sources (sodium thiosulfate, mercapto ethanol or carbon disulfide) and solvents (distilled water or anhydrous ethanol).\textsuperscript{113} They have shown that judicious choice of the polarity of both solvent and sulfur precursor results in differentiation of the product phase (cubic sphalerite or hexagonal wurtzite). The authors suggest the inclusion of both metal and sulfur-based radicals as critical to a plausible reaction mechanism.
1.4.5 **Synthesis through restricted reaction environments**

Highly porous host structures, comprised of extensive nanometer sized internal cavities, have been used as sites for various reaction schemes so that subsequent particle growth becomes restricted (typically to within 20 nm). Extensive research into restricted reaction environments has largely focused upon the use of micelles, polymers and zeolites (including molecular sieves).

1.4.5.1 **The use of zeolites**

Typically, cationic exchange within the reaction space precedes chalcogenation. This is exemplified in the two reaction schemes below, which utilise zeolites in the synthesis of nanoparticulate CdS and CdTe ($Z = \text{zeolite}; A = \text{Na or K}$).

\[
\begin{align*}
Z-2Na^+ + \text{Cd(NO}_3\text{)}_2(aq) & \rightarrow Z-\text{Cd}^{2+} + 2\text{NaNO}_3 \quad (\text{Na}^+\text{-Cd}^{2+} \text{ Ion Exchange}) \\
Z-\text{Cd}^{2+} + \text{H}_2\text{S}(g) & \rightarrow Z-2\text{H}^+(s) + \text{CdS}(s) \quad (\text{Cd}^{2+}\text{-H}^+ \text{ Ion Exchange})
\end{align*}
\]

Wang and Herron have shown that the exact size of the CdS nanoparticles was dependent upon the amount of cadmium used.\(^{114}\)

\[
\begin{align*}
Z-2A^+ + \text{Cd(NO}_3\text{)}_2(aq) & \rightarrow Z-\text{Cd}^{2+} + 2\text{A(NO}_3\text{)}_2(aq) \quad (\text{Na}^+/\text{K}^+ - \text{Cd}^{2+} \text{ Ion Exchange}) \\
Z-\text{Cd}^{2+} + \text{H}_2\text{(g)} & \rightarrow Z-2\text{H}^+(s) + \text{Cd}(s) \quad (450 \degree \text{C}, \text{Reduction by hydrogen}) \\
Z-\text{H}^+ + \text{Cd}(s) + \text{Te}(g) & \rightarrow Z-2\text{H}^+(s) + \text{CdTe}(s) \quad (\text{Elemental combination})
\end{align*}
\]

Mallouk et al. showed that altering the diameter of the zeolite pore size (through selection of either the potassium or sodium cationic resin) resulted in control of the CdTe clusters synthesised.\(^{114}\)

Other noteworthy variations upon this theme include growth of binary chalcogenides between the layers of 2-dimensional host structure. Cao et al., have utilised this method to synthesise a range of materials, the exact size of the nano-clusters being modified by the initial cationic concentration used (a general reaction scheme is described below).\(^{114}\)

\[
\begin{align*}
\text{Zr(O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2 + M^{2+} & \rightarrow M^{2+}[\text{Zr(O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2]^2+ + 2\text{H}^+ \quad (M = \text{Zn, Cd, Pb}) \\
M^{2+}[\text{Zr(O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2]^2+ + \text{H}_2\text{E} & \rightarrow \text{Zr(O}_3\text{PCH}_2\text{CH}_2\text{CO}_2\text{H})_2 + \text{ME} \quad (E = \text{S, Se})
\end{align*}
\]

45
The matrix itself may play a crucial role in deciding the final properties of the nanoparticulate material. Brus and co-workers have synthesised both ZnS and CdSe quantum dots (capped with either another semiconductor or phenyl groups) from inverse miscelle solutions, through reaction of silylchalcogenides with a microemulsion of metal cations. They have shown that the labile nature of miscelles allows further reaction between silyl groups and the excess $M^{2+}$ sites on the crystal surface. The effect is further crystal growth and so alternate surface capping.

1.4.5.2 The use of co-polymers

Extensive research has been undertaken into the use of polymer matrices in the synthesis of semiconducting nanocrystallites, since they not only provide good mechanical and optical properties to the final nanocrystal-polymer composite, but also give a high kinetic stability to nanometre-sized particles. In addition, they achieve an even spatial distribution of particles within the polymer matrix, and can be readily processed into thin films for future applications in device structures. However, it has often proved difficult to control particle size and obtain films of sufficient optical quality.

The work of Yi Yang et al. typifies this area of research. They have successfully synthesised nanoparticulate PbI$_2$, Fe$_2$O$_3$, PbS, CdS and ZnS in polymer matrices such that the final composite film can be easily processed and be of a sufficiently high optical purity. They have utilised a variety of methods, but the underlying principle (typical for this type of synthetic approach) is outlined by treatment of a metal alkyl polymer adduct with hydrogen sulfide (below for ZnS):

Copolymerisation of zinc methacrylate and styrene produced a lightly cross-linked Zn$^{2+}$ microgel (a zinc salt coordinated by polymer ligands, ‘Zn-P’), the cross-linking arising through the two C=C bonds in each zinc methacrylate molecule. The copolymer was then reacted in a sealed container with H$_2$S (a source of S$^{2-}$) in the correct molar ratio to yield a “ZnS-P” organosol.

Using these methods, the particle distribution can be controlled by the microstructure adopted by the block copolymer. However, the use of a solid-gas interface can lead to a variation in metal : sulfur ratio unless the morphology of the pre-formed polymer film is well controlled. Also, copolymers containing organometallic blocks often require complex reaction pathways, thereby restricting the predictability of the film growth and the microstructure adopted.
Recent synthetic routes to nanoparticulate magnets include the reduction of metal halides using organic solvents in the presence of lithium. Leslie-Pelecky et al. have used this technique to synthesise ultrafine cobalt particles, stabilised in a polymer matrix. The materials exhibited ferromagnetic behaviour at room temperature plus a ‘spin-glass-like’ transition at around 10K. Nanoparticulate magnets have also been reported by Zhang and Manthiram, through the reduction of ferrous (Fe\(^{2+}\)) ions to Fe by potassium borohydride (KBH\(_4\)) in aqueous solution.

1.4.6 Organometallic routes

1.4.6.1 Dual source precursors

Control over nanoparticulate morphology can be obtained through judicious selection of the properties of the capping ligands. Consequently, the use of reaction media that also act as capping ligands allows the possibility for a simple route (a single, reproducible step) to highly monodispersed nanoparticles. Crucially, however, it has been reported that a balance must be struck between the stability of the capping ligand and particle growth rate if nanoparticles of uniform size are to result. In other words, the ligands must be of sufficient Lewis basicity for suitable particle passivation, yet still be labile to allow particle growth. This is graphically highlighted by the recent work of O’Brien et al. with the preparation of ‘organically passivated gold nanoparticles’ by the reduction of AuCl\(_4\) solution by NaBH\(_4\) in a range of polar, Lewis base solvents. They found that the use of hot (190 °C) TOPO resulted in a range of both particle sizes (10-100 nm) and morphologies (triangular, spherical and square). However, replacing the TOPO with a mixture of TOPO and octadecylamine (1 : 0.57 molar ratio) resulted in heterogeneous ligand capping and controlled growth of spherical nanoparticles (8.59 ± 1.09 nm).

* Solution of gold (IV) chloride in 4-tert-butylpyridine

Binary (group 13-15) materials have proven to be more difficult to synthesise due to increased energetic barriers to crystal formation (resulting from the greater covalent character of these materials). Consequently, nucleation and particle growth become indiscernible in terms of experimental control. In addition, direct reaction between the reagents (suggested by Heath and Shiang as a crucial step in both nucleation and
growth)\textsuperscript{16} is hampered by the Lewis acidity of common group 13 precursors (e.g. gallium halides). Some notable advances are described below.\textsuperscript{16}

Kher and Well describe the synthesis of crystalline, glyme-capped gallium phosphide / arsenide by the solvent mediated metathesis reaction described below: \textsuperscript{16}

\[
\text{GaCl}_3 + A_3E \rightarrow \text{GaP} + 3\text{ACl} \quad (A = \text{Na, K}; \ E = \text{P, As}; \ \text{solvent mixture: toluene-glyme})
\]

A similar reaction scheme was employed by Sasaki \textit{et al.} in the synthesis of crystalline 1-8 nm particles of InAs in triglyme at elevated temperatures for prolonged time periods: \textsuperscript{16}

\[
\text{In(acac)}_3 + \text{As(SiMe}_3\text{)}_3 \rightarrow \text{InAs} + 3\text{SiMe}_3\text{(acac)} \quad (T = 216 \degree \text{C}; \ t = 70 \text{ h})
\]

Nozik and co-workers have shown that analogous gallium reaction resulted in nanoparticulate GaAs.\textsuperscript{16}

1.4.6.2 Single source precursors\textsuperscript{107,117}

Single source metal-organic precursors offer certain advantages in the synthesis of nanoparticulate material, notably in the avoidance of both volatile (e.g. silated pnictides) and highly toxic (chalcogen hydride) reagents. The synthetic approach largely centres upon the decomposition of the single source precursors in a variety of solvents, with the passivating Lewis base either being incorporated in the reaction scheme or added during the work-up.

P. O’Brien \textit{et al.} have used a range of metal diorganophosphides in the synthesis of nanoparticulate Cd\textsubscript{3}P\textsubscript{2}, InP and GaP, as described by the general reaction conditions below:

\[
[M\text{eCdP(Bu}^1\text{)j}] \quad \text{solvent mixture = TOPO, 4-ethyl pyridine; \ T = reflux.}
\]

They report the formation of InP / GaP quantum dots of approximately 8 nm in diameter, with a range in particle sizes of ± 20 %.

\[
\text{M(Pbu}^1\text{)}_3 \quad M = \text{Ga, In}; \ \text{solvent = 4-ethyl pyridine}; \ T = \text{reflux; } t = 70 \text{ d.}
\]
The TOPO capped Cd$_3$P$_2$ exhibited improved resistance to photodegradation. In addition, they observed that replacing the tertiary butyl ligand with either cyclohexyl or phenyl resulted in the decomposition to predominantly *bulk* cadmium phosphide, highlighting the importance of the capping ligand to particle structure. Further research into this reaction showed that the competing reactions of reductive elimination (resulting in cadmium formation) and β-elimination (leading to nanoparticulates) are temperature dependant, with the latter predominating at T < 150 °C.

Nanoparticulate materials have also been synthesised by the decomposition of single source precursors, a selection of which are described below:

1. Wells and co-workers have synthesised GaP by pyrolysis of either (Cl$_3$Ga$_2$P)$_n$ or [X$_2$Ga-P(SiMe$_3$)$_2$]$_2$ (X = Br, I) under vacuum.
2. Gibson *et al.* have shown that methanolysis of Cd[P(SiPh$_3$)$_2$]$_2$ yields methanol capped Cd$_3$P$_2$.
3. Janik and co-workers have thermolysed [H$_2$GaE(SiMe$_3$)$_2$]$_3$ in xylene at 450 °C, yielding 5 nm CdE (E = P, As).
4. Pyrolysis of either [Cd(SePh)$_2$][depe], Cd(SePh)$_2$, or [Cd$_2$(SeC$_6$H$_5$)$_4$(dppm)]$_n$ in high boiling point solvents, such as 4 ethylpyridine, results in nanoparticulate CdSe (Steigerwald *et al*).
1.5 Uses of metal chalcogenides

Metal and mixed metal chalcogenides have a wide range of commercial applications, particularly in the electronics industry. For instance, lanthanide chalcogenides (e.g. LnE₃) and ternary metal lanthanide sulphides (MLnS₂; M: Group Ia, IIA, IIIb) are refractory materials that exhibit a number of potential and actual technological uses. These range from infra red lenses\(^ {118} \) (transmission range ~1-14 µm), catalysts\(^ {119} \) colour phosphors\(^ {120} \) (e.g. television sets utilize Eu doped Y oxysulphides for the red pixels), to lasers (neodymium sulphide)\(^ {121} \) and semiconductor dopants to ionic conductors.\(^ {122} \) A selection of established, as well as potential, uses are explained below.

1.5.1 Binary semiconducting thin films

Phase pure, binary tin sulfides have several distinct semiconducting phases (trigonal SnS₂, tetragonal Sn₃S₄, rhombic Sn₂S₃ and orthorhombic SnS).\(^ {123} \) This series of compounds show a high degree of electronic diversity, varying in both band-gap width as well as type of conductance. For example, tin (IV) sulfide has an optical energy gap of 2.07 eV and shows n-type conductivity, whereas tin (II) sulfide is a p-type semiconductor with thermal and optical energy gaps of 1.20 eV and 1.08 eV respectively.\(^ {124} \) Furthermore, since the acceptor levels are created by the tin vacancies normally present in the lattice, an excess of tin would change the type of conductivity of SnS from p- to n-type. In addition, thin films of SnS find application as photovoltaic materials (due to their high energy conversion; 25%),\(^ {125} \) solar control coatings\(^ {126} \) and as heat mirrors.\(^ {127} \) It should be noted that the optical energy gap of SnS is similar to that of silicon.

The technological importance of new semiconductors to the electronics industry is apparent when you consider that about 95% of all commercial applications are based around silicon,\(^ {128} \) yet the development of optoelectronics (notably photonic communications and computing) is severely restricted by the inherently weak (unstable) photoemission efficiency resulting from its indirect band gap.\(^ {129} \) Groups 12-16 and 13-15 binary compounds are generally direct-transition band gap semiconductors (the latter forming the basis of most optical and optoelectronic devices at the present). The band gap energies of the 12-16 materials are larger than the 13-15 compounds, and so are potentially important for the emission, detection and modulation of light in the visible and near-UV regions.\(^ {130} \) In contrast, the 13-15 compounds are
suitable for visible (largely red) to near-IR radiation. Owing to the difficulty in making suitably refined and pure thin films necessary for such applications (re: section 1.3.2c, p. 37-39), binary 12-16 compounds have generally been limited to simple applications. These include optical coatings, gratings, photoconductors and a wide range of optical windows.\textsuperscript{83} The semiconductor and luminescent properties of zinc and cadmium sulfides and selenides have led to their specific use in the production of light emitting diodes L.E.D.'s.\textsuperscript{128} However, recent developments in MOCVD may open up new device applications by allowing the formation of composite thin films with a high degree of purity and homogeneity. ZnS and ZnSe are the most promising materials as fast switching devices, or for blue / blue-green laser diode devices (semiconducting composites that also contain n-GaAs with either ZnCdS or ZnCdSe)\textsuperscript{129} which could lead to high density optical storage systems. Thin film electroluminescent displays based on ZnS are commercially available via the MOCVD process. Cubic ZnSe can be used as a passivation layer for GaAs wafers.\textsuperscript{130} Applications for cadmium chalcogenides include the construction of solid state (n-CdS / p-CdTe) solar cells and photodetectors,\textsuperscript{83, 131} in field effect transistors, sensors and transducers.\textsuperscript{132} Its use in photoconducting cells is widespread due to its high photosensitivity.

In addition to the above compounds, the sesquichalcogenides of gallium and indium chalcogenides (M\textsubscript{2}E\textsubscript{3}) are also direct transition, wide band gap semiconductors, like the 12-16 materials.\textsuperscript{83} The alternative ME structures of these compounds generally have a reduced band gap, approaching those of 13-15 compounds.\textsuperscript{83} The sesquisulfides, therefore, are alternatives to the 13-15 materials as potential photovoltaic and optoelectronic materials. In general, groups III-VI materials fall into two different compound types - M\textsubscript{2}E\textsubscript{3} (M = Ga, In; E = S, Se, Te) : a zinc blende type (Ga) and a defect spinel (In); and ME (same layered structure as M\textsubscript{2}E\textsubscript{3}).

1.5.2 Bulk materials

Simple binary and ternary chalcogenides also exhibit commercial potential outside the electronics industry. A variety of transition metal sulfides have found uses as catalysts (e.g. MoS\textsubscript{2} is used as a petrochemical catalyst; cadmium and zinc sulfides are potential catalysts in the photo-decomposition of water).\textsuperscript{133} The disulfides of tin, titanium, zirconium and hafnium all crystallise in the wurtzite structure, consisting of a hexagonal close packed sulfide lattice with metal atoms
occupying the octahedral holes on alternate layers. The result is a two dimensional, or 'layered' lattice (typical also of molybdenum disulfide) which exhibits weak, inter-layer bonding. Certain bulk properties classical of early transition metal sulfides remain unaffected (such as high melting point). Consequently, these materials find commercial applications as high industrial lubricants,128 Layered transition metal dichalcogenides also find applications as battery cathodes,43, 127 and hydrodesulfurisation catalysts.129 Tin (IV) sulfide can also be used as a mosaic to produce artificial gold for reflective surfaces.6 Layered transition metal dichalcogenides form a wide range of solid solutions with either mixed metal or mixed anionic compositions.100-1, 130 Such solid solution compounds have been the focus of extensive study into the changes of structural and electronic / magnetic properties as a function of composition.130

The sulfides and selenides of zinc and cadmium are also used in reflective coatings and in the pigmentation of paints, rubber, and porcelain.128 Cadmium sulfide (CdS) can be used in the formation of synthetic yellows or light oranges. Exact shade of colour may be, in part, determined by the relative reflectance of a variation in particle sizes.134

1.5.3 Solid solutions

Colour determination may also be controlled through variation in compound stoicheometry; as in the synthesis of light yellows through the addition of zinc in a solid solution with CdS to form [(Cd,Zn)S]. Similarly, the formation of solid solutions of either cadmium sulfoselenides [Cd(S,Se)] or cadmium mercury sulfides [(Cd,Hg)S] can be used to synthesise a range of deep orange through to red pigments.134

It is common for commercial pigments to have a differential composition, employing differing particle sizes, variation in the actual amount of each coloured material and the even dispersion through the pigment of lithopones (a mixture of metal sulfide pigment, such as ZnS, with a metal sulfate, such as MgSO4).134

Each compound of the series Cd_xHg_yTe (0 <x,y <1; Σ(x, y) = 1) has regular band-gaps (variable by the percentage content of cadmium), which can be used, for example, in the standardisation of certain spectroscopic equipment.
1.5.4 Ternary semiconductors

Chalcopyrite-type ternary (I-III-VI$_2$) semiconductors have long been a subject of academic interest since the chalcopyrite structure is the simplest noncubic, ternary analogue of the well studied binary zinc blende structure. This noncubic atomic array results in several important differences in their band structure when compared to their analogous binary materials (these include the removal of degeneracy to 'allow' previously 'forbidden' electronic transitions). They show technological potential in the fields of IR and visible LED's, IR detectors and far IR generation. They are particularly useful as nonlinear optical materials, since their high degree of covalency results in high nonlinear coefficients whilst their noncubic structure allows these optical transitions to be phase matched. Their usefulness is extended further when considering that several of these materials can be made both p and n-type. Specifically, CuAlS$_2$ and CuGaS$_2$ not only have direct band gaps in the UV and visible, respectively, but also can be made p-type, thereby finding application in the area of heterojunctions with large bandgap II-VI semiconductors (which can only be obtained n-type). More recent interest has focused on CuInE$_2$ and their use in highly efficient, hard-radiation solar cells. Their high output stability may also prove them as suitable materials for cathode in photochemical devices.
1.6 Aims of this work

As previously mentioned, the primary focus of this project is to extend the understanding of how the properties of liquid ammonia may facilitate the formation of binary and ternary metal chalcogenides through two reaction pathways – elemental combination and solution phase metathesis.

With reference to elemental combination reactions, it has been known for some time that the metastable state of the solvated electrons produced upon dissolution of soluble metals in liquid ammonia allows a convenient, single step route to these metal chalcogenides by direct combination of the elements. Upon dissolution of sulfur in liquid ammonia, it is known that a complex system of equilibria exists between reduced sulfur-nitrogen species that include S-N rings and sulfur polyanions. However, the nature of these equilibria is still not fully understood. This thesis describes, chronologically, the research outlined above, which began with the hypothesis that perhaps the sulfur-nitrogen system contains species that could oxidise metals (and so promote formation of metal sulfides) that would otherwise be insoluble in liquid ammonia. From here a comparative study using aliphatic amines was undertaken, since it has been suggested that they form straight chain sulfur radicals. Thereby one hoped to determine the relative scope of these solvents towards the synthesis of metal sulfides. The primary stipulation as to the desired binary products was that they be of single phase, with a high degree of homogeneity.

Significant research has been undertaken in recent years into the use of solid state metathesis to synthesise specific chalcogenides and pnictides. It was clear that work needed to be done in order to see if the scope of the metathetical route could be extended to the synthesis of binary compounds from the main-group and d-block alike. In addition, specific examples existed that showed that these reaction-types may also be carried out in either uncoordinating (e.g. toluene) or coordinating solvents (e.g. diglyme), whether in solution or with the presence of a solution-solid interface. The addition of a medium (whether coordinating or uncoordinating) could lead to a dissipation of the heat generated by these otherwise highly exothermic reactions. One would expect this to result in either a reduction in particle size or in product crystallinity. The formation of both bulk nanometer and amorphous materials is of general scientific interest, particularly in the case of semiconductors. Specifically, the
use of liquid ammonia would be of interest due to its high specific heat capacity, whilst it’s coordination to a variety of metal halides may facilitate the reactions by reducing the dimensionality of the reagents. In the formation of metal mixed dichalcogenides, the high energy needed to sustain the propagation wave of filament-initiated SSM reactions results in enhancement of the more volatile chalcogen in the reaction product. Conversely, the relative low volatility of tellurium has resulted in insufficient energy being present to form MoTe₂ and WTe. The low energy of the analogous system carried out in liquid ammonia, as well as the emphasis on kinetic (rather than thermodynamic) driving forces to complete the reaction, may provide a suitable reaction mechanism to overcome both of the aforementioned problems. One may also expect that given the low temperature and inert atmosphere for liquid ammonia metathesis reactions oxygen contamination of the products would be limited.

As mentioned, the synthesis of solid solutions by both elemental combination and metathesis in liquid ammonia has been investigated. The degree of control over the final stoichiometry is of interest in designing new materials. This stems from the modification of certain bulk properties of the parent compounds that can be achieved (including conductivity type, band gap size and carrier concentration). There are some general requirements for the formation of solid solutions. Overall charge neutrality must be preserved. Both end-member phases of substitutional solid solutions must be of the same crystal structure. There is also a restriction in cationic radii. A difference of 15% has been suggested as the maximum that a common lattice structure can tolerate before phase segregation occurs. However, for main group systems this difference seems to be appreciably higher. Further scope for new materials is made possible by the introduction of ions of differing charge. However, in such cases interstitial solid solutions are likely to result since charge neutrality will be preserved through the formation of either interstitial ions or ion vacancies. It is less likely that double substitution reactions would succeed in preserving neutrality without some appreciable degree of interstitiality.
1.6.1 **Key spectroscopic methodologies**

In terms of analysis, it is beyond the scope of this thesis to obtain a fully quantitative classification of such compounds. Instead, it is the aim of this thesis to approach the question of whether the bulk material may be considered as truly nanocrystalline or amorphous and, where possible, observe any modifications to the bandgap of semiconducting compounds synthesised. In addition, where broadened Bragg peaks are observed by powder X-ray diffraction studies, an estimation of average particle size will be obtained using a modification of the formula derived by Scherrer (equation 1.36):

\[
D = 1.2\lambda \,(B\cos\theta)^{-1}
\]  

(1.36)

where: 
- \(D\) = average particle diameter
- \(\lambda\) = wavelength of incident X-ray radiation (1.5406 Å)
- \(\theta\) = angle of the reflection (half the number of degrees of measured peak)
- \(B\) = \(\sqrt{b^2 - b^2_0}\)

where \(b_0\) = FWHM of a theoretically infinitely narrow line (radians)
- \(b\) = width of Bragg peak at half its maximum height (radians)
- \(B\) = width of Bragg peak at half its maximum height (radians)

The factors determining the formation of solid solutions are understood only qualitatively, the formation and compositional extent of such materials usually being determined experimentally. X-ray powder diffraction plays a crucial role in the characterisation of solid solutions. By obtaining a qualitative ‘fingerprint’ pattern, it is possible to determine the presence of multiple crystalline phases (of concentration in excess of about 5%). Estimations of relative quantities within approximately 3 microns of the surface may be obtained by use of back-scattered electrons under a SEM. The compositions of solid solutions were determined by application of Vegard’s Law to the d-spacings of powder diffraction lines. For non-cubic crystals, these calculations were carried out on Bragg reflections along the same axis, since expansion of the unit cell of such crystal types may not be uniform in three dimensions. One must fully appreciate, however, the limitations in assuming a linear variation in cell parameters with composition. Vegard’s Law applies only to substitutional solid solutions that form a random distribution of the mixed ions (the actual stoichiometry referring only to the...
bulk material, and not the unit cell). Both positive and negative deviations from Vegard's linear relationship are possible. A smooth negative departure from Vegard’s Law in non-metallic materials is indicative of a net attractive force between unlike ions. If this ordering occurs over long range then one would expect evidence for superstructure from the ‘fingerprint’ powder pattern. A smooth positive deviation from Vegard’s law may be explained by the clustering of the mixed ions into segregated domains, giving rise to microscopic regions of varied composition (even though the solid solution may appear homogeneous on the macroscopic scale). In addition to this, abrupt deviations in Vegard’s Law will result at certain compositions from either a change in symmetry of the solid solution, or a change in the solid solution mechanism. The characterisation of interstitial solid solutions (rather than substitutional ones) is therefore likely to deviate somewhat from the generalisations of Vegard’s Law.
2.0 Synthesis of Binary Materials by Elemental Combination

Reactions in Liquid Ammonia

2.1 Binary chalcogenides

2.1.1 Binary sulfides: synthesis and characterisation

The addition of a range of transition- and main-group metals to solutions of sulfur dissolved in liquid ammonia ($S_{(am)}$) at room temperature, resulted in reactions that afforded binary metal sulfides in good yield (table 2.1; equations 2.1-2.7).

\[
M_{(s)} + S_{(am)} \rightarrow MS_{(s)} \quad (M = \text{Zn, Cd, Hg, Pb}) \quad (2.1)
\]

\[
\text{Cu}_{(s)} + S_{(am)} \rightarrow \text{Cu}_{1.5}S_{(s)} + \text{Cu}_{1.9}S_{(s)} + \text{Cu}_{1.3}S_{(s)} \quad (2.2)
\]

\[
2\text{Ag}_{(s)} + S_{(am)} \rightarrow \text{Ag}_2S_{(s)} \quad (2.3)
\]

\[
2\text{TI}_{(s)} + 3S_{(am)} \rightarrow \text{Tl}_2S_{(s)} + S_{(am)} \quad (2.4)
\]

\[
2\text{Tl}_{(s)} + S_{(am)} \rightarrow \text{Tl}_2S_{(s)} + \text{Tl}_{(s)} \quad (2.5)
\]

\[
2\text{As}_{(s)} + 3S_{(am)} \rightarrow \text{As}_2S_3_{(s)} \quad (2.6)
\]

\[
\text{Sn}_{(s)} + S_{(am)} \rightarrow \text{SnS}_{(s)} + \text{SnS}_2_{(s)} \quad (2.7)
\]

For these reactions, the solvated sulfur species lead to various colourations of the liquid ammonia (including blue, red and green). In all cases, the disappearance of the metal coincided with the formation of a new solid. Also, reaction of the sulfur from solution resulted in removal of the colour from the ammonia solution. After removal of the ammonia, the colour of the product invariably coincided with literature references for the desired metal sulfide. Examination of the powder by optical microscopy revealed a homogeneous solid (with the exception of the Tl and Sn reactions). SEM analysis of all sulfide powders revealed agglomerates of particles of typical size 2-5 μm.
Table 2.1 XRD data for metal sulfides synthesised from the elements in liquid ammonia at R.T.

| Ratio of elements | Product colour | Products as formed from reaction (identified by XRD) | Annealed reaction products (250-300 °C for 2h) | Lattice Parameters Å (± 0.01) | Lit. lattice parameters / Å
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni : S 1 : 1</td>
<td>Black</td>
<td>X-ray amorphous + Ni</td>
<td>NiS, heazlewoodite + [NiS]</td>
<td><em>a = c = 3.44</em></td>
<td>a = c = 3.43</td>
</tr>
<tr>
<td>Ni : S 3 : 2</td>
<td>Black</td>
<td>X-ray amorphous + Ni</td>
<td>NiS, heazlewoodite + [Ni]</td>
<td><em>a = c = 4.08</em></td>
<td>a = c = 4.08</td>
</tr>
<tr>
<td>Cu : S 1 : 1</td>
<td>Black</td>
<td>X-ray amorphous + Cu, Ni</td>
<td>Cu, NiS, diginite + [Cu, Ni]</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>Ag : S 2 : 1</td>
<td>Black</td>
<td>Ag₂S (acanthite)</td>
<td>Ag₂S (acanthite)</td>
<td><em>a = c = 4.47</em></td>
<td>a = c = 4.48</td>
</tr>
<tr>
<td>Zn : S 1 : 1</td>
<td>White</td>
<td>X-ray amorphous ZnS (wurzite)</td>
<td>ZnS, wurzite</td>
<td><em>a = 3.82</em></td>
<td>a = 3.82</td>
</tr>
<tr>
<td>Cd : S 1 : 1</td>
<td>Yellow</td>
<td>X-ray amorphous CdS (greenockite)</td>
<td>CdS, greenockite</td>
<td><em>a = 4.14</em></td>
<td>a = 4.14</td>
</tr>
<tr>
<td>Hg : S 1 : 1</td>
<td>Red</td>
<td>X-ray amorphous α-HgS (cinneabar)</td>
<td>α-HgS, cinneabar</td>
<td><em>a = 4.15</em></td>
<td>a = 4.15</td>
</tr>
<tr>
<td>Sn : S 1 : 1</td>
<td>Black</td>
<td>X-ray amorphous SnS (herzenbergite)</td>
<td>SnS, herzenbergite</td>
<td><em>a = 3.98</em></td>
<td>a = 3.99</td>
</tr>
<tr>
<td>Sn : S 1 : 2</td>
<td>Grey</td>
<td>X-ray amorphous SnS (herzenbergite)</td>
<td>SnS, herzenbergite</td>
<td><em>a = 3.98</em></td>
<td>a = 3.99</td>
</tr>
<tr>
<td>Pb : S 1 : 1</td>
<td>Black</td>
<td>PbS (galena)</td>
<td>PbS, galena</td>
<td><em>a = c = 5.94</em></td>
<td>a = c = 5.93</td>
</tr>
<tr>
<td>As : S 2 : 3</td>
<td>Yellow</td>
<td>X-ray amorphous As₂S₃</td>
<td>As₂S₃</td>
<td><em>a = 4.22</em></td>
<td>a = 4.22</td>
</tr>
</tbody>
</table>

*a All minor phases (< ca. 10 %) represented by square brackets. Where mineral structures have been synthesised, the mineral names are given in italics.

*b Unit cell parameters were determined for the major phase binary material only.
X-ray powder diffraction (XRD) analysis

Reactions of silver, thallium and lead with $S_{(am)}$ solution produced crystalline $\text{Ag}_2\text{S}$, $\text{TlS}$ and $\text{PbS}$ which indexed with literature cell parameters. Analysis of the X-ray powder diffraction (XRD) patterns using the Scherrer equation showed that these materials had crystallite sizes in the range of 500-800 Å. The XRD pattern for PbS is shown in figure 2.1. All the other reactions between sulfur and metals (As, Sn, Cu, Ni, Zn, Cd, Hg) in liquid ammonia produced a featureless XRD pattern, indicating that the elements had reacted to form an X-ray amorphous sulfide.

Figure 2.1  XRD spectrum of lead sulfide product (PbS)

![XRD spectrum of lead sulfide product (PbS)](image)

Key: Sample (top) – lead sulfide  Standard (bottom) – galena, PbS

Electron microscopy

Energy dispersive analysis by X-rays (EDXA) revealed the presence of only metal and sulfur with virtually uniform composition over many randomly chosen surface spots (electron beam focal width of 1 μm). Electron microprobe analyses of the products from reaction with zinc, mercury and lead were in excellent agreement with the empirical formulae for the binary metal sulfides ($\text{ZnS}$, $\text{HgS}$ and $\text{PbS}$), although in some cases a trace of metal in the powder was detected (typically 1% or less).
Figure 2.1 XPS spectrum of pre-annealed zinc sulfide product obtained by combination of zinc and sulfur in liquid ammonia at room at 298K showing the 2p sulfur doublet.

The spectrum shows the doublet associated with the 2p electrons from the S\(^{2-}\) anion of ZnS. It comprises two discrete peaks, indicative of the \(2p_{1/2}\) and \(2p_{3/2}\) electrons.

\(^1\) The spectrum shows the doublet associated with the 2p electrons from the S\(^{2-}\) anion of ZnS. It comprises two discrete peaks, indicative of the \(2p_{1/2}\) and \(2p_{3/2}\) electrons.
XPS analysis

The X-ray photoelectron spectrum (XPS) of ZnS showed the presence of metal and sulfur with little associated carbon and nitrogen. The binding energy values of 1022.1 eV for the Zn 2p₃/₂ and 161.6 eV for the S 2p are similar to the previously reported values for ZnS.* Figure 2.2 (p. 46) shows the expected doublet spectrum for S 2p electrons in S²⁻. The X-ray photoelectron spectrum suggests an elemental ratio of 1.00 Zn to 1.08 S. No elemental zinc or sulfur was observed in the spectrum, with only the values expected for single environments of Zn²⁺ and S²⁻ being observed. Microanalysis of the metal sulfides showed trace levels of nitrogen and hydrogen (typically less than 0.4 %).

* Zn Auger parameter observed at 2011.4 eV, ZnS = 2011.3 eV; sulfur binding energy for ZnS is 161.7 eV).

FT-IR and Raman analysis

IR and Raman analyses were consistent (for all reaction equations 2.1-2.7) with the formation of metal sulfides with vibrations between 600 and 250 cm⁻¹. Infra-red analyses of group 12 metal sulfides showed very weak bands at 3200 cm⁻¹ and 1450 cm⁻¹ (presumably as a result of N-H vibrations).

Annealing of samples

Heating the X-ray amorphous powders at 250-300 °C for 2h in vacuo induced sufficient crystallinity to enable the materials to be characterised by X-ray powder diffraction (table 2.1). This characterisation showed a single phase metal sulfide for zinc and cadmium (ZnS and CdS), two phases for mercury (predominantly α-HgS with a trace of β-HgS; figure 2.3) and three phases for copper (Cu₃S, Cu₁₆S and Cu₇₂S₄). SEM / EDXA analysis of the thermolysed powders showed, in general, a homogeneous solid of uniform composition (to within 2-3 atm. % of the empirical formulae described by XRD). The IR and Raman analyses of thermolysed powders showed the expected vibrations without the weak N-H bands.
Figure 2.3 XRD spectrum of mercury sulfide (HgS)

Reactions involving early transition metals

Reactions of early transition metals (Ti, Zr, Cr, Nb, Ta, V, Mo, W and Co) 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 both X-ray powder diffraction (which showed the patterns for the elements), and SEM / EDXA 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. However, a tentative assignment (based purely upon X-ray powder diffraction data) has been made for the formation of FeS upon facile heating under dinitrogen (250-300 °C; 2h) of 1:1 ratios of the elements after treatment in liquid ammonia.

Reaction of either nickel or tin with S\textsubscript{am} solution produced an inhomogeneous product:

Analysis of nickel sulfides (re: table 2.1 for XRD data)

The reaction of nickel with sulfur showed only the presence of nickel prior to annealing by XRD. EDXA studies of the material’s surface showed that elemental nickel was in fact a minor phase (ca. 5 %). Assuming the surface composition to be representative of the bulk material, EDXA showed the material to largely consist of a homogeneous
nickel sulfide, with approximate ratio of the elements of 1:1 (accuracy of 2-3 %). Heating the washed nickel product to 250-300 °C under dinitrogen, induced a sufficient degree of crystallinity in the material for it to be analysed by XRD. The combined analysis of electron microprobe and X-ray powder diffraction show the annealed material to be NiS\textsubscript{0.63}, with a minor amount (5-10 %) of NiS. Repeating the experiment with a 3:2 ratio of nickel : sulfur again resulted in the formation of X-ray amorphous material contaminated with approximately 5 % unreacted nickel. Similar analysis of the annealed product by electron probe confirmed the presence of Ni\textsubscript{3}S\textsubscript{2}, with a minor phase (ca. 5 %) of elemental nickel.

**Analysis of tin sulfides** (re: table 2.1 for XRD data)

The XRD pattern of the pre-annealed sample prepared from reaction of tin and sulfur in liquid ammonia showed just tin metal. However, Raman microscopy lead to the observation of three separate phases: one gold coloured (SnS\textsubscript{2}, ca. 35 %), one black (SnS, ca.65 %) and a minor amount of a grey phase (ca. 5 %). The minor phase was assigned as unreacted tin due to the absence of a Raman signature. The gold and black phases had the anticipated Raman signatures for SnS\textsubscript{2} (with absorption occurring at 208 cm\textsuperscript{-1} and 314 cm\textsuperscript{-1}) and SnS (with absorption at 95 cm\textsuperscript{-1}, 160 cm\textsuperscript{-1}, 185 cm\textsuperscript{-1} and 213 cm\textsuperscript{-1}). Confirmation of these two distinct binary tin sulfides was obtained with solid state \textsuperscript{119}Sn NMR spectroscopy, which showed the presence of two separate nuclear environments with chemical shift values of \(\delta\) 6871 and 7220 (figure 2.4). These values correspond to the tin (II) and tin (IV) environments respectively. SEM studies showed the particles of the three phases to have typical dimensions of 3-8 \(\mu\text{m}\), with the sulfides showing an aggregated structure.

During the heat treatment (300-350 °C) the whole product turned black, with the sublimation of some elemental sulfur. The X-ray powder diffraction pattern for this material showed a single phase, identified as tin (II) sulfide. This observation is consistent with the known thermal instability of SnS\textsubscript{2}.\textsuperscript{71} The stoichiometry of the black product was confirmed as SnS by microprobe analysis.
Figure 2.2 $^{119}$Sn NMR spectra of the reaction product obtained from the combination of tin and sulfur at room temperature in liquid ammonia (elemental ratio Sn:S of 1:2) $^1$

$^1$ Chemical shift values are given for each peak (± 5 ppm). Standard resonance peaks are expressed in bold type.

