ROOM TEMPERATURE SYNTHESIS OF THALLIUM CHALCOGENIDES IN AMMONIA AND n-BUTYLAMINE

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Abstract

A range of crystalline thallium chalcogenides have been prepared by direct combination of the elements at room temperature in liquid ammonia ($Tl[TlS_2]$, $Tl[TlSe_2]$, Tl_2Se, Tl_5Se_3, Tl_5Te_3 and (TlAgTe)) and n-butylamine ($Tl[TlE_2]$; E = S, Se) solvents. Solvent mediated metathesis reactions in liquid ammonia of TlCl with stoichiometric amounts of sodium chalcogenide (Na_2E, E = S, Se, Te) afforded a range of thallium chalcogenides ($Tl[TlE_2]$, E = S, Se; Tl_5Te_3) in addition to co-produced salt. Washing of the sub-micrometer, aggregated product mixture with water enabled isolation of crystalline binary chalcogenides in good yield. Products from both the elemental and metathesis reactions were characterised by X-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDXA), electron probe analysis and infra-red spectroscopy (IR).

Introduction

Thalllium chalcogenides have a range of stoichiometries including Tl_2E, Tl_4E_3, TlE, Tl_2E_3 and Tl_5E_3 (E = S, Se, Te). Thallium has two common oxidation states in these materials, Tl(I) and Tl(III), such that the material with emperical formula TlE is best regarded as $Tl(I)[Tl(III)E_2]$. Recent research into thallium chalcogenides have focused primarily on establishing parameters for semi-conducting properties[1-3]. Notable investigations have included the memory switching effect of both thallium monosulfide[4] and thallium selenide[5-7] single crystals (TlS), as well as the photoconductivity associated with bulk thallium selenide (TlSe, Tl_2Se).[8] Modification of the electrical responses of thallium chalcogenides have been achieved through substitution chemistry, forming materials such as $Tl_{2x}In_{2(1-x)}Se_2$ ($0< x \leq 1.0$).[9 10] Interest also lies in piezoelectric and dielectric properties of some transition-metal thallium-chalcogenides, notably vanadium thallium sulfide.[11]

Thallium-chalcogenides have been synthesised by a variety of means, including the reaction of H_2S with acidic solutions containing Tl^+ cations to afford phase pure Tl_2S.[12] Synthesis of thallium chalcogenides by elemental combination reactions[13] employ elevated temperatures, long processing times (*ca.* 800-1300°C; 3-7 days) and offer little control over product stoichiometry.[14] This processing is necessary to overcome the solid state diffusion barrier. We have previously reported single-step, room-temperature elemental-combination reactions in liquid ammonia[15] and n-butylamine[16] that afford transition metal chalcogenides.[15] We have also shown that metal chalcogenides can be formed in solid state metathetical reactions (SSM) between metal halides and sodium chalcognides[17]. The reactions are promoted by the formation of the co-formed salt and proceed with a synthesis wave or thermal flash. Recent extensions of these reactions have shown that the exothermic 'explosive' reaction can be controlled by the use of a solvent at reflux[18]. In this paper we report two new room temperature methods of forming thallium chalcogenides; elemental combination in N-based solvents (ammonia and n-butylamine) and metathesis reaction of thallium chloride with sodium chalcogenide in liquid ammonia.

Materials and methods

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. X-ray powder diffraction patterns were determined on a Siemens D5000 transmission powder diffractometer using germanium monochromated Cu-$K_{\alpha 1}$ radiation (λ = 1.504 Å). Powder patterns were compared to those of data-base standards.[19] They were indexed using either TREOR or METRIC-LS programmes (lattice parameters matched to within 0.01 Å of the literature[19]). SEM / EDXA measurements were determined on a Jeol JSM820 microscope, equipped with a Kevex Quantum Delta 4 detector and a Hitatchi SEM S-570 camera. The electron beam was focused (1 µm spot at the 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. Infra-red spectra were recorded on a Nicolet 205 spectrometer using KBr pressed disks. The spectra were compared with those obtained from the literature.[20] Reactions were carried out using Schlenk techniques in thick walled (3-4 mm), teflon-in-glass, Youngs-type Schlenk-tubes which were sealed by a large rota-flow tap and surrounded by safety netting. Na_2E (E = S, Se, Te) was prepared by the direct combination of stoichiometric quantities of sodium metal and elemental chalcogen in liquid ammonia. Once prepared, the sodium chalcogenide was immediately used in subsequent reactions.