$^{119}$Sn NMR at 13kHz, 298K

$^{119}$Sn NMR at 10kHz, 298K
2.1.2 Reaction of soluble metals with sulfur in liquid ammonia

Investigations were also carried out into reactions of calcium, strontium, barium, ytterbium and europium with the sulfur-ammonia solution under the same conditions outlined for the non-soluble metals. In each case, the metal dissolved into the ammonia to form a blue, and then bronze, solution characteristic of an increasing concentration of solvated electrons. The dissolved sulfur species were found to react with this solution, affording a light purple or brown precipitate, with the solution colour fading to colourless through the loss of solvated electrons. Evaporation of the ammonia produces a further change in the colour of the precipitates to the characteristic reddish-brown of the binary metal sulfide, suggesting the possible loss of complexed ammonia molecules. In each case, the powders were found to be X-ray amorphous and contaminated with up to 5% unreacted metal (as determined by optical microscopy). Precipitation of metal fragments from solution upon the removal of ammonia tend to be pyrophoric in nature (due to a high surface area), thus making the work up of these materials in air problematic. Consequently, as far as possible, manipulations of the products were carried out using Schlenk techniques. EDXA and IR analysis were consistent with the formation of the binary sulfide. Annealing the powders at 250-300 °C for 2h was sufficient to induce a high enough degree of crystallinity to allow characterisation by XRD, which confirmed the materials to be the binary sulfides MS (M = Ca, Sr, Ba, Yb or Eu).

2.1.3 Binary selenides and tellurides: synthesis and characterisation

The reactions of selenium and tellurium with various transition- and main-group elements in liquid ammonia were also investigated – tables 2.3, 2.4; equations 2.8-2.19 (minor phases, defined as ca. 5-10% by optical microscopy, are expressed in italics).

\[ M(s) + E(s) \rightarrow ME(s) \quad (M = \text{Zn, Cd, or Hg}, \ E = \text{Se or Te}; \ M = \text{Pb}, \ E = \text{Se}) \]  
\[ 2\text{Ag}(s) + \text{Se}(s) \rightarrow \text{Ag}_2\text{Se}(s) \]  
\[ 2\text{Ag}(s) + \text{Te}(s) \rightarrow \text{Ag}_2\text{Te}(s) + \text{As}_x\text{Te}_y(s) \]  
\[ \text{Cu}(s) + \text{Se}(s) \rightarrow \text{Cu}_{2-x}\text{Se}(s) + \text{CuSe}(s) \]
\[
\begin{align*}
\text{Cu}(s) + \text{Te}(s) & \rightarrow \text{Cu}_{2-3x}\text{Te}(s) + \text{Cu}_{2.7}\text{Te}_{2x}(s) + \text{CuTe}(s) \quad (2.12) \\
\text{Ni}(s) + \text{Se}(s) & \rightarrow \text{NiSe}(s) + \text{NiSe}_{2x}(s) + \text{Ni}(s) + \text{Se}(s) \quad (2.13) \\
2\text{Ni}(s) + 2\text{Te}(s) & \rightarrow \text{NiTe}_2(s) + \text{Ni}(s) + \text{Te}(s) \quad (2.14) \\
2\text{Tl}(s) + \text{Se}(s) & \rightarrow \text{Tl}_2\text{Se}(s) + \text{Tl}_{3}\text{Se}_{3x}(s) + \text{TlSe}(s) \quad (2.15) \\
2\text{Tl}(s) + 3\text{Se}(s) & \rightarrow \text{Tl}_2\text{Se}(s) + \text{Se}(s) \quad (2.16) \\
2\text{Tl}(s) + \text{Te}(s) & \rightarrow \text{Tl}_2\text{Te}(s) + \text{Te}(s) \quad (2.17) \\
2\text{Tl}(s) + 3\text{Te}(s) & \rightarrow \text{Tl}_2\text{Te}(s) + \text{Te}(s) \quad (2.18) \\
\text{Pb}(s) + \text{Te}(s) & \rightarrow \text{Pb}(s) + \text{Te}(s) \quad (2.19)
\end{align*}
\]

Unlike the reactions with sulfur, in none of these reactions did any colour appear in the ammonia. Product work up and analysis were identical to the cases described for sulfur above.

**Transition metal selenides / tellurides**

Crystalline products were synthesised for both selenides and tellurides of copper, silver (Ag$_2$Se, figure 2.5), cadmium (CdSe, figure 2.6) and mercury (table 2.2, p.54). Facile heating (250-300 °C, 2h) was required to form a crystalline ZnSe, CdSe, NiSe and nickel telluride which were all shown to be amorphous to X-rays as formed. All the tellurides were crystalline prior to heating, with the exception of nickel. All products were confirmed as binary materials prior to annealing, rather than an intimate mixture of the elements, by SEM / EDXA, microprobe, IR and, in some cases, XPS (CdSe, HgTe and Ag$_2$Te).
Figure 2.5 XRD spectrum of pre-annealed silver selenide (Ag₃Se) formed from the reaction of silver and selenium in liquid ammonia at room temperature

Key: Sample (top) - silver selenide Standard (bottom) - naumannite, Ag₃Se

Figure 2.6 XRD spectrum of pre-annealed mercury selenide (HgSe) formed from the reaction of silver and selenium in liquid ammonia at room temperature

Key: Sample (top) - cadmium selenide Standard (bottom) - cadmesolite, CdSe
Table 2.2 XRD data for binary transition metal selenides and tellurides (synthesised from combination of the elements in liquid ammonia at room temperature)

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)(^a)</th>
<th>Annealed reaction products ((250 - 300 , ^\circ C; , 2h))(^a)</th>
<th>Lattice Parameters (\AA (\pm 0.01))(^b)</th>
<th>Literature(^{139}) Lattice parameters /(\AA)</th>
</tr>
</thead>
</table>
| Ni : Se 1 : 1    | Black          | X-ray amorphous + Ni                                      | NiSe                                                     | \(a = 3.66\)  
\(c = 5.33\)         | NiSe\(_2\) Characterised using standardised XRD patterns |
| Ni : Te 1 : 1    | Black          | X-ray amorphous + Ni + Te                                 | NiTe\(_2\) \((melonite)\) + Ni + [Te]                   | \(a = 3.78\)  
\(c = 6.06\)         | \(a = 3.78\)  
\(c = 6.06\)         |
| Cu : Se 1 : 1    | Black          | Cu\(_{2.3}\)Se \((berzelianite)\) [CuSe, klockmannite]   | Cu\(_{2.3}\)Se \((berzelianite)\)                       | \(a = c = 5.76\) | \(a = c = 5.77\) |
| Cu : Te 1 : 1    | Black          | Cu\(_{2.3}\)Te \((rickardite)\) + Cu\(_{2.3}\)Te + CuTe   | Cu\(_{2.3}\)Te \((rickardite)\) + Cu\(_{2.7}\)Te + CuTe | Characterised using standardised XRD patterns |
| Ag : Se 2 : 1    | Black          | Ag\(_2\)Se \((naumannite)\)                              | Ag\(_2\)Se \((naumannite)\)                             | \(a = 4.33\)  
\(b = 7.06\)  
\(c = 7.76\) | \(a = 4.33\)  
\(b = 7.06\)  
\(c = 7.76\)         |
| Ag : Te 2 : 1    | Silver         | Ag\(_2\)Te \((hessite)\) + [Ag\(_7\)Te\(_4\), stuetzite] | Ag\(_2\)Te \((hessite)\) + [Ag\(_7\)Te\(_4\), stuetzite] | \(a = 8.10\)  
\(b = 4.47\)  
\(c = 8.97\) | \(a = 8.09\)  
\(b = 4.47\)  
\(c = 8.96\) |
| Zn : Se 1 : 1    | Red            | X-ray amorphous                                          | ZnSe \((stilleite)\)                                    | \(a = c = 5.66\) | \(a = c = 5.62\) |
| Zn : Te 1 : 1    | Black          | X-ray amorphous                                          | ZnTe                                                     | \(a = c = 6.10\) | \(a = c = 6.07\) |
| Cd : Se 1 : 1    | Red            | CdSe \((cadmesolite)\)                                   | CdSe \((cadmesolite)\)                                  | \(a = 4.30\)  
\(c = 7.01\)         | \(a = 4.30\)  
\(c = 7.01\)         |
| Cd : Te 1 : 1    | Black          | CdTe                                                     | CdTe                                                     | \(a = 4.30\)  
\(c = 10.26\)        | \(a = 4.30\)  
\(c = 10.26\)        |
| Hg : Se 1 : 1    | Black          | HgSe \((tiemannite)\)                                    | HgSe \((tiemannite)\)                                   | \(a = c = 6.08\) | \(a = c = 6.07\) |
| Hg : Te 1 : 1    | Black          | HgTe \((coloradoite)\)                                   | HgTe \((coloradoite)\)                                  | \(a = c = 6.46\) | \(a = c = 6.45\) |

\(^a\) All minor phases (< ca. 10 %) represented by square brackets. Where mineral structures have been synthesised, the mineral names are given in italics.

\(^b\) Unit cell parameters were determined for the major phase binary material only.

---

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Main-group metal selenides / tellurides (table 2.3)

It is clear from both XRD studies (table 2.3) and EDXA that the reactions of thallium with selenium / tellurium (equations 2.15-2.18) and the reaction of lead with selenium (equation 2.8) afford crystalline binary material. A 1:1 ratio of lead and selenium results in the formation of lead selenide (PbSe). The reactions of thallium and selenium produce inhomogeneous material dependant upon the ratio of reacting elements. A 2:1 ratio of Tl:Se results in multiple binary phases (Tl$_2$Se, Tl$_3$Se$_3$, TlSe), whilst a 2:3 ratio produces a single binary phase (TlSe). Applying the same elemental ratios to the reactions of thallium with tellurium, however, result only in the synthesis of Tl$_3$Te$_5$ (figure 2.7 shows the XRD spectrum obtained for the stoichiometric ratio of Tl:Te of 2:1).

Table 2.3 XRD data for binary main-group metal selenides and tellurides (synthesised from combination of the elements in liquid ammonia at room temperature)

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)$^a$</th>
<th>Annealed reaction products (250-300 °C, 2h)$^a$</th>
<th>Lattice Parameters Å (± 0.01)$^b$</th>
<th>Literature$^{159}$ Lattice parameters /Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl:Se 2:1</td>
<td>Black</td>
<td>Tl$_2$Se$_3$</td>
<td>Tl$_2$Se$_3$</td>
<td>a = 8.02 c = 7.00</td>
<td>a = 8.02 c = 7.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl$_2$Se + [TlSe]</td>
<td>Tl$_2$Se + [TlSe]</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>Tl:Se 2:3</td>
<td>Black</td>
<td>TlSe + [Se]</td>
<td>TlSe + [Se]</td>
<td>a = 8.02 c = 7.00</td>
<td>a = 8.02 c = 7.00</td>
</tr>
<tr>
<td>Tl:Te 2:1</td>
<td>Black</td>
<td>Tl$_2$Te$_3$</td>
<td>Tl$_2$Te$_3$</td>
<td>a = 8.93 c = 12.62</td>
<td>a = 8.92 (5) c = 12.61 (5)</td>
</tr>
<tr>
<td>Tl:Te 2:3</td>
<td>Black</td>
<td>Tl$_2$Te$_3$</td>
<td>Tl$_2$Te$_3$</td>
<td>a = 8.93 c = 12.62</td>
<td>a = 8.92 (5) c = 12.61 (5)</td>
</tr>
<tr>
<td>Sn:Se 1:2</td>
<td>Grey</td>
<td>Sn + Se</td>
<td>Sn + Se</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td>Sn:Te 1:1</td>
<td>Grey</td>
<td>Sn + Te</td>
<td>Sn + Te</td>
<td>No reaction</td>
<td></td>
</tr>
<tr>
<td>Pb:Se 1:1</td>
<td>Black</td>
<td>PbSe (clausthalite)</td>
<td>PbSe (clausthalite)</td>
<td>a = c = 6.12</td>
<td>a = c = 6.12</td>
</tr>
<tr>
<td>Pb:Te 1:1</td>
<td>Black</td>
<td>Pb + Te</td>
<td>PbTe (altaite)</td>
<td>a = c = 6.45</td>
<td>a = c = 6.46</td>
</tr>
</tbody>
</table>

$^a$ All minor phases (< ca. 10 %) represented by square brackets. Where mineral structures have been synthesised, the mineral names are given in italics.

$^b$ Unit cell parameters were determined for the major phase binary material only.
In the case of the reaction between lead and tellurium (equation 2.19), the reaction was heat initiated, the pre-annealed product showing the presence of unreacted elements by XRD (table 2.3) and EDXA. Tin was found not to react with either selenium or tellurium, even after annealing. Both EDXA and XRD studies showed inhomogeneous reaction products comprising of the unreacted elements.

2.1.4 Observable trends in the synthesis of binary metal chalcogenides
The lead and silver selenides were crystalline prior to annealing, as had been observed for the sulfides. The selenides of copper and mercury also formed crystalline products directly from reaction in liquid ammonia, yet they formed amorphous sulfides. Only cadmium and zinc showed amorphous products prior to heating when treated with any of the chalcogens. The metals that produced single phased materials for all the chalcogens were from group 12, in addition to lead. Silver reacted to give both a single phase selenide and sulfide, but two phases resulted form the reaction with tellurium. Thallium reacted with either sulfur or tellurium to form a single phase binary material. Fundamental differences between the two materials exist, however. The thallium telluride can be described as a slightly metal deficient phase of thallium (+1) telluride (Tl$_3$Te$_3$, rather than Tl$_2$Te), whereas the sulfide is of a completely different stoichiometry.
to those of the reagents. It is TIS, a mixed oxidation state material, more accurately 
described as Tl\textsubscript[I]Tl\textsuperscript[III]S\textsubscript[2]. In the case of the selenide material, both multiple phases and 
different oxidation states of thallium are accessible.

Annealing changed the initial product composition of two reactions involving transition 
metals. The trace CuSe (equation 2.11) disappeared and only berzelianite (Cu\textsubscript[2-x]Se) was 
observed. A trace of AgTe was formed upon heating the product of equation 2.10.

### 2.1.5 ‘Heat initiated reactions’ – elemental combination reactions initiated by 
annealing (under dinitrogen) the initial reaction product from liquid ammonia 
(at room temperature)

As already stated, heating the initial reaction product at 250-300 °C for 2h under 
dinitrogen promoted the reaction between lead and tellurium (equation 2.19), resulting 
in the formation of PbTe. Similar heat initiated reactions to that of Pb/Te were observed 
in the formation of the sulfides of gallium, indium, antimony and bismuth, plus the 
tellurides of arsenic and bismuth (equations 2.20-2.30; table 2.4).

\[
\begin{align*}
2\text{Ga(s)} + 3\text{Se(s)} & \rightarrow \text{Ga}\textsubscript[2]Se\textsubscript[3](s) & 523 K \text{, 2h}, > \text{Ga}\textsubscript[2]Se\textsubscript[3](s) \quad (2.20) \\
\text{In}(s) + \text{S}(\text{am}) & \rightarrow \text{In}(s) + \text{InS}(s) & 523 K \text{, 2h}, > \text{InS}(s) \quad (2.21) \\
2\text{In}(s) + 3\text{S}(\text{am}) & \rightarrow \text{In}(s) + \text{InS}(s) + \text{In}_2\text{S}_3(s) & 523 K \text{, 2h}, > \text{In}_2\text{S}_3(s) + \text{InS}(s) \quad (2.22) \\
\text{In}(s) + \text{Se}(s) & \rightarrow \text{In}(s) + \text{Se}(s) + \text{InSe}(s) & 523 K \text{, 2h}, > \text{InSe}(s) + \text{In}(s) + \text{Se}(s) \quad (2.23) \\
2\text{In}(s) + 3\text{Se}(s) & \rightarrow \text{In}(s) + \text{Se}(s) + \text{In}_2\text{Se}_3(s) & 523 K \text{, 2h}, > \text{In}_2\text{Se}_3(s) \quad (2.24) \\
2\text{Sb}(s) + 3\text{S}(s) & \rightarrow 2\text{Sb}(s) + 3\text{S}_2(s) & 523 K \text{, 2h}, > \text{Sb}_2\text{S}_3(s) \quad (2.25) \\
2\text{Sb}(s) + 3\text{Se}(s) & \rightarrow 2\text{Sb}(s) + 2\text{Se}(s) & 523 K \text{, 2h}, > \text{Sb}_2\text{Se}(s) \quad (2.26) \\
\text{Bi}(s) + 2\text{S}(\text{am}) & \rightarrow \text{Bi}(s) + 2\text{S}(\text{am}) & 523 K \text{, 2h}, > \text{Bi}_2\text{S}_3(s) \quad (2.27) \\
\text{Bi}(s) + 2\text{Se}(s) & \rightarrow \text{Bi}(s) + 2\text{Se}(s) & 523 K \text{, 2h}, > \text{Bi}_2\text{Se}_3(s) \quad (2.28) \\
\text{Bi}(s) + 2\text{Te}(s) & \rightarrow \text{Bi}(s) + 2\text{Te}(s) & 523 K \text{, 2h}, > \text{Bi}_2\text{Te}_3(s) + \text{Te}(s) \quad (2.29) \\
2\text{As}(s) + 3\text{Te}(s) & \rightarrow \text{As}(s) + \text{Te}(s) + \text{As}_2\text{Te}_3(s) & 523 K \text{, 2h}, > \text{As}_2\text{Te}_3(s) + \text{Te}(s) \quad (2.30)
\end{align*}
\]
Formation of single phase main-group metal chalcogenides of high purity resulted from facile heating of the elements, once stirred in liquid ammonia. Further reactions to those described above were carried out, although the characterization was more tentative since products of insufficient crystallinity for the use by XRD were obtained. The products of the reactions involving arsenic with either sulfur or selenium was found to be X-ray amorphous (even after annealing at 550 °C for 2 h). EDXA / electron probe studies and Raman spectroscopy suggest that the reaction products to be $\text{As}_2\text{S}_3$ and $\text{As}_2\text{Se}_3$ respectively. Similar analysis suggests that the pre-annealed, amorphous product of the reaction between gallium and sulfur to be $\text{Ga}_2\text{S}_3$. 
Table 2.4 XRD data for heat initiated, elemental combination reactions

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)</th>
<th>Annealed reaction products (250-300 °C, 2h)</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature Lattice parameters Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga : Se 2 : 3</td>
<td>Black</td>
<td>Ga + Se</td>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = 6.66</td>
<td>a = 6.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 11.65</td>
<td>c = 11.65</td>
</tr>
<tr>
<td>In : S 1 : 1</td>
<td>Grey</td>
<td>In + InS</td>
<td>InS</td>
<td>a = 3.90</td>
<td>a = 3.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 4.02</td>
<td>b = 4.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 10.78</td>
<td>c = 10.78</td>
</tr>
<tr>
<td>In : S 2 : 3</td>
<td>Grey</td>
<td>In + In&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt; + InS</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = c = 10.77</td>
<td>a = c = 10.78</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>InS</td>
<td>a = 3.90</td>
<td>a = 3.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 4.02</td>
<td>b = 4.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 10.78</td>
<td>c = 10.78</td>
</tr>
<tr>
<td>In : Se 1 : 1</td>
<td>Grey</td>
<td>In + Se + [InSe]</td>
<td>InSe + [In&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>a = 4.11</td>
<td>a = 4.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 11.00</td>
<td>c = 11.02</td>
</tr>
<tr>
<td>In : Se 2 : 3</td>
<td>Grey</td>
<td>In + Se + [In&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = 7.11</td>
<td>a = 7.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 19.36</td>
<td>c = 19.37</td>
</tr>
<tr>
<td>As : Te 2 : 3</td>
<td>Grey</td>
<td>As + Te + [As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>As&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt; + [Te]</td>
<td>a = 4.05</td>
<td>a = 4.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 29.61</td>
<td>b = 29.59</td>
</tr>
<tr>
<td>Sb : S 2 : 3</td>
<td>Silver</td>
<td>Sb + S</td>
<td>Sb&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = 11.33</td>
<td>a = 11.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 11.30</td>
<td>b = 11.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 3.83</td>
<td>c = 3.83</td>
</tr>
<tr>
<td>Sb : Se 2 : 3</td>
<td>Silver</td>
<td>Sb + Se</td>
<td>Sb&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = 11.64</td>
<td>a = 11.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 11.78</td>
<td>b = 11.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 3.97</td>
<td>c = 3.97</td>
</tr>
<tr>
<td>Bi : S 1 : 2</td>
<td>Silver</td>
<td>Bi + S</td>
<td>Bi&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt; (bismuthinite)</td>
<td>a = 11.13</td>
<td>a = 11.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 11.26</td>
<td>b = 11.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 3.97</td>
<td>c = 3.97</td>
</tr>
<tr>
<td>Bi : Se 1 : 2</td>
<td>Black / Metallic</td>
<td>Bi + Se</td>
<td>Bi&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>a = c = 9.42</td>
<td>a = c = 9.42</td>
</tr>
<tr>
<td>Bi : Te 1 : 2</td>
<td>Black / Metallic</td>
<td>Bi + Te</td>
<td>[Te] + Bi&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt; (tellurobismuthite)</td>
<td>a = c = 10.14</td>
<td>a = c = 10.14</td>
</tr>
</tbody>
</table>

* Liquid ammonia treated elements heated (under dinitrogen) to 250-300 °C, 2h.

b All minor phases (< ca. 10 %) represented by square brackets. Where mineral structures have been synthesised, the mineral names are given in italics.

<sup>c</sup> Unit cell parameters were determined for the major phase binary material only.
2.2 Discussion of the synthesis of binary metal chalcogenides

2.2.1 Scope of elemental combination reactions

Chalcophilic considerations

The reaction of sulfur-ammonia solutions with insoluble metals seems to be limited to the chalcophilic late transition and main group metals (a ‘dividing line’ in reactivity being observed at cobalt). The later elements (Ni, Cu, Ag, Zn, Cd, Hg, Sn, Pb, Tl, In, Ga and, to a limited degree, As) all react with sulfur-ammonia solutions at room temperature to form metal sulfides, whereas the earlier transition metals and Au do not react under comparable conditions. Therefore, the reactions that work are those of soft metals (as defined in Pearson’s terms).

Redox considerations

The reactions are all of the redox type, with the metal being oxidised in most cases to the II oxidation state, with the exception of copper, thallium and tin discussed below. The nature of the oxidizing agent in the sulfur-ammonia solution has yet to be quantified. As previously discussed (section 1.2a), sulfur-ammonia solutions have been shown to contain various sulfur imides (e.g. $S_2NH$), in addition to sulfur-nitrogen anions and sulfur polyanions (e.g. $S_4N^2^-$, $S_8^2^-$ and $S_{12}^2^-$). One or more of these could be responsible for the redox chemistry.

In the case of copper, only Cu$^+$ sulfides are observed. In the formation of the selenides and tellurides, however, Cu$^{n\text{th}}$ materials are apparent in trace quantities, with CuSe being reduced to Cu$^{2\text{nd}}$Se during annealing. Copper is soluble in liquid ammonia in the presence of oxygen, as indicated by the potentials below,\textsuperscript{154} giving rise to a solution dominated by the Cu(I) complex ions.

\[
\begin{align*}
\text{Cu} + 2\text{NH}_3 & \rightarrow [\text{Cu(NH}_3)_2]^+ \quad E^\circ = -0.12 \text{ V} \\
[\text{Cu(NH}_3)_2]^+ + 2\text{NH}_3 & \rightarrow [\text{Cu(NH}_3)_4]^{2+} \quad E^\circ = -0.01 \text{ V}
\end{align*}
\]

However, so long as an inert atmosphere is maintained, copper metal will remain insoluble in liquid ammonia, thereby restricting reactions to the solid state. The propensity for Cu$^+$ products is likely to result from their greater stability than Cu$^{n\text{th}}$: Cu$_3$S is found to be more thermodynamically stable than CuS, being traditionally synthesised from heating copper and sulfur in the absence of air.\textsuperscript{154} Heating copper (II) products for
prolonged time periods may, therefore, induce some degree of reduction to a more metal rich phase.

The reactions of thallium show an interesting trend in oxidation states that seems to be dependent upon the chalcogen used. With sulfur, the product, Tl[S\text{S}_2], formed independently of the ratio of elemental thallium to sulfur (whether it be 2:1 or 2:3). With selenium it appears that the ratio of reagents is crucial. With a 2:1 ratio of metal to selenium then the products are predominantly Tl\text{I} (Tl_2Se and Tl_2Se_3) with a minor phase of TlSe. When the ratio is 2:3 then a single phase of TlSe results, with the stoichiometric excess of selenium appearing as the unreacted element. With tellurium, however, the sole product is the metal deficient Tl\text{I} product Tl_2Te_3, irrespective of the ratios of the starting materials (2:3 or 2:1). These materials are highly covalent, the trend being indicative of the so called ‘inert pair’ effect being exhibited by thallium. Reduction in bond enthalpy of the metal-chalcogen bond upon increasing the size of the chalcogen (due to a reducing integral orbital overlap) results in a progressive preference for thallium to remain in the more energetically accessible Tl\text{I} oxidation state rather than Tl\text{III}.

In the case of tin, it appears that the oxidizing nature of the soluble sulfur-ammonia solution is required to promote elemental combination, since the formation of both tin selenide and tin telluride from reaction of the elements in liquid ammonia is inhibited (even after annealing). A mixture of SnS and SnS_2 results, irrespective of the Sn:S ratios used, showing that both Sn\text{II} and Sn\text{IV} states are made accessible by the S-N species present in liquid ammonia at room temperature. The stoichiometric excess of tin remains as unreacted element and a minor phase. However, the presence of tin exclusively in the II oxidation state after thermolysis (300-350 °C) suggests that the conditions during annealing lead to comproportionation of the SnS_2 and the tin metal present, resulting in complete conversion of SnS_2 to the more thermodynamically stable SnS. Given that the relative proportions of the oxidation states in the pre-annealed mixture were Sn(IV) > Sn(II) > Sn (0), as assessed by optical microscopy, one can rationalise complete conversion of the tin (IV) to tin (II) sulfide during annealing, with the removal of all tin metal and the formation of free sublimed sulfur (equation 3.31).

\[ 2\text{Sn}_{(s)} + 4\text{S}_{(am)} \rightarrow \text{SnS}_{(s)} + \text{SnS}_{2(s)} + \text{S}_{(s)} + \text{Sn}_{(s)} \quad \text{ca.600 K, 2h} \rightarrow 2\text{SnS}_{(s)} + \text{S}_{(subl)} \] (3.31)
2.2.2 Role of liquid ammonia in the formation of metal chalcogenides

The use of other (non N-based) solvents

The reactions of metals (M) with sulfur, selenium and tellurium (M = Cu, Ag, Cd, Zn, Hg, Pb) were repeated under similar reaction conditions in a variety of common non N-based solvents (CS₂, C₆H₆, C₅H₅N, CH₂Cl₂, CH₃OH, H₂O, acetone and THF). It is apparent that liquid ammonia plays a crucial role in room temperature syntheses of the aforementioned metal chalcogenides since, generally, no significant (> 10%) elemental combination was observed in the other common solvents mentioned. The singular exception where a reaction did occur was with lead and sulfur / selenium in water. This was likely to result from the highly chalcophilic nature of lead, but at no point was a single phase seen, but rather a mixture of lead chalcogenide, lead oxide and lead oxy-chalcogenide. In addition, such reactions took place over an extended period of time (60 h for the aqueous lead-sulfur reaction compared to less than 12 h in liquid ammonia).

The reactions observed in sulfur-ammonia solutions are time dependent. No reaction occurs until the sulfur has dissolved into the ammonia, with the onset of the blue colouration. Then anywhere from 2 h to 4 days are required for appreciable amounts of product to precipitate (as assessed by the removal of both the metal and the colour (sulfur) from the ammonia). Whilst the particle size of the metal did have an observed effect on the rate of all the reactions discussed (with powders reacting faster than discrete pieces), 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 is seen clearly in the relative reaction times of sulfur with the 3d elements of groups 10-13: nickel (ca. 60 h), copper (ca. 36 h) and zinc (ca. 12 h).

Elemental combination in liquid ammonia

In the synthesis of metal sulfides, it is likely that the sulfur species first generated upon dissolution of sulfur play an important mechanistic role, since sulfur-ammonia solutions can take up to 1,000 hours to fully equilibriate.¹³ It is known that some metals will react directly with sulfur at room temperature (such as mercury).³ Such reactions are, however, largely surface limited and for most metals slow. This may result from the presence of a passivating oxide layer. Liquid ammonia may act to remove this coating and so facilitate contact between the metal and dissolved sulfur. Thereby liquid ammonia may play a dual role – production of active sulfur species in solution as well
as activating the metal surface. This would result in a lowering the free energy of activation such that the reaction can occur at ambient temperatures.

**Types of product formed**

The sulfide formed tends to be the most thermodynamically stable product. Alteration of the metal to sulfur ratios was investigated to try to form other sulfide phases (ZnS, AgS or CuS). It was found that only ZnS, AgS CuS (i.e. a mixed state material) was observed. If a reaction was stopped prior to completion and inspected by SEM / EDXA, an intimate mixture of metal sulfide, unreacted metal and sulfur was observed.

One may extend the observation of the product stoichiometry being that of the most thermodynamically stable binary material to the remaining binary chalcogenide synthesised. Although the metal selenide and telluride reactions were fundamentally different to the sulfur-ammonia solutions (in that none of the elements appeared to dissolve in the ammonia during the course of the reaction), attempts at altering the product stoichiometry by using excess selenium or tellurium (or excess metal) did not have any bearing on the product formed. However, it was observed that reaction rate generally increased from sulfur to selenium to tellurium.

It should be noted that exceptions to the intransient nature of elemental stoichiometry were observed in the formation of thallium selenides and the reaction between nickel and sulfur, where a 3:2 ratio of Ni:S produced NiS₂ (heazlewoodite).

**Effect of annealing**

The heat treatment used to induce crystallinity in the amorphous powders is much lower than the combination temperature required from the individual elements. In the majority of cases, comparative reactions of intimately ground powders of the elements under similar heat treatment (250-300 °C) even after prolonged time periods (ca. 6h) failed to occur. Where it did occur (ZnS and CdS) the product was less crystalline than the ammonia treated powders. This may result from a better mixing of the particles, with sulfur species effectively coating the metal surface and so increasing the contact area. The removal of the metal oxide coatings by ammonia previously described may also contribute to sulfide formation, as well as allowing the elemental combination of metals with insoluble chalcogens. This potential activation of the metal surface is borne out by the heat initiated reactions of lead and tellurium (equation 2.9), gallium / indium with selenium (equation 2.20 and 2.26), arsenic with tellurium (equation 2.30) and antimony / bismuth with selenium / tellurium (equations 2.25-2.29). The elements reacted only
when heated to 250-300 °C, yet without treatment in liquid ammonia (or upon exposure to atmospheric oxygen) the reaction did not proceed. The remaining reactions involving main-group metals show that although the initial products may be of varying stoichiometry (or contain unreacted metal), facile heating of the mixture, without exposure to air, will also result in the most thermodynamically stable single phase at 250-300 °C. This is normally the metal sesquisulfide (M$_2$E$_3$). In addition, whilst the conversion of tin (II / IV) sulfide mixture to tin (II) sulfide upon annealing may be rationalised in terms of thermodynamic stability of SnS, the proposed comproportionation route would be facilitated by the activation of the tin metal present.

2.3 Experimental

All reagents were of 99.9 % purity, or better, and purchased from Aldrich Chemical Co. They were used without further purification. Ammonia was purchased from BOC and used without drying. All manipulations were carried out in a dinitrogen filled glove box. Reactions were carried out (using Schlenk techniques) in thick walled (3-4 mm), teflon-in-glass, sealed Youngs-type 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-K$_{\alpha}$ radiation ($\lambda = 1.504$ Å). They were indexed using either TREOR or METRIC-LS programmes (lattice parameters matched to within 0.02 Å with literature). The SEM / EDXA measurements were determined on a Jeol JSM820 microscope, equipped with a Kevex Quantum Delta 4 detector and a Hitachi SEM S-570 camera. The electron beam was focused (1 μm spot at surface) with an excitation energy of 20 keV. Electron-probe analyses were conducted on a Jeol EMA, using polished samples, and compared to metal and chalcogen standards. XPS measurements were performed with a VG ESCALAB 220i XL instrument using focused (300 μm spot) monochromatic Al-K$_{\alpha}$ 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 Is peak at 284.8 eV. Infra-red spectra were recorded on a Nicolet 205 spectrometer using KBr pressed disks. Raman spectra were recorded on a Dilor XY spectrometer. The 514.53 nm line of an argon laser (50 mW) was the excitation source; the slit width was 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 (7600-6300 ppm) for two different spin rates (10 KHz and 13 KHz), using a Bucker 300 MHz spectrometer. The sample was referenced against C(SnMe$_3$)$_4$, the chemical shift for which was taken to be 48.2 ppm. Thermolysis studies were performed in a Lenton Thermal Designs tube furnace.

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

2.3.1 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 ca. 10 cm$^3$ liquid ammonia 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 ca. 15h. From the onset of dissolution of the sulfur, the ammonia was observed to change to a dark blue, to green and finally colourless, with the formation of a pale blue precipitate. Within 1 h of warming to room temperature, all of the sulfur had dissolved. The zinc metal could initially be seen but had been consumed within 6-10 h. The precipitate was collected by cooling the solution back to -77 °C and allowing the ammonia to evaporate at atmospheric pressure 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 0.268 g, 0.275 mmol, 90 %). Part of the material was heated to 250-300 °C for 2 h. The unthermolysed and thermolysed materials were analysed by X-ray powder diffraction (Table 2.1), Fourier-transform IR and Raman spectroscopies, microanalysis, SEM / EDXA (or electron probe studies), magnetic moment measurements and X-ray photoelectron spectroscopy.

**X-ray photoelectron spectroscopy (pre-annealed ZnS)**

<table>
<thead>
<tr>
<th></th>
<th>Observed values</th>
<th>Literature values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc Auger Parameter (eV)</td>
<td>2011.4</td>
<td>2011.3 eV (ZnS); 2009.8 eV (ZnO)</td>
</tr>
<tr>
<td>Sulfur 2p binding energy (eV)</td>
<td>161.6</td>
<td>161.7 (ZnS)</td>
</tr>
</tbody>
</table>
Elemental composition (pre-annealed ZnS)

<table>
<thead>
<tr>
<th></th>
<th>Observed abundance</th>
<th>Calculated abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microanalysis</td>
<td>C (0.2 %), H (0.0 %),</td>
<td>S (32.8 %)</td>
</tr>
<tr>
<td></td>
<td>N (0.15 %), S (32.6 %)</td>
<td></td>
</tr>
<tr>
<td>Standardised electron probe</td>
<td>Zn 66.2 %, S 33.8%</td>
<td>Zn 66.5 %, S 33.5 %</td>
</tr>
</tbody>
</table>

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 (weak bands at 3200 and 1450 cm⁻¹ were also observed in the unthermolysed sample, identified as free ammonia N-H stretches).⁶⁸

Standardised EDXA analysis of all the metal sulfides were typically within 1 % of the expected elemental ratios for sulfur and metal.

All the metal sulfide powders were diamagnetic. The ¹¹⁹Sn NMR spectra confirmed the presence of two separate nuclear tin environments with chemical shift values of δ 6870 ppm and 7220 ppm, corresponding to tin (II) and tin (IV) respectively.

2.3.2 Reactions of Ag and Pb with sulfur in liquid ammonia

The same reaction condition conditions and scale were used in the reactions as detailed above for ZnS, except that in the silver reaction an 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 further heating for characterisation.

Microanalysis for Ag₂S showed C (0.05 %), H (0.01 %) and N (0.3 %).

Standardised electron probe analysis for PbS showed lead 86.5 % (calc. 86.6 %) and sulfur 13.5 % (calc. 13.4 %).

2.3.3 Reactions of selenium and tellurium in liquid ammonia

The same reaction condition conditions and scale were used in the reactions as detailed above for zinc-sulfur reactions. These reactions typically required 48-52 h to go to completion. During this time no colour was evident in the liquid ammonia, yet the elements were converted in to a black powder. No traces of the metal were observed after ca. 24 h, and no precipitation from the solution was seen. Ammonia was evaporated by passing dinitrogen at −77 °C and the products were analysed by XRD (Table 2.1), SEM / EDXA, electron micrprobe, FT-IR and XPS. Some of the products were amorphous to X-rays (Table 2.1) and were heated to 250-300 °C in vacuo for 2h in order to induce sufficient crystallinity for characteristaion.
XPS data obtained for pre-annealed CdSe, HgTe Ag$_2$Te

<table>
<thead>
<tr>
<th>Pre-annealed material</th>
<th>Observed binding energy</th>
<th>Auger parameter$^{23,32}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe</td>
<td>3d$_{5/2}$ peak – 491.7 eV</td>
<td>Cd 3d$_{5/2}$ peak – 786.7 eV</td>
</tr>
<tr>
<td>HgTe</td>
<td>5d$_{5/2}$ peak – 572.4 eV</td>
<td>Te d$_{5/2}$ peak – 491.7 eV</td>
</tr>
<tr>
<td>Ag$_2$Te</td>
<td>Te d$_{5/2}$ peak – 572.5 eV</td>
<td>Te d$_{5/2}$ peak – 491.7 eV</td>
</tr>
</tbody>
</table>

IR and Raman analyses showed broad bands at *ca.* 350-180 cm$^{-1}$ for the selenides and 250-160 cm$^{-1}$ for the tellurides.$^{24}$

2.3.4 **Reactions of Ca, Sr, Ba, Eu and Yb 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 liquid ammonia first, and the resultant blue or bronze solution was magnetically stirred during the addition of the chalcogen. Over a period of 2h the ammonia solution faded, yielding either a purple or brown precipitate. The materials were worked up as before and analysed by X-ray powder diffraction, IR spectroscopy and SEM / EDXA.

2.3.5 **Reactions of strontium and barium in 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 of the solution to room temperature, produced a deep bronze solution. Within 2 h the bronze colouration faded to blue, and after 20 h to colourless with the precipitation of a white solid. Cooling the solution back to −77 °C and allowing the evaporation of the ammonia under a dinitrogen flow (by warming under atmospheric pressure), yielded an X-ray amorphous white solid which analysed as M(NH$_2$)$_2$.

Nitrogen analysis : Sr(NH$_2$)$_2$ 23.7 % (calc. 23.71 %); Ba(NH$_2$)$_2$ 8.1 % (calc. 8.35 %).

IR analysis (both samples) : $\nu = 3200$ and 1450 cm$^{-1}$.

Dissolution of Ca, Yb or Eu in liquid ammonia without the addition of chalcogens was also found to result 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 IR (the latter showing strong N-H vibrations in each sample at both $\nu_{\text{N-H}}$ 3200 cm$^{-1}$ and $\nu_{\text{N-H}}$ 1450 cm$^{-1}$).
<table>
<thead>
<tr>
<th>Target Material&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Range of particle sizes (microns)&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Ratio of elements / atm. % (experimental error ± 2-3 atm %)&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Elemental ratio</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2 – 8</td>
<td>Ni : S</td>
<td>60 : 40 (major)</td>
<td>60 : 40 (Ni&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>Ni : S</td>
</tr>
<tr>
<td>NiS</td>
<td>2 – 8</td>
<td>Ni : S</td>
<td>50 : 50 (major)</td>
<td>50 : 50 (NiS)</td>
<td>Ni : S</td>
</tr>
<tr>
<td>NiSe</td>
<td>2 – 8</td>
<td>Ni : Se pre-annealed material only</td>
<td>50 : 50 (major)</td>
<td>50 : 50 (NiSe)</td>
<td>Ni : Se</td>
</tr>
<tr>
<td>NiTe</td>
<td>2 – 8</td>
<td>Ni : Te</td>
<td>33 : 67 (major)</td>
<td>33 : 67 (NiTe&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>Ni : Te</td>
</tr>
<tr>
<td>CuS</td>
<td>2 – 8</td>
<td>Cu : S</td>
<td>28 : 72</td>
<td>33 : 67 (Cu&lt;sub&gt;2&lt;/sub&gt;S)</td>
<td>Cu : S</td>
</tr>
<tr>
<td>CuSe</td>
<td>2 – 8</td>
<td>Cu : Se</td>
<td>50 : 50 (major)</td>
<td>50 : 50 (CuSe)</td>
<td>Cu : Se</td>
</tr>
<tr>
<td>CuTe</td>
<td>2 – 8</td>
<td>Cu : Te</td>
<td>67 : 33 (50%)</td>
<td>67 : 33 (Cu&lt;sub&gt;2&lt;/sub&gt;Te)</td>
<td>Cu : Te</td>
</tr>
<tr>
<td>Cu : Te</td>
<td>70 : 30 (25%)</td>
<td>73 : 27 (Cu&lt;sub&gt;2&lt;/sub&gt;Te)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>2 – 8</td>
<td>Ag : S</td>
<td>67 : 33</td>
<td>67 : 33</td>
<td>Ag : S</td>
</tr>
<tr>
<td>Ag&lt;sub&gt;2&lt;/sub&gt;Se</td>
<td>2 – 8</td>
<td>Ag : Se</td>
<td>67 : 33</td>
<td>67 : 33</td>
<td>Ag : Se</td>
</tr>
<tr>
<td>Ag&lt;sub&gt;2&lt;/sub&gt;Te</td>
<td>2 – 8</td>
<td>Ag : Te</td>
<td>67 : 33 (major)</td>
<td>67 : 33 (Ag&lt;sub&gt;2&lt;/sub&gt;Te)</td>
<td>Ag : Te</td>
</tr>
<tr>
<td>ZnS</td>
<td>2 – 8</td>
<td>Zn : S</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Zn : S</td>
</tr>
<tr>
<td>ZnSe</td>
<td>2 – 8</td>
<td>Zn : Se</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Zn : Se</td>
</tr>
<tr>
<td>ZnTe</td>
<td>2 – 8</td>
<td>Zn : Te</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Zn : Te</td>
</tr>
<tr>
<td>CdS</td>
<td>2 – 8</td>
<td>Cd : S</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Cd : S</td>
</tr>
<tr>
<td>CdSe</td>
<td>2 – 8</td>
<td>Cd : Se</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Cd : Se</td>
</tr>
<tr>
<td>CdTe</td>
<td>2 – 8</td>
<td>Cd : Te</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Cd : Te</td>
</tr>
<tr>
<td>HgS</td>
<td>2 – 8</td>
<td>Hg : S</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Hg : S</td>
</tr>
<tr>
<td>HgSe</td>
<td>2 – 8</td>
<td>Hg : Se</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Hg : Se</td>
</tr>
<tr>
<td>HgTe</td>
<td>2 – 8</td>
<td>Hg : Te</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td>Hg : Te</td>
</tr>
</tbody>
</table>

<sup>1</sup> Prepared from combination of stoichiometric quantities of elements in liquid ammonia at room temperature.

<sup>2</sup> Assessed by SEM.

<sup>3</sup> As assessed by EDXA (spot size - 1 micron). Results displayed are for both pre-annealed and annealed material (unless otherwise stated). Approximate surface abundance of multiple phases (as assessed using back-scattered electrons) is expressed either as a percentage or as **major** (>90%) / **minor** (<10 %).
## Table 2.6 SEM / EDXA data for heat initiated reaction products

<table>
<thead>
<tr>
<th>Target Material</th>
<th>Range of particle sizes (microns)</th>
<th>Ratio of elements / atm % (experimental error ± 2-3 %)</th>
<th>Elemental ratio</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb : Te</td>
<td>5 – 8</td>
<td>Pb : Te</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td></td>
</tr>
<tr>
<td>Ga₂Se₃</td>
<td>5 – 8</td>
<td>Ga : Se</td>
<td>40 : 60</td>
<td>40 : 60</td>
<td></td>
</tr>
<tr>
<td>As₂Te₃</td>
<td>5 – 8</td>
<td>As : Te</td>
<td>40 : 60</td>
<td>40 : 60</td>
<td></td>
</tr>
<tr>
<td>Sb₂S₃</td>
<td>5 – 8</td>
<td>Sb : S</td>
<td>40 : 60</td>
<td>40 : 60</td>
<td></td>
</tr>
<tr>
<td>Sb₂Se₃</td>
<td>5 – 8</td>
<td>Sb : Se</td>
<td>40 : 60</td>
<td>40 : 60</td>
<td></td>
</tr>
<tr>
<td>BiS₂</td>
<td>5 – 8</td>
<td>Bi : S</td>
<td>33 : 67 (80 %)</td>
<td>33 : 67 (Bi₂S₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi : S</td>
<td>5 : 95 (20 %)</td>
<td>0 : 100 (S)</td>
<td></td>
</tr>
<tr>
<td>BiSe₂</td>
<td>5 – 8</td>
<td>Bi : Se</td>
<td>33 : 67 (80 %)</td>
<td>33 : 67 (Bi₂Se₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi : Se</td>
<td>5 : 95 (20 %)</td>
<td>0 : 100 (Se)</td>
<td></td>
</tr>
<tr>
<td>BiTe₂</td>
<td>5 – 8</td>
<td>Bi : Te</td>
<td>33 : 67 (80 %)</td>
<td>33 : 67 (Bi₂Te₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bi : Te</td>
<td>5 : 95 (20 %)</td>
<td>0 : 100 (Te)</td>
<td></td>
</tr>
<tr>
<td>In₂S₃</td>
<td>5 – 8</td>
<td>In : S</td>
<td>40 : 60 (80 %)</td>
<td>40 : 60 (In₂S₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>In : S</td>
<td>50 : 50 (20 %)</td>
<td>50 : 50 (InS)</td>
<td></td>
</tr>
<tr>
<td>In₂Se₃</td>
<td>5 – 8</td>
<td>In : Se</td>
<td>40 : 60 (90 %)</td>
<td>40 : 60</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>In : Se</td>
<td>95 : 5 (5 %)</td>
<td>100 : 0 (In)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>In : Se</td>
<td>5 : 95 (5 %)</td>
<td>0 : 100 (Se)</td>
<td></td>
</tr>
<tr>
<td>InS</td>
<td>5 – 8</td>
<td>In : S</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td></td>
</tr>
<tr>
<td>InSe</td>
<td>5 – 8</td>
<td>In : Se</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td></td>
</tr>
</tbody>
</table>

**Note:** For the majority of samples, the pre-annealed material was composed of discrete elements only (experimental ratio of elements ≥ 95 %). Exceptions were observed for the reactions shown below.

<table>
<thead>
<tr>
<th>Target material</th>
<th>Ratio of elements of pre-annealed material / atm % (experimental error ± 2-3 %)</th>
<th>Elemental ratio</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>InS</td>
<td>In : S</td>
<td>50 : 50 (20 %)</td>
<td>50 : 50 (InS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In : S</td>
<td>98 : 2 (80 %)</td>
<td>100 : 0 (In)</td>
<td></td>
</tr>
<tr>
<td>In₂S₃</td>
<td>In : S</td>
<td>40 : 60 (20%)</td>
<td>40 : 60 (In₂S₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In : S</td>
<td>50 : 50 (20%)</td>
<td>50 : 50 (InS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In : S</td>
<td>98 : 2 (60%)</td>
<td>100 : 0 (In)</td>
<td></td>
</tr>
<tr>
<td>InSe</td>
<td>In : Se</td>
<td>50 : 50 (20%)</td>
<td>50 : 50 (InS)</td>
<td></td>
</tr>
<tr>
<td>In₂Se₃</td>
<td>In : Se</td>
<td>40 : 60 (20%)</td>
<td>40 : 60 (In₂S₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Free element</td>
<td></td>
<td>Free element (80%)</td>
<td></td>
</tr>
</tbody>
</table>

---

⁴ Obtained from stirring stoichiometric quantities of the elements in liquid ammonia at room temperature.
SEM / EDXA results obtained for material annealed at 250-300 °C for 2h.
⁵ Assessed by SEM
⁶ Assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple phases is expressed as a percentage (as assessed using back-scattered electrons).
2.4 Binary Pnictides

Various elemental combination reactions were carried out in liquid ammonia in order to ascertain whether binary pnictide compounds could be synthesised at room temperature in liquid ammonia. The reaction schemes initially undertaken to produce both main-group and late transition metal ‘pnictides’ are shown (that is phosphides, arsenides, antimonides and bismuthides). They are shown since they represent a broad range of target compounds, both in terms of varying pnictide connectivity as well as containing those metals that exhibit a high affinity for the pnictide atoms (specifically zinc, copper, cadmium and thallium). The schemes comprise some well documented main-group binaries, including classic group 13-15 semiconducting materials. The reaction schemes investigated were split into three main categories, as described by the reactions below (equations 2.31 to 2.40).

A. Transition metal phosphides

\[
\begin{align*}
3M(s) + P_{(am)} &\rightarrow M_3P(s) \quad (M = Cu, Ag) \\
3M(s) + 2P_{(am)} &\rightarrow M_3P_2(s) \quad (M = Cu, Zn, Cd) \\
M(s) + 2P_{(am)} &\rightarrow MP_2(s) \quad (M = Cr, Co, Ti)
\end{align*}
\]

B. Transition metal arsenides and antimonides

\[
\begin{align*}
3M(s) + Pn_{(s)} &\rightarrow M_3Pn(s) \quad (M = Cu, Ag, Pn = As, Sb) \\
3M(s) + 2Pn_{(s)} &\rightarrow M_3Pn_2(s) \quad (M = Cd, Zn, Pn = As, Sb) \\
xM(s) + yAs_{(s)} &\rightarrow M_xAs_y(s) \quad (M = Ag, x : y = 7:1; M = Cd, x : y = 5:2) \\
Cd(s) + Sb(s) &\rightarrow CdSb(s)
\end{align*}
\]

C. Main-group pnictides

\[
\begin{align*}
M(s) + Pn_{(s)} &\rightarrow MPn_{(s)} \quad (M = Ga, In, Pn = As, Sb) \\
3Tl(s) + Pn_{(s)} &\rightarrow Tl_3Pn_{(s)} \quad (Pn = As, Sb) \\
xTl(s) + yBi_{(s)} &\rightarrow Tl_xBi_y(s) \quad (x : y = 3:1, 7:2 or 1:2) \\
4Sn_{(s)} + 3P_{(am)} &\rightarrow Sn_4P_{3(s)}
\end{align*}
\]
2.4.1 Synthesis and characterisation

The experimental procedure for these reactions is the same as that used in the synthesis of the analogous metal chalcogenides. Initial products showed no direct reaction between the elements after 60h of mixing in liquid ammonia. The XRD patterns showed the presence of individual elements. EDXA showed regions of discrete elements far in excess of the 1 μm excitation width, a pattern that is consistent with an intimate mix of the elements rather than being indicative of any elemental combination.

The products were then annealed (250-300 °C for 2h in dinitrogen) without exposure to the atmosphere. Subsequent analysis by XRD showed a mixture of unreacted elements and binary metal pnictides. EDXA confirmed the presence of unreacted elements as the major constituents (ca. 60-80 % of the sample surface), as well as multiple phases of metal pnictides. The exception to this was the annealed product of the reaction between tin and phosphorus, as discussed below.

2.4.2 Choice of phosphorus reagent

The metal phosphide reactions were initially carried out using the polymeric, or red, form of phosphorus. These reactions were then repeated using the white isomer, which fully dissolves in liquid ammonia to afford a red solution consisting of discrete P₄ tetrahedra. The reactions were left for 48h, after which the red colouration was seen to disappear. The results obtained were similar to those for the annealed samples. That is, both XRD and EDXA showed the predominance for unreacted elements, whilst quantitative EDXA showed the presence of many phases of metal phosphide. Annealing the products showed little appreciable increase in the percentage of elementally combined products. A single exception to this was the reaction between tin and phosphorus. Pre-annealed samples showed uncombined elements, yet after annealing the XRD pattern showed the presence with a single tin phosphide phase of desired stoichiometry (Sn₄P₄, figure 2.8) with some unreacted tin. Interestingly, the product mixture was not pyrophoric and elemental analysis showed the phosphorus content to have remained unchanged. ³¹P solid state NMR showed two broad bands (δ + 47.60 and - 442.65 ppm) and one sharp peak (δ + 6.55 ppm) indicative of the polymeric form of phosphorus (spectroscopic chemical shifts obtained for a red phosphorus standard of 99.9+ % purity were δ 7.21, 53.92 and - 442.89 ppm). This suggests that after 48 h in liquid ammonia at room temperature, white phosphorus is fully converted to the thermodynamically more stable red form, which offers an overwhelming kinetic barrier
towards elemental combination with metals. This observation is similar to those recorded for the reaction between white phosphorus and a mixture of atomic and excited molecular nitrogen\textsuperscript{142} (produced by subjecting dinitrogen to a static electrical discharge), described by equation 2.42.

\[
\text{N}_2^{(g)} + P_4^{(s)} \rightarrow P_4^{(s)} + \text{some phosphorus nitrides} \quad (2.42)
\]

Figure 2.6 XRD spectrum of tin phosphide (Sn\textsubscript{3}P\textsubscript{4})

![XRD spectrum of tin phosphide (Sn\textsubscript{3}P\textsubscript{4}]

Key: Sample of annealed Sn\textsubscript{4}P\textsubscript{3} (top) Standards (bottom) of Sn\textsubscript{4}P\textsubscript{3} (blue), Sn metal (red)

2.4.3 Discussion of binary metal pnictides

Owing to the insolubility in liquid ammonia of red phosphorus, arsenic, antimony and bismuth, one can assume the elemental reactions carried out using these pnictogens to be purely solid state. For the most part, the failure to produce binary metal pnictides without thermolysis suggests that the energy of activation is too high for elemental combination at room temperature in liquid ammonia. Although binary products were observed after annealing the liquid ammonia treated elements at 250-300 °C, they showed a range of stoichiometries. Although the temperature of elemental combination is lower than may be expected (as was observed for the formation of certain metal chalcogenides after treatment of the elements in liquid ammonia), the synthesis of a
single phase was not observed. Unlike binary metal chalcogenides, the analogous pnictides show a wider range of allowed stoichiometries, the energies of formation of which appear to be too similar to be distinguishable under the reaction conditions adopted.

In the majority of cases, the use of white phosphorus in the formation of metal phosphides showed a more extensive formation of binary products than when red phosphorus was employed (although they were minor phases). EDXA analysis showed regions of metal phosphide consistent with the synthesis of a range of stoichiometries. One can surmise these reactions were now made accessible by the dissolution of the phosphorus into discrete \( \text{P}_4 \) tetrahedra, thereby greatly increasing the surface area of the reaction interface. It would then seem likely that they were prevented from going to completion by the conversion of white to red phosphorus. As was observed for the annealed products mentioned earlier, it also appears that under the conditions employed, there is no preference for the formation of a metal phosphide of single phase / stoichiometry.
3.0 Synthesis of Ternary Materials by Elemental Combination
Reactions in Liquid Ammonia

3.1 Ternary chalcogenides; general synthesis and characterisation

Attempts at forming single phased substitutional solid solutions of late transition metals via combination of the elements in liquid ammonia met with some success. Three types of ternary material were synthesised – ‘mixed metal chalcogenides’ (sulfides and tellurides), ‘metal mixed chalcogenides’ (mainly sulfur selenides) and ‘metal mixed pnictide chalcogenides’ (groups 11-15-16). In addition, two types of reaction were studied, one involving the use of metals soluble in liquid ammonia and one with the use of insoluble metals. Initial discussions in this chapter relate to the first two types of material, the 11-15-16 materials will be dealt with separately (section 3.7).

Stoichiometric determination was obtained with the use of EDXA (or standardised electron probe) coupled with the application, where possible, of Vegard’s Law to the X-ray powder diffraction pattern. However, all reaction products described as metal mixed chalcogenides, as well as those involving soluble metals, were initially amorphous to X-rays. Once isolated, they required heating at 250-300 °C for 2h in order to induce sufficient crystallinity for characterisation. Consequently, annealing was carried out in a static, inert atmosphere to limit any loss of chalcogen from the product.

For all the reactions described, FT-IR analyses of the products showed broad stretches in the region of 600-200 cm⁻¹, characteristic of M-S and M-M stretching frequencies. As with the binary materials described in the previous chapter, no absorptions were observed above 600 cm⁻¹, indicating the absence of any appreciable N-H based ligands in the product. Whilst reaction times for the associated binary compounds were typically less than 24 h, 1-2 days was necessary for complete reaction of the ternary chalcogenides. SEM studies showed that for all samples, the synthesised products were comprised of aggregates of size 2-8 µm, both before and after heating.

3.1.2 General experimental
The same general reaction procedure and reaction scale was used as described for the binary metal chalcogenides in section 2.3, except that either two metals or two chalcogenides were added to the liquid ammonia in predetermined ratios. Product work-up and analyses were also carried out as for the binary materials. The samples that
required annealing were heated to 250-300 °C under static dinitrogen in order to induce sufficient crystallinity for analysis by X-ray powder diffraction.

3.2 Combination of soluble metals with chalcogens
Reactions of chalcogens with liquid ammonia solutions of fully dissolved metal \((M_{(am)})\) at room temperature afforded a range of single phase ternary mixed metal chalcogenides in good yield (equations 3.1-3.3).

\[
M_{(am)} + Sr_{(am)} + 2E_{(am)} \rightarrow MSrE_{2(s)} \quad (M = Mg, Ca, Ba, Yb; E = S, Se, Te) \quad (3.1)
\]

\[
xSr_{(am)} + yBa_{(am)} + 2S_{(am)} \rightarrow Sr_{x}Ba_{y}S_{2(s)} \quad (\Sigma(x,y) = 1.00; \quad x = 0.25, 0.50 \text{ or } 0.75) \quad (3.2)
\]

\[
Eu_{(am)} + Yb_{(am)} + 2E_{(am)} \rightarrow EuYbE_{2(s)} \quad (E = S, Se \text{ or } Te) \quad (3.3)
\]

The ternary products produced through the employment of soluble metals were all of single phase. For the strontium barium sulfides, the XRD pattern of the annealed material showed them all to be solid solutions. Exact stochiometries were thus calculated directly from a comparative study of the lattice parameters obtained from the product’s XRD spectra with those of the related binary metal chalcogenides by invoking Vegard’s law.\(^{160}\) Analysis of the products of general formula \(ABE_2\) \((A = Mg, Ca, Ba, Yb; B = Sr / Eu; \quad E = S, Se, Te)\) relied upon EDXA studies, since annealing to temperatures in excess of 550 °C failed to induce sufficient crystallinity for successful characterisation by X-ray powder diffraction. EDXA confirmed the elemental ratios expected for the stoichiometries described by equations 3.1 and 3.3 to within 1% over many randomly selected surface spots (focal width of electron beam being 1 micron). The materials exhibited characteristic colour and IR absorption (compared to literature).

3.3 Insoluble element combination (metal mixed chalcogenides)
In addition to the aforementioned reactions using soluble metals, attempts were made to synthesise ternary metal mixed chalcogenides of varying stoichiometry using the insoluble, chalcophilic metals Cu, Zn, Cd, Ag, Hg, Tl and Pb (equations 3.4-3.9).

\[
M(s) + xS_{(am)} + ySe_{(am)} \rightarrow MS_{x}Se_{y(s)} \quad (M = Zn, Cu; \quad x = y = 0.50) \quad (3.4)
\]

\[
Cd(s) + xS_{(am)} + ySe_{(am)} \rightarrow Cds_{x}Se_{y(s)} \quad (\Sigma(x, \; y) = 1; \quad x = 0.20, 0.40, 0.50, 0.60, 0.80) \quad (3.5)
\]
The reactions described by equations 3.4 and 3.5 resulted in materials of single phase. The powders were amorphous to X-rays prior to annealing. The diffraction patterns of the annealed samples are intermediate between those of binary metal sulfide and metal selenide. Stoichiometric determination of these substitutional solid solutions was undertaken by application of Vegard’s Law (figure 3.1). These results were confirmed by SEM and EDXA of the unthermolysed materials, which showed a single phase under back-scattered electrons and a uniform elemental composition by EDXA, over many surface spots, consistent with the desired stoichiometry (to within 2-3 atm. %). Figure 3.1 (below) shows an XRD plot of CdS$_{0.50}$Se$_{0.50}$ compared with CdS (eq. 2.1) and CdSe (eq. 2.8) prepared in liquid ammonia. The plot clearly shows that the solid solution exhibits variation in lattice dimensions with retention of the crystal type (in accordance with Vegard’s law):

**Figure 3.1** XRD plot of CdS$_{0.50}$Se$_{0.50}$ compared to CdS and CdSe (all synthesised from elemental combination reactions in liquid ammonia at room temperature)

The samples of this series were also analysed by Laser Induced Fluorescence (LIF).
3.3.2 Laser Induced Fluorescence of cadmium sulfur selenides

It is possible to obtain a Laser Induced Fluorescence (LIF) spectrum for each member of the series CdS$_x$Se$_{1-x}$, where 0 ≤ $x$ ≤ 1; $\Sigma(x, y) = 1; \Delta x = 1.0$. Notable features common to all these spectra include the range of peak intensities (500 – 5000 units) and the range of frequencies within which these solid solutions fluoresce – from $\lambda \approx 480$ nm (CdS) to $\lambda \approx 640$ nm (CdSe); $\Delta \lambda \approx 160$ nm. These excitation frequencies lie in the visible region, and have led to these solid solutions being widely used as pigments for artists requiring colours ranging from yellow to red (the degree of red pigmentation being directly related to the percentage composition of selenium in the base compound).

Compounds from this series synthesised by direct combination of the elements in liquid ammonia (section 3.1.3) were also analysed by the LIF technique prior to annealing. The spectra obtained are shown in figure 3.2. Notably, all the pre-annealed samples appeared yellow. The LIF analysis showed that all the fluorescence frequencies lie within a greatly reduced range (Δλ ≈ 15 nm) whose parameters lie at shorter wavelengths than the standard for CdS – from $\lambda \approx 440$ nm to $\lambda \approx 455$ nm. The synthesised samples fluoresced with a much lower intensity, with one showing no fluorescence at all (intensity range: 0-350 units). Given the semiconducting nature of cadmium sulfur selenides, the observed blue shift in fluorescence of the samples may indicate that the material contains quantum confined nanoparticles. It was also observed that upon increasing the intensity of the incident radiation, the irradiated region darkened towards the expected characteristic colour of that sample. Sequential scans showed a red shift in the fluorescence frequencies, in some cases with a subsequent increase in intensity, perhaps in response to laser induced heating and a subsequent sintering of fine particles.
Equations 3.10-3.13 describe the synthesis of ternary mixed chalcogenides of Ag, Hg, Tl and Pb (equations 3.11-3.16).

\[
\begin{align*}
2M(s) + S_{(am)} + Se_{(s)} &\rightarrow MS_{(s)} + MSe_{(s)} \\
4M(s) + S_{(am)} + Se_{(s)} &\rightarrow M_2S_{(s)} + M_2Se_{(s)} \\
4Tl(s) + Se_{(s)} + Te_{(s)} &\rightarrow Tl_2Se_{(s)} + Tl_2Te_{(s)} \\
2Ag(s) + Se_{(s)} + Te_{(s)} &\rightarrow Ag_2Se_{(s)} + Te_{(s)}
\end{align*}
\] 

(Equations 3.10, 3.11, 3.12, 3.13)

The metals employed in equations 3.10 and 3.11 all formed crystalline binary chalcogenides without annealing. Combined EDXA and XRD studies showed that the elements combined to form a mixture of binary metal sulfides and selenides rather than a single ternary material (tables 3.1, 3.2 and 3.3).

The phases synthesised were the same as those observed in chapter 2. With reference to equations 3.13 and 3.14, discrete binary metal selenides and tellurides were synthesised where sufficient metal was present (equation 3.13), as with the analogous sulfur-selenium mix. However, equation 3.14 shows a preference for a single phase of silver selenide over a non-stoichiometric mix of selenide and telluride (where the metal content was stoichiometrically deficient to form \(Ag_2Se\) and \(Ag_3Te\)).
Table 3.1 XRD data for metal mixed chalcogenides (synthesised from direct combination of the elements in liquid ammonia at room temperature)

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed by reaction (identified by XRD)*</th>
<th>Lattice Parameters (Å (±0.01))b</th>
<th>Literature(^{139}) Lattice Parameters / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag : S : Se</td>
<td>Black</td>
<td>Ag(_2)S (acanthite)</td>
<td>(a = c = 4.48)</td>
<td>(a = c = 4.46)</td>
</tr>
<tr>
<td>4 : 1 : 1</td>
<td></td>
<td>Ag(_2)Se (naumannite)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
</tr>
<tr>
<td>Ag : Se : Te</td>
<td>Black</td>
<td>Ag(_2)Se (naumannite) + Te</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
</tr>
<tr>
<td>2 : 1 : 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl : S : Se</td>
<td>Black</td>
<td>Tl(_2)Se</td>
<td>(a = 12.20) (c = 18.17)</td>
<td>(a = 12.20) (c = 18.17)</td>
</tr>
<tr>
<td>4 : 1 : 1</td>
<td></td>
<td>Tl(_2)Se Characterised using standardised XRD patterns</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tl : Se : Te</td>
<td>Black</td>
<td>Tl(_2)Se + Tl(_2)Te</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>4 : 1 : 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg : S : Se</td>
<td>Black</td>
<td>HgS metacinnebar [HgS cinnebar]</td>
<td>(a = c = 5.85)</td>
<td>(a = c = 5.85)</td>
</tr>
<tr>
<td>2 : 1 : 1</td>
<td></td>
<td>HgSe tiemannite</td>
<td>(a = c = 6.07)</td>
<td>(a = c = 6.07)</td>
</tr>
<tr>
<td>Pb : S : Se</td>
<td>Black</td>
<td>PbS galena</td>
<td>(a = c = 5.93)</td>
<td>(a = c = 5.93)</td>
</tr>
<tr>
<td>2 : 1 : 1</td>
<td></td>
<td>PbSe clausthalite</td>
<td>(a = c = 6.12)</td>
<td>(a = c = 6.12)</td>
</tr>
</tbody>
</table>

* All minor phases (< 10 %) represented in square brackets. Where a phase synthesised corresponds to a mineral structure, the mineral name appears in italics.

\(^{139}\) Cell parameters are calculated for the major binary phase.
Table 3.2  SEM / EDXA data for ternary mixed metal-thallium-tellurides

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size (microns)</th>
<th>Elemental ratio</th>
<th>Experimental values (pre-annealed)</th>
<th>Experimental values (annealed)</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>TlAgTe</td>
<td>2 - 8</td>
<td>Tl : Ag : Te</td>
<td>33 : 33 : 33 (major)</td>
<td>33 : 33 : 33 (major)</td>
<td>33 : 33 : 33 (AgTlTe)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Ag : Te</td>
<td>50 : 0 : 50 (minor)</td>
<td>50 : 0 : 50 (minor)</td>
<td>50 : 0 : 50 (TlTe)</td>
</tr>
<tr>
<td>TlAlTe2</td>
<td>2 - 8</td>
<td>Tl : Al : Te</td>
<td>65 : 0 : 35 (major)</td>
<td>66 : 0 : 34 (minor)</td>
<td>63 : 0 : 37 (Tl2Te)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Al : Te</td>
<td>50 : 0 : 50 (minor)</td>
<td>50 : 0 : 50 (major)</td>
<td>50 : 0 : 50 (TlTe)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Al : Te</td>
<td>0 : 100 : 0 (major)</td>
<td>0 : 100 : 0 (minor)</td>
<td>0 : 100 : 0 (Al)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Al : Te</td>
<td>0 : 0 : 100 (major)</td>
<td>0 : 0 : 100 (minor)</td>
<td>0 : 0 : 100 (Te)</td>
</tr>
<tr>
<td>TlGaTe2</td>
<td>2 - 8</td>
<td>Tl : Ga : Te</td>
<td>64 : 0 : 36 (major)</td>
<td>66 : 0 : 35 (minor)</td>
<td>63 : 0 : 37 (Tl2Te)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Ga : Te</td>
<td>50 : 0 : 50 (minor)</td>
<td>50 : 0 : 50 (major)</td>
<td>50 : 0 : 50 (TlTe)</td>
</tr>
<tr>
<td>TlCrTe2</td>
<td>2 - 8</td>
<td>Tl : Cr : Te</td>
<td>38 : 2 : 60 (major)</td>
<td>40 : 0 : 60 (minor)</td>
<td>40 : 0 : 60 (Tl2Te)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Cr : Te</td>
<td>0 : 100 : 0 (major)</td>
<td>3 : 95 : 2 (minor)</td>
<td>0 : 100 : 0 (Cr)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Cr : Te</td>
<td>0 : 0 : 100 (major)</td>
<td>0 : 0 : 100 (minor)</td>
<td>0 : 0 : 100 (Te)</td>
</tr>
</tbody>
</table>

Table 3.3  SEM / EDXA data for ternary metal mixed chalcogenides

<table>
<thead>
<tr>
<th>Material</th>
<th>Aggregate size (microns)</th>
<th>Elemental ratio</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag4SSe</td>
<td>2 - 8</td>
<td>Ag : S : Se</td>
<td>67 : 33 : 0 (50 %)</td>
<td>67 : 33 : 0 (AgS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag : S : Se</td>
<td>67 : 0 : 33 (50 %)</td>
<td>67 : 0 : 33 (AgS)</td>
</tr>
<tr>
<td>Ag2SeTe</td>
<td>2 - 8</td>
<td>Ag : Se : Te</td>
<td>67 : 33 : 0 (50 %)</td>
<td>67 : 33 : 0 (AgS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag : Se : Te</td>
<td>0 : 0 : 100 (50 %)</td>
<td>0 : 0 : 100 (Te)</td>
</tr>
<tr>
<td>Tl2SSe</td>
<td>2 - 8</td>
<td>Tl : S : Se</td>
<td>67 : 33 : 0 (50 %)</td>
<td>67 : 33 : 0 (TlS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : S : Se</td>
<td>67 : 0 : 33 (50 %)</td>
<td>67 : 0 : 33 (TlS)</td>
</tr>
<tr>
<td>Tl2SeTe</td>
<td>2 - 8</td>
<td>Tl : Se : Te</td>
<td>67 : 33 : 0 (50 %)</td>
<td>67 : 33 : 0 (TlS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tl : Se : Te</td>
<td>67 : 0 : 33 (50 %)</td>
<td>67 : 0 : 33 (TlS)</td>
</tr>
<tr>
<td>Hg2SSe</td>
<td>2 - 8</td>
<td>Hg : S : Se</td>
<td>50 : 50 : 0 (50 %)</td>
<td>50 : 50 : 0 (HgS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hg : S : Se</td>
<td>50 : 0 : 50 (50 %)</td>
<td>50 : 0 : 50 (HgS)</td>
</tr>
<tr>
<td>Pb2SSe</td>
<td>2 - 8</td>
<td>Pb : S : Se</td>
<td>50 : 50 : 0 (50 %)</td>
<td>50 : 50 : 0 (PbS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb : S : Se</td>
<td>50 : 0 : 50 (50 %)</td>
<td>50 : 0 : 50 (PbS)</td>
</tr>
</tbody>
</table>

1 Material prepared from combination of stoichiometric quantities of elements in liquid ammonia at room temperature. Results obtained are for both pre-annealed and annealed material (unless otherwise stated).
2 Range of particle sizes assessed by SEM.
3 Elemental composition of phase assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple binary phases (assessed qualitatively using back-scattered electrons) is expressed either as a percentage or as major / minor.
3.4 Insoluble element combination (mixed metal chalcogenides)

3.4.1 Mixed transition metal chalcogenides

Reactions were also undertaken to synthesise ternary mixed metal chalcogenides using chalcophilic late transition metals (Cu, Zn, Cd, Hg) by direct, room temperature elemental combination. These metals are insoluble in liquid ammonia, the products of which are described in equations 3.8-3.10 (minor phases in italics).

\[
0.45 \text{Zn}(s) + 0.55 \text{Cd}(s) + S_{(am)} \rightarrow \text{Zn}_{0.45}\text{Cd}_{0.55}S_{(s)}
\] (3.8)

\[
\text{Zn}(s) + \text{Cu}(s) + 2S_{(am)} \rightarrow \text{ZnS}(s) + 0.625 \text{Cu}_{1.6}S_{(s)} + 0.375 S_{(am)}
\] (3.9)

\[
x\text{Cd}(s) + y\text{Hg}(s) + 2\text{Te}(s) \rightarrow '\text{Cd}_x\text{Hg}_y\text{Te}_2'(s); \ (x,y) = 1; \ x = 0.25, 0.50 \text{ or } 0.75
\] (3.10)

Attempts at forming substitutional solid solutions of mixed metal chalcogenides proved difficult under the conditions employed. Success was obtained in the synthesis of zinc cadmium sulfide (Zn$_{0.45}$Cd$_{0.55}$S$_2$). Both EDXA and XRD of the heated and annealed samples respectively, confirm the presence of a ternary material. Application of Vegard’s Law shows the material to be slightly cadmium rich, with a derived formula of Zn$_{0.46}$Cd$_{0.54}$S (equation 3.4). The values obtained for the product were $a = 3.97$ (ZnS 3.82; CdS 4.14 Å) and $c = 6.47$ (ZnS 6.26; CdS 6.71 Å).

However, for the elemental combination of zinc with copper and sulfur, EDXA analysis of the unthermolysed surface showed variation in elemental composition. In addition, although the XRD patterns of the annealed material showed broadened peaks, lines due to binary metal sulfides were observed. They showed the presence of ZnS, sphalerite, and Cu$_{1.6}$S, geerite (equation 3.5). Similarly, electron probe studies of Cd$_x$Hg$_y$Te$_2$ (equation 3.6) showed uniform aggregates of variable elemental composition across the sample’s surface. The metal content would typically vary by ca. 10% with occasional regions of binary sulfide.

3.4.2 Ternary (mixed metal) thallium tellurides

Following on from the synthesis of binary thallium chalcogenides described in chapter 2 (equations 2.4-5, 2.15-18) it was decided to investigate the formation of mixed transition metal telluride solid solutions. For simplicity, based upon the binary
reactions, the sulfide and selenide analogues were not attempted since it was only with tellurium that the thallium adopted exclusively the Tl\textsuperscript{I} oxidation state. The transition metals used were silver, gallium, chromium and aluminium. The reaction products are described by table 3.4 and equations 3.14-3.17.

\[\text{Tl}_2 + \text{Ag}_2 + \text{Te}_2 \rightarrow \text{AgTlTe}_2 + \text{Tl}_2\text{Te}_3\]  
(3.14)*

\[\text{Tl}_2 + \text{Al}_2 + 2\text{Te}_2 \rightarrow \text{Tl}_2\text{Te}_3 + \text{Te}_2 + \text{Al}_2 + \text{Al}_2\]  
(3.15)*

\[\text{Tl}_2 + \text{Ga}_2 + 2\text{Te}_2 \rightarrow \text{Tl}_2\text{Te}_3 + \text{Tl}_2\text{Te}_3 + \text{Ga}_2\]  
(3.16)

\[2\text{Tl}_2 + 2\text{Cr}_2 + 4\text{Te}_2 \rightarrow \text{Tl}_2\text{Te}_3 + \text{Te}_2 + \text{Cr}_2 + \text{Cr}_2\]  
(3.17)*

* Minor phases of TlTl and Tl were detected by XRD detected prior to annealing.

# Minor phases of TlTl and Tl detected by XRD after annealing.

3.4 XRD data for mixed metal - thallium tellurides (synthesised from direct combination of the elements in liquid ammonia at room temperature)

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction</th>
<th>Annealed reaction products (250-300 °C, 2h)</th>
<th>Lattice Parameters (a \pm 0.01)</th>
<th>Literature Lattice Parameters (\Delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl : Ag : Te 1 : 1 : 1</td>
<td>Black</td>
<td>AgTlTe, Te</td>
<td>AgTlTe, Te</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>Tl : Al : Te 1 : 1 : 2</td>
<td>Grey</td>
<td>Tl\textsubscript{2}Te\textsubscript{3} + Te</td>
<td>Tl\textsubscript{2}Te\textsubscript{3} + Al + [Tl\textsubscript{2}Te\textsubscript{3}, Tl]</td>
<td>(a = 8.93) (c = 12.63) (a = 8.92) (c = 12.61)</td>
<td></td>
</tr>
<tr>
<td>Tl : Ga : Te 1 : 1 : 2</td>
<td>Grey</td>
<td>Tl\textsubscript{2}Te\textsubscript{3}</td>
<td>Not annealed</td>
<td>(a = 8.93) (c = 12.62) (a = 8.92) (c = 12.61)</td>
<td></td>
</tr>
<tr>
<td>Tl : Cr : Te 1 : 1 : 2</td>
<td>Grey</td>
<td>Tl\textsubscript{2}Te\textsubscript{3} + Te</td>
<td>Tl\textsubscript{2}Te\textsubscript{3} + Cr + [TlTlTe, Tl, Te]</td>
<td>(a = 17.39) (b = 6.54) (c = 7.90) (a = 17.41) (b = 6.55) (c = 7.91)</td>
<td></td>
</tr>
</tbody>
</table>

* Added to liquid ammonia at room temperature

* Minor phases in square brackets

* Lattice parameters calculated for major binary phase only

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3.4.2a Characterisation and discussion of mixed metal-thallium tellurides

Solid solutions of mixed metal thallium tellurides appear to be successful only with the use of silver. The major phase observed was for the anticipated monovalent thallium-silver coupling, giving rise to the synthesis of a single phase of AgTlTe. However, the product as a whole was not homogeneous, with a minor, binary thallium telluride phase detected by X-ray powder diffraction (XRD) in the pre-annealed sample. Both XRD and EDXA showed this phase to be a binary material consistent with the empirical formula TlTe. The limited success of these ternary reactions is probably indicative of the similar ionic radii of Tl(I) and Ag(I) (compared to Cr(III), Al(III) or Ga(III)) which may allow more thermodynamically stable solid solutions. Also, the coupling of Tl(I) with Ag(I) is more likely to result in similar crystal structures to that of the associated binary metal (I) tellurides.