Elemental combination reaction of a 2:1 ratio of thallium to sulfur in liquid ammonia

Thallium metal (1250 mg, 6.12 mmol) and sulfur (98 mg, 3.06 mmol) were added to liquid ammonia (*ca.* 10 cm^3) condensed in a Schlenk tube at –77 °C. The system was sealed, allowed to warm to room temperature and magnetically stirred for 15 h. The sulfur dissolved in the ammonia to generate a dark blue solution that faded to green and after 10 h became colourless, with a black precipitate. Within 1 h of warming to room temperature, all the sulfur had dissolved. The thallium metal was not observed to dissolve during the course of the reaction, but was consumed within 6-10 h and replaced by the black precipitate. The precipitate was collected by cooling the solution back to –78 °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 30 min. The solid was collected and analysed. Part of the material was heated to 250 °C for 2 h. The unthermolysed and thermolysed materials were analysed by X-ray powder diffraction (Table 1), FTIR, microanalysis, SEM / EDXA and electron probe studies.

Analogous reactions, work up procedures and characterisations were carried out on the elemental reactions of Tl with Se and Te in ammonia. Notably in these reactions no species was observed to dissolve in the ammonia.

Elemental combination reaction of a 2:1 ratio of thallium to selenium in n-butylamine

Thallium metal (235 mg, 1.15 mmol) and selenium (45.8 mg, 0.58 mmol) were added in stoichiometric amounts to 20 cm^3 of n-butylamine in a 40 cm^3 sample tube at room temperature. The mixture was magnetically stirred for 48 h. Selenium reacted directly with the thallium to afford a black solid without dissolution. The black solid was isolated by first decanting off the amine, then washing with acetone (20 cm^3) followed by CS_2 (2 x 20 cm^3) before being air-dried and annealed for 2 h at 250 °C. The product was analysed (before and after annealing) by XRD (Table 1), SEM / EDXA and FTIR spectroscopy. XRD analysis was also carried out on the pre-washed product.

Analogous reactions, work up procedures and characterisations were carried out on the elemental reactions of Tl with S in n-butylamine. Sulfur dissolved in the n-butylamine to afford a red solution. This red solution reacted with thallium to form thallium sulfide, yet at no time was the thallium observed to dissolve in n-butylammine. No reaction was observed between thallium and tellurium in n-butylamine even after stirring for 1 week at RT.

Metathetical reaction of sodium telluride with thallous chloride in liquid ammonia.

Ammonia (*ca.* 15 cm^3) was condensed over freshly prepared sodium telluride (100 mg, 0.58 mmol). Thallium (I) chloride (138 mg, 1.15 mmol) was added with continuous stirring. The system was sealed and allowed to warm to room temperature. The sodium telluride partially dissolved whilst the TlCl remained as a solid throughout the course of the reaction. After 12-18 h the ammonia was cooled to *ca.* -77 °C and allowed to evaporate under a nitrogen gas flow. Part of the product was then triturated with 3 x 20 cm^3 of water, yielding a black material. This was dried *in vacuo* at RT, then annealed for 2 h at 200-250 °C. The product was analysed (before and after annealing) by XRD, SEM / EDXA and IR spectroscopy. XRD analysis was also carried out on the pre-washed reaction product.