Even though in the majority of cases binary thallium tellurides were synthesised, there is a notable difference to the binary elemental reactions carried out solely between thallium and tellurium (section 2.1.3, p. 55). That is, Tl(III)-Te bond formation with presence of metals prior to annealing, either as minor phases (M = Ag, Ga) or as major phase (M = Cr). This is exemplified in figure 3.1, which shows the XRD pattern for the product obtained for M = Cr. In addition, annealing in the presence of aluminium leads to major product conversion from Tl3Te5 (Tl(I)) to TlTe (Tl(I), Tl(III)). It is possible that the metals (Ag, Ga, Cr, Al) act to facilitate transfer of electrons from the thallium atoms to the tellurium without formation of metal tellurides. Such a role would require an effective reduction in the ionisation potentials of thallium, thereby enabling access to the Tl(III) oxidation state at ambient temperatures. Whilst it is known that thallium can form alloy-type compounds with a variety of transition- and main-group metals, the existence of such materials as transient species in the reactions described above is purely speculative. However, the existence of a transient ternary (mixed metal) species may also explain the presence of evenly distributed, sub-micrometer particles of X-ray amorphous metal in the pre-annealed reaction mixture. It has been observed that reactions in which a metal reagent does not participate result in discrete metal particles of at least 5 micrometers in size, commonly of sufficiently high crystallinity to be detected by XRD. The combined XRD-EDXA data for the reactions described by equations 3.4-3.7 suggests that the unreacted metals (Cr, Ga, Al and to a lesser extent Ag) may have been precipitated from some ‘Tl-M-E’ species, but whether such a species exists in solution or on the interface of reacting metals is unknown.
3.4.2b Effect of annealing on mixed metal-thallium telluride product mixtures

Analysis of major / minor phases upon annealing show two effects of heat upon the initial product mixture. First, crystallisation of free metal occurs, allowing detection by XRD to be enhanced. Secondly, the conversion of the majority of thallium (I) telluride (but a minor amount of thallium (III) telluride) to the mixed Tl\textsuperscript{I-III} telluride (TlTe) was observed (as described by the reaction scheme below).

\[
\begin{align*}
\text{Tl}_2\text{Te}_3(s) & \rightarrow \text{Tl}\{\text{TlTe}_2\}_{(s)} \leftarrow \text{Tl}_2\text{Te}_3(s) \\
(\text{Tl})_{\text{major}} & \rightarrow (\text{Tl}^{\text{I-III}}) \leftarrow (\text{Tl}^{\text{III}})_{\text{minor}}
\end{align*}
\]

(\leftrightarrow: \text{annealing at } T = 250-300 \degree \text{C, 2h})

This supports the proposed role of the metals present as electron transfer catalysts, since not only was TlTe not observed in the analogous binary reactions of the previous chapter, but also thermodynamic considerations (re: tellurium bond formation) would favour the conversion of Te\textsuperscript{0} \rightarrow Te\textsuperscript{II} (Tl\textsuperscript{I} \rightarrow Tl\textsuperscript{III}) to a greater degree than Te\textsuperscript{II} \rightarrow Te\textsuperscript{0} (Tl\textsuperscript{III} \rightarrow Tl\textsuperscript{I}).
It should be noted that annealing the reaction product involving gallium (equation 3.6) was not carried out since it would have resulted in a phase change of gallium (m.p. ca. 30 °C).

3.5 Discussion of elemental combination reactions

3.5.1 Ternary chalcogenides

It is apparent that the use of soluble metals gives excellent control over the target chalcogenide, the elements reacting stoichiometrically to form single phases of high purity. It is likely that these reactions proceeded via direct reduction of the chalcogen by the highly reducing nature of the metallo-ammonia solutions. Equivalent crystal modifications of the composite binary chalcogenides and complete dissolution of the metals ensures that highly efficient mixing of reagents resulted in a single phased substitutional solid solution.

Difficulty arose in forming solid solutions of mixed metal chalcogenides when using metals insoluble in liquid ammonia. EDXA showed a variable elemental composition across the sample surface, and XRD studied showed broadened peaks with lines corresponding to individual binary chalcogenides. This indicates that although some metal doping has occurred in the corresponding chalcogenide lattice, phase segregation has occurred. This is most likely a result of the individual binary materials adopting a different crystal modification. This would also explain the relative success of transition metal sulfur selenides, as the binary sulfide and selenide of late transition metals often have the same crystal structure. For example, the CdS,Se$_{1-x}$ series of ternary materials all crystallised in the cubic (wurtzite) phase adopted by CdS (greenockite structure) and CdSe (cadmesolite structure) synthesised from liquid ammonia at room temperature.

3.5.2 Degrees of amorphous character of the products

The question of how amorphous the samples unresolved by X-rays truly are, is addressed with reference to the ternary materials of general formula CdS,Se$_{1-y}$. Increasing the intensity of the incident radiation resulted in an observed red shift in the frequencies of the LIF spectra. This suggests a level of localised annealing has occurred, resulting in regional induction of a more ordered structure and so a shift in fluorescence frequency towards that of the highly crystalline standards used for spectral comparison. Reflectance XRD studies of the cadmium sulfide sample, formed from elemental combination in liquid ammonia and taken prior to annealing, showed the sample...
nanoparticulate CdS. If the existence of small ordered crystallites of binary chalcogenides (largely undetected by transmission X-ray powder diffraction) in the CdS$_x$Se$_y$ compounds were the fluorescent material, then this would explain the LIF spectra obtained. Minor crystalline phases of fluorescent binary material would result in less intense fluorescence with small frequency variation. The shift to higher fluorescent frequencies than those normally observed for these compounds would suggest a blue shift in the band gap of these materials. This would lead to the suggestion that such small binary crystallites may exhibit properties of quantum confinement, but without further investigation with microscopies of higher resolution than those already carried out, this is mere conjecture.

3.5.3 Solid state reaction mechanisms of ternary metal mixed chalcogenides

**Amorphous materials**

The ternary structures observed by XRD do not show evidence for super cell structure - there is an absence of 'additional' Bragg reflections in the powder patterns, and the CdS$_x$Se$_y$ series do not exhibit a negative deviation in Vegard’s law for values of $0 < x, y < 1$. This suggests that the chalcogen atoms of the metal mixed chalcogenide materials are randomly distributed within the lattice, rather than being evenly dispersed within the unit cell. Consequently, it seems unlikely that a mechanism describing these elemental combination reactions would include formation of heteroleptic chalcogenide species prior to reaction with the metal (whether in solution or the solid state).

The creation of amorphous sulfide materials would not necessarily stem just from the low temperature at which the reactions were carried out. The dissolved S-N species in ammonia have sulfur coordinations that differ from that of the cubic-based structure of a final crystalline material. These species may disrupt the formation of long range order within the resultant lattice if such species are present at the formation of the M-S or S-Se bonds.

**Crystalline products**

The formation of highly crystalline binary chalcogenide materials of silver, mercury, lead and thallium at room temperature suggest that these materials offer accessible barriers to solid state diffusion under the reaction conditions employed. This would allow the necessarily intimate mixing of the metal and chalcogen atoms during formation of the lattice structure. Interestingly, these same metals do not allow
formation of ternary mixed chalcogenide materials to any degree (as described by reactions 3.11-3.14), even though such solid solutions are known to exist.\textsuperscript{144} This suggests that there is an appreciable difference in the rates, and so extent, of solid state diffusion of the chalcogen species present in liquid ammonia. Depending upon the number of molar equivalents of metal present, this difference would result in either the formation of both binary metal chalcogenides (re: equation 3.13) or the preferential formation of one over the other (equation 3.14), based upon the same thermodynamic consideration that governed the syntheses of chapter 2.

Crucially, it has been observed that formation of such crystalline materials proceed in the solid state by diffusion of the chalcogen \textit{into} the metal (re: chapter 4 discussions). It is possible that, unlike selenium / tellurium, the solvated sulfur species would first have to undergo conversion to discrete $S^{2-}$ anions if a highly ordered metal sulfide lattice is to result, thereby reacting at a slower rate than the heavier congeners.

\textbf{General overview of mechanisms}

It appears that successful ternary solid solutions of metal mixed chalcogenides appear to be restricted to those highly chalcophilic metals whose related binary materials are amorphous and adopt the same crystal structure (e.g. cadmium and zinc). One may rationalise that poor solid state diffusion into the metal would result in the chalcogen species (and so the reaction interface) being largely restricted to the metal surface. This would result in both solvated sulfur species and insoluble selenium / tellurium remaining in close proximity, allowing the formation of ternary mixed chalcogenide materials. It would also result in the sulfur remaining with a coordination other than that of the final crystalline lattice, thereby encouraging the formation of X-ray amorphous materials (as proposed in section 3.5.2).
3.6 Metal mixed pnictide chalcogenides (M₃PnE₃ / MPnE₂)

‘Metal mixed pnictide chalcogenides’ are a class of ternary compounds described by the combination of a chalcogen (typically sulfur or selenium) with both a pnictogen (arsenic or antimony) and a transition metal (copper or silver). The transition metal is formally in its I oxidation state, whilst the pnictogen is commonly found in its III, rather than V, oxidation state. These compounds have been well characterised, occur naturally in mineral form and commonly adopt one of two empirical formulae, although others are possible through the allowed variation in oxidation state of both the pnictogen and copper. The common formulae are M₃PnE₃ and MPnE₂ (where M = Ag, Cu; Pn = As, Sb; E = S, Se, Te). This class of compounds offers an opportunity to probe elemental combination reactions in liquid ammonia in terms of the formation of ternary materials and stoichiometric control of the products. In addition, interest lies in which binary products (if any) preferentially form from the elemental ratios present. To some extent this last statement has limited implications since we already know, from the binary material synthesis described in chapter 2, that both copper and silver do not react directly with either arsenic or antimony in liquid ammonia. In addition, only silver reacted with antimony during annealing of the elements after treatment in liquid ammonia (affording Ag₃Sb after 2h at 250-300 °C). To limit the number of possible binary side reactions, initial reactions were carried out with M = Ag since previous work has shown that, unlike copper, elemental reactions in liquid ammonia involving silver result in exclusively Ag⁺ species.

3.6.1 Experimental, synthesis and characterisation

Suitable ratios of the elements were added to liquid ammonia at -77 °C under a flow of dinitrogen, such that an exact stoichiometric combination would yield the products M₃PnE₃ and MPnE₂ (i.e. M : Pn : E of 1:1:2 and 3:1:3). Initial reactions involved the use of silver along with both arsenic and antimony, with E = S, Se and Te. The reactions were stirred in liquid ammonia at room temperature for 48 h. In the case of the sulfide reactions, it was observed that the ammonia became colourless after 48 h, indicative of the removal of dissolved sulfur species. The reaction mixture was isolated and a sample annealed at 250-300 °C for 2 hours, as described for the binary elemental reactions in chapter 2.

Owing to the similarity of the IR absorptions for all the possible binary and ternary metal chalcogenides that could be formed when the elements had reacted, material
analysis relied upon X-ray powder diffraction used in conjunction with SEM and EDXA. A representative number of samples analysed by IR as a pressed KBr disc, showed absorption frequencies in the region 600-200 cm\(^{-1}\) (typical of M-E stretching modes). No peaks were observed for any N-H based ligands. The X-ray results of the ternary silver materials are shown in tables 3.5, 3.6 and represented by equations 3.17-3.27. EDXA confirmed the presence of all the phases described by the powder patterns to an accuracy of 2-3 atm. %. Following the usual work-up, the samples were annealed at 250-300 °C for 2h (denoted by \(\Delta\)).

\[
\begin{align*}
3\text{Ag}(s) + \text{As}(s) + 3\text{S}_{(am)} & \rightarrow \text{Ag}_3\text{AsS}_3(s) \quad \text{(unaffected by annealing)} \quad (3.17) \\
3\text{Ag}(s) + 3\text{As}(s) + 6\text{S}_{(am)} & \rightarrow \text{Ag}_3\text{AsS}_3(s) + 2\text{As}(s) + 3\text{S}_{(am)} \quad \text{(unaffected by annealing)} \quad (3.18) \\
9\text{Ag}(s) + 3\text{As}(s) + 9\text{Se}_{(s)} & \rightarrow x\text{Ag}_2\text{Se}_{(s)} + 3\text{As}(s) + (9-x)\text{Se}_{(s)} + (9-2x)\text{Ag}(s) \\
\Delta: & \text{3Ag}_2\text{Se}_{(s)} + \text{Ag}_3\text{AsSe}_{1.5(s)} + 2\text{AsSe}_{1.5(s)} \quad (3.19) \\
2\text{Ag}(s) + 2\text{As}(s) + 4\text{Se}_{(s)} & \rightarrow \text{Ag}_2\text{Se}_{(s)} + 2\text{AsSe}_{(s)} + \text{Se}_{(s)} \quad \text{(unaffected by annealing)} \quad (3.20) \\
3\text{Ag}(s) + \text{As}(s) + 3\text{Te}_{(s)} & \rightarrow \text{Ag}_2\text{Te}_{(s)} + \text{Te}_{(s)} \quad \text{(*) unaffected by annealing} \quad (3.21) \\
\text{* Minor phase of Ag}_2\text{Te}_4 \text{ was detected by XRD.} \\
2\text{Ag}(s) + 2\text{As}(s) + 4\text{Te}_{(s)} & \rightarrow \text{Ag}_2\text{Te}_{(s)} + \text{Te}_{(s)} + 2\text{AsTe}_{(s)} \quad \text{(unaffected by annealing)} \quad (3.22) \\
3\text{Ag}(s) + \text{Sb}(s) + 3\text{S}_{(am)} & \rightarrow \text{Ag}_3\text{SbS}_3(s) \quad \text{(*) unaffected by annealing} \quad (3.22) \\
\text{* Minor phase of Ag}_3\text{SbS}_2 \text{ detected by XRD.} \\
3\text{Ag}(s) + 3\text{Sb}(s) + 6\text{S}_{(am)} & \rightarrow \text{Ag}_3\text{SbS}_3(s) + 2\text{Sb}(s) + 3\text{S}_{(am)} \quad \text{(unaffected by annealing)} \quad (3.24) \\
2\text{Ag}(s) + 2\text{Sb}(s) + 4\text{Se}_{(s)} & \rightarrow \text{Ag}_2\text{Se}_{(s)} + 2\text{Sb}(s) + 3\text{Se}_{(s)} \quad \text{(*) unaffected by annealing} \quad (3.25) \\
\text{* Minor phase of Ag}_2\text{Se}_3 \text{ detected by XRD.} \\
6\text{Ag}(s) + 2\text{Sb}(s) + 6\text{Te}_{(s)} & \rightarrow 3\text{Ag}_2\text{Te}_{(s)} + 2\text{Sb}(s) + 3\text{Te}_{(s)} \\
\Delta: & \text{Ag}_2\text{Te}_{3(s)} + 2\text{Sb}(s) + 3\text{Te}_{(s)} + \text{Ag}(s) \quad (3.26) \\
2\text{Ag}(s) + 2\text{Sb}(s) + 4\text{Te}_{(s)} & \rightarrow \text{Ag}_2\text{Te}_{(s)} + 2\text{Sb}(s) + 3\text{Te}_{(s)} \quad \text{(unaffected by annealing)} \quad (3.27)
\end{align*}
\]
Table 3.5 XRD data for 11-15-16 chalcopryites

\( \text{ABE}_2 / \text{A}_3\text{BE}_4; \ A = \text{Ag; } B = \text{As; } E = \text{S, Se, Te}) \)

Materials were synthesised from direct combination of the elements in liquid ammonia at room temperature

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (pre-washed)</th>
<th>Washed and annealed reaction products (250-300 °C, 2h)</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature Lattice Parameters / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag:As:S 3:1:3</td>
<td>Black</td>
<td>Ag₃AsS₃ \textit{Prousite}</td>
<td>Ag₃AsS₃</td>
<td>a = 10.80 c = 8.69</td>
<td>a = 10.80 c = 8.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag:As:S 1:1:2</td>
<td>Black</td>
<td>Ag₃AsS₃ \textit{Prousite}</td>
<td>Ag₃AsS₃</td>
<td>a = 10.80 c = 8.69</td>
<td>a = 10.80 c = 8.69</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag:As:Se 3:1:3</td>
<td>Black</td>
<td>Ag₂Se \textit{(naumannite)} + Ag + As + Se</td>
<td>Ag₂Se \textit{(naumannite)}</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
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<td></td>
<td></td>
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<td></td>
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<td></td>
<td>AsSe₁.₅</td>
<td>Characterised using standard XRD patterns</td>
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</tr>
<tr>
<td>Ag:As:Se 1:1:2</td>
<td>Black</td>
<td>Ag₂Se \textit{(naumannite)}</td>
<td>Ag₂Se \textit{(naumannite)}</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
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<tr>
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<td></td>
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<td>AsSe + Se</td>
<td>Characterised using standardised XRD patterns</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag:As:Te 3:1:3</td>
<td>Black</td>
<td>Ag₂Te \textit{(altaite)} + Te + [Ag₂Te₄]</td>
<td>Ag₂Te \textit{(altaite)} + Te + [Ag₂Te₄]</td>
<td>a = 8.10 b = 4.47 c = 8.97</td>
<td>a = 8.09 b = 4.47 c = 8.96</td>
</tr>
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<td></td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>Ag:As:Te 1:1:2</td>
<td>Black</td>
<td>Ag₂Te \textit{(altaite)} + Te</td>
<td>Ag₂Te \textit{(altaite)} + Te</td>
<td>a = 8.10 b = 4.47 c = 8.97</td>
<td>a = 8.09 b = 4.47 c = 8.96</td>
</tr>
<tr>
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<td>AsTe</td>
<td>Characterised using standard XRD patterns</td>
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</tbody>
</table>

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Table 3.6 XRD data for 11-15-16 chalcopyrites

(ABEÆ / A₃BE₃; A = Ag; B = Sb; E = S, Se)

Materials were synthesised from direct combination of the elements in liquid ammonia
at room temperature

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (pre-washed)</th>
<th>Washed and annealed reaction products (250-300 °C, 2h)</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature¹³⁹ Lattice Parameters / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag:Sb:S 3:1:3</td>
<td>Black</td>
<td>Ag₃SbS₃ + [Ag, AgSbS₂]</td>
<td>Ag₃SbS₃ + [Ag, AgSbS₂]</td>
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<td>a = 11.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 8.73</td>
<td>c = 8.73</td>
</tr>
<tr>
<td>Ag:Sb:S 1:1:2</td>
<td>Black</td>
<td>Ag₃SbS₃ + Sb + S</td>
<td>Ag₃SbS₃ + Sb</td>
<td>a = 11.04</td>
<td>a = 11.04</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 8.73</td>
<td>c = 8.73</td>
</tr>
<tr>
<td>Ag:Sb:Se 1:1:2</td>
<td>Black</td>
<td>Ag₂Se (naumannite) + Sb + Se + [AgSbSe₂]</td>
<td>Ag₂Se (naumannite) + Sb + Se + [AgSbSe₂]</td>
<td>a = 4.33</td>
<td>a = 4.33</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>b = 7.06</td>
<td>b = 7.06</td>
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<tr>
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<td>c = 7.76</td>
<td>c = 7.76</td>
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<tr>
<td>Ag:Sb:Te 3:1:3</td>
<td>Black</td>
<td>Ag₂Te (altaite)</td>
<td>Ag₃Te₃ + Sb + Te</td>
<td>a = 8.10</td>
<td>a = 8.09</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td>b = 4.47</td>
<td>b = 4.47</td>
</tr>
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<td>c = 8.97</td>
<td>c = 8.96</td>
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<tr>
<td>Ag:Sb:Te 1:1:2</td>
<td>Black</td>
<td>Ag₂Te (altaite)</td>
<td>Ag₃Te₃ + Sb + Te</td>
<td>a = 8.10</td>
<td>a = 8.09</td>
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<td></td>
<td>b = 4.47</td>
<td>b = 4.47</td>
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<td></td>
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<td></td>
<td>c = 8.97</td>
<td>c = 8.96</td>
</tr>
</tbody>
</table>

Following on from the successes of the reactions involving elemental silver, the synthesis of the following copper based ternary materials were carried out:

Cu₃AsE₃ (E = S, Se) and Cu₃SbE₃ (E = S, Se, Te)

NB: No data base XRD pattern could be found for Cu₃AsTe₃.

3Cu₉(s) + As₈(s) + 3S₈(am) → Cu₃AsS₄* + amorphous material

\[ \Delta: Cu_{1.96}S_{(am)} \rightarrow CuAsS \]  

(3.28)

* Minor phases of Cu₃AsS₄ and As₂S₃ detected by XRD.
\[ 3\text{Cu}(s) + \text{As}(s) + 3\text{Se}(s) \rightarrow 2\text{CuSe}(s) + \text{CuAsSe}(s) \] *(unaffected by annealing) (3.29)

* Unresolved by XRD prior to annealing due to overlapping peaks.

\[ 3\text{Cu}(s) + \text{Sb}(s) + 3\text{S}(s) \rightarrow \text{Cu}_{1.75}\text{S}(s) + \text{Sb}(s) \] *(unaffected by annealing) (3.30)

* Minor phase of Cu\(_{1.75}\)S\(_s\) was detected by XRD.

\[ 3\text{Cu}(s) + 3\text{Se}(s) \rightarrow 3\text{CuSe}(s) + \text{Sb}(s) \]

\[ \Delta: \text{Cu}_{1-x}\text{Se}(s) + \text{Cu}_{1-x}\text{Se}_2(s) + (1+2x)\text{Cu}(s) + \text{Sb}(s) \] *(amorphous to X-rays) (3.31)

\[ 6\text{Cu}(s) + 2\text{Sb}(s) + 6\text{Te}(s) \rightarrow 3\text{Cu}_{2-x}\text{Te}(s) + 2\text{Sb}(s) + 3\text{Te}(s) \] *(unaffected by annealing) (3.32)

The 1:1:2 ratio of elements was not conducted here for reasons based upon an efficient use of time and the results obtained for the analogous silver reactions. It was observed that where ternary materials formed, an apparent preference for the 3:1:3 ratio existed. If the copper materials were to show a preference for the 1:1:2 ratio, however, then one would simply expect associated formation of Cu\(_{2-x}\)E (re: the formation of binary copper chalcogenides; equations 2.2, 2.11 and 2.12).
Table 3.7 XRD data for 11-15-16 chalcoprytes

(ABE<sub>2</sub> / A<sub>3</sub>BE<sub>5</sub>; A = Cu; B = As, Sb; E = S, Se, Te)

Materials were synthesised by elemental combination in liquid ammonia at R.T.

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Products as formed from reaction (pre-washed)</th>
<th>Washed and annealed reaction products (250-300 °C, 2h)</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature&lt;sup&gt;19&lt;/sup&gt; Lattice Parameters / Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu : As : S 3 : 1 : 3</td>
<td>Black</td>
<td>CuAsS (&lt;i&gt;lautite&lt;/i&gt;)</td>
<td>CuAsS (&lt;i&gt;lautite&lt;/i&gt;)</td>
<td>a = 11.35</td>
<td>a = 11.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>[Cu&lt;sub&gt;3&lt;/sub&gt;AsS&lt;sub&gt;4&lt;/sub&gt;, As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>[Cu&lt;sub&gt;3&lt;/sub&gt;AsS&lt;sub&gt;4&lt;/sub&gt;, As&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;]</td>
<td>b = 5.55</td>
<td>b = 5.55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Amorphous material</td>
<td>Cu&lt;sub&gt;1.90&lt;/sub&gt;S (&lt;i&gt;diginite&lt;/i&gt;)</td>
<td>c = 3.75</td>
<td>c = 3.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu : As : Se 3 : 1 : 3</td>
<td>Black</td>
<td>CuSe (&lt;i&gt;klockmannite&lt;/i&gt;)</td>
<td>CuSe (&lt;i&gt;klockmannite&lt;/i&gt;)</td>
<td>a = 3.92</td>
<td>a = 3.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 17.21</td>
<td>b = 17.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CuAsSe</td>
<td>CuAsSe</td>
<td>a = 11.77</td>
<td>a = 11.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 6.78</td>
<td>b = 6.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 19.23</td>
<td>c = 19.21</td>
</tr>
<tr>
<td>Cu : Sb : S 3 : 1 : 3</td>
<td>Black</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt; + Sb + [Cu&lt;sub&gt;7&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt; + Sb + [Cu&lt;sub&gt;7&lt;/sub&gt;S&lt;sub&gt;2&lt;/sub&gt;]</td>
<td>a = 7.88</td>
<td>a = 7.89</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 7.85</td>
<td>b = 7.84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 10.99</td>
<td>c = 11.01</td>
</tr>
<tr>
<td>Cu : Sb : Se 3 : 1 : 3</td>
<td>Black</td>
<td>CuSe (&lt;i&gt;klockmannite&lt;/i&gt;)</td>
<td>Cu&lt;sub&gt;1.3&lt;/sub&gt;S&lt;sub&gt;4&lt;/sub&gt;Se + Cu&lt;sub&gt;1.5&lt;/sub&gt;Se&lt;sub&gt;2&lt;/sub&gt; + Sb + Cu</td>
<td>a = 3.94</td>
<td>a = 3.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 17.20</td>
<td>c = 17.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu : Sb : Te 3 : 1 : 3</td>
<td>Black</td>
<td>Cu&lt;sub&gt;2.4&lt;/sub&gt;Te + Sb + Te</td>
<td>Cu&lt;sub&gt;2.4&lt;/sub&gt;Te + Sb + Te</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
</tbody>
</table>
### Table 3.8 SEM / EDXA data for ternary silver arsenic chalcopryites

<table>
<thead>
<tr>
<th>Target material$^4$</th>
<th>Particle size (microns)</th>
<th>Ratio of elements / atm. % (experimental error ± 2-3 %)$^6$</th>
<th>Elemental ratio</th>
<th>Experimental values (pre-annealed)</th>
<th>Experimental values (annealed)</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}_2\text{AsS}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>43 : 14 : 43</td>
<td>43 : 14 : 43</td>
<td>43 : 14 : 43 ($\text{Ag}_2\text{AsS}_3$)</td>
</tr>
<tr>
<td>$\text{AgAsS}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>43 : 14 : 43</td>
<td>43 : 14 : 43</td>
<td>43 : 14 : 43 ($\text{Ag}_2\text{AsS}_3$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsSe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{AsSe}_3$)</td>
</tr>
<tr>
<td>$\text{AgAsS}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>43 : 14 : 43 (minor)</td>
<td>43 : 14 : 43 (minor)</td>
<td>43 : 14 : 43 ($\text{Ag}_2\text{AsSe}_3$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsSe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>0 : 40 : 60 (minor)</td>
<td>0 : 40 : 60 (minor)</td>
<td>0 : 40 : 60 ($\text{AsS}_2$)</td>
</tr>
<tr>
<td>Unreacted Ag / As / Se</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{AgAsSe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Se}$)</td>
</tr>
<tr>
<td>$\text{AgAsS}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>0 : 50 : 50 (minor)</td>
<td>0 : 50 : 50 (minor)</td>
<td>0 : 50 : 50 ($\text{AsSe}_2$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Te}$)</td>
</tr>
<tr>
<td>$\text{AgAsTe}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>63 : 0 : 37 (minor)</td>
<td>63 : 0 : 37 (minor)</td>
<td>63 : 0 : 37 ($\text{Ag}_2\text{Te}_4$)</td>
</tr>
<tr>
<td>Unreacted As / Te</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{AgAsTe}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Te}_4$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsSe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 ($\text{Ag}_2\text{Se}_3$)</td>
</tr>
<tr>
<td>$\text{Unreacted Sb, Se}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 ($\text{Ag}_2\text{Te}_4$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{AsTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
</tbody>
</table>

### Table 3.9 Morphology of ternary silver antimony chalcopryites

<table>
<thead>
<tr>
<th>Target material$^1$</th>
<th>Particle size (microns)</th>
<th>Ratio of elements / atm. % (experimental error ± 2-3 %)$^3$</th>
<th>Elemental ratio</th>
<th>Experimental values (pre-annealed)</th>
<th>Experimental values (annealed)</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}_2\text{SbS}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>43 : 14 : 43 (major)</td>
<td>43 : 14 : 43 (major)</td>
<td>43 : 14 : 43 ($\text{Ag}_2\text{SbS}_3$)</td>
</tr>
<tr>
<td>$\text{AgSbS}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 (minor)</td>
<td>25 : 25 : 50 ($\text{Ag}_2\text{SbS}_3$)</td>
</tr>
<tr>
<td>Unreacted Ag</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{AgSbS}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>43 : 14 : 43 (major)</td>
<td>43 : 14 : 43 (major)</td>
<td>43 : 14 : 43 ($\text{Ag}_2\text{SbS}_3$)</td>
</tr>
<tr>
<td>Unreacted Sb, S</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{AgSbSe}_2$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Se}$)</td>
</tr>
<tr>
<td>$\text{Unreacted Sb, Sb}$</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{SbTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Te}$)</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{SbTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>63 : 0 : 37 (minor)</td>
<td>63 : 0 : 37 (minor)</td>
<td>63 : 0 : 37 ($\text{Ag}_2\text{Te}_4$)</td>
</tr>
<tr>
<td>Unreacted Sb, Te</td>
<td></td>
<td>(minor)</td>
<td>-</td>
<td></td>
<td></td>
<td>95% abundant</td>
</tr>
<tr>
<td>$\text{Ag}_3\text{SbTe}_3$</td>
<td>2 - 8</td>
<td></td>
<td></td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 ($\text{Ag}_2\text{Te}_4$)</td>
</tr>
</tbody>
</table>

$^4$ Material prepared from combination of stoichiometric quantities of elements in liquid ammonia at room temperature. Results obtained are for both pre-annealed and annealed material (unless otherwise stated).

$^5$ Range of particle sizes assessed by SEM.

$^6$ Elemental composition of phase assessed by EDXA (spot size - 1 micron). Relative surface abundance of multiple phases (assessed qualitatively using back-scattered electrons) is expressed as major / minor.
Table 3.10 Morphology of ternary 11-15-16 chalcopyrites

\( (A_3B_3E_3; \ A = \text{Cu}; \ B = \text{As, Sb}; \ E = \text{S, Se, Te}) \)

<table>
<thead>
<tr>
<th>Target material(^7)</th>
<th>Particle size(^a) (microns)</th>
<th>Ratio of elements / atm. % (experimental error ± 2-3 %)(^9)</th>
<th>Elemental ratio</th>
<th>Experimental values (pre-annealed)</th>
<th>Experimental values (annealed)</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cu}_2\text{AsS}_3 )</td>
<td>2 - 8</td>
<td>( \text{Cu} : \text{As} : \text{S} )</td>
<td>33 : 33 : 33 (40 %)</td>
<td>33 : 33 : 33 (40 %)</td>
<td>33 : 33 : 33 (( \text{CuAsS} ))</td>
<td>( \text{Cu}_2\text{S}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{As} : \text{S} )</td>
<td>67 : 0 : 33 (40 %)</td>
<td>67 : 0 : 33 (40 %)</td>
<td>67 : 0 : 33 (( \text{Cu}_2\text{S}_3 ))</td>
<td>( \text{Cu}_2\text{S}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{As} : \text{S} )</td>
<td>38 : 12 : 50 (minor)</td>
<td>38 : 12 : 50 (minor)</td>
<td>38 : 12 : 50 (( \text{Cu}_2\text{AsS}_3 ))</td>
<td>( \text{Cu}_2\text{S}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{As} : \text{S} )</td>
<td>30 : 0 : 70 (minor)</td>
<td>30 : 0 : 70 (minor)</td>
<td>29 : 0 : 71 (( \text{As}_2\text{S}_3 ))</td>
<td>( \text{Cu}_2\text{S}_3 )</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{AsSe}_3 )</td>
<td>2 - 8</td>
<td>( \text{Cu} : \text{As} : \text{Se} )</td>
<td>50 : 0 : 50 (50 %)</td>
<td>50 : 0 : 50 (50 %)</td>
<td>50 : 0 : 50 (( \text{CuSe} ))</td>
<td>( \text{Cu}_2\text{Se} )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{As} : \text{Se} )</td>
<td>33 : 33 : 33 (50 %)</td>
<td>33 : 33 : 33 (50 %)</td>
<td>33 : 33 : 33 (( \text{CuAsSe} ))</td>
<td>( \text{Cu}_2\text{Se} )</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{SbS}_3 )</td>
<td>2 - 8</td>
<td>( \text{Cu} : \text{Sb} : \text{S} )</td>
<td>63 : 0 : 37 (major)</td>
<td>63 : 0 : 37 (major)</td>
<td>63 : 0 : 37 (( \text{CuSbS}_3 ))</td>
<td>( \text{CuSbS}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{Sb} : \text{S} )</td>
<td>80 : 0 : 20 (minor)</td>
<td>80 : 0 : 20 (minor)</td>
<td>80 : 0 : 20 (( \text{Cu}_2\text{S}_2 ))</td>
<td>( \text{Cu}_2\text{S}_2 )</td>
</tr>
<tr>
<td></td>
<td>Unreacted Sb</td>
<td></td>
<td></td>
<td></td>
<td>≥ 95 % abundant</td>
<td>( \text{CuSbS}_3 )</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{SbSe}_3 )</td>
<td>2 - 8</td>
<td>( \text{Cu} : \text{Sb} : \text{Se} )</td>
<td>50 : 0 : 50 (major)</td>
<td>50 : 0 : 50 (40 %)</td>
<td>50 : 0 : 50 (( \text{CuSe} ))</td>
<td>( \text{CuSbSe}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{Sb} : \text{Se} )</td>
<td>-</td>
<td>33 : 0 : 67 (40 %)</td>
<td>33 : 0 : 67 (( \text{CuSe} ))</td>
<td>( \text{CuSbSe}_3 )</td>
</tr>
<tr>
<td></td>
<td>Unreacted ( \text{Cu} / \text{Sb} / \text{Se} )</td>
<td></td>
<td>(minor)</td>
<td>(minor)</td>
<td>≥ 95 % abundant</td>
<td>( \text{CuSbSe}_3 )</td>
</tr>
<tr>
<td>( \text{Cu}_2\text{SbTe}_3 )</td>
<td>2 - 8</td>
<td>( \text{Cu} : \text{Sb} : \text{Te} )</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (major)</td>
<td>67 : 0 : 33 (( \text{Cu}_2\text{Te} ))</td>
<td>( \text{CuSbTe}_3 )</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{Cu} : \text{Sb} : \text{Te} )</td>
<td>(minor)</td>
<td>(minor)</td>
<td>≥ 95 % abundant</td>
<td>( \text{CuSbTe}_3 )</td>
</tr>
</tbody>
</table>

\(^7\) Material prepared from combination of stoichiometric quantities of elements in liquid ammonia at room temperature. Results obtained are for both pre-annealed and annealed material (unless otherwise stated).

\(^a\) Range of particle sizes assessed by SEM.

\(^9\) Elemental composition of phase assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple phases (assessed qualitatively using back-scattered electrons) is expressed either as a percentage or as major / minor.
Figure 3.4 XRD spectrum of silver arsenic telluride (Ag$_3$AsTe$_3$) formed directly from combination of the elements at room temperature in liquid ammonia

Key: Sample (top) – Ag$_3$AsTe$_3$, Standard (bottom) – hessite, Ag$_2$Te (blue), Te (red)

Figure 3.5 XRD spectrum of silver antimony sulfide (Ag$_3$SbS$_3$) formed directly from combination of the elements at room temperature in liquid ammonia

Key: Sample (top) – Ag$_3$SbS$_3$, Standard (bottom) – Ag$_3$SbS$_3$ (blue), AgSbS$_2$ (red)
3.6.2 Discussion of ternary metal pnictogen chalcogenides

The results show that the elemental combination of chalcogens (group 16) and group 11 metals with either arsenic or antimony (group 15) at room temperature in liquid ammonia affords a range of crystalline materials. Depending upon which elements are used, these materials, prior to annealing, fall into one of two categories (ignoring minor phases):

2. A mixture of binary chalcogenide materials with unreacted chalcogen / pnictogen.

Consider the reactions involving elemental sulfur. It is clear that when the metal used is silver then there is a preference for forming a ternary material based upon the stoichiometry Ag₅PnS₅. This occurs whether the pnictogen (Pn) used is arsenic or antimony, and irrespective of the initial elemental ratios (Ag₅SbS₅, figure 3.6). When the transition metal is replaced by copper, a marked difference in product type is observed. When arsenic is used then a new ternary phase appears as the major product, presumably on the grounds of thermodynamic stability – CuAsS. When antimony is employed as the pnictogen then we see phase segregation occurring, resulting in an inhomogeneous mixture of copper (I) sulfide and unreacted antimony.

When the chalcogen source is insoluble in liquid ammonia (Se, Te) we see significant phase segregation occurring. The use of arsenic generally favours the formation of both transition- and main-group metal chalcogenides, whereas antimony persists as unreacted element. It is likely that thermodynamic considerations dictate the identity of the binary materials synthesised, with stoichiometric excesses persisting as unreacted elements (Ag₅AsTe₅, figure 3.5).

As was observed for the analogous binary reactions described in chapter 2, both copper and silver show a marked preference for the I oxidation state. A notable exception to this was the reactions involving copper, selenium and arsenic / antimony which afforded copper (II) selenide.
3.6.3 Effect of annealing samples (250-300 °C, 2h)

Where annealing was carried out (re: equations 3.17-3.32) it is clear that, with few exceptions, heat treatment has little effect on the product composition (notably with the retention of minor phases). Where heating affected product composition, only in the case of Ag/As/Se did elemental combination to a ternary material occur (equation 3.19). Otherwise, the affect of annealing was restricted to either changes in the stoichiometry of binary phases (equations 3.26 and 3.31) or crystallisation of amorphous materials (equation 3.28). This supports the hypothesis that where phase segregation has occurred, the most thermodynamically stable products result.

\[3\text{Ag}_2\text{Te}(s) + 2\text{Sb}(s) + 3\text{Te}(s) \rightarrow \text{Ag}_5\text{Te}_3(s) + 2\text{Sb}(s) + 3\text{Te}(s) + \text{Ag}(s) \quad (3.26)\]

\[\text{CuAsS}(s) \rightarrow \text{amorphous material} \rightarrow \text{Cu}_{1.96}\text{S}(s) + \text{CuAsS} \quad (3.28)\]

\[3\text{CuSe}(s) + \text{Sb}(s) \rightarrow \text{Cu}_{1.01}\text{Se}(s) + \text{Cu}_{1.01}\text{Se}_2(s) + (1+2x)\text{Cu}(s) + \text{Sb}(s) \quad (3.31)\]

3.6.4 Mechanistic evaluation

Prior to annealing, the only reactions that formed exclusively ternary 11-15-16 compounds as a major product are those that included sulfur as the chalcogen source. It seems unlikely that the formation of these ternary materials in liquid ammonia would result from a solid state reaction akin to the formation of metal mixed sulfur selenides, since the composite binary materials usually adopt a different crystal structure. In addition, it is clear that at room temperature in liquid ammonia it is not possible to form binary group 11 arsenides and antimonides by elemental combination reactions. Therefore, speculation towards a plausible mechanism must address two crucial points - the need for sulfur to be present for combination between the transition metal and the pnictogen, and the fact that the use of selenium or tellurium results in extensive phase segregation. In order to elucidate the problem, two plausible mechanisms have been developed, addressing the necessary redistribution of electrons involved in this elemental combination in terms of a concerted and non-concerted process.

Non-concerted electron transfer

A possible non-concerted reaction scheme is described below (Pn = As, Sb).

This involves the reaction between the group 11 metal and a solvated group 15 sulfide species - \([\text{Pn}^{III}\text{S}_n]^{(n\cdot)}\). The scheme as it stands is self-contained, yet assumes that the initial generation of a suitable concentration of solvated electrons at room temperature

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originates from the oxidizing nature of the sulfur-ammonia solution. Without such equilibria between the chalcogen and the solvent itself, such a reaction scheme as described above would not occur. Such would be the case for the use of selenium and tellurium, resulting in analogous solid state reactions to those described in chapter 2, and so the extensive formation of binary materials.

\[ 3 \text{S}^-_{(am)} + 3e^-_{(am)} \rightarrow 3\text{S}^2-_{(am)} \]
\[ 3\text{S}^2-_{(am)} + \text{Pn(s)} \rightarrow [\text{Pn}^{III}\text{S}_3]^{+}_{(am)} \]
\[ [\text{Pn}^{III}\text{S}_3]^{+}_{(am)} + 3\text{Ag(s)} \rightarrow \text{Ag}_3\text{PnS}_3 + 3e^-_{(am)} \]

\* S\(^-\)(am) is a univalent S-N anion (S\(^-\)N\(^\)') formed upon dissolution of sulfur in liquid ammonia

Concerted electron transfer

If one considers the redistribution of electrons as a concerted process, then success of the sulfide reactions could be the result of kinetic factors. For with the greatly increased surface area associated with the dissolution of sulfur, it is more likely that a reaction interface would exist between the chalcogen, transition- and main-group metal atoms. Conversely, the insolubility of both selenium and tellurium may crucially limit the likelihood of the transition metal atom being in close approach to the group 15-16 coupling (and in the necessary stoichiometric ratio) to initiate a ternary reaction. This in turn would result in a greater probability of formation of binary materials, with any ternary material being a minor phase in the product mixture.

Irrespective of what type of process the electron transfer is, one general result needs to be addressed - the reactions involving silver produce a wider range of more stoichiometrically exact ternary phases than the analogous copper reactions. As described earlier, the variable oxidation states made accessible by copper in liquid ammonia allow a wider range of binary materials that are thermodynamically stable at room temperature. In addition to this, it is likely that the relative size of the M\(^+\) and Sb\(^{3+}\) cations would make the Ag\(^+\)-Sb\(^{3+}\) interaction more stable than Cu\(^+\) / \(^{2+}\)-Sb\(^{3+}\). Consequently, under our manipulations, only the combination of silver with antimony is accessible at room temperature.
3.7 General conclusions of elemental combination reactions in liquid ammonia

Chalcogen-ammonia solutions react directly with some elemental metals at room temperature, affording a low-temperature pathway to both binary and, to a lesser extent, ternary metal chalcogenides. The synthesised materials are either highly crystalline or largely amorphous in character. The ease and scope of reaction is dependant upon the metal used, with product formation 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 often of high purity, notably with respect to the formation of binary chalcogenides. Crystallinity can be induced in the X-ray amorphous materials, whilst for the most part unaltering the product composition, by facile heating at 250-300 °C for 2h in a static, inert atmosphere. A wide range of ternary solid solutions have been synthesised with regards to mixed transition-metal and mixed transition-main-group metal chalcogenides (as well as mixed-chalcogenide materials), using both insoluble and soluble metals. In some cases, notably with certain ternary compounds, single phases of high purity (> 90%), do result. There are also cases where there is not complete control over the stoichiometry of the product or the oxidation state of the metal (re: copper and thallium binary chalcogenides). However, liquid ammonia does allow the synthesis of a remarkably wide range of materials utilising a simple two step process, as well as consistently facilitating particle sizes within the range of 2-8 μm.

3.7.1 Context of this work in relation to alternative synthetic routes

Liquid ammonia plays an intrinsic role in enabling the reactions studied to occur at room temperature, resulting in a truly low-temperature mechanistic route to metal chalcogenides. The reactions occur at significantly lower temperatures (ca. 25 °C) than both self-propagating high temperature synthesis (which can generate temperatures in excess of 1000 °C) and solid state metathesis (in which the reaction temperature is limited to the melting point of the co-produced salt; ca. 600-800 °C). Traditional elemental combination routes to metal chalcogenides also involve elevated temperatures (ca. 1150 °C), in addition to prolonged reaction times (ca. 3 days) and the use of multiple steps.
The liquid ammonia reactions described are also more straightforward than the molecular precursor routes to metal sulfides and selenides, which require the synthesis of materials with a specific decomposition pathway and a reaction temperature often in excess of 200 °C. The use of liquid ammonia reactions have some correlation 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). Subsequently, the ammonia promoted, metal chalcogenide reactions may be viewed as similar to the work of Rauchfuss et al. where the elements are made to react at the reflux temperature of a strongly coordinating solvent to afford binary materials.

3.7.2 Previously proposed mechanisms for the formation of the sulfide anion ($S^{2-}$)

In reference to the mechanisms for production of the $S^{2-}$ proposed by Dubois et al., the work outlined in chapters 2 and 3 have shown that the amide anion is only likely to be formed in sulfur-ammonia solutions upon dissolution of a soluble metal. It is likely that these metals react to form subsequent chalcogenides by direct reduction of the chalcogen; the process being facilitated by the stabilisation of the solvated electron afforded by liquid ammonia. In the case of the reduction of sulfur in liquid ammonia, an understanding of the intricacies of the sulfur-ammonia system of equilibria may be (for the most part) superfluous, since either the cyclic S-N species or the $in situ$ $H_2S$ are likely to be reduced directly to the $S^{2-}$ anion. It is interesting to note, however, that no evidence was observed of higher order polyanionic sulfur species being formed in the reaction product, even though the predominant species initially formed upon dissolution of sulfur is reported to include $S_n^{2-}$. It is conceivable that the formation of any amide during the reaction of soluble metals would act to facilitate the conversion of the S-N rings and sulfur polyanions present to the $S^{2-}$ anion. The observation of the partial or complete dissolution of zinc, cadmium and lead prior to the precipitation of the corresponding metal sulfide (which does not include any metal amide), does lend itself to the reduction of $H_2S$ by the metal as a means of forming solely the MS product. This is, however, largely unsubstantiated. Even so, if this were the dominant mechanism in play, it may explain the slight reduction in the reaction rate of the sulfides when compared to the selenides or tellurides (which must proceed via a solid state route). That is, the acidic environment of the ammonia solution ($pH < 5.8$) would lend itself only to the reduction of $H_2S$ to HS', thereby generating a kinetic barrier to the complete reduction to $S^{2-}$. This of course assumes that HS' does not react directly with the metal.
in the same manner as \( S^2 \). A possible role of the sulfur-ammonia system as an oxidising medium, intrinsic to the formation of metal mixed pnictide chalcogenides, has been suggested (section 3.5.4), although this is only speculative.
4.0 Synthesis of Binary Materials by Elemental Combination

Reactions in n-Butylamine

4.1 Synthesis and Characterisation

The room temperature reactions of silver, lead, mercury, thallium and copper with sulfur, selenium or tellurium in n-butylamine produces, after 24 h, crystalline metal chalcogenides of general formula $\text{Ag}_x\text{E}$, $\text{PbE}$, $\text{HgE}$ (where $E = \text{S, Se, Te}$), $\text{TIE}$ ($E = \text{S, Se}$), $\text{Cu}_{2+x}\text{Se}$ and $\text{Cu}_{2-x}\text{Se}$ (equations 4.1 – 4.5), in practically quantitative yield (table 4.1). In the case of mercury sulfide, black wurtzite phase (metacinnebar, $\beta$-HgS) formed after 24 h. With an evaporating solvent, the mercury product was found to contain significant quantities ($\geq 10\%$) of the red cubic phase (cinnebar, $\alpha$-HgS) after 24 h.

\begin{align*}
2\text{Ag} + \text{E(amine)} & \rightarrow \text{Ag}_2\text{E} \quad (E = \text{S, Se, Te}) \\
\text{M} + \text{E(amine)} & \rightarrow \text{ME} \quad (\text{Hg, Pb}; E = \text{S, Se, Te}) \\
(2-x)\text{Cu} + \text{Se(amine)} & \rightarrow \text{Cu}_{2-x}\text{Se} \\
2\text{Cu} + \text{Te(amine)} & \rightarrow \text{Cu}_{0.64}\text{Te}_{0.36} \\
2\text{Tl} + 3\text{E(amine)} & \rightarrow \text{Tl}[\text{TIE}_2] + \text{E} \quad (E = \text{S, Se}) \quad \text{‘TIE’}
\end{align*}

The metal chalcogenides were characterised by both FT-IR and Raman spectroscopic analyses, which showed characteristic broad absorption bands within the region of 600 - 200 cm$^{-1}$ (depending upon the sample). Vibrational spectroscopy invariably matched that of authentic samples. No IR stretches were observed for N-H vibrations. In addition, microanalyses showed negligible amounts of carbon, hydrogen and nitrogen ($< 0.3\%$) in the bulk materials. Consequently, one can surmise that amine is not bound to the products. The X-ray powder diffraction patterns obtained for the products from all the reactions undertaken in n-butylamine are summarised in table 4.1, both before and after annealing at 250 – 300 °C for 2h. in an inert atmosphere (dinitrogen).
Table 4.1 XRD data for chalcogenides of Cu, Ag, Hg, Tl and Pb (produced by combination of the elements in n-butylamine at room temperature)

<table>
<thead>
<tr>
<th>Ratio of elements</th>
<th>Product colour</th>
<th>Reaction time / h</th>
<th>Products as formed from reaction (identified by XRD)(^a)</th>
<th>Annealed reaction products (250-300 °C, 2h)(^a)</th>
<th>Lattice Parameters (\Delta \pm 0.01)(^b)</th>
<th>Lit. lattice parameters (\Delta)(^1\text{39})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu : S 1 : 1</td>
<td>Black</td>
<td>24</td>
<td>X-ray amorphous Cu(_2)S (chalcolite) + S</td>
<td>(a = 3.96) (c = 6.77) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = 3.96) (c = 6.78)</td>
<td></td>
</tr>
<tr>
<td>Cu : Se 1 : 1</td>
<td>Black</td>
<td>12</td>
<td>Cu(<em>{2.8})Se (berzelianite) Cu(</em>{2-x})Se (berzelianite)</td>
<td>(a = c = 5.74) (\Delta)(^1\text{39})</td>
<td>(a = c = 5.77)</td>
<td></td>
</tr>
<tr>
<td>Cu : Te 1 : 1</td>
<td>Black</td>
<td>72</td>
<td>Cu(<em>{0.65})Te(</em>{0.35}) + [Cu(_4)Te(_3)]</td>
<td>Cu(<em>{2-x})Te (rickardite) Cu(</em>{2-x})Te (weissite)</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>Ag : S 2 : 1</td>
<td>Black</td>
<td>48</td>
<td>Ag(_2)S (acanthinite) Ag(_2)S (acanthinite)</td>
<td>(a = c = 4.48) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 4.46)</td>
<td></td>
</tr>
<tr>
<td>Ag : Se 2 : 1</td>
<td>Black</td>
<td>48</td>
<td>Ag(_2)Se (naumannite) Ag(_2)Se (naumannite)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76) (\Delta)(^1\text{39})</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
<td></td>
</tr>
<tr>
<td>Ag : Te 2 : 1</td>
<td>Silver</td>
<td>48</td>
<td>Ag(_2)Te (hessite) + [Ag]</td>
<td>Ag(_2)Te (hessite)</td>
<td>(a = 8.07) (b = 4.47) (c = 8.94) (\Delta)(^1\text{39})</td>
<td>(a = 8.09) (b = 4.47) (c = 8.96)</td>
</tr>
<tr>
<td>Hg : S 1 : 1</td>
<td>Black</td>
<td>24</td>
<td>HgS (metacinnebar) HgS (metacinnebar)</td>
<td>(a = c = 5.85) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 5.85)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Red</td>
<td>24</td>
<td>HgS (cinnebar) HgS (cinnebar)</td>
<td>(a = 4.15) (b = 9.50) (\Delta)(^1\text{39})</td>
<td>(a = 4.15) (b = 9.50)</td>
<td></td>
</tr>
<tr>
<td>Hg : Se 1 : 1</td>
<td>Black</td>
<td>24</td>
<td>HgSe (tiemannite) HgSe (tiemannite)</td>
<td>(a = c = 6.07) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 6.07)</td>
<td></td>
</tr>
<tr>
<td>Hg : Te 1 : 1</td>
<td>Black</td>
<td>24</td>
<td>HgTe (coloradoite) HgTe (coloradoite)</td>
<td>(a = c = 6.45) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 6.45)</td>
<td></td>
</tr>
<tr>
<td>Tl : S 2 : 3</td>
<td>Black</td>
<td>48</td>
<td>TlS + S TlS + S</td>
<td>TlS + S</td>
<td>(a = 7.79) (c = 6.80) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = 7.79) (c = 6.80)</td>
</tr>
<tr>
<td>Tl : Se 2 : 3</td>
<td>Black</td>
<td>48</td>
<td>TlSe + Se TlSe + Se</td>
<td>TlSe + Se</td>
<td>(a = 8.02) (c = 7.00) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = 8.02) (c = 7.00)</td>
</tr>
<tr>
<td>Pb : S 1 : 1</td>
<td>Black</td>
<td>48</td>
<td>PbS (galena) + [Pb]</td>
<td>PbS (galena)</td>
<td>(a = c = 5.93) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 5.93)</td>
</tr>
<tr>
<td>Pb : Se 1 : 1</td>
<td>Black</td>
<td>48</td>
<td>PbSe (clausthalite) PbSe (clausthalite)</td>
<td>(a = c = 6.12) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 6.12)</td>
<td></td>
</tr>
<tr>
<td>Pb : Te 1 : 1</td>
<td>Black</td>
<td>48</td>
<td>PbTe (altaite) PbTe (altaite)</td>
<td>(a = c = 6.45) (\pm 0.01) (\Delta)(^1\text{39})</td>
<td>(a = c = 6.46)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) All minor phases (< 10 %) represented in square brackets. Where a phase synthesised corresponds to a mineral structure, the mineral name appears in italics.

\(^b\) Cell parameters are calculated for the major binary phase.
Table 4.2  SEM / EDX characterisation of binary chalcogenides of Cu, Ag, Hg, Tl, Pb produced from elemental combination in n-butylamine

<table>
<thead>
<tr>
<th>Target material</th>
<th>Aggregate size (microns)</th>
<th>Ratio of elements (± 2-3 %)</th>
<th>Elemental ratio</th>
<th>Experimental values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuS</td>
<td>2 - 8</td>
<td>Cu : S</td>
<td>67 : 33</td>
<td>67 : 33 (CuS)</td>
<td></td>
</tr>
<tr>
<td>CuSe</td>
<td>2 - 8</td>
<td>Cu : Se</td>
<td>65 : 35</td>
<td>67 : 33 (CuS,Se)</td>
<td></td>
</tr>
<tr>
<td>CuTe</td>
<td>2 - 8</td>
<td>Cu : Te (pre-annealed)</td>
<td>65 : 35 (90 %)</td>
<td>64 : 36 (Cu0.64Te0.36)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu : Te (pre-annealed)</td>
<td>57 : 33 (10 %)</td>
<td>57 : 33 (Cu0.57Te0.43)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cu : Te (annealed)</td>
<td>65 : 35</td>
<td>67 : 33 (Cu1Te)</td>
<td></td>
</tr>
<tr>
<td>Ag2S</td>
<td>2 - 8</td>
<td>Ag : S</td>
<td>67 : 33</td>
<td>65 : 33</td>
<td></td>
</tr>
<tr>
<td>Ag2Se</td>
<td>2 - 8</td>
<td>Ag : Se</td>
<td>67 : 33</td>
<td>67 : 33</td>
<td></td>
</tr>
<tr>
<td>Ag2Te</td>
<td>2 - 8</td>
<td>Ag : Te</td>
<td>67 : 33 (95 %)</td>
<td>67 : 33</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ag : Te</td>
<td>95 : 5 (5 %)</td>
<td>100 : 0 (Ag)</td>
<td></td>
</tr>
<tr>
<td>HgS</td>
<td>2 - 8</td>
<td>Hg : S</td>
<td>67 : 33</td>
<td>65 : 33</td>
<td></td>
</tr>
<tr>
<td>HgSe</td>
<td>2 - 8</td>
<td>Hg : Se</td>
<td>67 : 33</td>
<td>67 : 33</td>
<td></td>
</tr>
<tr>
<td>HgTe</td>
<td>2 - 8</td>
<td>Hg : Te</td>
<td>67 : 33</td>
<td>67 : 33</td>
<td></td>
</tr>
<tr>
<td>Tl2S3</td>
<td>2 - 8</td>
<td>Tl : S</td>
<td>50 : 50</td>
<td>50 : 50 (TlS)</td>
<td></td>
</tr>
<tr>
<td>Tl2Se3</td>
<td>2 - 8</td>
<td>Tl : Se</td>
<td>50 : 50</td>
<td>50 : 50 (TlSe)</td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>2 - 8</td>
<td>Pb : S</td>
<td>50 : 50 (95 %)</td>
<td>50 : 50 (PbS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb : S</td>
<td>98 : 2 (95 %)</td>
<td>100 : 0 (Pb)</td>
<td></td>
</tr>
<tr>
<td>PbSe</td>
<td>2 - 8</td>
<td>Pb : Se</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td></td>
</tr>
<tr>
<td>PbTe</td>
<td>2 - 8</td>
<td>Pb : Te</td>
<td>50 : 50</td>
<td>50 : 50</td>
<td></td>
</tr>
</tbody>
</table>

1 Material synthesised by room temperature elemental combination in n-butylamine. Results obtained are for both pre-annealed and annealed material (unless otherwise stated).
2 Assessed by SEM
3 As assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple phases is expressed as a percentage (as assessed by back-scattered electrons). Analysis carried out after washing with CS2.
Table 4.3 SEM / EDXA characterisation of binary chalcogenides of Fe, Ni, As, Sb, Bi synthesised from reaction of the elements at room temperature in n-butylamine

<table>
<thead>
<tr>
<th>Target material</th>
<th>Aggregate size (microns)</th>
<th>Elemental composition / atm. % (experimental error ± 2-3 %)</th>
<th>Elemental Ratio</th>
<th>Pre-annealed values</th>
<th>Annealed values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiS</td>
<td>2 - 8</td>
<td>Ni : S</td>
<td>Elementa Rratio</td>
<td>50 : 50 (5 %)</td>
<td>50 : 50 (95 %)</td>
<td>50 : 50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unreacted Ni</td>
<td></td>
<td>(95 %)</td>
<td>(5 %)</td>
<td>≥ 95 % abundance</td>
</tr>
<tr>
<td>AsS₃</td>
<td>2 - 8</td>
<td>As : S</td>
<td>40 : 60 (90 %)</td>
<td>40 : 60 (90 %)</td>
<td>40 : 60 (As₂S₃)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unreacted As</td>
<td>(10 %)</td>
<td>(10 %)</td>
<td></td>
<td>≥ 95 % abundance</td>
</tr>
<tr>
<td>As₂Se₃</td>
<td>2 - 8</td>
<td>As : Se</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (As₂Se₃)</td>
<td></td>
</tr>
<tr>
<td>As₂Te₃</td>
<td>2 - 8</td>
<td>As : Te</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (As₂Te₃)</td>
<td></td>
</tr>
<tr>
<td>Sb₂S₃</td>
<td>2 - 8</td>
<td>Sb : S</td>
<td>40 : 60 (10 %)</td>
<td>40 : 60 (10 %)</td>
<td>40 : 60 (Sb₂S₃)</td>
<td></td>
</tr>
<tr>
<td>Sb₂Se₃</td>
<td>2 - 8</td>
<td>Sb : Se</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (Sb₂Se₃)</td>
<td></td>
</tr>
<tr>
<td>Sb₂Te₅</td>
<td>2 - 8</td>
<td>Sb : Te</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (Sb₂Te₅)</td>
<td></td>
</tr>
<tr>
<td>Bi₂Se₅</td>
<td>2 - 8</td>
<td>Bi : Se</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (Bi₂Se₅)</td>
<td></td>
</tr>
<tr>
<td>Bi₂Te₅</td>
<td>2 - 8</td>
<td>Bi : Te</td>
<td>Unreacted elements</td>
<td>40 : 60</td>
<td>40 : 60 (Bi₂Te₅)</td>
<td></td>
</tr>
</tbody>
</table>

Note: For the following reactions, an intimate mix of unreacted elements (≥ 95 % atm. % by EDXA) was observed for both pre-annealed and annealed materials:
1. Fe + E (E = S, Se, Te)
2. Ni + E (E = Se, Te)
3. Bi + S

---

¹ Material synthesised by room temperature elemental combination in n-butylamine. Results obtained are for both pre-annealed and annealed material (unless otherwise stated).
² Assessed by SEM.
³ As assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple phases is expressed as a percentage (as assessed using backscattered electrons). Analysis carried out after washing with CS₂.

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4.1.1 Characterisation of reaction products of Cu, Ag, Hg, Tl and Pb with S, Se, Te in n-butylamine

SEM revealed small, irregularly shaped aggregates (typically 3-8 microns in size). In the majority of samples, EDXA showed only the metal and chalcogenide to be present in the expected elemental ratios, and over many surface spots (of excitation width 1 micron). In some samples (Ag$_2$Te, PbS) small regions of unreacted metal were observed (<5 % as assessed by surface analysis using back-scattered electrons).

In the case of the product from the reaction of silver and tellurium in n-butylamine, EDXA could not be used to distinguish such regions as either an elemental mixture (Ag$_2$Te / Te) or the phase AgTe. The XPS spectra of this sample (figure 4.1), showed binding energy values of 367.6 eV for Ag 3d$_{5/2}$ and 571.8 eV for Te 3d$_{5/2}$, which are consistent with literature values for the formation of silver telluride, Ag$_2$Te (367.2 eV for Ag 3d$_{5/2}$ and 571.3 eV for Te 3d$_{5/2}$). Furthermore, integration of these peaks over many surface spots shows a consistent elemental ratio, concordant with a stoichiometry of Ag$_2$Te$_{1.03(5)}$.

For the reaction between mercury and sulfur, two types of product were synthesised. By maintaining a constant volume of solvent a black product was obtained, whilst a reddish brown material resulted by allowing the n-butylamine to evaporate. Under optical microscopy, both materials were observed to be intimate mixtures of two discrete phases (one black and the other red), each of different proportions, as shown in the table below.

<table>
<thead>
<tr>
<th>Black product</th>
<th>&lt;5 % red phase + &gt;95 % black phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Red-brown product</td>
<td>&gt;10 % red phase + &lt;90 % black phase</td>
</tr>
</tbody>
</table>

Raman spectroscopic analysis (figure 4.2) showed the red phase to be cinnebar and the black phase to be metacinnebar. Figure 4.2 shows the Raman spectra obtained for each phase. The red phase showed a pattern characteristic of α-HgS (also known as the pigment ‘vermillion’), with absorption at 345 cm$^{-1}$ and 252 cm$^{-1}$ (the later peak having a shoulder at high wavenumbers). The black phase produced a more ambiguous Raman pattern, comprising of a largely featureless regime with one discernible peak at ca. 170 cm$^{-1}$. This absorption is neither characteristic of α-HgS nor the elements (sulfur, mercury) and so suggests synthesis of a different phase of mercuric sulfide (β-HgS, as confirmed by XRD, figure 4.3). These observations are consistent with β-HgS being...
Raman inactive, with the absorption (being at low wavenumbers) tentatively assigned to a possible lattice vibration. Upon thermolysing each phase \textit{in situ} using increased power to the incident laser, a transformation to the red phase was observed.

**Figure 4.1** XPS spectrum of pre-annealed silver sulfide (prepared by elemental combination in n-butylamine at 298K) showing silver 3d doublet

\[\text{The spectrum shows the doublet associated with the 3d electrons from the Ag}^{II} \text{ cation of Ag}_{2}\text{Te. It is comprised of two discrete peaks, indicative of the } 3d_{3/2} \text{ and } 3d_{5/2} \text{ electrons.}\]
Optical microscopic analysis of the thermolysed samples also showed that annealing each sample at 250 – 300 °C for 2h increased the relative proportions of the red phase (typically by ca. 20 %). Figure 4.4 shows the XRD spectrum of the annealed black phase (metacinnabar), confirming the presence of both metacinnabar (major phase) and cinnebar (minor phase). These observations are consistent with α-HgS being the thermodynamically more stable form of mercuric sulfide.\textsuperscript{446}

Figure 4.2 \textsuperscript{5} Raman spectra of α-HgS (top) and β-HgS (bottom)

\textsuperscript{5}Single peaks are labeled with their centre of gravity in wavenumbers (cm\textsuperscript{-1}). The smoothed spectra as shown (100-700 cm\textsuperscript{-1}), lie within the expected range for M-S absorption (200-600 cm\textsuperscript{-1}).
Figure 4.3  XRD spectrum of mercuric sulfide (black phase) formed directly from the elements in n-butylamine at room temperature

![XRD spectrum of mercuric sulfide](image)

Key: sample (top) – HgS  
Standard (bottom) – *metacinnabar*, HgS

Figure 4.4  XRD spectrum of mercuric sulfide (black phase) after annealing at 250-300 °C for 2 hours

![XRD spectrum after annealing](image)

Key: Sample (black) – HgS  
Standard mercuric sulfide – *cinnebar* (blue), *metacinnabar* (red)
The X-ray powder diffraction patterns of the products produced from the reactions of silver, lead, thallium (figure 4.5 shows TlSe) and mercury with chalcogens in n-butylamine (table 4.1) showed the formation of crystalline metal chalcogenide powders that indexed well to give cell parameters that were in good agreement (± 0.01 Å) with literature measurements.\(^{139}\) Crystallite sizes were of the order of 300 - 700 Å (as determined by the Scherrer equation).\(^{138}\) For all these reactions, a single phase metal chalcogenide product was obtained, with the exceptions of the reactions of silver with tellurium and lead with sulfur, where small traces of unreacted metal were detected (ca. 2 - 3 % on surface, as assessed by EDXA / SEM). Upon annealing these powders (250 – 300 °C for 2 h) the trace of metal disappears, presumably either because of incorporation within the metal chalcogenide phase or by reaction with trace amounts of X-ray amorphous chalcogen. The reaction product of thallium and tellurium showed no elemental combination, both by EDXA and XRD.

Treatment of copper with sulfur in n-butylamine produced a black X-ray amorphous material that upon thermolysis at 250 – 300 °C for 2 h produced crystalline Cu\(_2\)S (characterised by EDXA and XRD). Reaction of selenium and tellurium with copper in n-butylamine produced black crystalline solids – Cu\(_{2.36}\)Se and Cu\(_{0.64}\)Te\(_{0.36}\) (with a trace of Cu\(_4\)Te\(_3\)). 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. This is shown in figure 4.6 in the formation of copper (I) selenide. The excess chalcogen in the reaction would have been removed by the washing with CS\(_2\). Combination of the elements in the 2:1 ratio also produces ‘Cu\(_2\)E’ but without the need for CS\(_2\) washing.

It should be noted that only the metal chalcogenides of general formula Ag\(_2\)E, PbE, HgE (E = S, Se, Te), TIE (E = S, Se) and Cu\(_{2-x}\)E (Se, Te) formed crystalline phases at room temperature from elemental combination reactions in n-butylamine.
Figures 4.5 XRD spectrum of thallium selenide (Tl:Se 2:3) formed directly from the elements in n-butylamine at room temperature

Figure 4.6 XRD spectrum of copper selenide (Cu:Se 1:1) after annealing at 250-300 °C for 2 hours

Key: Sample (top) – thallium selenide (Tl:Se 2:3), Standard (bottom) – TlSe (blue), Se (red)

Key: Sample (top) – copper selenide (Cu:Se 1:1), Standard (bottom) – Cu$_{2-x}$Se (blue), Se (red)
4.1.2 Characterisation of the reaction of Fe, Ni with S, Se, Te in n-butylamine

The reaction of iron or nickel either with sulfur, selenium or tellurium at room temperature in n-butylamine produced a slight colour change in the solid. However, both XRD and EDXA studies of the materials showed the presence of unreacted elements. Only in the case of nickel with sulfur did heating the material at 250 – 300 °C for 2 h show formation of a crystalline chalcogenide of desired stoichiometry (NiS). The cell parameters \(a = c = 3.43 \pm 1 \text{ Å}\) matched those of literature \(a = c = 3.42 \text{ Å}\).\(^{139}\)

4.1.3 Characterisation of the reaction of As, Sb, Bi with S, Se, Te in n-butylamine

Arsenic reacted with sulfur in n-butylamine to afford a yellow solid that was amorphous to X-rays, even after heating at 550 °C for 2h. EDXA analysis showed the correct elemental ratios of arsenic to sulfur over many surface spots to conclude that the major product from the reaction (> 90 %) was arsenic (III) sulfide (As\(_2\)S\(_3\)). Similar analyses 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\(_2\)S\(_3\). In both cases, the initial starting materials were in the ratio of 2:5 not 2:3, as the products suggest, indicating a preference for the lower oxidation state sulfides for these elements. As already observed, the excess sulfur present after the reaction would have been removed by trituration of the products with CS\(_2\). There was no observed reaction between bismuth and either sulfur, selenium or tellurium at room temperature in n-butylamine after 7 days (as assessed by EDXA and XRD). The initial ratios of reagents were 2:5 (Bi:E), the sulfur having been removed, still in solution, whilst decanting off the solvent. Upon annealing the selenide and telluride reactions (250-300 °C, 2h; inert atmosphere) a single phased product was observed (characterised by XRD), of stoichiometry Bi\(_2\)E\(_3\). Figure 4.7 shows the XRD spectrum obtained for the formation of bismuth selenide. Repeating the analogous reactions with arsenic and antimony also afforded phase pure, crystalline As\(_2\)E\(_3\) and Sb\(_2\)E\(_3\) (E = Se, Te). Heating the elements under the same conditions but without prior treatment in n-butylamine showed a mixture of unreacted metal (XRD) and a minor phase of the sesquichalcogenide (< ca. 10 % as assessed by EDXA).
Attempts at forcing an elemental reaction between sulfur and tin or cadmium by refluxing the n-butylamine, both by conventional means (12h) as well as by microwave irradiation (2h), failed to produce a discernible sulfide product. Reactions between sulfur and silver or lead in n-hexylamine did proceed to form the metal chalcogenide, but over a prolonged period of time (7 days).

4.1.4 Reactions in other N-based solvents
Reactions were also investigated between the more chalcophilic metals used (Ag, Pb, Hg) and the chalcogens (S, Se, Te) at room temperature in a variety of N-based solvents (n-hexylamine, ethylenediamine, aqueous ammonia), as well a non-coordinating solvent (cyclohexane). Although these reactions proceeded in n-hexylamine, they were significantly slower (requiring about 7 days to go to completion). In each case, the same crystalline phases were observed as for n-butylamine. Repeating these reactions at room temperature in either cyclohexane or ethylenediamine failed to result in any elemental combination, even after a prolonged period of time (14 days). The use of aqueous ammonia as a solvent, facilitated the formation of PbS within 48 h. However, the product was significantly contaminated with quantities of both metal oxide and
unreacted metal (ca. 75% in total, as assessed by EDXA). There was no observed reaction between sulfur and either mercury or silver in aqueous ammonia after 48 h. In neither of these alternative solvents was the transition of α-HgS to β-HgS observed.

4.2 Discussion of elemental reactions in n-butylamine

4.2.1 Solution state mechanisms

Mercuric sulfide (HgS) occurs in two mineral forms. The red form (cinnebar, or α-HgS) adopts a distorted sodium chloride lattice, with the formation of zigzag Hg-S chains similar to those in HgO. The black phase (metacinnebar, or β-HgS) adopts the zinc blende structure found for HgSe and HgTe. The black phase is metastable, and so may be converted to the red either by heating or by treatment with alkali polysulfides or mercurous chloride. It is this phase that predominates from the elemental reaction of mercury and sulfur in both n-butylamine and, to a lesser extent, liquid ammonia. Literature reports the black phase to be rare, forming from either the action of H$_2$S on the metal or from precipitation from aqueous solution. The absence of solvated mercury species upon addition of the element to n-butylamine (or indeed to liquid ammonia) thereby suggests the possible presence of _in situ_ H$_2$S, formed upon the dissolution of sulfur in n-butylamine, may play a critical role in the subsequent reaction. Upon dissolution in either primary or secondary amines, it has been reported that the S$_8$ ring undergoes stepwise nucleophilic attack by the amine. The initial products are the _in situ_ release of H$_2$S with the formation of N,N'-polythiobisamines. In a solution just containing dissolved sulfur, these S-N species co-exist with a secondary product (amine polysulfides) formed by the subsequent attack of the aliphatic amine by H$_2$S. It is plausible, however, that the H$_2$S formed may be the source of sulfur for direct combination with the metal. Moreover, these new sulfur-amine species contain long straight chains of sulfur that are inherently less stable than the original S$_8$ rings. Hodgson _et al._ suggests that as a consequence, these solvated species would undergo subsequent homolytic scission to achieve a degree of resonance stability, thereby creating sulfur based radicals. The possibility exists, therefore, that sulfur radicals may play an intrinsic role in the formation of metal sulfides by elemental combination at room temperature. Indeed, it has been shown that the _in situ_ formation of both metal and sulfur based radicals is the key mechanistic pathway to the room temperature synthesis
of nanoparticulate zinc and cadmium sulfides, by γ-irradiation of solutions of metal halides and metal thiolates.\textsuperscript{117}

4.2.2 Solid state mechanisms

It should be noted that both selenium and tellurium are insoluble in n-butylamine yet also react with elemental silver, copper, lead and mercury. The reactions of selenium and tellurium appear to be solid state reactions, although the presence of extremely low concentrations of solvated species cannot be ruled out. The time taken for complete reaction (table 4.1) suggest that the rate of elemental solid state diffusion is excellent, especially since crystalline material results. It might be expected that the rates of reaction of sulfur with either silver or mercury 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 HgSe and Ag\textsubscript{2}Se (> 95 % for both cases, as determined by EDXA / XRD). It was not possible to form solid solutions (MS\textsubscript{2}Se\textsubscript{y}, where M = Hg, Ag, Pb) as a major product. This may indicate two discrete reaction types in operation, one intrinsic to solvated sulfur species, whilst the other is solid state. In the later case, the amine solvent may play a role in activating the reagent surface, whilst allowing good contact between the elements.

4.2.3 Role of n-butylamine

It seems unlikely, however, that the syntheses involving selenium and tellurium are simply room temperature solid state reactions working independently of the solvent (even though the metals that react are amongst the most chalcophilic). First, no elemental combination was observed for the elements on refluxing. Secondly, both cadmium and tin (both highly chalcophilic in nature) failed to react with chalcogens in n-butylamine, even at reflux, and there was only a marginal degree of reactivity observed between zinc and sulfur once the solvent had been raised to reflux and left for 7 days. Thirdly, although the formation of M\textsubscript{2}E\textsubscript{5} (M = Sb, Bi, E = Se, Te) did not occur at room temperature in n-butylamine, the direct combination of the elements did occur after facile heating in an inert atmosphere (250 – 300 °C, 2h). This afforded the most thermodynamically stable products (the sesquichalcogenide M\textsubscript{2}E\textsubscript{3}) as a pure, crystalline, single phase. This was not found to be the case after similar heating of the elements
without treatment by n-butylamine. This ‘activation’ of the metal surface was also exhibited by liquid ammonia (as discussed in section 2.2.2, p. 62-63).

Finally, n-butylamine appears to allow thallium to react with both sulfur and selenium at room temperature by obtaining the Tl^{III} oxidation state. The single phased product from each reaction is ‘TIE’ – a mixed oxidation state metal chalcogenide, more accurately described as Tl^{I} [Tl^{III} S_{2}]. Altering the reagent ratios to either 2:1 or 2:3 (Tl:E) has no effect on the product stoichiometry. The failure of the analogous reaction between thallium and tellurium may be a result of insufficient bond enthalpy to drive the reaction at room temperature. Interestingly, n-butylamine does not appear to allow the formation of the kinetic phases of thallium (I) selenide or telluride exhibited by liquid ammonia (Tl_{2}E or Tl_{2}E_{3}). These products would appear to be more energetically accessible at low reaction temperatures when one considers the ‘inert pair’ effect exhibited by thallium.¹⁴³

4.3 Discussion of elemental reactions in N-based solvents

4.3.1 Comparison of n-butylamine and liquid ammonia
As previously discussed (chapter 2), the reaction of chalcogens with late transition- and main-group metals (Zn, Cd, Hg, Ag, Cu, Pb) in liquid ammonia at room temperature in a pressure vessel (ca. 7 atm.), produced a range of single phased metal chalcogenides. The reactions of lead and silver produces crystalline metal sulfides, whilst the remaining reactions produced X-ray amorphous materials that could be crystallised by facile heating (250 – 300 °C for 2 h). Similar results were obtained for n-butylamine, with comparable phases being observed, but for three notable exceptions. First, the reaction of mercury and sulfur in liquid ammonia afforded an X-ray amorphous material, identified as a mixture of both cinnebar and metacinnebar. Yet in n-butylamine the composition of the two phases of mercuric sulfide may be altered by changing the dynamics of the solvent. For ‘analogous’ solvent conditions (i.e. a sealed system), the reaction product in n-butylamine showed a marked preference for the zinc blende phase (metacinnebar), whilst with an evaporating solvent the more thermodynamically stable distorted rock salt structure (cinnebar) was dominant. Secondly, the reactions of copper with selenium or tellurium in n-butylamine produced predominantly single phased materials of CuI, whilst in liquid ammonia a mixture of phases was observed (which included significant amounts of CuTe and CuSe). Thirdly, elemental reactions in liquid
ammonia gave a greater scope in that zinc, cadmium and tin all reacted to form X-ray amorphous chalcogenides (with crystalline materials resulting after annealing these powders at 250 – 300 °C for 2h). In n-butylamine no reaction was observed for these reactions, even at reflux, except in the case of zinc and sulfur where, as already stated, the formation of 5 - 10 % amorphous ZnS was obtained on the surface of the zinc after 7 days. In the absence of heating, n-butylamine does not facilitate extensive reaction between chalcogens and Sb, Bi, In and As (Se, Te).