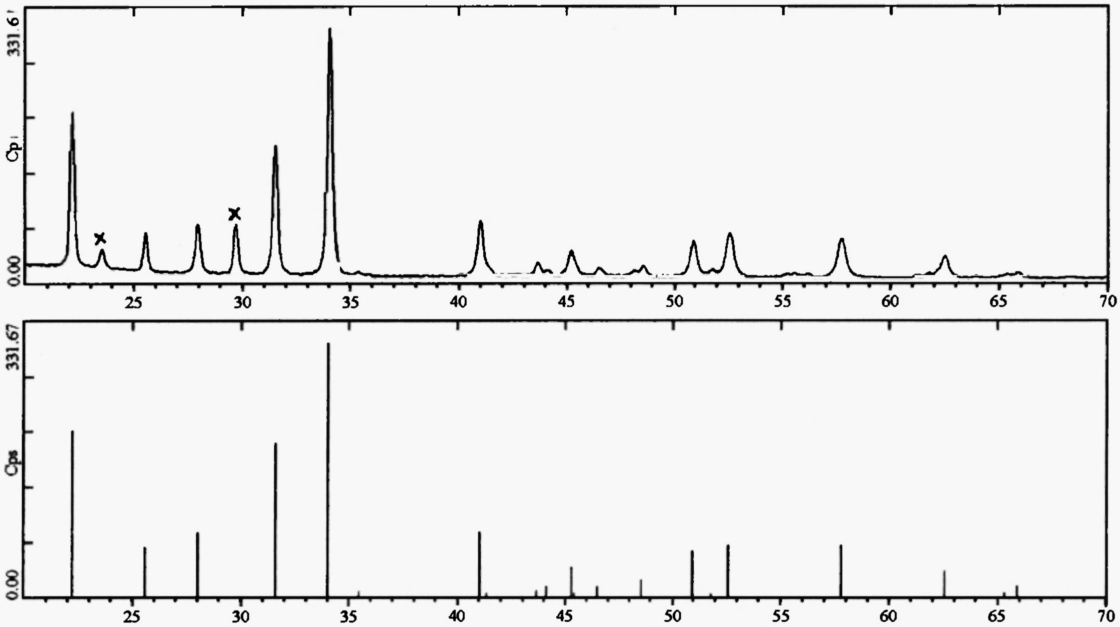

Figure 1 Top Trace; X-ray powder diffraction pattern of the product of the elemental reaction of Selenium and Thallium in n-butylamine at RT. Bottom trace powder XRD stick pattern of Tl[TlSe$_2$].
• = Se metal

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. Thallium salts are very toxic.

Results

Liquid ammonia; synthesis and characterisation of binary thallium chalcogenides

The addition of thallium metal to stoichiometric ratios of chalcogen (Tl:E; 2:1, 7:4 and 2:3) in liquid ammonia at RT, resulted in reactions that afforded crystalline binary thallium chalcogenides in good yield (> 90%); Table 1, (1)-(6). Minor phases observed in the reaction, defined as less than *ca.* 5-10 % as determined by optical microscopy, are expressed in italics.

$$\mathrm{Tl_{(s)} + S_{(am)} \rightarrow Tl[TlS_2]_{(s)}} \quad (1)$$
$$\mathrm{2Tl_{(s)} + 3S_{(am)} \rightarrow Tl[TlS_2]_{(s)} + S_{(am)}} \quad (2)$$

$$\mathrm{7Tl_{(s)} + 4Se_{(s)} \rightarrow Tl_2Se_{(s)} + Tl_5Se_{3(s)}} \quad (3)$$
$$\mathrm{2Tl_{(s)} + 3Se_{(s)} \rightarrow 2Tl[TlSe_2]_{(s)}} + \mathit{Se}_{(s)} \quad (4)$$

$$\mathrm{6Tl_{(s)} + 3Te_{(s)} \rightarrow Tl_5Te_{3(s)}} + \mathit{Tl}_{(s)} \quad (5)$$
$$\mathrm{10Tl_{(s)} + 15Te_{(s)} \rightarrow 2Tl_5Te_{3(s)} + 9Te_{(s)}} \quad (6)$$

Table 1 X-ray powder diffraction data for metal sulfides synthesised from the elements in liquid ammonia and n-butylamine at R.T.