4.3.2 Role of the N-based solvents

For the most part one can say that the elemental combination reactions we carried out in N-based solvents at room temperature (NH3, NH3aq, CH3(CH2)3NH2, CH3(CH2)3NH2, and NH2(CH2)3NH(x) produced phases of the metal chalcogenides that were the same as the most common mineral forms of these species. The materials formed with silver were formally Ag (I) d10, with mercury Hg (II) d10, and with lead Pb (II) d10s2. Copper was predominantly Cu (I) d10, with some deviance in liquid ammonia to Cu (II) d9. It is known that some chalcophilic elements will react on contact with chalcogens, in the absence of a solvent, at room temperature. We discovered that the products from the reaction of mercury and sulfur in the absence of a solvent (cinnebar and metacinnebar) were not crystalline, and the reaction stopped after an initial period (ca. 60 h) to leave only partly coated reacting particles. In order to test the rate of solid state reaction of silver metal and elemental sulfur, disks of the elements were pressed together and the interface observed every 7 days. The silver disk was seen to gradually darken with the formation of crystalline acanthite (Ag2S). The reaction progressed from the elemental boundary into the silver disk to a depth of 0.5-1 mm per month. It is probable, therefore, that the mechanical stirring of the elements in a solvent would assist the formation of metal chalcogenides by removing the powdered product from the surface of the metal, effectively regenerating clean surfaces for subsequent reaction. In line with the results obtained, one would expect liquid ammonia to be more efficient at regenerating the metal surface when compared to the organic N-based solvents. For not only does its reduced size and increased pressure allow greater crowding of the solvent at the reaction sites, but its increased polarity allows a more extensive solvent sphere, thereby increasing mobility of the product away from the metal surface.

Significant differences in the reactivity of elemental combination reactions are also apparent in the remaining N-based solvents used (ethylenediamine, aqueous ammonia
and n-hexylamine). Rauchfuss et al. report\textsuperscript{19} that the strongly coordinating ethylenediamine solvent can be used in the synthesis of amorphous copper sulfide. They observe the elemental combination of copper and sulfur at room temperature and pressure, affording a low energy route to $[\text{Cu(en)}_2]^{2+}[\text{S}_6]^{2-}$. This complex can be thermally decomposed at 500 °C to amorphous CuS. Interestingly, the stability afforded to the copper (II) cation by this bidentate ligand does not appear to be extended to either the mercury (II), silver (I) or lead (II) cation, with none of these metals reacting at room temperature to form a $[\text{M(solv)}_2(\text{S}_6)]$ complex (even after a prolonged time period of 14 days). This is likely to result from the increased strain on the ‘bite angle’ upon coordinating to a significantly larger cation (when compared to copper II), thereby reducing the stabilising effect of the bidentate ligand.

Reactions occur more slowly in n-hexylamine than n-butylamine, and not at all in non-N-based solvents such as cyclohexane. It is possible that the increased basicity of the N-based solvents mentioned remove passivating oxide layers from the metal, thereby allowing the reactions to occur by lowering the energy of activation to a point made accessible at room temperature. The marked increase in the scope of reactions for liquid ammonia may be the result of the higher pressures at which this solvent is maintained (\textit{ca.} 7 atm.), resulting in an increase in the surface action of the solvent molecules. One should also consider that increasing the size of the organic substituents on the nitrogen atom would result in an increase in its dielectric constant, thereby reducing its effectiveness at solvating these oxide layers. Consequently, the scope of the reactions would become limited to those that form the more thermodynamically stable products. This is supported by the use of aqueous ammonia, which although allowed the formation of lead sulfide, also resulted in increased reaction time (48 h compared to 60 h) and significant product contamination (metal oxide). The presence of ammonium hydroxide in this solution not only reduces the 'cleaning' property of ammonia, but also allows an additional reaction between the hydroxide and the activated metal surface.
4.4 Conclusions of reactions in n-butylamine

Areas of current research into metal chalcogenide synthesis include the preparation of nanoparticulate materials (section 1.4, p. 31-35). They may be broadly divided into two groups – synthesis from gas phase (usually by the use of molecular precursors) and synthesis from solution (either via autoclave techniques or by refluxing solvents). These synthetic approaches offer chalcogenides of high purity with a high degree of control (resulting in very precise particle sizes) with distributions that are usually stabilised in a polymer matrix, micelle or framework structure. However, they frequently make use of H$_2$E (a toxic and lachrymatory precursor) as the chalcogen source. The bulk materials synthesised in n-butylamine have a restricted particle range of 300 – 700 Å. The elemental reactions studied are arguably more straightforward than many of the new methods, in that they do not require elevated temperatures, synthetic precursors, special reaction vessels or the use of H$_2$E. Reaction times are moderate, taking between 12 and 60 h. However, the amine promoted elemental reactions studied have little control over product crystallinity, with the materials formed being of two extremes, either X-ray amorphous (Cu$_2$S) or highly crystalline (PbS). The single phase reaction products seem also to be limited to some of the highly chalcophilic elements (in Pearson’s terms), namely the chalcogenides of silver, copper, mercury and lead.

The reactions with selenium or tellurium appear to proceed via the solid state. The solvent may act to allow intimate mixing of the reagents, removing partly reacted material to expose activated fresh metal surfaces. In terms of the sulfide reactions, it appears that the onus of reaction may lie with a mechanism involving solvated sulfur species, possibly inclusive of sulfur based radicals.

4.5 Experimental of elemental reactions in n-butylamine

All reagents were of 99.9% purity, or better, purchased from Aldrich Chemical Co. and used without further purification. Manipulations and weightings were carried out in air, with reactions in 40 cm$^3$ sample tubes. All analyses of the products were carried out using the same spectroscopic equipment as outlined in Chapter 2.

Reactions of Hg, Ag and Pb with S, Se and Te in n-butylamine

The same general reaction procedure and scale was adopted for all the reactions, as exemplified here for the synthesis of PbS.
Powdered lead metal (0.612 g, 3.06 mmol) and sulfur (0.098 g, 3.06 mmol) were added in stoichiometric amounts to 20 cm$^3$ of n-butylamine at room temperature. The mixture was magnetically stirred for 48 h. Sulfur dissolved in the n-butylamine to give a red solution, which reacted with the powdered lead to afford a black solid. The lead was not observed to dissolve into the amine solution, but rather become used up during the course of the reaction. The black solid was isolated by decanting off the amine followed by washing with first acetone (20 cm$^3$) and then CS$_2$ (2 x 20 cm$^3$). The reaction product was characterised as PbS; 0.659 g, 2.74 mmol (90 %).

All of the mercury, silver and lead chalcogenides were analysed by X-ray powder diffraction (table 4.1), FT-IR and Raman spectroscopy, SEM / EDXA 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. Notably, there were neither IR absorptions observed for N-H stretches, nor Raman absorptions for elemental sulfur. The mercury, lead and silver chalcogenides were all diamagnetic. Microanalysis (CHN) for Ag$_2$Se showed C = 0.29 %, H = 0.15 %, N = 0.08 %; and 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 procedure was adopted as outlined for PbS, the results of which are also summarised in table 4.1. The reaction of copper with sulfur produced X-ray amorphous black material, whilst with both selenium and tellurium a crystalline black material was synthesised (Cu$_{2-x}$Se and Cu$_{0.64}$Te$_{0.36}$). The reactions of arsenic and antimony with sulfur in n-butylamine produced yellow and red solids respectively, which were isolated by first decanting off the solvent and then triturating with CS$_2$ (40 cm$^3$). This procedure was also adopted for the reactions of nickel and iron with sulfur, selenium and tellurium (all of which afforded black materials). All of the reaction products mentioned were X-ray amorphous both before and after thermolysis (250 – 300 °C for 2h), with the exception of nickel with sulfur which was characterised as NiS (millerite) after the heat treatment. Reaction of zinc with sulfur in n-butylamine did produce a small amount of X-ray amorphous white solid after 7 days, which was identified as ZnS by EDXA. This analysis also suggested that the reaction only went, at best, to a 10% yield.
5.0 **Synthesis of Binary Metal Chalcogenides by Solid State Metathesis**

5.1 **Synthesis and characterisation**

The solid state reaction of metal halides MXₙ (n = 1, 2) with stoichiometric amounts of sodium chalcogenide (Na₂S₂ or Na₂E where E = S, Se, Te), in evacuated ampoules at 300 °C for 48 h, affords a range of transition- and main-group metal chalcogenides in good yield in addition to the co-produced salt (equations 5.1-5.12). Repeated washing of the highly sintered, fused product mixture with distilled water resulted in isolation of crystalline binary chalcogenides, typically of a single phase. The single phase materials synthesised are described below:

<table>
<thead>
<tr>
<th>ME₂ (M = Fe, Co, E = S, Te; NiS₂(0.4)</th>
<th>ME (MnS, FeSe, SnSe and SnTe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(0.4)E (M = Fe, Co, E = S)</td>
<td>Ni(0.4)E (E = S, Se, Te)</td>
</tr>
<tr>
<td>Ag₂E (E = S, Se, Te)</td>
<td></td>
</tr>
</tbody>
</table>

The reaction products were characterised by X-ray powder diffraction, SEM/EDX and Infra-red spectroscopy. In each case, a colour change throughout the reaction mixture was observed in the temperature range 170-220 °C, irrespective of which reagents are used, resulting in the formation of a fused black product. These reactions were not observed to proceed via a synthesis wave. The yields obtained for all reactions were typically > 90 %. All the products mentioned were characteristically black in appearance. All reaction products, after washing, showed characteristic IR absorptions for binary metal chalcogenides (broad bands between 600 and 400 cm⁻¹).

The results of the SSM reactions described above are shown in Table 5.1 and equations 5.1-5.12. With the exception of chromium trichloride (equation 5.12), all the reaction products were of sufficient crystallinity to be characterised by XRD. The phases produced, in the majority of cases, can thus be accurately determined by comparison of the derived unit cell parameters with those from literature (Table 5.1).
Table 5.1 XRD data for single phase binary transition metal chalcogenides synthesised by SSM

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Products as formed from reaction</th>
<th>Product colour</th>
<th>Phases obtained after annealing the washed material</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature Lattice Parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>2AgF + Na2S</td>
<td>NaF</td>
<td>Black</td>
<td>Ag2S (acanthite)</td>
<td>a = c = 4.46</td>
<td>a = c = 4.46</td>
</tr>
<tr>
<td>2AgF + Na2Se</td>
<td>NaF</td>
<td>Black</td>
<td>Ag2Se (naumannite)</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
<td>a = 4.33 b = 7.06 c = 7.76</td>
</tr>
<tr>
<td>2AgF + Na2Te</td>
<td>NaF</td>
<td>Black</td>
<td>Ag2Te (hessite)</td>
<td>a = 8.09 b = 4.47 c = 8.96</td>
<td>a = 8.09 b = 4.47 c = 8.96</td>
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<tr>
<td>2MnF + Na2S</td>
<td>NaF</td>
<td>Black</td>
<td>MnS (alabandite)</td>
<td>a = c = 5.24</td>
<td>a = c = 5.24</td>
</tr>
<tr>
<td>2MnF + Na2S2</td>
<td>NaF</td>
<td>Black</td>
<td>MnS (alabandite)</td>
<td>a = c = 5.24</td>
<td>a = c = 5.24</td>
</tr>
<tr>
<td>FeCl2 + Na2S</td>
<td>Black</td>
<td>Fe1.0S (x = 0.04)</td>
<td>a = 3.43 c = 3.79</td>
<td>a = 3.43</td>
<td></td>
</tr>
<tr>
<td>FeCl2 + Na2S2</td>
<td>Black</td>
<td>FeS2 (pyrite)</td>
<td>a = c = 5.41</td>
<td>a = c = 5.41</td>
<td></td>
</tr>
<tr>
<td>FeCl2 + Na2Se</td>
<td>Black</td>
<td>FeSe</td>
<td>a = 3.77 b = 5.52 c = 6.26</td>
<td>a = 3.77</td>
<td></td>
</tr>
<tr>
<td>FeCl2 + Na2Te</td>
<td>Black</td>
<td>FeTe2</td>
<td>a = 3.85 b = 5.34 c = 6.26</td>
<td>a = 3.85</td>
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<tr>
<td>CoCl2 + Na2S</td>
<td>NaCl</td>
<td>Black</td>
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<td>a = 3.38 c = 5.15</td>
<td>a = 3.38 c = 5.15</td>
</tr>
<tr>
<td>CoCl2 + Na2S2</td>
<td>NaCl</td>
<td>Black</td>
<td>CoS2</td>
<td>a = c = 5.54</td>
<td>a = c = 5.54</td>
</tr>
<tr>
<td>CoCl2 + Na2Te</td>
<td>NaCl</td>
<td>Black</td>
<td>CoTe2</td>
<td>a = 3.88 b = 5.30 c = 6.30</td>
<td>a = 3.88 b = 5.30 c = 6.30</td>
</tr>
<tr>
<td>NiCl2 + Na2S</td>
<td>NaCl</td>
<td>Black</td>
<td>Ni1.0S (x = 0.02)</td>
<td>a = c = 3.42</td>
<td>a = c = 3.42</td>
</tr>
<tr>
<td>NiCl2 + Na2S2</td>
<td>NaCl</td>
<td>Black</td>
<td>NiS2.0 (x = 0.02)</td>
<td>a = c = 5.62</td>
<td>a = c = 5.62</td>
</tr>
<tr>
<td>NiCl2 + Na2Se</td>
<td>NaCl</td>
<td>Black</td>
<td>Ni1.0Se (x = 0.06)</td>
<td>a = 3.66 c = 5.33</td>
<td>a = 3.66 c = 5.33</td>
</tr>
<tr>
<td>NiCl2 + Na2Te</td>
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<td>Black</td>
<td>Ni1.0Te (x = 0.45)</td>
<td>a = 3.78 c = 6.06</td>
<td>a = 3.78 c = 6.06</td>
</tr>
</tbody>
</table>

---

* Reagents shown with molar ratios.

b Phases characterised by X-ray powder diffraction prior to work-up of reaction product. All minor phases (< ca. 10 %) represented by square brackets.

c Colour of isolated phases (the solid material remaining after reaction product work-up).

d Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h.

* Unit cell parameters were determined for major phase binary material only.
The XRD pattern of each reaction product showed the presence of crystalline sodium halide, which was easily removed by trituration with distilled water without alteration of the metal chalcogenide. In each case, analysis by SEM showed the product to be a highly sintered, fused mass. EDXA analyses of the washed material confirmed the presence, for the majority of cases, of homogeneous products, whose elemental ratio was in good agreement with that observed by the XRD pattern (to within 2-3 atm. %). The notable exceptions to this were the reactions tin sulfide (eq. 5.10) and chromium sulfide (eq. 5.11).

5.1.1 Stoichiometrically exact crystalline products of single phase (mono-chalcogenides)
A single crystalline phase of desired stoichiometry was obtained for the following SSM reactions heated to 300 °C for 48h in sealed, evacuated glass ampoules(equations 5.1-5.4).

\[ 2\text{AgF} + \text{Na}_2\text{E} \rightarrow \text{Ag}_2\text{E} + \text{NaF} \quad (E = \text{S, Se, Te}) \]  
\[ \text{MnF}_2 + \text{Na}_2\text{S} \rightarrow \text{MnS} + 2\text{NaF} \]  
\[ \text{FeBr}_2 + \text{Na}_2\text{Se} \rightarrow \text{FeSe} + 2\text{NaBr} \]  
\[ \text{SnBr}_2 + \text{Na}_2\text{E} \rightarrow \text{SnE} + 2\text{NaBr} \quad (E = \text{Se, Te}) \]

The XRD spectra obtained for the washed Ag$_2$Se product is shown below (figure 5.1)

**Figure 5.1 XRD of washed silver selenide synthesised by SSM reactions**

![XRD spectra](image)

Key: Sample (top) – silver selenide, Ag$_2$Se  
Standard (bottom) – naumannite, Ag$_2$Se
The spectra obtained for the unwashed product of manganese sulfide is shown below (figure 5.2), showing the formation of the co-produced salt (NaF).

**Figure 5.2 XRD of unwashed manganese disulfide synthesised by SSM reactions heated to 300 °C for 48h**

![XRD graph](image)

---

Key: Sample (top) – MnS  
Standard (bottom) – abalandite, MnS (blue), NaF (red)

### 5.1.2 Non-stoichiometric monochalcogenide crystalline products of single phase

In addition, a series of SSM reactions heated to 250-300 °C for 48h in sealed, evacuated glass ampoules, afforded single crystalline phases of metal deficient chalcogenides with stoichiometry $M_{(1-x)}E$ (equations 5.5-5.7).

\[
\begin{align*}
MX_2 + Na_2S & \rightarrow M_{(1+x)}S + 2NaCl \quad (MX_2 = FeBr_2, CoCl_2) \quad (5.5) \\
NiCl_2 + Na_2E & \rightarrow Ni_{(1+x)}E + 2NaCl \quad (E = S, Se, Te) \quad (5.6) \\
MX_2 + Na_2Te & \rightarrow M_{0.5}Te + 0.5M + 2NaX \quad (M = Fe, Co) \quad (5.7)
\end{align*}
\]

Accurate stoichiometries of all the products described in equations 5.5 and 5.6 were derived from application of Vegard’s law to the X-ray diffraction peak positions. The results are
shown in Table 5.1, and represent an average stoichiometric value of the four most intense peaks in the range \(20^\circ \leq \theta \leq 70^\circ\). In the case the products described in equation 5.7, the X-ray powder diffraction pattern only showed the presence of \(\text{MTe}_2\) and the co-produced salt. Upon analysis by EDXA, however, regions of metal were detected. Consequently, one can surmise the reaction conditions were insufficient to induce sufficient crystallinity in the X-ray amorphous elemental metal.

5.1.3 Stoichiometrically exact crystalline products of single phase (disulfides)

The reactions that afforded a single phase of crystalline metal dichalcogenides, under the same reactions conditions described above, are described in equation 5.8.

\[
\text{MX}_3 + \text{Na}_3\text{S}_3 \rightarrow \text{MS}_2 + 2\text{NaX} \quad \text{(MX}_3 = \text{FeBr}_2, \text{CoCl}_2) \quad (5.8)
\]

Figure 5.3 (below) shows the spectra obtained for the unwashed sample of \(\text{FeS}_2\). Note both the formation of the co-produced salt (NaBr) as well as a single (pyrite) phase of iron disulfide.

**Figure 5.3 XRD of unwashed iron disulfide synthesised by SSM reactions**

heated to \(300^\circ\) C for 48h

Key: Sample (top) – iron disulfide

Standard (bottom) – *pyrite*, \(\text{FeS}_2\) (red), NaBr (blue)
In addition to the aforementioned reactions (equation 5.8), a slightly sulfur deficient phase of nickel disulfide (Ni$_{x}$S$_{2}$) was synthesised from the reaction of Na$_2$S$_2$ with NiCl$_2$. The XRD spectrum of the *unwashed* material is shown in below (figure 5.4). Note both the formation of the co-produced salt (NaCl) as well as the shift in 20 values to lower angles when compared to the standard peak positions for vaesite.

**Figure 5.4 XRD of unwashed nickel disulfide synthesised by SSM reactions**

heated to 300 °C for 48h

Key: Sample (spectrum) – nickel disulfide Standards (sticks) – *vaesite*, Ni$_2$S$_2$ (red), NaCl (blue)

5.1.4 Crystalline and amorphous products of multiple phases

Equations 5.9-5.12 show those reactions that did not produce products of single phase from SSM reactions heated to 250-300 °C for 48h in sealed, glass ampoules.

\[
\text{ZnCl}_2 + \text{Na}_2\text{S}_2 \rightarrow \text{ZnS}^* + 2\text{NaCl} + \text{S} \quad (5.9)
\]

* Two distinct phases of zinc sulfide were characterised by XRD (sphalerite and α-wurtzite-2H).

Whilst it was not possible to synthesise ZnS$_2$ from the reaction of ZnCl$_2$ with Na$_2$S$_2$, the resultant metathesis afforded both cubic and hexagonal structures of ZnS with the
formation of free sulfur (reaction 9). Interestingly, previous studies have shown that the reaction of ZnCl\textsubscript{2} with Na\textsubscript{2}S results only in the more thermodynamically stable hexagonal phase, suggesting that the reactions studied here may follow a less energetic route.

SnBr\textsubscript{2} + Na\textsubscript{2}S → SnS + Sn\textsubscript{2}S\textsubscript{3}* + Sn\textsubscript{2}S\textsubscript{4} + 2NaCl \hspace{1cm} (5.10)

* These are minor phases

The reaction product of SnBr\textsubscript{2} with Na\textsubscript{2}S (annealed at 300 °C) showed appreciable differences in atomic distribution by EDXA. X-ray powder diffraction studies showed the presence of two tin sulfide phases (SnS and Sn\textsubscript{2}S\textsubscript{3}). Upon increasing the annealing temperature to 500-550 °C, the proportion of tin sesquisulfide in the reaction product was greatly reduced (to a regional deviation of 2-5 % from a 1:1 ratio of Sn : S, as assessed by EDXA). This is in agreement with the formation of tin sulfide thin films\textsuperscript{168} by APCVD (via the reaction of SnCl\textsubscript{4} with H\textsubscript{2}S). These studies show that for a substrate temperature of 525 °C Sn\textsubscript{2}S\textsubscript{3} predominates, whilst at T = 545 °C SnS was deposited.

2VCl\textsubscript{3} + 3Na\textsubscript{2}S → V\textsubscript{2}S\textsubscript{3} + 6NaCl + VOCl\textsuperscript{+} + Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}.5H\textsubscript{2}O\textsuperscript{+} \hspace{1cm} (5.11)

* The origin of these impurities is unknown, although it is likely to be the result of both slightly impure vanadium (III) chloride and moisture within the reaction vessel.

2CrCl\textsubscript{3} + 3Na\textsubscript{2}S → NaCl + ‘amorphous material’ \hspace{1cm} (5.12)

The reaction of CrCl\textsubscript{3} with Na\textsubscript{2}S shows the formation of a co-produced salt (reaction 5.11), suggesting that a metathesis reaction has occurred. However, the chromium product was amorphous to X-rays, even after annealing at 300 °C for 48h. EDXA studies of this X-ray amorphous material, both before and after washing, showed variable elemental composition of Cr and S over many surface spots, suggesting either the existence of different chromium sulfide phases or impurities resulting from oxygen contamination (the X-ray detector used excludes the analysis of elements lighter than sodium). The origin of impurities is unknown, although contamination from the reaction vessel has been observed in SSM reactions before.\textsuperscript{61-68} However, one must appreciate the inaccuracy of such characterisation. It should be remembered that the Cr-S system has six discrete phases in the composition...
range \( \text{Cr}_{0.95} \text{S} \) to \( \text{Cr}_{1.2} \text{S} \), each of which may also be encountered in a non-stoichiometric form.\(^4\)

### 5.2 Discussion and mechanistic evaluation

#### 5.2.1 Role of chalcogenide precursor

As already mentioned in section 1.3a (p. 19-23), previous studies have shown that metathetical reactions between solid alkali metal chalcogenide and liquid metal halide occur very rapidly, with a massive evolution of heat. Often this gives rise to a characteristic thermal flash, with temperatures in excess of 1000 °C being reported. This shows that the reactions proceed from initiation once the solid-state diffusion barrier has been overcome. For solid-state reactions, it has been shown that propagation will only occur once the heat of reaction is sufficient to melt the co-produced salt, which proceeds through the reaction mixture. In the reactions observed here, however, a uniform change in colour of the reagents (rather than a thermal flash) occurs once the surroundings reach approximately 200 °C, irrespective of which metal halide was used. This suggests that a phase change occurred in the sodium chalcogenide. In addition, the heats of reaction are 200 - 250 KJmol\(^{-1}\), and so are of insufficient exothermicity to proceed via a propagation wave.\(^5\) Instead, it is likely that the intimate mix of reagents allows neighbouring grains to react via close contact once the sodium chalcogenide undergoes a phase change, giving rise to an observed ‘dark wave’ front through the material.\(^6\) This process would be enhanced by the small particle sizes of the chalcogenide precursor (freshly prepared from a room temperature elemental combination reaction in liquid ammonia.), by allowing both a high surface area of contact with the metal halide and a lower initiation temperature. This would support propagation of a less exothermic reaction through the material without the massive evolution of heat normally associated with SSM reactions.

The reactions were characteristically rapid, with a dark, fused mass being formed within a few minutes. With the exception of the reaction of chromium trichloride and sodium sulfide, the reactions showed limited crystallinity once the reaction was complete. Exposing the reaction to elevated temperatures for prolonged periods of time, therefore, served only to anneal the products, thereby enhancing their crystallinity. These reactions are likely to exhibit an enhanced reaction rate. It has been recorded that a reduction in the reagent
particle size increases the rate of reaction by reducing the maximum size of the diffusion barrier created by the formation of the reaction products. 56

5.2.2 Kinetic products
The relatively low temperatures at which these SSM reactions occur allow some degree of stoichiometric control in the reaction by varying the sulfur content of the precursor. Thus it is possible to form both 'MS' and 'MS2' (where M = Fe, Co, Ni) from the metal (II) halide by using Na2S and Na2S2 respectively. In addition, the low reaction temperature may allow the formation of kinetic products, and so the formation of mixed phases of tin sulfide. Within the reaction temperature range SnS, SnS3 and SnS2 are all kinetically stable (the greater thermodynamic stability of SnS only occurring at temperatures above 300 °C, as shown by SEM analysis of the sample annealed at 500 °C).

5.2.3 Mechanistic pathway
Solid state metathetical reactions are believed to proceed via two possible pathways, 56, 67 reductive recombination or ionic metathesis. The latter involves the exchange of ions within a sodium halide melt. However, we believe the reactions resulting in metal mono-chalcogenides proceeded via partial reduction of the reagents to the elements, followed by their recombination to form the product (equations 5.14 and 5.15).

\[ \text{MX}_2(s) + \text{Na}_2\text{E}(s) \rightarrow [\text{M} + \text{E} + 2\text{NaX}] \rightarrow \text{ME}(s) + 2\text{NaX}(s) \quad (5.14) \]

\[ \text{MX}_2(s) + \text{Na}_2\text{S}_2(s) \rightarrow [\text{M} + 2\text{S} + 2\text{NaX}] \rightarrow \text{MS}_2(s) + 2\text{NaX}(s) \quad (5.15) \]

First there is the presence of elemental metal in the synthesis of the metal ditellurides (equation 5.7). Secondly, both the metal halides used and metal chalcogenides observed have a high degree of covalency. This may be rationalised both in terms of the small divalent cations interacting with 'soft' polarizable anions, as well as the structures that the metal chalcogenides adopt (the nickel arsenide structure exhibits significant metal-metal interaction). Finally, the formation of kinetic products may allow a departure from a purely metathetical reaction mechanism to one which incorporates a degree of redox (since both SnII and SnIV states are present). This in turn supports the theory that the transition state of the SSM reactions studied may involve discrete elements as opposed to solely an exchange
of the parent ions. This is further supported by the reactions affording metal tellurides; with particular attention being drawn to those of FeBr₂ and CoCl₂ with twice the molar ratio of Na₂Te. The synthesis of Na₂Te from grey tellurium and sodium in liquid ammonia shows minor phases of NaTe and NaTe₂ by XRD analysis. Upon reaction, however, the only metal tellurides observed were those of the target compound, FeTe₂ and CoTe₂, with any excess tellurium appearing as the element after washing. There was no evidence in any of the products of polytelluride anions, even though they persist in the precursor above 300 °C.

The synthesis of metal disulfides as stoichiometrically exact, single phase materials, may suggest preservation of the [S-S]²⁻ unit present in the Na₅S₂ precursor. If this is the case then these reactions would follow an ionic exchange within the phase change of the sodium sulfide precursor (equation 5.16).

\[
M_{2(\alpha)} + Na₂S_{2(\alpha)} \rightarrow [M^{2+} + S_{2}^{2-} + 2NaX] \rightarrow MS_{2(\alpha)} + 2NaX_{(\alpha)}
\] (5.16)

However, one must also consider that these materials formed the most thermodynamically stable sulfides as well as the more thermodynamically stable phase of the disulfide - the distorted NaCl (pyrite) structure as opposed to the less regular marcasite structure. Consequently, so long as the in situ ratio of the elements remains uniform and exact, reductive recombination remains a plausible mechanistic pathway.

5.2.4 Metal deficient binary chalcogenides - M(1-x)E

The metal deficient, binary transition metal chalcogenides (M(1-x)E) synthesised by the solid state metathetical reaction between metal halide and sodium chalcogenide (as described in section 5.1) may be broadly classified according to their exact stoichiometry (described in the table below).

<table>
<thead>
<tr>
<th>M(1-x)E where X is small</th>
<th>M = Co, Fe, Ni</th>
<th>E = S</th>
<th>0.03 &lt; X &lt; 0.07</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(1-x)E where X is large</td>
<td>M = Co, Fe, Ni</td>
<td>E = Te</td>
<td>X = 0.5 (Fe, Co), X = 0.45 (Ni)</td>
</tr>
</tbody>
</table>

Defect solids with small x-values

It is well known that the sulfides and tellurides of iron, cobalt and nickel adopt the structure of nickel arsenide. Therefore, they may be described as octahedrally coordinated metal
atoms with two near metal neighbours that are coplanar with four of the chalcogenide atoms. This close approach of dipositive metal atoms (2.60-2.68 Å in FeS, CoS and FeS) accounts for their semiconductor, semimetallic or alloylike behaviour, and infers a high degree of covalency within the solid.

They are also well known for their non-stoichiometric phases. FeS has been well characterised in the literature and is typical of these types of transition metal chalcogenide. They commonly adopt the nickel arsenide structure within a limited compositional range (50-55 atm. % sulfur for the Fe-S system). Stoichiometric unity is rare, the apparent excess of chalcogen arising through the occurrence of randomly distributed vacancies of metal ions within the lattice. In the case of iron (II) sulfide, electroneutrality is preserved through the presence of suitable quantities of Fe$^{3+}$. Indeed, it is electron transfer from Fe$^{2+}$ to Fe$^{3+}$ that results in the p-type conduction of metal deficient FeS (via a virtual migration of Fe$^{3+}$ ions). Such materials are single compounds with a variety of possible phases, and are therefore best described as having a stoichiometry of Me$_{(1-x)}$E. Retention of the structure over a range of x-values denotes characteristics of a solid solution, and so has allowed application of Vegard's Law to determine accurately the extent of the non-stoichiometric defects in the materials synthesised by deriving an exact stoichiometry (table 5.1). For small x-values one can rationalise the introduction of defects into an initially perfect structure on the basis that the marked increase in entropy is large enough to overcome the unfavourable reduction in bonding energy. So long as the TAS term is large enough to outweigh the loss in ΔH, then the free energy of formation of defects will occur, up to a limiting defect concentration.

**Defect solids with large x-values (metal ditellurides)**

Literature shows that the tellurides of iron, cobalt and nickel can adopt the nickel arsenide structure for values of 0.5 ≤ x ≤ 1. Metal atoms may be progressively removed from the structure at unity (MTe) until alternate planes of metal atoms are missing ('MTe$_2$'). It is energetically more likely that electroneutrality of the structure is preserved through the formation of polytelluride anions (Te$_2^2$) rather than the formation of M$^{IV}$ cations. The metathetical reactions undertaken to form the tellurides of iron and cobalt from metal (II) halides and disodium telluride may thus be expressed as equation 5.13.
\[ \text{MX}_{2\text{s}} + \text{Na}_2\text{Te}_{2\text{s}} \rightarrow \frac{1}{2}\text{MTe}_{2\text{s}} + \frac{1}{2}\text{M}_{(s)} + 2\text{NaX}_{(s)} \quad (M = \text{Fe, Co}) \quad (5.13) \]

Since the \(\Delta S\) term is small for a purely solid state system, it is more useful to rationalise the formation of \(\text{M}_{2\text{s}},\text{Te}\) rather than \(\text{MTe}\), it is more useful to discuss the relative thermodynamic stabilities of the two possible products, as described by the product equilibrium (equation 5.14).

\[ \text{MTe}_{(s)} \leftrightarrow \text{M}^{II}[\text{Te}^{II}_{(s)}] + \text{M}^{0}_{(s)} \quad (5.14) \]

By considering the comparative heats of formation of \(\text{M-Te}, \text{M-M}\) and \(\text{Te-Te}\), it is apparent that for the low temperature at which these SSM reactions occurred, the most thermodynamic product was one with 50% of the metal ions removed. Increasing the reaction temperature would favour the reverse reaction, and so the synthesis of \(\text{MTe}\).

5.3 General Conclusions

The aforementioned study has shown that solid state metathesis reactions of low oxidation state metal halides with sodium chalcogenides offer a convenient dual step route to the synthesis of a range of crystalline transition metal chalcogenides in high yield (>90 %). In addition, we have extended the scope of this general procedure to the synthesis of binary mono-chalcogenides of manganese, iron, cobalt, nickel, silver and tin, in addition to the disulfides of iron, cobalt and nickel. In the majority of cases a single, crystalline and stoichiometric phase is produced.

Most conventional syntheses of metal chalcogenides require either multiple steps with long processing times, the existence of specific precursors or the use of highly toxic reagents. These problems are circumvented by the metathetical solid state reaction of metal halides with alkali metal chalcogenides. Once initiated, these intimately mixed reagents undergo a rapid, self-propagating reaction to produce highly sintered metal chalcogenides and a co-produced salt. The alkali metal halide co-produced salt is easily removed by trituration, affording pure metal chalcogenide.
The mechanistic studies of the synthesis of ME₂ (M = Mo, W; E = S, Se, Te) from filament initiated SSM reactions involving MoCl₅ and WCl₆ (carried out by Kaner et al.),²⁶ suggest that since the temperature of reaction is limited by the melting point of the co-produced salt (with Hess’s Law calculations showing that approximately 90% of the reaction enthalpy originating from the heat of formation of the highly crystalline alkali metal halide), both product crystallinity and stoichiometry would be optimised by the use of high oxidation state metal fluorides or chlorides. Consequent work resulted in the formation of stoichiometrically exact and crystalline NiS₂ (vaesite) from the reaction of Na₂S with K₂[NiF₆].¹⁵ We have shown that metal halides in their common low oxidation states can be used in conjunction with facile heating (300 °C for 48 h) to afford a selection of crystalline binary metal mono- and dichalcogenides with, for the most part, preservation of the oxidation state of the metal. Application of Vegard’s Law to the XRD spectrum of the Ni₁₋₀ₓS₂ product obtained, showed it to be a slightly metal deficient phase (with an empirical formula of NiS₁₋₀₂). By changing the sulfide precursor to Na₂S₂, the vaesite structure was obtained. However, upon close examination of the XRD spectrum (figure 5.4) a shift in peak position to lower 2θ values is observed, signifying a slight increase in size of the unit cell. This observation is consistent with the formation of a slightly metal deficient phase NiS₂₋ₓ, and was not reported with the use of K₂[NiF₆].¹⁵ With the use of alkali metal chalcogenide reagents prepared from a room temperature synthesis, it is possible to achieve a low temperature SSM reaction, thereby allowing the possibility of kinetic product formation and amorphous materials. The synthesis of tin sesquisulfide (as a minor product), as well as single phases of both cobalt and iron ditelluride, suggest that these three reactions proceed via a reductive recombination pathway as opposed to one solely involving metathetical exchange of ions.

5.4 Experimental

All the initial reagents used were of 99.9 % purity, or better, and purchased from Aldrich Chemical Company and were used without further purification. Ammonia was purchased from BOC and used without drying. All manipulations were carried out in a dinitrogen filled glove box. Reactions involving the synthesis of the sodium chalcogenide precursors
were carried out (using Schlenk techniques) in thick walled (3-4 mm), teflon-in-glass, sealed Youngs-type Schlenk tubes (sealed by a large rota-flow tap) which were surrounded by safety netting. The solid state metathesis reactions were performed in sealed, evacuated ampoules using a Lenton Thermal Designs tube furnace. X-ray powder diffraction patterns were determined on a Siemens D5000 transmission powder diffractometer using germanium monochromated Cu-Kα1 radiation (λ = 1.504 Å). They were indexed using either TREOR or METRIC-LS programmes (lattice parameters matched to within 0.02Å with literature). The SEM / EDXA measurements were determined on a Jeol JSM820 microscope, equipped with a Kevec Quantum Delta 4 detector and a Hitachi SEM S-570 camera. The electron beam was focused (1μm spot at surface) with an excitation energy of 20 keV. Electron-probe analyses were conducted on a Jeol EMA, using polished samples, and compared to metal and chalcogen standards. FT-IR spectra were recorded using a Nicolet 205 FT-IR spectrometer.

**Preparation of sodium chalcogenide**

Na₂E (E = S, Se, Te) and Na₂S₂ were prepared by the direct combination of stoichiometric quantities of sodium metal and elemental chalcogen in liquid ammonia. These reactions were carried at room temperature in teflon-in-glass Youngs-type pressure vessels, using Schlenk techniques. Once prepared, the sodium chalcogenide was used immediately in the SSM reactions.

**Reaction of sodium chalcogenide with metal halide**

The same general reaction scale and procedure was adopted for all these reactions, as exemplified here for FeS₂.

Freshly prepared disodium disulfide (100 mg, 0.91 mmol.) and iron (II) bromide (200 mg, 0.91 mmol.) were ground together inside a glove box, using an agate pestle and mortar, until intimately mixed. The mixture was added to an ampoule, which was then sealed under vacuum and heated slowly (ca. 20 °C/min). In each case, a colour change throughout the mixture was observed once the temperature reached 170-220 °C, resulting in the formation of a fused black product. A synthesis wave was not observed. The product was then annealed for 48 h at 300 °C, after which the product was triturated with 3x20 cm³ distilled water, before being dried under vacuum. The resultant black powder was analysed by XRD,
SEM / EDXA and IR spectroscopy. XRD analysis was also carried out on the pre-washed reaction product.

Table 5.2 SEM / EDXA data for all products of SSM reactions heated to 250-300 °C for 48h in sealed glass ampoules

<table>
<thead>
<tr>
<th>Target Material</th>
<th>Description of product morphology</th>
<th>Ratio of elements (± 2-3 %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Elemental ratio</td>
</tr>
<tr>
<td>AgS</td>
<td>Fused black and white matter</td>
<td>Ag : S</td>
</tr>
<tr>
<td>AgSe</td>
<td>Fused black and white matter</td>
<td>Ag : Se</td>
</tr>
<tr>
<td>AgTe</td>
<td>Fused black and white matter</td>
<td>Ag : Te</td>
</tr>
<tr>
<td>MnS</td>
<td>Fused black and white matter</td>
<td>Mn : S</td>
</tr>
<tr>
<td>MnS2</td>
<td>Fused black and white matter</td>
<td>Mn : S</td>
</tr>
<tr>
<td>FeS</td>
<td>Fused black and white matter</td>
<td>Fe : S</td>
</tr>
<tr>
<td>FeSe</td>
<td>Fused black and white matter</td>
<td>Fe : Se</td>
</tr>
<tr>
<td>FeTe</td>
<td>Fused black and white matter</td>
<td>Fe : Te</td>
</tr>
<tr>
<td>CoS</td>
<td>Fused black and white matter</td>
<td>Co : S</td>
</tr>
<tr>
<td>CoTe</td>
<td>Fused black and white matter</td>
<td>Co : Te</td>
</tr>
<tr>
<td>NiS</td>
<td>Fused black and white matter</td>
<td>Ni : S</td>
</tr>
<tr>
<td>NiSe</td>
<td>Fused black and white matter</td>
<td>Ni : Se</td>
</tr>
<tr>
<td>NiTe</td>
<td>Fused black and white matter</td>
<td>Ni : Te</td>
</tr>
<tr>
<td>FeS₂</td>
<td>Fused black and white matter</td>
<td>Fe : S</td>
</tr>
<tr>
<td>CoS₂</td>
<td>Fused black and white matter</td>
<td>Co : S</td>
</tr>
<tr>
<td>NiS₂</td>
<td>Fused black and white matter</td>
<td>Ni : S</td>
</tr>
<tr>
<td>ZnS₂</td>
<td>Fused black and white matter</td>
<td>Zn : S</td>
</tr>
<tr>
<td>SnS (300 °C)</td>
<td>Fused black and white matter</td>
<td>Sn : S</td>
</tr>
<tr>
<td>SnS (550 °C)</td>
<td>Fused black and white matter</td>
<td>Sn : S</td>
</tr>
<tr>
<td>V₂S₃</td>
<td>Fused black and white matter</td>
<td>V : S</td>
</tr>
<tr>
<td>Cr₂S₃</td>
<td>Fused black and white matter</td>
<td>Cr : S</td>
</tr>
</tbody>
</table>

¹ Materials synthesised by SSM reactions of transition metal halides with sodium chalcogenides.
² Assessed by SEM prior to washing with distilled water.
³ As assessed by EDXA (spot size - 1 micron) of washed samples. Approximate surface abundance of multiple phases is expressed as a percentage (assessed using back-scattered electrons).
6.0 Metathetical reactions in liquid ammonia

6.1 General introduction

The addition of stoichiometric amounts of low valent metal halides to liquid ammonia solutions of disodium chalcogenide afforded a range of both crystalline and X-ray amorphous metal chalcogenides in good yield (> ca. 95 %). The reaction times, although varied, were all assessed to be within 36 h from the formation of material characteristic in colour to the desired product. In most cases, XRD analysis of the pre-annealed material showed the presence of crystalline alkali metal halide, suggesting that the reactions proceed via a metathetical route. Repeated washing of the material with CS₂ and then distilled water resulted in isolation of the metal chalcogenides. IR studies of the isolated products showed absorptions characteristic of the desired material, with no N-H stretches being detected. Facile annealing of the isolated X-ray amorphous material at 250-300 °C for 48h induced sufficient crystallinity for analysis by X-ray powder diffraction. Both binary and ternary materials have been synthesised, and fully characterised by XRD in conjunction with SEM / EDXA.

As the final chapter in this thesis the reactions undertaken, where possible, will be described with comparison to previous chapters.

6.2 Binary chalcogenides

A selection of both crystalline and X-ray amorphous binary metal chalcogenides were synthesised by metathesis in liquid ammonia at room temperature. The results are summarised in table 6.1 (crystalline materials) and 6.2 (X-ray amorphous materials).

6.2.1 Crystalline materials

\[
PbCl_{2(s)} + 2Na_2E \rightarrow PbE_{(s)} + 2NaCl_{(s)} \quad (E = S, Se, Te) \quad (6.1)
\]

\[
2AgF_{(s)} + 2Na_2E \rightarrow M_2E_{(s)} + 2NaF_{(s)} \quad (E = S, Se, Te) \quad (6.2)
\]
Lead chalcogenides crystallised at room temperature in the familiar mineral forms of galena (PbS), clausthalite (PbSe) and altaite (PbTe) - table 6.1; figure 6.1

Table 6.1 XRD data for crystalline binary transition metal chalcogenides synthesised by metathetical reactions in liquid ammonia at room temperature

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Products as formed from reaction (identified by XRD)</th>
<th>Product colour</th>
<th>Phases obtained after annealing the washed material</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature(^a^) Lattice Parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>2AgF + Na(_2)S</td>
<td>Ag(_2)S (acanthite) + NaF</td>
<td>Black</td>
<td>Ag(_2)S (acanthite)</td>
<td>(a = c = 4.48)</td>
<td>(a = c = 4.46)</td>
</tr>
<tr>
<td>2AgF + Na(_2)Se</td>
<td>Ag(_2)Se (naumannite) + NaF</td>
<td>Black</td>
<td>Ag(_2)S (naumannite)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
<td>(a = 4.33) (b = 7.06) (c = 7.76)</td>
</tr>
<tr>
<td>2AgF + Na(_2)Te</td>
<td>Ag(_2)Te (hessite) + NaF</td>
<td>Black</td>
<td>Ag(_2)S (acanthite)</td>
<td>(a = 8.07) (b = 4.47) (c = 8.94)</td>
<td>(a = 8.09) (b = 4.47) (c = 8.96)</td>
</tr>
<tr>
<td>2TlCl + Na(_2)S</td>
<td>Tl[Tl(_2)S(_2)] + NaCl</td>
<td>Black</td>
<td>Tl[Tl(_2)S(_2)]</td>
<td>(a = 7.79) (c = 6.80)</td>
<td>(a = 7.79) (c = 6.80)</td>
</tr>
<tr>
<td>TlCl + Na(_2)Se</td>
<td>Tl[Tl(_2)Se(_2)] + NaCl</td>
<td>Black</td>
<td>Tl[Tl(_2)Se(_2)]</td>
<td>(a = 8.02) (c = 7.00)</td>
<td>(a = 8.02) (c = 7.00)</td>
</tr>
<tr>
<td>2TlCl + Na(_2)Te</td>
<td>Tl(_2)Te(_3) + NaCl</td>
<td>Black</td>
<td>Tl(_2)Te(_3)</td>
<td>(a = 8.93) (c = 12.62)</td>
<td>(a = 8.92 (c = 12.61 ) (5)</td>
</tr>
<tr>
<td>PbCl + Na(_2)S</td>
<td>PbS (galena) + NaCl</td>
<td>Black</td>
<td>PbS (galena)</td>
<td>(a = c = 5.93)</td>
<td>(a = c = 5.93)</td>
</tr>
<tr>
<td>PbCl + Na(_2)Se</td>
<td>PbSe (clausthalite) + NaCl</td>
<td>Black</td>
<td>PbSe (clausthalite)</td>
<td>(a = c = 6.12)</td>
<td>(a = c = 6.12)</td>
</tr>
<tr>
<td>PbCl + Na(_2)Te</td>
<td>PbTe (altaite) + NaCl</td>
<td>Black</td>
<td>PbTe (altaite)</td>
<td>(a = c = 6.46)</td>
<td>(a = c = 6.46)</td>
</tr>
</tbody>
</table>

\(^a^\) Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.
\(^b^\) Phases characterised by X-ray powder diffraction prior to work-up of reaction product.
\(^c^\) Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.
\(^d^\) Unit cell parameters were determined for the binary material only.
Figure 6.1 XRD patterns of pre-annealed lead selenide (top spectrum) and lead telluride (bottom spectrum) obtained from metathetical reactions in liquid ammonia at room temperature

Key: * peaks relating to co-produced salt (NaCl)
Top display: Sample (spectrum) – lead selenide Standard (green sticks) – claustralite, PbSe
Bottom display: Sample (spectrum) – lead telluride Standard (red sticks) – altaite, PbTe

Similarly, silver chalcogenides were found to crystallise at room temperature in the common mineral forms of acanthite (Ag₂S), naumannite (Ag₂Se) and hessite (Ag₂Te); table 6.1.

Reaction of a 2:1 ratio of TlCl and Na₂E allows two theoretical products - Tl₂E (by the simple metathetical exchange of ions) or Tl[TIE₂] (‘TIE’ by partial redox of the ions, section 3.3.3). The reactions undertaken in liquid ammonia are described by equations 6.3, 6.4 (minor phases in italic).

\[
4\text{TiCl}_4(\text{s}) + 2\text{Na}_2\text{E}_{(\text{am})} \rightarrow \text{Tl}[\text{TlE}_2]_{(\text{s})} + \text{Tl}^+ + 2\text{NaCl}_{(\text{s})} \quad (E = \text{S, Se}) \quad (6.3)
\]

\[
6\text{TiCl}_4(\text{s}) + 3\text{Na}_2\text{Te}_{(\text{am})} \rightarrow \text{Tl}_{(6-x)}\text{Te}_{3(\text{s})} + 2\text{NaCl}_{(\text{s})} + \text{Tl}^+ \quad (x = 1) \quad (6.4)
\]
Comparison with the analogous elemental combination reactions in both liquid ammonia (equations 2.5, 2.15 and 2.17) and n-butylamine (reactions 4.5) show that the formation of an inhomogeneous product consisting of a single, crystalline phase of TlS and Tl(6-x)Te_3 and corresponding excess element is common. The metathetical approach to the formation of thallium (I) selenide is similar to n-butylamine assisted elemental combination in the formation of crystalline TlSe. Only by elemental combination in liquid ammonia was multiple crystalline phases of thallium selenide observed (Tl_xSe_y, Tl_2Se, TlSe; equation 2.17)

6.2.2 X-ray amorphous materials (minor phases given in italics)

Equations 6.5-6.6 describe liquid ammonia mediated, solid state metathesis reactions that afforded amorphous materials after 36h at room temperature. In each case, annealing the products at 250-300 °C for 3h under dinitrogen afforded sufficient crystallinity for full characterisation by X-ray powder diffraction (data given in table 6.2)

\[
\begin{align*}
MCl_{2(\text{am})} + \text{Na}_2\text{S}_{(\text{am})} & \rightarrow \text{MS}_{(s)} + 2\text{NaCl}_{(s)} \quad (M = \text{Ni, Zn, Cd, Hg}) \\
\text{HgCl}_{2(\text{am})} + \text{Na}_2\text{E}_{(\text{am})} & \rightarrow \text{HgE}_{(s)} + 2\text{NaCl}_{(s)} \quad (E = \text{Se, Te})
\end{align*}
\]

(6.5) (6.6)

Annealing led to product crystallisation as common mineral structures: millerite (NiS), wurtzite (ZnS), greenockite (CdS), tiemannite (HgSe) and colaradoite (HgTe). Interestingly, only β-HgS (metacinnebar) was present after annealing. Since it is less thermodynamically stable than α-HgS, one may assume that β-HgS is the sole product from the metathetical reaction. This suggests that liquid ammonia can support formation of kinetic phases from metathetical reactions.

The XRD patterns of ZnS (figure 6.2), CdS (figure 6.3) and HgS show broadened peaks indicative of the formation of bulk materials with restricted (nanometer) particle size. Average particle size was determined by application of the Scherrer equation\textsuperscript{138} to the spectra. Interestingly, the average size of the crystallites is the direct result of the annealing conditions under which the X-ray amorphous powders were annealed.

Richard, 155
Figure 6.2 XRD pattern for annealed zinc sulfide, ZnS (250-300 °C)

This pattern shows a single phase of ZnS (wurtzite) with average particle size of 9.9(6) nm.

Figure 6.3 XRD pattern for annealed cadmium sulfide, CdS (250-300 °C)

This pattern shows a single phase of CdS (greenockite) with average particle size of 38.9 nm. The annealed sample of mercury sulfide β-HgS had an average particle size of 23.9 nm. The remaining binary materials described show average particle sizes typical of HgSe (tiemannite) with 52.6(8) nm.
Table 6.2 XRD data for amorphous binary transition metal chalcogenides

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Pre-wash material</th>
<th>Product colour</th>
<th>Phases obtained after annealing the washed material</th>
<th>Lattice Parameters (Å (± 0.01))</th>
<th>Literature Lattice Parameters / Å&lt;sup&gt;139&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Black</td>
<td>NiS (millerite)</td>
<td>$a = c = 3.42$</td>
<td>$a = c = 3.42$</td>
</tr>
<tr>
<td>ZnCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Yellow</td>
<td>ZnS (wurzite)</td>
<td>$a = 3.82$</td>
<td>$c = 6.25$</td>
</tr>
<tr>
<td>CdCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Yellow</td>
<td>CdS (greenockite)</td>
<td>$a = 4.14$</td>
<td>$c = 6.72$</td>
</tr>
<tr>
<td>2CuBr + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaBr</td>
<td>Black</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;S (chalocite) + [Cu&lt;sub&gt;1-8&lt;/sub&gt;S, Cu&lt;sub&gt;9&lt;/sub&gt;S]</td>
<td>$a = 3.96$</td>
<td>$c = 6.78$</td>
</tr>
<tr>
<td>CuCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Black</td>
<td>CuS (covelite)</td>
<td>$a = 3.76$</td>
<td>$c = 16.21$</td>
</tr>
<tr>
<td>CuCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;Se</td>
<td>NaCl</td>
<td>Black</td>
<td>CuSe (klockmannite) + [CuSe&lt;sub&gt;2&lt;/sub&gt; (krutaite)]</td>
<td>$a = 3.93$</td>
<td>$c = 17.20$</td>
</tr>
<tr>
<td>CuCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;Te</td>
<td>NaCl</td>
<td>Black</td>
<td>Cu&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;2&lt;/sub&gt; + Cu&lt;sub&gt;4&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Identified by standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>HgCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Black</td>
<td>β-HgS metacinnebar</td>
<td>$a = c = 5.85$</td>
<td>$a = c = 5.85$</td>
</tr>
<tr>
<td>HgCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;Se</td>
<td>NaCl</td>
<td>Black</td>
<td>HgSe (tiemannite)</td>
<td>$a = c = 6.08$</td>
<td>$a = c = 6.07$</td>
</tr>
<tr>
<td>HgCl&lt;sub&gt;2&lt;/sub&gt; + Na&lt;sub&gt;2&lt;/sub&gt;Te</td>
<td>NaCl</td>
<td>Black</td>
<td>HgTe (coloradoite)</td>
<td>$a = c = 6.46$</td>
<td>$a = c = 6.45$</td>
</tr>
<tr>
<td>2GaCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Black</td>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = 3.68$</td>
<td>$c = 6.03$</td>
</tr>
<tr>
<td>2GaCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;Se</td>
<td>NaCl</td>
<td>Black</td>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = 6.66$</td>
<td>$c = 11.65$</td>
</tr>
<tr>
<td>2GaCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;Te</td>
<td>NaCl</td>
<td>Black</td>
<td>Ga&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = c = 5.90$</td>
<td>$a = c = 5.90$</td>
</tr>
<tr>
<td>2InCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>NaCl</td>
<td>Black</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;S&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = c = 10.78$</td>
<td>$a = c = 10.78$</td>
</tr>
<tr>
<td>2InCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;Se</td>
<td>NaCl</td>
<td>Black</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;Se&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = 7.12$</td>
<td>$c = 19.37$</td>
</tr>
<tr>
<td>2InCl&lt;sub&gt;3&lt;/sub&gt; + 3Na&lt;sub&gt;2&lt;/sub&gt;Te</td>
<td>NaCl</td>
<td>Black</td>
<td>In&lt;sub&gt;2&lt;/sub&gt;Te&lt;sub&gt;3&lt;/sub&gt;</td>
<td>$a = c = 18.51$</td>
<td>$a = c = 18.49$</td>
</tr>
</tbody>
</table>

* Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.

* Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.
Copper chalcogenides (re: table 6.2)

\[
\begin{align*}
2\text{CuBr}_{(\text{am})} + \text{Na}_2\text{S}_{(\text{am})} & \rightarrow \text{Cu}_2\text{S}_{(s)} + 2\text{NaBr}_{(s)} + \text{Cu}_{2-x}\text{S}_{(s)} \quad (x = 0.1, 0.2) \\
\text{CuCl}_{2(\text{am})} + \text{Na}_2\text{S}_{(\text{am})} & \rightarrow \text{CuS}_{(s)} + 2\text{NaCl}_{(s)} + \text{Cu}_{2-x}\text{S}_{(s)} \quad (x = 0.2)
\end{align*}
\]

(6.7) (6.8)

\[
\begin{align*}
\text{CuCl}_{2(\text{am})} + \text{Na}_2\text{Se}_{(\text{am})} & \rightarrow \text{CuSe}_{(s)} + \text{CuSe}_{2(\text{am})} + 2\text{NaCl}_{(s)} \\
\text{CuCl}_{2(\text{am})} + \text{Na}_2\text{Te}_{(\text{am})} & \rightarrow \text{CuTe}_{x-0.5(\text{am})} + x\text{Te}_{(s)} + 2\text{NaCl}_{(s)}
\end{align*}
\]

(6.9) (6.10)

*Two phases of non-stoichiometric (tellurium deficient) Cu\textsuperscript{II} telluride were characterised by XRD - Cu\textsubscript{2.72}Te\textsubscript{2} and Cu\textsubscript{4}Te\textsubscript{3}.

Comparisons with the elemental combination reactions in liquid ammonia (equations 2.2, 2.11 and 2.12) show significant differences in the two synthetic approaches. Elemental combination favours the formation of copper (I) chalcogenides (only CuSe and CuTe were synthesised as minor phases). It is clear from equations 6.7 - 6.10 that the oxidation state of the copper precursor is preserved as a major phase product. In addition, the metathetical reactions show a more restricted variation in stoichiometry. Where copper deficient phases are present, they are either minor phases or closer in formulation to unity. Exact stoichiometries were only observed for minor phases from elemental combination.

Preservation of oxidation state and tight stoichiometric control would be expected from a low temperature SSM reaction scheme. However, although it was observed that these reactions are largely solid state in nature, copper halides do dissolve in liquid ammonia, affording copper-ammonia adducts. It is the increased stability of solvated Cu\textsuperscript{I} species in liquid ammonia (relative to Cu\textsuperscript{II}) that may account for the presence of copper (I) products from copper (II) precursors.\textsuperscript{154}

**Group 13 chalcogenides**

A selection of group 13 sesqui-chalcogenides was also synthesised as single phases (table 6.2).

\[
2\text{MCl}_{3(s)} + 3\text{Na}_2\text{E} \rightarrow \text{M}_{2}\text{E}_{2(s)} + 6\text{NaCl}_{(s)} \quad (M = \text{Ga, In}; \; \text{E} = \text{S, Se, Te})
\]

(6.11)
Gallium and indium sesqui-chalcogenides have useful semi-conducting properties both as crystalline and amorphous materials. Crystallisation of the bulk, X-ray amorphous powders was induced by facile heating material (250-300 °C, 3h).

Interestingly, annealing both the selenide and telluride materials at 250-300 °C for 48h in the presence of oxygen affords the metal chalcogenate rather than the metal oxide (in accordance with equation 6.12).

\[ \text{M}_2\text{E}_3(\text{s}) + 4.5\text{O}_2(\text{am}) \rightarrow \text{M}_2\text{E}_3\text{O}_{10}(\text{s}) \quad (M = \text{Ga, In}; \ E = \text{Se, Te}) \] (6.12)

6.2.3 Discussion of reactions - role of solvent

The metal chalcogenide materials synthesised may be considered as products of solvent mediated metathetical reactions. Although the reactions were observed to be largely solid state in nature and their products comply with metathetical predictions, there are marked differences from the purely SSM reactions described in the previous chapter. The reactions observed in liquid ammonia metathesis (LAM) are both initiated and proceed at room temperature without the need of an external heat source. It is possible that the liquid ammonia itself initiates the reactions by creating a change in state of the precursors (dissolution of the disodium chalcodenide and formation of metallo-ammonia adducts). The reaction is likely to proceed both in the solid state (through surface limited reactions) and in solution (via solvent mediated reactions). The solvent serves to facilitate the reactions in two ways. The surface area of the reaction interface is greatly increased by the formation of solvated species. Furthermore, stirring the insoluble reagents results in exposure of new surfaces by the attrition of suspended particles.

6.2.4 Discussion - product morphology

As is typical of solvent mediated metathesis reactions, liquid ammonia metathesis results in notable differences in product morphology when compared to SSM. Completion of these highly exothermic reactions at room temperature shows the liquid ammonia to be acting as a heat sink. The high heat capacity of liquid ammonia allows efficient dissipation and absorption of reaction enthalpy, whilst the unreactive nature of the solvent towards the precursors allows effective dispersion of insoluble particles. The reaction temperature
thereby becomes limited by both the boiling point of the liquid and the reduced thermal mass of the reaction mixture. Consequently, product annealing is reduced and so particle size becomes restricted. Liquid ammonia metathesis affords spherical nanocrystallites agglomerated into aggregates of < 1 micron, whereas SSM characteristically results in a fused, highly sinterable mass in excess of 10 microns in diameter. This has direct effects on the bulk properties of the resultant material. For example, often the reaction products from liquid ammonia metathesis are X-ray amorphous yet can be crystallized in a single step by facile heating (250-300 °C, 48h). This has led to the synthesis of nanocrystalline 12-16 semiconductors (ZnS, CdS), whose particle size is a consequence of the annealing conditions. Subsequently, this synthetic approach not only requires less energy and processing time but also offers an effective, reproducible conversion between crystalline and X-ray amorphous materials.

6.2.5 Comparison with other mediating solvents

Recent developments in metathesis reactions have resulted in a variety of mediating solvents being studied. LAM offers similar morphologies to the bulk chalcogenide material but with a reduction in total energy input to the reaction system. To date, liquid ammonia offers the only room temperature route to metathesis reactions. It is, however, restricted in its application in three ways:

First, the use of a strongly coordinating solvent, such as ammonia, may result in the formation of kinetically stable adduct of the metal halide precursors. The dissolution of both nickel and zinc bromide afforded Ni(NH$_3$)$_6$Br$_2$ and Zn(NH$_3$)$_2$Br$_2$ which persisted as untreated reagents, even after annealing the reaction mixture.

Secondly, the use of a highly volatile solvent under pressure may result in failure of the reaction system. It was found that LAM reactions were limited to metal halide precursors with an oxidation state less than +III. When MoCl$_5$, WCl$_4$ and WCl$_6$ were used in the attempted synthesis of MoS$_2$, WS$_2$ and WS$_3$, resultant heating of the solvent exceeded the tolerance level of the reaction vessel. Calculations based upon Hess’ Law have shown that the critical value in determination of the reaction enthalpy is the heat of formation of the co-produced salt. Therefore, the molar ratio of salt to chalcogenide product is crucial in minimising localised heating within the reaction vessel.
Finally, the scope of LAM reactions is restricted by the need to both avoid competing reaction pathways (as described below by the use of group 14 halides), and adhere to salt balanced equations. Consequently, only NiS (and not Ni$_3$S$_2$) can be produced by the metathetical reaction between NiCl$_2$ and Na$_2$S.

**Group 14 restriction**

It should be noted that the use of group 14 halides as presursors to the synthesis of single phase products in liquid ammonia is largely restricted due to their propensity towards solvolysis. It is well documented that silicon tetrahalides undergo sequential ammonolysis, affording Si(NH)(NH$_2$)$_2$ up to 140 °C in conjunction with two molar equivalents of ammonium halide.$^{150}$ It has been shown here that PbCl$_2$ reacts *upon addition* to sodium chalcogenides in liquid ammonia, allowing complete conversion to lead chalcogenide via a metathetical route. However, this was shown as an exception. Analogous reactions involving tin halide (SnCl$_2$ or SnL$_2$) show highly crystalline ammonium halide to be present in addition to the expected co-produced sodium salt. One can therefore envisage the beginning of two competitive reaction types upon ascending group 14 - metathesis and ammonolysis. Since these covalent metal halides do not offer a very high degree of insolubility (with the exception of PbCl$_2$), one cannot eliminate significant material contamination with metal amide / imide when carrying out metathetical reactions.

### 6.3 Binary pnictides (Pn = As, Sb)

The stoichiometric quantities required for metathetical reactions are dictated by the need for salt balanced equations. To assume such reactions proceed via the metathetical exchange of ions greatly restricts the pnictide structures that can be synthesised. For example, the target nickel pnictide material from NiCl$_2$ and Na$_3$Pn is Ni$_3$Pn$_2$. However, as previously discussed in section 5.2.3 (p. 123), the highly covalent nature of these materials and the formation of the 'nickel arsenide' structure, suggest that elemental recombination is more likely.

#### 6.3.1 Pnictides of iron, cobalt and nickel (Fe$_3$Pn$_2$, Co$_3$Pn$_2$, and Ni$_3$Pn$_2$)

Stoichiometric quantities of MCl$_2$ (M = Fe, Co, Ni) and Na$_3$Pn (Pn = As, Sb) were stirred in liquid ammonia for 36h at room temperature. Each product was observed to be inhomogeneous, containing both white and black material. XRD analysis prior to work-up
showed the presence of alkali metal halide (NaCl), suggesting that a metathetical reaction had taken place. After repeated washings with distilled water, the black material was isolated and shown to be X-ray amorphous. EDXA showed elemental variation (pnictogen and metal only) over many surface spots. SEM analysis using backscattered electrons showed the presence of two intimately mixed phases, hence accurate quantitative results were difficult to obtain. EDXA of the samples after annealing at 250-300 °C for 48h showed little change in either the number or distribution of phases observed. However, XRD analysis of the annealed samples showed the presence of a single binary pnictide phase which was fully characterised as MPn (figure 6.4 shows the spectrum obtained for CoSb). In some cases (NiAs and NiSb) unreacted transition metal was observed as minor peaks. The weakness in intensity suggests that the facile annealing may induce a limited degree of crystallinity into the otherwise X-ray amorphous transition metal pnictide. The variation in elemental composition detected by EDXA is therefore likely to be an uneven dispersion of transition metal amongst the binary pnictide. One may surmise that the reaction proceeds in accordance with equation 6.13.

\[ 3MCl_2(s) + 2Na_3Pn(s) \rightarrow 2MPn(s) + 6NaCl(s) + M(s) \quad (M = \text{Co, Fe, Ni}; \ Pn = \text{As, Sb}) \ (6.13) \]
6.2.2 Group 12 pnictides (Zn₃P₃, and Cd₃P₃)

Experimental procedure and analytical analyses were carried out as described in the previous section. XRD analysis of the reaction products again showed a mixture of co-produced salt (NaCl) and black, X-ray amorphous material. SEM / EDXA of the isolated black material showed variable elemental composition resulting from the presence of three intimately mixed phases, whose relative distributions seemed unaffected by annealing. XRD analysis of the annealed material showed the presence of a single binary metal pnictide (of stoichiometry M₃P₃), in addition to both elemental metal and pnictogen. These results differ markedly from the reactions of cobalt, iron and nickel halides, in that the reactions of group 12 chlorides from the salt balanced stoichiometry, yet appear not to go to completion (as described by equation 6.12).

\[ 3MCl_{2(s)} + 2Na₃P₃_{(s)} \rightarrow 1-xM₃P₃_{2(s)} + 2NaCl_{(s)} + xM_{(s)} + xP₃_{(s)} \quad (M = Zn, Cd; P₃ = As, Sb) \] (6.14)
Table 6.3 XRD data for binary transition metal pnictides synthesised by liquid ammonia mediated metathesis reactions at room temperature

<table>
<thead>
<tr>
<th>Reagents *</th>
<th>XRD of pre-washed material</th>
<th>Product colour</th>
<th>Phases obtained after annealing the washed material b</th>
<th>Lattice Parameters Å (± 0.01)</th>
<th>Literature Lattice Parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>3FeCl₂ + 2Na₃As</td>
<td>NaCl</td>
<td>Black</td>
<td>FeAs</td>
<td>a = 5.39</td>
<td>a = 5.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 5.93</td>
<td>b = 5.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 3.27</td>
<td>c = 3.27</td>
</tr>
<tr>
<td>3FeCl₂ + 2Na₃Sb</td>
<td>NaCl</td>
<td>Black</td>
<td>FeSb</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>3CoCl₂ + 2Na₃As</td>
<td>NaCl</td>
<td>Black</td>
<td>CoAs (orthorhombic)</td>
<td>a = 3.46</td>
<td>a = 3.46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>b = 5.87</td>
<td>b = 5.87</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 5.29</td>
<td>c = 5.29</td>
</tr>
<tr>
<td>3CoCl₂ + 2Na₃Sb</td>
<td>NaCl</td>
<td>Black</td>
<td>CoSb (hexagonal)</td>
<td>a = 3.88</td>
<td>a = 3.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 5.19</td>
<td>c = 5.19</td>
</tr>
<tr>
<td>3NiCl₂ + 2Na₃As</td>
<td>NaCl</td>
<td>Black</td>
<td>NiAs (hexagonal) + [Ni]</td>
<td>a = 3.62</td>
<td>a = 3.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 5.01</td>
<td>c = 5.01</td>
</tr>
<tr>
<td>3NiCl₂ + 2Na₃Sb</td>
<td>NaCl</td>
<td>Black</td>
<td>NiSb (hexagonal) + [Ni]</td>
<td>a = 3.93</td>
<td>a = 3.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 5.13</td>
<td>c = 5.13</td>
</tr>
<tr>
<td>3ZnCl₂ + 2Na₃As</td>
<td>NaCl</td>
<td>Black</td>
<td>Zn₃As₂ + [Zn, As]</td>
<td>a = c = 5.81</td>
<td>a = c = 5.81</td>
</tr>
<tr>
<td>3ZnCl₂ + 2Na₃Sb</td>
<td>NaCl</td>
<td>Black</td>
<td>Zn₃Sb₂ + [Zn, Sb]</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
<tr>
<td>3CdCl₂ + 2Na₃As</td>
<td>NaCl</td>
<td>Black</td>
<td>Cd₃As₂ + [Cd, As]</td>
<td>a = 8.93</td>
<td>a = 8.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 12.68</td>
<td>c = 12.68</td>
</tr>
<tr>
<td>3CdCl₂ + 2Na₃Sb</td>
<td>NaCl</td>
<td>Black</td>
<td>Cd₃Sb₂ + [Cd, Sb]</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
</tbody>
</table>

* Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.

b Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.
6.2.3 Discussion of pnictide reactions

The presence of unreacted element in the reaction mixture strongly supports the suggestion that these metathetical reactions proceed via elemental recombination. Prior to annealing, the elements are X-ray amorphous, suggesting that they have precipitated from solution. EDXA show variable elemental compositions with either two or three distinct phases being present. After annealing, the presence of both binary pnictide and unreacted elements becomes apparent by XRD studies with little variation in the EDXA results.

6.2.4 Comparison with previous pnictide synthesis (described in section 2.5)

The aforementioned reaction products do not follow the predicted salt balanced equations and are therefore inhomogeneous materials. However, it is worth noting that unlike the analogous elemental combination reactions, binary transition metal pnictide materials were synthesised with both single phase and greater yield via metathesis. If one assumes the metathetical reactions to be elemental recombination then they principally have strong similarities with those of the direct combination of the elements. Crucially, however, the stability afforded by the formation of the crystalline co-produced salt results in the precipitation of metal and pnictogen from solution. This elemental mix thereby has a greatly increased surface area, allowing the formation of the kinetically most favourable binary phase. Whether this elemental recombination occurs at room temperature or during annealing is unresolved.
6.3 Ternary chalcogenides

This final section is concerned with the synthesis of ternary chalcogenide materials by liquid ammonia mediated, metathesis reactions at room temperature. Reactions were devised to synthesise materials summarised by the general formulae $\text{ABE}_2$ ($A = \text{Cu}, \text{Ag}; B = \text{Al}, \text{Ga}, \text{In}; E = \text{S}, \text{Se}$), $\text{CuSbE}_2$ ($E = \text{S}, \text{Se}, \text{Te}$), $\text{MFeS}_2$ ($M = \text{Cu}, \text{Zn}, \text{Cd}$), $\text{AB}_2\text{E}_4$ ($A = \text{Zn}, \text{Cd}; B = \text{Cr}, E = \text{S}; B = \text{V}, E = \text{Se}$) and $\text{CdHg}_x\text{Te}$ ($\Sigma x, y = 1.00$). The following section (6.3.1) is concerned with general experimental results and observations that are common to all the ternary reactions described.

6.3.1 General experimental results for ternary materials

Condensation of ammonia over disodium chalcogenide led to partial dissolution, resulting in characteristic colours of the ammonia solution (blue for Na$_2$S and red for Na$_2$Se). Such solutions are believed to contain fully dissociated sodium and chalcogenide ions ($\text{Na}^+, \text{S}^2-$ and $\text{Se}^2-$). It is also known that the dissolution of certain metal halides to ammonia results in characteristic colour changes through the formation of metallo-ammonia adducts ($\text{Cu(NH}_3)_x\text{Br}_y$, $\text{Ga(NH}_3)_x\text{Br}_y$). In the majority of cases, completion of the reactions in liquid ammonia at room temperature resulted in product material being suspended in a clear liquid. However, it should be noted that the reagents were not observed to fully dissolve before precipitation of the products, suggesting that the bulk of the reagents react in the solid state. Reaction times, although varied, were all observed to reach completion within one hour.

The reactions afforded an inhomogeneous product consisting of white crystallites and aggregates of spherical, black particles. X-ray powder diffraction studies of the unwashed reaction product showed only the presence of the co-produced, sodium halide salt (NaBr, NaCl, NaF, NaCl$_2$Br$_{2-x}$), suggesting the presence of X-ray amorphous black material. Repeated washings with distilled water (3 x 20ml) lead to the removal of this salt, along with any unreacted reagents. SEM studies of the X-ray amorphous material showed extensive aggregated structures, typically of a few hundred nanometres. FT-IR analyses showed stretches of 600-400 cm$^{-1}$, which have been assigned to metal-sulfur connectivities. Elemental analysis showed no significant N or H content. Annealing the purified products
at 200-250°C for 48 hours allowed full characterisation by XRD, which generally confirmed a single phased, crystalline product of the desired stoichiometry. The Bragg peaks of these materials showed significant broadening, corresponding to an average particle size of 52.3–64.6 nm (Scherrer equation). EDXA studies of the annealed samples showed elemental compositions and distributions in accordance with the XRD characterisation (to within an accuracy of ± 2 – 3% atm).

6.3.2 Mixed (transition- main-group) metal chalcopyrite materials

This section is concerned with the synthesis of two types of ternary chalcopyrite materials of general stoichiometry ABE₂ – chalcopyrites of groups 11-13-16 (section 6.3.2a) and groups 11-15-16 (section 6.3.2b).

A = monovalent transition-metal – group 11 (Cu, Ag)
B = trivalent-main group metal - groups 13 (Ga, In) or 15 (Sb)
E = chalcogen (S, Se)

6.3.2a Group 11-13-16 chalcopyrites

Chalcopyrite-type ternary semiconductors of general formula ABE₂ (A = Cu, Ag; B = Ga, In; E = S, Se) were successfully prepared by solution phase metathetical reactions of sodium chalcogenide (Na₂S, Na₂Se) with the appropriate metal halides (CuBr, AgF, GaBr₃, InCl₃). The reactions are described by equation 6.15. XRD data is represented in tables 6.4 and 6.5. Figure 6.5 shows the XRD pattern obtained for AgInSe₂. With a stoichiometric deficiency of gallium bromide an inhomogenous product was isolated, comprising of a minor phase of binary copper (I) sulfide (Cu₂S₄, anilite) and CuGaS₂ (gallite), rather than a gallium deficient ternary material (figure 6.6). Attempts at the formation of the aluminium analogues of these materials resulted in the preferential formation of the binary group 9 chalcogenide (table 6.5).

AXₐ + BX₃ₒ + 2Na₂Eₒ → ABE₂ₒ + 4NaXₒ  (A = Cu, Ag; B = Ga, In; E = S, Se) (6.15)
The mode of addition of the reagents also appears to be important. Initial reactions in the formation of CuInSe$_2$ were carried out by adding the metal halides individually to the partially solvated disodium selenide. The product was characterised by EDXA as a mixture of both binary copper selenide (CuSe) and the copper deficient ternary phase. After the described work-up and thermolysis, XRD studies confirmed the presence of CuIn$_2$Se$_{3.5}$ (figure 6.7), with the binary material remaining X-ray amorphous. This suggests that the reaction begins upon addition of the metal halides to the ammonia solution, and so efficient mixing of both the halide precursors and reaction mixture is important in the synthesis of a single phase of desired stoichiometry. Similar results were observed for the initial reaction carried out for AgInS$_4$, which produced a reaction mixture containing AgIn$_2$S$_4$ and Ag$_2$S (In$_2$O$_3$ and AgO were also detected by XRD after annealing).