Ratio of elements	Product colour	Solvent	Products as formed from reaction (identified by XRD)	Annealed reaction products (250-300 °C for 2h)[a]	Lattice Parameters Å (± 0.01)[b]	Lit. lattice parameters / Å[19]
Tl : S 2 : 1	Black	$NH_{3\,(l)}$	$Tl[TlS_2]$	$Tl[TlS_2]$ + Tl	$a = 7.79$ $c = 6.80$	$a = 7.79$ $c = 6.80$
Tl : S 2 : 3	Black	$NH_{3\,(l)}$	$Tl[TlS_2]$	$Tl[TlS_2]$ + S	$a = 7.79$ $c = 6.80$	$a = 7.79$ $c = 6.80$
Tl : Se 2 : 1	Black	$NH_{3\,(l)}$	Tl_5Se_3	Tl_5Se_3	$a = 8.02$ $c = 7.00$	$a = 8.02$ $c = 7.00$
			Tl_2Se + [TlSe]	Tl_2Se + [TlSe]	standardised XRD patterns[19]	
Tl : Se 2 : 3	Black	$NH_{3\,(l)}$	TlSe + [Se]	TlSe + [Se]	$a = 8.02$ $c = 7.00$	$a = 8.02$ $c = 7.00$
Tl : Te 2 : 1	Black	$NH_{3\,(l)}$	Tl_5Te_3 + [Te]	Tl_5Te_3 + [Te]	$a = 8.93$ $c = 12.62$	$a = 8.92$ $c = 12.61$
Tl : Te 2 : 3	Black	$NH_{3\,(l)}$	Tl_5Te_3 + [Te]	Tl_5Te_3 + [Te]	$a = 8.93$ $c = 12.62$	$a = 8.92$ $c = 12.61$
Tl : S 2 : 3	Black	n-butyl amine	$Tl[TlS_2]$ + S	$Tl[TlS_2]$ + S	$a = 7.79$ $c = 6.80$	$a = 7.79$ c = 6.80
Tl : Se 2 : 3	Black	n-butyl amine	$Tl[TlSe_2]$ + Se	$Tl[TlSe_2]$ + Se	$a = 8.02$ $c = 7.00$	$a = 8.02$ c = 7.00

[a] All minor phases (< *ca.* 10 %) represented by square brackets

[b] Unit cell parameters were determined for the major phase only.

Dissolution of sulfur in liquid ammonia lead to blue/green solutions[15, 20]. The disappearance of insoluble thallium metal in the sulfur ammonia solution coincided with the formation of a black solid and loss of colour from the ammonia. In the reactions of thallium with selenium and tellurium the chalcogen did not appear to dissolve or any colour appear in the ammonia. In these reactions formation of the thallium chalcogenide product coincided with consumption of the metal. Work–up of these powders by trituration with acetone and carbon disulfide proved effective in removing the small amount of unreacted chalcogenide. This was achieved both by dissolution of the chalcogenide and separation of the thallium chalcogenide by density driven separation. Examination of the products of the washed reactions by optical microscopy revealed a homogeneous solid. SEM analysis of these powders revealed agglomerates of particles of typical size 2-5 microns.

XRD analyses of the as-formed product from reactions of thallium with chalcogens in liquid ammonia showed them to be crystalline (Table 1). The chalcogenides indexed with literature cell parameters.[19] Where the reactions involved either sulfur or tellurium, a single binary phase of thallium chalcogenide is produced irrespective of the initial ratio of the elements ($Tl[TlS_2]$, Tl_5Te_3). The reactions of thallium and selenium produce mixed-phase thallium-chalcogenides dependant upon the ratio of reacting elements. A 2:1 initial ratio of Tl:Se results in the binary phases, Tl_2Se and Tl_5Se_3, whilst a 2:3 initial ratio produces single phase $Tl[TlSe_2]$. Analysis of the X-ray powder diffraction patterns using the Scherrer equation,[21] showed that the as made materials had crystallite sizes in the range of 500-800 Å. Annealing the materials at 250 °C for 2 h slightly improved the crystallinity of the products, with an average crystallite size of 800-1000 Å.

Standardised EDXA analysis of the metal sulfide products were within 1 % of the expected elemental ratios for $Tl[TlS_2]$, showing virtually uniform composition over many randomly chosen surface spots (electron beam focal width of 1 μm). Similar analyses also confirmed the presence of all phases of thallium telluride to within 2-3 atm. % of the phase predicted by XRD. Electron probe analysis of the mixed phase Tl_2Se and Tl_5Se_3 product (3) showed regions on the micron scale that corresponded to the individual phases. Microanalysis of all of the thallium chalcogenides synthesised in ammonia had negligible (less than 0.2%) CHN content, indicating that an amide was not formed in the reactions.

The thallium-sulfide showed a strong absorption band at 450-300 cm^{-1} in the IR spectra, corresponding to an M-S stretch. Notably, there were no bands at 3200 and 1450 cm^{-1} in the unthermolysed sample, showing the absence of N-H stretches from either ammonia or metal amides.[19] Infra-red analyses showed broad bands at *ca.* 350-180 cm^{-1} for the thallium selenides and 250-160 cm^{-1} for the thallium telluride.[19]

Attempts at forming single-phase, substitutional solid-solutions of thallium chalcogenides (Tl_2SSe, Tl_2SeTe, TlAgTe and $TlMTe_2$, where M = Al, Ga, Cr, Ag) *via* elemental combination in liquid ammonia met with limited success. Phase segregation occurred in all cases except for the formation of AgTlTe.

n-Butylamine; synthesis and characterisation of binary thallium chalcogenides

Room temperature reactions of thallium with either sulfur or selenium (Tl:E ratios of 2:1 or 2:3) in n-butylamine produced, after 24 h, crystalline thallium chalcogenides of general formula $Tl[TlE_2]$ (E = S, Se), (7), in practically quantitative yield (> 90%). Sulfur dissolved in the n-butylamine to give a red solution, which reacted with the thallium to afford a black solid. The thallium was not observed to dissolve into the n-butylamine, but rather become used up during the course of the reaction. In the selenium / thallium reaction neither element dissolved in n-butylamine. The reaction was complete in 24 h. No reaction was observed between thallium and tellurium in n-butylamine even after 1 week at room temperature.

$$2Tl_{(s)} + 2E_{(amine)} \rightarrow Tl[TlE_2]_{(s)} \qquad (E = S, Se) \qquad (7)$$

The thallium chalcogenides were characterised by FT-IR spectroscopic analysis, which showed a characteristic broad absorption bands within the region of 600 - 200 cm^{-1}. Vibrational spectra invariably matched that of authentic samples.[20] No IR stretches were observed for N-H vibrations. In addition, microanalyses (CHN) showed negligible amounts of carbon, hydrogen and nitrogen (< 0.2 %) in the bulk materials, indicating that amine is not bound to the product. The X-ray powder diffraction patterns obtained for the as-made products indexed well with literature cell parameters (Table 1, Figure 1).[19] Crystallite sizes as assessed by the Scherrer equation were 600 - 800 Å. As with analogous reactions in liquid ammonia, annealing at 250 – 300 °C for 2 h in an inert atmosphere had no discernible affect on product composition (as assessed by EDXA).

SEM revealed small, irregularly shaped aggregates (typically 3 - 8 μm 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 (excitation width of 1 μm).

The X-ray powder diffraction patterns of the products produced from the reactions of thallium with chalcogens in n-butylamine showed the formation of crystalline thallium chalcogenide powders. These indexed well to give cell parameters that were in good agreement (± 0.01 Å) with literature measurements.[18] Crystallite sizes were of the order of 300 - 700 Å (from line broadening analysis). The product of the reaction of thallium with tellurium showed that no elemental combination had occurred, both by EDXA and XRD.

Solvent mediated metathetical reactions in liquid ammonia

Reaction of stoichiometric amounts of thallous chloride with disodium chalcogenide in liquid ammonia at room temperature afforded single-phase thallium-chalcogenides in good yield (> ca. 95 %). The reactions were all assessed to be complete within 36 h. Whilst both disodium sulfide and selenide were observed to dissolve in liquid ammonia, thallous chloride did not. XRD analysis of the pre-annealed product showed the presence of crystalline alkali metal halide, suggesting that the reactions proceed via a metathetical route. Repeated washing of the material with CS_2 and then distilled water resulted in isolation of the thallium chalcogenides largely free of thallium metal. Infra-red studies of the isolated products showed absorptions characteristic of the desired material, with no N-H stretches being detected (broad band at ca 400 cm^{-1}). Facile annealing of the isolated material at 250 - 300 °C for 48 h improved the crystallinity for X-ray analysis without changing product identity, Table 2, (8), (9).

$$4TlCl_{(s)} + 2Na_2E_{(am)} \rightarrow Tl[TlE_2]_{(s)} + Tl_{(s)} + 2NaCl_{(s)} \quad (E = S, Se) \qquad (8)$$

$$6TlCl_{(s)} + 3Na_2Te_{(s/am)} \rightarrow Tl_{(6-x)}Te_{3(s)} + 2NaCl_{(s)} + \mathit{Tl}_{(s)} \quad (x = 1) \qquad (9)$$