Figure 6.5 XRD spectrum of washed silver indium selenide (AgInSe$_2$)

annealed at 250-300 °C for 48h

Key: Sample (top) – annealed AgInSe$_2$ Standard (bottom) – silver indium selenide, AgInSe$_2$
**Table 6.4 XRD data for 11-13-16 chalcopyrites**

(\(\text{ABE}_2; \ A = \text{Cu, Ag}; \ B = \text{Ga, In}; \ E = \text{S, Se}\) )

<table>
<thead>
<tr>
<th>Reagents (^a)</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)(^b)</th>
<th>Phases obtained after annealing the washed material (^c)</th>
<th>Lattice Parameters (\bar{A} \pm 0.01)(^d)</th>
<th>Literature(^\text{139}) Lattice Parameters, (\bar{A})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CuBr + GaCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Green</td>
<td>NaBr</td>
<td>(\text{CuGaS}_2) (\textit{gallite}) + [\text{Cu}_3\text{S}_4])</td>
<td>(a = 5.36) (c = 10.49)</td>
<td>(a = 5.36) (c = 10.49)</td>
</tr>
<tr>
<td>(\text{CuBr + GaCl}_3 + 2\text{Na}_2\text{Se})</td>
<td>Black</td>
<td>NaBr</td>
<td>(\text{CuGaSe}_2)</td>
<td>(a = 5.61) (c = 10.99)</td>
<td>(a = 5.61) (c = 10.99)</td>
</tr>
<tr>
<td>(\text{AgF + GaCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Black</td>
<td>NaBr</td>
<td>(\text{AgGaS}_2)</td>
<td>(a = 5.74) (c = 11.62)</td>
<td>(a = 5.74) (c = 11.62)</td>
</tr>
<tr>
<td>(\text{AgF + GaCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Black</td>
<td>NaBr</td>
<td>(\text{AgGaSe}_2)</td>
<td>(a = 5.97) (c = 10.88)</td>
<td>(a = 5.97) (c = 10.88)</td>
</tr>
<tr>
<td>(\text{CuBr + InCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Black</td>
<td>(\text{NaBr + NaCl}_x\text{Br}_y)</td>
<td>(\text{CuInS}_2)</td>
<td>(a = 5.52) (c = 11.12)</td>
<td>(a = 5.52) (c = 11.12)</td>
</tr>
<tr>
<td>(\text{CuBr + InCl}_3 + 2\text{Na}_2\text{Se})</td>
<td>Black</td>
<td>(\text{NaBr + NaCl}_x\text{Br}_y)</td>
<td>(\text{CuInSe}_2)</td>
<td>(a = 5.78) (c = 11.62)</td>
<td>(a = 5.78) (c = 11.62)</td>
</tr>
<tr>
<td>(\text{AgF + InCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Black</td>
<td>NaCl</td>
<td>(\text{AgInS}_2)</td>
<td>(a = 5.82) (c = 11.17)</td>
<td>(a = 5.82) (c = 11.17)</td>
</tr>
<tr>
<td>(\text{AgF + InCl}_3 + 2\text{Na}_2\text{S})</td>
<td>Black</td>
<td>NaCl</td>
<td>(\text{AgInSe}_2)</td>
<td>(a = 5.77) (c = 11.55)</td>
<td>(a = 5.77) (c = 11.55)</td>
</tr>
</tbody>
</table>

\(^a\) Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.

\(^b\) Phases characterised by X-ray powder diffraction prior to work-up of reaction product.

\(^c\) Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.

\(^d\) Unit cell parameters were determined for the binary material only.

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Figure 6.6 XRD spectrum of washed copper gallium sulfide (CuGaS$_2$) annealed at 250-300 °C for 48h.

Key: Sample (top) – annealed CuGaS$_2$ Standards (bottom) – CuGaS$_2$ (blue), Cu$_2$S$_4$ (red)

Figure 6.7 XRD spectrum of washed copper indium selenide (CuInSe$_2$) annealed at 250-300 °C for 48h.

Key: Sample (top) – annealed CuInSe$_2$ (black) Standard (bottom) – CuIn$_{1.20}$Se$_{3.30}$ (blue)
Comparative reactions to form ABE$_2$ (A = Cu, Ag; B = Al)

EDXA of both pre-annealed and thermolysed samples of washed AAIE$_2$ (A = Ag, Cu; E = S, Se) showed comparative regional variation in elemental composition over many surface spots (focal width ca. 1 micron), with Cu / Ag, Al and E being detected in each scan. SEM analysis by back-scattered electrons showed an intimate (< 2 microns) inhomogeneous mix of material over the sample surface, making resolution of each phase by EDXA difficult. Elemental ratios of A : E frequently indicated the formation of Ag E and Cu E to within an accuracy of ± 2 – 3% atm, suggesting that variation in energies of the backscattered electrons results from differing composition of aluminium. Regions of > 90 % S / Se were also detected, suggesting the presence of free chalcogen. Upon closer examination of the annealed samples by XRD, Cu$_2$E was in fact a mixture of CuE and E. The XRD data is given in table 6.5.

Table 6.5 XRD data for 11-13-15 chalcopryrites (ABE$_2$: A = Cu, Ag; B = Al; E = S, Se)

<table>
<thead>
<tr>
<th>Reagents $^a$</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)$^b$</th>
<th>Phases obtained after annealing the washed material $^c$</th>
<th>Lattice Parameters Å (± 0.01)$^d$</th>
<th>Literature $^{139}$ Lattice Parameters, Å</th>
</tr>
</thead>
</table>
| CuBr + AlCl$_3$ + 2Na$_2$S | Grey | NaCl, Br$_y$ | CuS (covelite) + S | a = 3.76  
c = 16.20  | a = 3.76  
c = 16.19 |
| CuBr + AlCl$_3$ + 2Na$_2$S | Grey | NaBr + NaCl, Br$_y$ | CuSe (klockmannite) + [CuSe$_2$, Se] | a = 3.93  
c = 17.22  | a = 3.93  
c = 17.22  |
| AgF + AlCl$_3$ + 2Na$_2$S | Black | NaCl | Ag$_2$S (acanthite) + S | a = c = 4.48  | a = c = 4.46 |
| AgF + AlCl$_3$ + 2Na$_2$S | Black | NaCl | Ag$_2$Se (naumannite) + Se | a = 4.33  
b = 7.06  
c = 7.76  | a = 4.33  
b = 7.06  
c = 7.76  |

$^a$ Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.

$^b$ Phases characterised by X-ray powder diffraction prior to work-up of reaction product.

$^c$ Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.

$^d$ Unit cell parameters were determined for the binary material only.
Pre-annealed XRD patterns showed the presence of co-produced salt and the absence of unreacted metal halide, suggesting that metathesis had occurred. Annealed spectra of AgAlE\textsubscript{2} show the metathetical formation of binary Ag\textsubscript{x}E (equation 6.16). The production of chalcogen suggests elemental reaction intermediates.

\[
\text{AgF}(s) + \text{AlCl}_3(s) + 2\text{Na}_2\text{E}(s) \rightarrow \text{Ag}_2\text{E}(s) + \text{E}(s) + \text{Al}(s) + 4\text{NaBr}(s) \quad (E = \text{S, Se}) \quad (6.16)
\]

* The presence of aluminium was detected by EDXA only.

However, similar spectra show the formation of binary CuE rather than Cu\textsubscript{2}E (as described by the metathesis reaction between CuBr and Na\textsubscript{2}S; equation 6.7). A minor phase of CuSe\textsubscript{2} (a copper deficient phase of copper (II) selenide) was also detected.

\[
\text{CuBr}(s) + \text{AlCl}_3(s) + 2\text{Na}_2\text{E}(s) \rightarrow \text{CuE}(s) + \text{E}(s) + \text{Al}(s) + 4\text{NaBr}(s) \quad (E = \text{S, Se})^* \quad (6.17)
\]

* The presence of aluminium was detected by EDXA only.

The cell parameters for the binary materials prepared in both reaction schemes compare well with the mineral structures.\textsuperscript{139} This suggests that aluminium is present as part of a discrete species to the sample and there is no significant doping of aluminium in any of the group 9 chalcogenide lattices. This may show a limitation of this synthetic route to the formation of aluminium doped semiconducting materials (such as GaAlAsSb).

6.3.2b Group 11-15-16 chalcopyrite materials

The following LAM reactions were studied in conjunction with the elemental combination pathway described in section 3.6. As previously shown, the synthesis of copper antimony chalcogenides (sulfides, selenides and tellurides) resulted in phase separation to the binary copper chalcogenide and elemental antimony / chalcogen. The aim was to investigate whether the use of precursors would allow metathetical formation of ternary materials and if so, whether a degree of stoichiometric control is possible. To this end, equation 6.18 describes the synthesis of CuSbE\textsubscript{2} (E = S, Se, Te), and equation 6.19 the synthesis of Cu\textsubscript{3}SbS\textsubscript{3} (the alternative stoichiometry of copper antimony sulfide adopted in section 3.6).
The XRD data is given in table 6.6. XRD patterns obtained after annealing the isolated product are shown for Cu$_3$SbS$_4$ (figure 6.8) and CuSbS$_2$ (figure 6.9).

\[
\text{CuBr}(s) + \text{SbBr}_3(s) + 2\text{Na}_2E(s) \rightarrow \text{CuSbE}_x(s) + 4\text{NaBr}(s), \quad (E = \text{S, Se, Te})(6.18)
\]

\[
12\text{CuBr}(s) + 4\text{SbBr}_3(s) + 16\text{Na}_2\text{S}(s) \rightarrow \text{Cu}_3\text{Sb}_2\text{S}_{16-x}(s) + 32\text{NaBr}(s) \quad (x = 3) \quad (6.19)^* \]

* Where M = Sb; E = S: an inhomogeneous mixture of Cu$_{12}$Sb$_4$S$_{13}$ (tetrahedrite, major phase) and Cu$_3$SbS$_4$ (famatinite, minor phase) was characterised by XRD – figure 6.8

LAM reactions allow the formation of ternary copper antimony chalcogenides (CuSbE$_x$). However, whilst it was possible to form with two discrete general formulas of copper antimony sulfide (CuSbE$_2$ and Cu$_3$Sb$_2$(S$_{3+x}$)), two distinct phases of Cu$_3$Sb$_2$(S$_{3+x}$) were accessible under the reaction conditions employed - tetrahedrite (x = 0.25) and famatinite (x = 1).

Table 6.6 XRD data for 11-15-16 chalcopyrites (ABE$_x$: A = Cu, Ag; B = As, Sb; E = S, Se)

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Product colour</th>
<th>Products as formed from reaction (identified by XRD)$^b$</th>
<th>Phases obtained after annealing the washed material $^c$</th>
<th>Lattice Parameters Å (± 0.01)$^d$</th>
<th>Literature $^{139}$ Lattice Parameters, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>3CuBr + SbBr$_3$ + 4Na$_2$S</td>
<td>Black</td>
<td>NaBr</td>
<td>Cu$_{12}$Sb$<em>4$S$</em>{13}$ + [Cu$_3$SbS$_4$]</td>
<td>$a = c =$ 10.36</td>
<td>$a = c = 10.36$</td>
</tr>
<tr>
<td>CuBr + SbBr$_3$ + 2Na$_2$S</td>
<td>Black</td>
<td>NaBr</td>
<td>CuSbS$_2$ chalcostibite</td>
<td>$a = 6.02$ $b = 3.80$ $c = 11.50$</td>
<td>$a = 6.02$ $b = 3.80$ $c = 11.50$</td>
</tr>
<tr>
<td>CuBr + SbBr$_3$ + 2Na$_2$Se</td>
<td>Black</td>
<td>NaBr</td>
<td>CuSbSe$_2$</td>
<td>$a = 6.02$ $b = 3.80$ $c = 17.22$</td>
<td>$a = 6.02$ $b = 3.80$ $c = 17.22$</td>
</tr>
<tr>
<td>CuBr + SbBr$_3$ + 2Na$_2$Te</td>
<td>Black</td>
<td>NaBr</td>
<td>CuSbTe$_2$</td>
<td>Characterised using standardised XRD patterns</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.

$^b$ Phases characterised by X-ray powder diffraction prior to work-up of reaction product.

$^c$ Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.

$^d$ Unit cell parameters were determined for the binary material only.
Figure 6.8 XRD spectrum of washed copper antimony sulfide (Cu$_3$Sb$_4$S$_9$) annealed at 250-300 °C for 48h

Key: Sample (top) - Cu$_3$Sb$_4$S$_9$ (black)  Standard - Cu$_{12}$Sb$_7$S$_{13}$ (blue), Cu$_3$Sb$_4$S$_9$

Figure 6.9 XRD spectrum of washed copper antimony sulfide (CuSb$_2$) annealed at 250-300 °C for 48h

Key: Sample (top) - annealed CuSb$_2$  Standard (bottom) - copper antimony sulfide, CuSb$_2$
6.3.2 Discussion of ternary transition- main-group chalcogenide reactions

It has been shown to be difficult to maintain the stoichiometry of CuInE₂ during its deposition into thin films (notably during deposition from the vapour phase).\textsuperscript{158} As a result, copper deficient films can result. Studies in both the solid state\textsuperscript{157} and a non-coordinated solvent at reflux (toluene)\textsuperscript{158} have shown that metathesis reactions do not produce copper deficient species. In the absence of any appreciable solubility of the reagents in the toluene, the reactions can be described as a slow solid state reaction, which is thermally assisted by the solvent. Long reaction times allow the solid state diffusion barrier to be overcome. This has been explained in terms of the calculated exothermicity of both reactions lying below the threshold required for a propagation wave. Therefore, the materials formed are the kinetic products of the reactions, their formation being preferred over phase segregation that would result in thermodynamically more stable products. It is not surprising, therefore, that the comparative solvent mediated reactions in liquid ammonia (carried out at significantly lower temperatures) should also yield the same stoichiometrically exact products. When comparing the results obtained from liquid ammonia to those of toluene, the comparative decrease in reaction time (<1h compared to 72h) and reduction in reaction temperature (25°C compared to 110°C) may be a result of the partial dissolution of the reagents. This would lead to a dramatic lowering of the same energies of activation, thereby allowing the reactions to occur at an accelerated rate at ambient temperatures (and so result in the formation of the kinetic product). This process would be further facilitated by the intimate mixing of the reagents. It is important to reiterate that successful stoichiometric control results from prudent mixing of the metal halides and the maintenance of an intimate mix. The reacting halides should be kept in the solid state for as long as possible. That is to say, too large a difference in the solubility of the halides may result in the formation from solution of minor phases, such as binary chalcogenides. Owing to the stoichiometric nature of the reagents used, this would in turn lead to the formation of sub-stoichiometric ternary materials (re: formation of CuIn\textsubscript{12}Se\textsubscript{3.5} and CuSe).

It is unclear whether the reaction product is truly a ternary material or an intimate mix of the constituent binary materials. The fine aggregate structure of nanoparticulate material created by solvent mediated metathesis reactions may create a mixture whose particles
cannot be resolved by the EDXA technique. Annealing such fine powders may lead directly to the ternary material with facile heating, in accordance with the reactions below:

\[ 2\text{CuS}_{(s)} + \text{In[InS}_2]_{(s)} \rightarrow 2\text{CuInS}_{2(s)} \quad (\text{Cu}^{II} \text{sulfide} + \text{‘InS’}) \]
\[ \text{Cu}_2\text{S}_{(s)} + \text{In}_2\text{S}_3_{(s)} \rightarrow 2\text{CuInS}_{2(s)} \quad (\text{Cu}^{I} \text{sulfide} + \text{In}^{III} \text{sulfide}) \]

This may explain why, assuming the preferential formation of \( \text{CuGaS}_2 \) as the kinetic phase, a mix of copper gallium disulfide and \( \text{Cu}_7\text{S}_4 \) resulted from the use of a substoichiometric amount of gallium halide rather than a single, gallium deficient, ternary phase. In addition, the use of high intensity X-rays (synchrotron radiation) in determining the powder pattern for \( \text{CuInS}_2 \) synthesised in refluxing toluene has shown the presence of copper sulfide crystallites in an otherwise amorphous reaction product.\(^{159}\)

6.3.4 Mixed (transition) metal chalcogenides

The synthesis of three general structures were tried: (a) chalcopyrite, (b) spinels and (c) substitutional solid solutions of group 12.

Whilst each structural class will be discussed separately, the XRD data for this section is described in table 6.7 (p. 150).
<table>
<thead>
<tr>
<th>Reagents (^a)</th>
<th>Products as formed from reaction (identified by XRD)(^b)</th>
<th>Product colour</th>
<th>Phases obtained after annealing the washed material (^c)</th>
<th>Lattice Parameters (\AA (± 0.01))^d</th>
<th>Literature (^{139}) Lattice Parameters, (\AA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{CuBr} + \text{FeCl}_2 + 2\text{Na}_2\text{S})</td>
<td>(\text{NaBr}) Black</td>
<td>(\text{CuFeS}_2) (chalcopyrite) [(\text{Cu}_5\text{FeS}_4\text{bornite})]</td>
<td>(a = 5.24) (c = 10.31)</td>
<td>(a = 5.24) (c = 10.30)</td>
<td></td>
</tr>
<tr>
<td>(\text{MCl}_2 + \text{FeCl}_2 + \text{Na}_2\text{S}) ((M = \text{Zn, Cd}))</td>
<td>(\text{NaCl}) Black</td>
<td>(\text{ZnS (wurtzite)}) (\text{CdS (greenockite)}) (\text{FeS}_2) (pyrite)</td>
<td>(a = 3.82) (c = 6.26)</td>
<td>(a = 3.82) (c = 6.26)</td>
<td>(a = c = 5.41)</td>
</tr>
<tr>
<td>(\text{MCl}_2 + 2\text{CrCl}_3 + 4\text{Na}_2\text{S}) ((M = \text{Zn, Cd}))</td>
<td>(\text{NaCl}) Black</td>
<td>(\text{ZnS (wurtzite)}) (\text{CdS (greenockite)}) (\text{CrS} + \text{S})</td>
<td>(a = 3.82) (c = 6.26)</td>
<td>(a = 3.82) (c = 6.26)</td>
<td>(a = c = 5.32)</td>
</tr>
<tr>
<td>(\text{MCl}_2 + 2\text{VCl}_3 + 4\text{Na}_2\text{Se}) ((M = \text{Zn, Cd}))</td>
<td>(\text{NaCl}) Black</td>
<td>(\text{ZnSe (stilbite)}) (\text{CdSe (cadmesolite)}) (\text{VSe}) (\text{VSe}_{(2-x)} + [\text{Se}])</td>
<td>(a = c = 5.66)</td>
<td>(a = c = 5.62)</td>
<td>(a = 4.30) (c = 7.01)</td>
</tr>
<tr>
<td>(x\text{CdCl}_2 + y\text{HgCl}_2 + \text{Na}_2\text{Te}) (x = 0.25, 0.50, 0.75) (\Sigma (x,y) = 1.00)</td>
<td>(\text{NaCl}) Black</td>
<td>(\text{CdTe}) (\text{HgTe coloradoite})</td>
<td>(a = 4.30) (c = 10.26)</td>
<td>(a = 4.30) (c = 10.26)</td>
<td>(a = c = 6.45)</td>
</tr>
</tbody>
</table>

\(^a\) Reagents (expressed with molar ratios) stirred in liquid ammonia at room temperature for 36h.
\(^b\) Phases characterised by X-ray powder diffraction prior to work-up of reaction product.
\(^c\) Phases characterised by X-ray powder diffraction after annealing at 250-300 °C for 48h. All minor phases (< ca. 10 %) represented by square brackets.
\(^d\) Unit cell parameters were determined for the binary material only.
\(^e\) Cell parameter given for VSe\(_2\).
6.3.4a Chalcogenides adopting the chalcopyrite structure

The synthetic approach adopted for mixed (transition- main-group) metal chalcopyrite materials was extended to include ternary, mixed transition-metal chalcogenide. Copper iron sulfide was chosen to further test the degree of stoichiometric control that this synthetic route offers since it offers a wide range of possible stoichiometries. The target material was CuFeS₂, or ‘chalcopyrite’ (from which this class of compound takes its name). The same experimental procedure and modes of analysis was adopted as before, with the precursors being left for 36h. XRD analysis of the initial reaction product showed it to be a mixture of X-ray amorphous black material and crystalline sodium chloride. SEM / EDXA analysis of the purified product showed the presence of 2 phases. The major (ca. 90-95 % of surface) phase showed an elemental composition in good agreement with the target stoichiometry (± 1%) over many surface spots. The minor phase showed a consistent deficiency in the percentage of iron of ca. 20 % with respects to copper. In addition, the percentages of copper and sulfur appeared to be similar. Annealing of the isolated black material at 250-300 °C for 48h showed very little variation in either the initial percentage composition of the two phases or their relative abundance. XRD analysis of the annealed material (figure 6.10) allowed complete characterisation of the major product as CuFeS₂ (chalcopyrite). The spectrum for the minor phase is in good agreement with the standard pattern for Cu₅FeS₄ (bornite). The reaction may thus be summarised by equation 6.20

\[ \text{CuBr}_{(am)} + \text{FeBr}_2_{(am)} + 2\text{Na}_2\text{S}_{(am)} \rightarrow \text{CuFeS}_2_{(s)} + 4\text{NaBr}_{(s)}^* \]  

* Minor phase of Cu₅FeS₄ was also observed.

These results highlight the fact that salt balanced, solvent (liquid ammonia) mediated metathesis reactions may result in multiple phases.
6.3.4b Chalcogenides adopting spinel structures

The scope of ternary LAM reactions was tested through the synthesis of a different structural type. The synthesis of spinels of general formula $\text{AB}_2\text{E}_4$ ($\text{A} = \text{Zn, Cd}; \text{B} = \text{Fe, Cr, V}; \text{E} = \text{S, Se}$) was attempted through the stoichiometric addition of an intimate mix of ACI$_2$ and BCI$_3$ to a liquid ammonia solution of Na$_2\text{E}$. The XRD pattern of the reaction product showed only the formation of the co-produced salt (NaCl). Removal of the salt by trituration with distilled water afforded a black, X-ray amorphous powder. SEM / EDXA analysis of these materials showed the presence of multiple phases with varying elemental ratios. The ratios suggested formation of an intimate mix of binary, rather than ternary, chalcogenide material. XRD studies of the powders after annealing (250-300 °C, 3h) confirmed the presence of multiple binary metal chalcogenide phases. The patterns were
sufficiently crystalline to allow full characterisation of the materials by XRD (table 6.7).
The reactions are described by equations 6.21-6.23 (minor phases in italics).

\[
\begin{align*}
\text{ACl}_2(s) + 2\text{FeCl}_3(s) + 4\text{Na}_2\text{S}(am) & \rightarrow \text{AS}(s) + \text{FeS}_2(s) + \text{FeS}_3(s) + 8\text{NaCl}(s) \\
\text{ACl}_2(s) + 2\text{CrCl}_3(s) + 4\text{Na}_2\text{S}(am) & \rightarrow \text{AS}(s) + 2\text{CrS}(s) + \text{S}(s) + 8\text{NaCl}(s) \\
\text{ACl}_2(s) + 2\text{VCl}_3(s) + 4\text{Na}_2\text{Se}(am) & \rightarrow \text{ASe}(s) + \text{VSe}_{(2-x)}(s) + \text{VSe}_x(s) + \text{S}(s) + 8\text{NaCl}(s)
\end{align*}
\]

For each reaction described, \( A = \text{Zn or Cd} \).

It is apparent that phase separation to binary transition metal chalcogenides occurs in preference to the formation of ternary spinel structures. For each reaction, both zinc and cadmium chalcogenide adopted the familiar mineral structures (table 6.7) of wurtzite (ZnS), greenockite (CdS), stilleite (ZnSe) and cadmesolite (CdSe). Both iron sulfide and vanadium selenide adopted both the mono- and di-chalcogenide phases observed in previous SSM reactions (re: chapter 5). Interestingly, although the presence of FeS was detected by EDXA, the phase remained X-ray amorphous after annealing. In the reaction of chromium (III) chloride, two molar equivalents of chromium (II) sulfide (CrS) were synthesised with the corresponding oxidation of one molar equivalent of \( \text{S}^2\) to elemental sulfur (equation 6.22). It appears that the reaction products reflect the most thermodynamically stable (binary) phases allowed by the stoichiometric ratio of the elements. Furthermore, it is likely that these materials result from elemental intermediates in the reaction rather than by direct metathetical exchange of the ions.

6.3.4c Mixed cadmium mercury tellurides

The final study carried out into ternary LAM reactions involved the synthesis of mixed cadmium mercury tellurides. These substitutional solid solutions are described by the general formula \( \text{Cd}_x\text{Hg}_y\text{Te}_2 \) (where \( \Sigma(x, y) = 1.00 \)). For comparison with the results obtained by elemental combination reactions (section 3.3.4), the reactions undertaken were the stoichiometries of \( x = 0.25, 0.50 \) and 0.75. They are described in table 6.7 and by equation 6.24.

\[
\begin{align*}
x\text{CdCl}_2(s) + y\text{HgCl}_2(s) + 2\text{Na}_2\text{Te}(am) & \rightarrow x\text{CdTe}(s) + y\text{HgTe}(s) + 4\text{NaCl}(s)
\end{align*}
\]

Note: \( \Sigma (x,y) = 1.00; \ x = 0.25, 0.50 \) or 0.75
As with the use of elemental combination, the products of LAM reactions were black, X-ray amorphous powders (only the formation of the co-produced salt (NaCl) was detected by XRD). However, SEM studies showed the metathetical products to consist of uniform aggregates of a few hundred nanometres, rather than a few microns for elemental combination. Furthermore, EDXA showed a more extensive variation in metal composition for the LAM products, which varied little with annealing the material at 300 °C for 3h. XRD analysis of the annealed samples showed complete phase separation to binary metal tellurides. The metals adopted the same structures for CdTe and HgTe (colaradoite) as have been observed in the synthesis of these binary materials in liquid ammonia by both metathetical and elemental combination routes (re: lattice parameters in tables 2.2 and 6.1).

When comparing LAM to elemental combination routes to these materials it is apparent that although metathesis offers greater particle size restriction, it does not allow formation of cadmium-mercury solid solutions, but rather the more thermodynamically stable binary metal tellurides.

6.4 Conclusions of liquid ammonia metathesis (ternary materials)

Solution phase metathetical reactions of low valent metal halides with the appropriate sodium chalcogenide (Na2E) in liquid ammonia at room temperature, affords a convenient, single step route to a wide range of bulk ternary chalcopyrite materials in good yield (>95 %). These include the synthesis of high quality ternary I-III-VI2 semiconductors. Compared to conventional syntheses of the bulk material (elemental combination), this route offers significantly lower reaction times (<1 hour compared to ca. 3 days) as well as lower temperatures (ca. 25°C compared with ca. 1150°C). Restricted particle size and range is also achieved owing to the liquid ammonia acting as a heat sink to absorb reaction energy. Moreover, this ‘solvent effect’ enables X-ray amorphous materials to be produced which can be easily converted to a crystalline single phase by annealing at relatively low temperatures for short time periods (200-250°C, 3h). With pruditious reagent preparation, this route leads to neither metal deficient nor metal rich ternary (ABE2) materials (such as CuIn3S8, AgIn5S8 or Ag9GaSe8). Within the short reaction time required for these reactions to occur, we believe that the products formed are the most kinetically stable for this reaction.
system. The necessity for salt balanced equations results in tighter stoichiometric control (although this may also restrict the range of stoichiometries obtainable). The use of metal precursors reduces the dependency of the reaction upon the chalcophilicity of the metal. Thus, a wider use of transition metals was employed than with elemental combination reactions. This synthetic approach does, however, seems to be highly selective in the type of material structure synthesised. Often complete phase segregation can occur, resulting in the preferential formation of binary transition metal chalcogenides.

**Particle size restriction**

It is unlikely that the restriction in the particle sizes observed resulted from the reaction of the ammonia from the terminal metal-halide bonds of a product nanoparticulate. Whilst this would restrict any further particle growth via reaction with either type of reagent, neither FT-IR nor XRD analyses support this hypothesis. Not only does the XRD of the unwashed product fail to show any ammonium salt, but FT-IR studies also fail to show the stretching frequency characteristic of metal-amine functionalities. Moreover, washing of such a capped material with water would lead to incorporation of the hydroxyl group into the material. Consequently, after annealing one would expect a characteristic stretches of metal-hydroxy / metal oxide functionalities in the infra-red or, if in sufficient quantities, the presence of the metal oxide / hydroxide in the XRD pattern. These results strongly suggest that particle size restriction primarily from the high specific heat capacity of the ammonia absorbing the heat of reaction. They also support the leading reaction mechanism as solid state metathesis, compared to an approach inclusive of ammonia coordination.

**6.6 Experimental procedure**

The reactions described were initially carried out in the manner described below for zinc sulfide. In each case, the alkali metal chalcogenide was freshly prepared from direct combination of the elements in liquid ammonia, with all manipulation undertaken using Schlenk techniques to avoid exposure to either air or water moisture (as described below). Once isolated, product work-up and characterisation of all products were carried out as for the solid state metathetical products described in chapter 5.
Reaction of zinc sulfide (from the reaction of sodium sulfide with zinc chloride)

The same general reaction scale and procedure was adopted for all these reactions, as exemplified here for ZnS.

Freshly prepared disodium sulfide (100 mg, 1.28 mmol.) and zinc chloride (175 mg, 1.28 mmol.) were ground together inside a glove box, using an agate pestle and mortar, until intimately mixed. The mixture was added to a Youngs-type pressure tube containing ca. 15 cm$^3$ at ca.-1% °C using Schlenk techniques. The tube was then sealed at allowed to warm to room temperature with continuous stirring of the reaction mixture. In each case, although the liquid ammonia was observed to change colour upon addition of the reagents (suggesting the presence of solvated species), the bulk of the mixture remained solid state in nature throughout the course of the reaction. After 12-18 h (or once the liquid ammonia was observed to turn colourless) the ammonia was allowed to evaporate under dinitrogen gas flow. Part of the product (typically a mixture of black and white material) was then triturated with 3x20 cm$^3$ of distilled water, typically yielding a black material, before being dried under vacuum. The isolated product was then annealed for 2 h at 200-250 °C. The isolated product was typically analysed (before and after annealing) by XRD, SEM / EDXA and IR spectroscopy. XRD analysis was also carried out on the pre-washed reaction product.

Slight modifications to the general experimental procedure were then developed. First, condensation of the ammonia over either the sodium sulfide or selenide resulted in complete dissolution of the material, thereby affording excellent contact between the reagents. It should be noted, however, that such a procedure only resulted in partial dissolution of sodium telluride. Finally, as described earlier, the synthesis of ternary materials may be sensitive to mode of addition of the metal halides (possibly resulting from a differential in reagent solubilities). In an attempt to limit this effect, these precursors were added as an intimately ground mix, with the least soluble halides available being used.
Preparation of sodium chalcogenide

$\text{Na}_2\text{E} \ (\text{E} = \text{S, Se, Te})$ was prepared by the direct combination of stoichiometric quantities of sodium metal and elemental chalcogen in liquid ammonia. These reactions were carried at room temperature in teflon-in-glass Youngs-type pressure vessels, using Schlenk techniques. Once prepared, the sodium chalcogenide was used immediately in the liquid ammonia metathesis without exposure to atmospheric conditions.
### Table 6.8 SEM / EDXA data of Binary metal chalcogenides synthesised by metathetical reaction in liquid ammonia at room temperature

<table>
<thead>
<tr>
<th>Reagents $^1$</th>
<th>Particle morphology $^2$</th>
<th>Ratio of elements (expt. error ± 2-3 atm.%$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\mu$m = microns</td>
<td>Elemental ratio</td>
</tr>
<tr>
<td></td>
<td>nm = nanometers</td>
<td>Ni : S</td>
</tr>
<tr>
<td>NiCl$_2$ + Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Irregular particles &lt; 50 nm</td>
<td>Zn : S</td>
</tr>
<tr>
<td>CdCl$_2$ + Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Cd : S</td>
</tr>
<tr>
<td>2CuBr + Na$_2$S</td>
<td>1-8 $\mu$m aggregates. Irregular particles &lt; 100 nm</td>
<td>Cu : S</td>
</tr>
<tr>
<td>CuCl$_2$ + Na$_2$S</td>
<td>1-8 $\mu$m aggregates. Spherical particles &lt; 100 nm</td>
<td>Cu : S</td>
</tr>
<tr>
<td>CuCl$_2$ + Na$_2$Se</td>
<td>1-8 $\mu$m aggregates. Irregular particles &lt; 100 nm</td>
<td>Cu : Se</td>
</tr>
<tr>
<td>CuCl$_2$ + Na$_2$Te</td>
<td>1-8 $\mu$m aggregates. Spherical particles &lt; 100 nm</td>
<td>Cu : Te</td>
</tr>
<tr>
<td>2AgF + Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ag : S</td>
</tr>
<tr>
<td>2AgF + Na$_2$Se</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ag : Se</td>
</tr>
<tr>
<td>2AgF + Na$_2$Te</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ag : Te</td>
</tr>
<tr>
<td>HgCl$_2$ + Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Hg : S</td>
</tr>
<tr>
<td>HgCl$_2$ + Na$_2$Se</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Hg : Se</td>
</tr>
<tr>
<td>HgCl$_2$ + Na$_2$Te</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Hg : Te</td>
</tr>
<tr>
<td>2GaCl$_3$ + 3Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ga : S</td>
</tr>
<tr>
<td>2GaCl$_3$ + 3Na$_2$Se</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ga : S</td>
</tr>
<tr>
<td>2GaCl$_3$ + 3Na$_2$Te</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Ga : Te</td>
</tr>
<tr>
<td>2InCl$_3$ + 3Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>In : S</td>
</tr>
<tr>
<td>2InCl$_3$ + 3Na$_2$Se</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>In : S</td>
</tr>
<tr>
<td>2InCl$_3$ + 3Na$_2$Te</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>In : Te</td>
</tr>
<tr>
<td>2TlCl + Na$_2$S</td>
<td>1-8 $\mu$m aggregates. Irregular particles &lt; 200 nm</td>
<td>Tl : S</td>
</tr>
<tr>
<td>2TlCl + Na$_2$Se</td>
<td>1-8 $\mu$m aggregates. Irregular particles &lt; 200 nm</td>
<td>Tl : S</td>
</tr>
<tr>
<td>2TlCl + Na$_2$Te</td>
<td>1-8 $\mu$m aggregates. Irregular particles &lt; 200 nm</td>
<td>Tl : Te</td>
</tr>
<tr>
<td>PbCl$_2$ + Na$_2$S</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Pb : S</td>
</tr>
<tr>
<td>PbCl$_2$ + Na$_2$Se</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Pb : S</td>
</tr>
<tr>
<td>PbCl$_2$ + Na$_2$Te</td>
<td>1-5 $\mu$m aggregates. Spherical particles &lt; 50 nm</td>
<td>Pb : Te</td>
</tr>
<tr>
<td>3MCl$_2$ + 3Na$_2$Pn</td>
<td>1-5 $\mu$m aggregates. Irregular particles 50-100nm</td>
<td>M : Pn</td>
</tr>
<tr>
<td>M = Fe, Co, Ni; Pn = As, Sb</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3MCl$_2$ + 3Na$_2$Pn</td>
<td>1-8 $\mu$m aggregates. Irregular particles 50-100nm</td>
<td>M : Pn</td>
</tr>
</tbody>
</table>

$^1$ Molar ratios of reagents given for the room temperature, liquid ammonia metathesis reaction of transition metal halides with sodium chalcogenides. Subsequent analyses were obtained from samples washed with distilled water, and refer to both pre-annealed and annealed material (unless stated).

$^2$ Assessed by SEM at maximum magnification.

$^3$ Elemental composition of phase assessed by EDXA (spot size - 1 micron). Approximate surface abundance of multiple phases (assessed qualitatively using back-scattered electrons) is expressed either as a percentage or as major / minor phases.

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**Table 6.9**  SEM / EDXA data of Ternary metal chalcogenides synthesised by metathetical reactions in liquid ammonia at room temperature

<table>
<thead>
<tr>
<th>Reagents</th>
<th>Particle morphology</th>
<th>Ratio of elements (expt error ± 2-3 atm %)</th>
<th>Elemental ratio</th>
<th>Expt values</th>
<th>Theoretical values</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgF + GaBr₃ + 2Na₂S</td>
<td>1-5 μm agg. Spherical pts &lt; 50 nm</td>
<td>Ag:Ga:S</td>
<td>25:25:50</td>
<td>25:25:50 AgGaS₂</td>
<td>Ag:Ga:S 65:2:33</td>
</tr>
<tr>
<td>AgF + GaBr₃ + 2Na₂Se</td>
<td>1-5 μm agg. Spherical pts &lt; 50 nm</td>
<td>Ag:Ga:Se</td>
<td>25:25:50</td>
<td>25:25:50 AgGaSe₂</td>
<td>Ag:Ga:Se 65:2:33</td>
</tr>
<tr>
<td>AgF + InCl₃ + 2Na₂S</td>
<td>1-5 μm agg. Spherical pts &lt; 50 nm</td>
<td>Ag:In:S</td>
<td>25:25:50</td>
<td>25:25:50 AgInS₂</td>
<td>Ag:In:S 65:2:33</td>
</tr>
<tr>
<td>AgF + InCl₃ + 2Na₂Se</td>
<td>1-5 μm agg. Spherical pts &lt; 50 nm</td>
<td>Ag:In:Se</td>
<td>25:25:50</td>
<td>25:25:50 AgInSe₂</td>
<td>Ag:In:Se 65:2:33</td>
</tr>
<tr>
<td>CuBr + AlCl₃ + 2Na₂S</td>
<td>1-5 μm agg. irregular pts &lt; 200 nm</td>
<td>Cu:Al:S*</td>
<td>50:0:50</td>
<td>50:0:50 CuS</td>
<td>Cu:Al:S* 67:0:33</td>
</tr>
<tr>
<td>CuBr + AlCl₃ + 2Na₂Se</td>
<td>1-5 μm agg. irregular pts &lt; 200 nm</td>
<td>Cu:Al:Se*</td>
<td>50:0:50</td>
<td>50:0:50 CuSe</td>
<td>Cu:Al:Se* 67:0:33</td>
</tr>
<tr>
<td>AgF + AlBr₃ + 2Na₂S</td>
<td>1-5 μm agg. irregular pts &lt; 200 nm</td>
<td>Ag:Al:S*</td>
<td>67:0:33</td>
<td>67:0:33 Ag₂S</td>
<td>Ag:Al:S* 67:0:33</td>
</tr>
<tr>
<td>AgF + AlBr₃ + 2Na₂Se</td>
<td>1-5 μm agg. irregular pts &lt; 200 nm</td>
<td>Ag:Al:Se*</td>
<td>67:0:33</td>
<td>67:0:33 Ag₂Se</td>
<td>Ag:Al:Se* 67:0:33</td>
</tr>
<tr>
<td>CuBr + FeCl₃ + 2Na₂Se</td>
<td>1-5 μm agg. irregular pts &lt; 100 nm</td>
<td>Cu:Fe:Se</td>
<td>25:25:50</td>
<td>25:25:50 CuFeSe₂</td>
<td>Cu:Fe:Se 50:10:40</td>
</tr>
<tr>
<td>MCl₂ + CrCl₃ + 2Na₂S</td>
<td>1-5 μm agg. Spherical pts &lt; 150 nm</td>
<td>M:Cr:S</td>
<td>50:1:49</td>
<td>50:0:50 MS</td>
<td>M:Cr:S 2:48:50</td>
</tr>
<tr>
<td>MCl₂ + VCl₃ + 2Na₂S</td>
<td>1-5 μm agg. Spherical pts &lt; 150 nm</td>
<td>M:V:S</td>
<td>50:0:50</td>
<td>50:0:50 MS</td>
<td>M:V:S 2:48:50</td>
</tr>
<tr>
<td>CdCl₂ + HgCl₂ + 2Na₂Te</td>
<td>1-5 μm agg. Spherical pts &lt; 50 nm</td>
<td>Cd:Hg:Te</td>
<td>47:3:50</td>
<td>50:0:50 CdTe</td>
<td>Cd:Hg:Te 3:48:49</td>
</tr>
</tbody>
</table>

*Aluminium was only detected in sub-micron regions of >95 atm % abundance. In addition, regions of free chalcogen (>95 atm %) were also detected.

** Minor phases
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