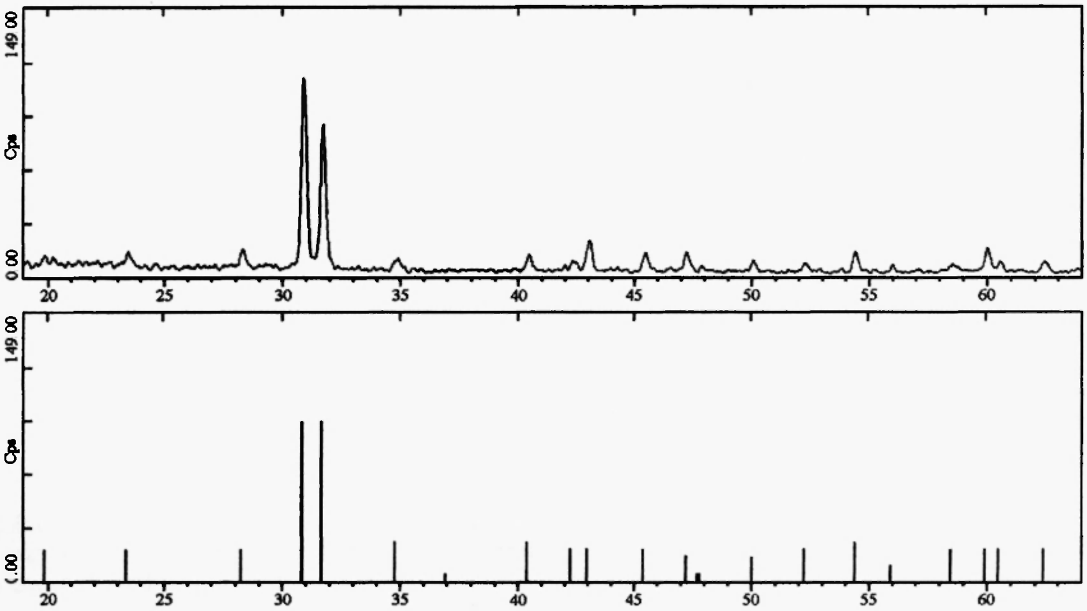

Figure 2 Top trace; X-ray Powder diffraction pattern of the product obtained from reaction of TlCl and Na_2Te in ammonia. Bottom trace; standard stick pattern for Tl_5Te_3.

Table 2 X-Ray powder diffraction data for thallium chalcogenides synthesised by metathetical reactions in liquid ammonia at RT

Reagents [a]	Products as formed from reaction (identified by XRD)[b]	Product colour	Phases obtained after annealing the washed material [c]	Lattice Parameters Å (± 0.01)	Literature[19] Lattice Parameters, Å
2TlCl + Na_2S	$Tl[TlS_2]$ + NaCl	Black	$Tl[TlS_2]$	a = 7.79 *c* = 6.80	a = 7.79 *c* = 6.80
TlCl + Na_2Se	$Tl[TlSe_2]$ + NaCl	Black	$Tl[TlSe_2]$	a = 8.02 *c* = 7.00	*a* = 8.02 *c* = 7.00
2TlCl + Na_2Te	Tl_5Te_3 + NaCl	Black	Tl_5Te_3	a = 8.93 *c* = 12.62	a = 8.92 *c* = 12.61

[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.

Discussion

Elemental combination reactions in liquid ammonia

Thallium metal reacts with either sulfur or tellurium to form the single phase binary material $Tl[TlS_2]$, Tl_5Te_3. The thallium telluride Tl_5Te_3 can be described thallium (+I) telluride due to tellurium-tellurium bonding, whereas the thallium sulfide is TlS, a mixed oxidation state material, more accurately described as $Tl^{I}[Tl^{III}S_2]$. In the case of the selenide product from the elemental reaction multiple phases are produced Tl_2Se and Tl_5Se_3 both of which have thallium in the Tl(I) state.

Formation of thallium chalcogenides from elemental reactions with sulfur-ammonia solutions is in agreement with previous work carried out on other chalcophillic metals[15]. It is known that some metals will react directly with chalcogens at room temperature, such reactions are largely surface limited and for most metals slow. These elemental reactions are largely solid state in nature and rapid, reaching completion in less than 48 h. We believe, that liquid ammonia plays a dual role in removing passivating oxide layers from insoluble reagents as well as producing active sulfur species in solution. This would result in a lowering the activation energy, such that the reaction can occur at ambient temperatures.

The elemental reactions of thallium with chalcogenides show an interesting trend in oxidation states that seem to be dependent upon the chalcogen used. With sulfur, the product, $Tl[TlS_2]$, formed independently of the initial ratio of 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 the products are predominantly Tl^{I} (Tl_2Se and Tl_5Se_3). When the initial Tl:Se ratio is 2:3 a single phase of $Tl[TlSe_2]$ results, with the stoichiometric excess of selenium appearing as the unreacted element. With tellurium, however, the sole metal chalcogenide product is Tl_5Te_3, irrespective of the ratios of the starting materials (2:3 or 2:1).

Solid solutions of mixed metal thallium telluride are only successful with the use of silver. The phase observed from the elemental combination reaction of thallium, silver and tellurium was AgTlTe. In previous elemental combination reactions silver was unique in that it reacted directly with the chalcogenides in ammonia and n-butylamine to form crystalline silver chalcogenides. The other metals that were employed form solid solutions with thallium and chalcogenides; Al, Ga and Cr do not react with the chalcogenides in ammonia. The ease of the formation of the TlAgTe solid solution is probably a reflection of the chalcophilicity of silver and thallium.

Elemental combination reactions in n-butylamine

The possible presence of *in situ* H_2S, formed upon the dissolution of sulfur in n-butylamine may play a critical role in the subsequent elemental reaction of Tl and S. Upon dissolution, the S_8 ring undergoes stepwise nucleophilic attack by either primary or secondary amines. The initial products are the *in situ* release of H_2S with the formation of N,N'-polythiobisamines.[22, 16] In a solution just containing dissolved sulfur, these S-N species co-exist with amine polysulfides, formed by the subsequent attack of the aliphatic amine by H_2S. It is plausible, however, that the H_2S formed may be the source of sulfur for direct combination with the metal. Moreover, these new straight chain sulfur-amine species are inherently less stable than the original S_8 rings. Hodgson *et al*[22] suggests that these solvated species would undergo homolytic scission to achieve a degree of resonance stability, creating sulfur based radicals. Sulfur radicals may be intrinsic in the formation of metal sulfides by elemental combination at room temperature in n-butylamine. Indeed, it has been reported 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.[23]

It should be noted that selenium is insoluble in n-butylamine yet also reacts with elemental thallium. However the analogous tellurium reaction does not form a thallium telluride in n-butylamine whereas in ammonia the reaction was facilitated. We have no ready explanation of this except perhaps that the extra pressure of the ammonia solution may promote the process.

Metathetical reactions in liquid ammonia

The thallium chalcogenide materials synthesised by metathesis reactions in ammonia 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 purely solid state metathetical reactions. The solvent mediated reactions are both initiated and proceed at room temperature without the need of an external heat source. The reaction also proceeds without a solid flame or synthesis wave. This has important consequences for the particle sizes of the materials obtained from the reactions.

As is typical of solvent mediated metathesis reactions, liquid ammonia metathesis results in notable differences in product morphology when compared to purely solid state metathesis reactions. Completion of these at room temperature and without a thermal flash shows the liquid ammonia to be acting as a heat sink. The reaction temperature thereby becomes limited by both the boiling point of the liquid and, with effective dispersion of insoluble particles, the reduced thermal mass of the reaction mixture. Consequently, product annealing is reduced and so particle size becomes restricted. Liquid ammonia metathesis affords spherical nanocrystaliites agglomerated into aggregates of < 1 micron, whereas SSM characteristically results in a fused, highly sinterable mass in excess of 10 microns in diameter.[25]

Conclusions

The formation of highly crystalline thallium chalcogenides by elemental combination in ammonia suggest that these materials offer accessible barriers to solid state diffusion under the reaction conditions employed. Interestingly, formation of ternary mixed chalcogenide materials are not formed, with the exception of TlAgTe, even though such solid solutions are known to exist.[17]

Liquid ammonia and n-butylamine both play an intrinsic role in enabling the elemental reactions 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 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 reactions described here are also more straight forward 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).[26] 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.[27]

Recent developments in metathesis reactions have resulted in a variety of mediating solvents being studied.[28] Liquid ammonia offers similar morphologies to the bulk chalcogenide materials 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.

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