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Solid state synthesis of binary metal chalcogenides

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Solid state reaction of metal halides MX_n ($n = 1$ or 2) with stoichiometric amounts of sodium chalcogenide (Na_2S_2 or Na_2E where E = S, Se or Te) at 300 °C for 48 h in evacuated ampoules affords a range of transition and main-group metal chalcogenides: ME_2 (M = Fe or Co, E = S or Te); $M_{(1-x)}E$ (M = Fe or Co, E = S); Ag_2E (E = S, Se or Te), $Ni_{(1-x)}E$ (E = S, Se or Te); NiS_2, MnS, FeSe, SnSe and SnTe along with co-formed salt. Washing of the highly sintered, fused product mixture with water resulted in isolation of crystalline binary chalcogenides, typically of a single phase in good yield (90%). The products were characterised by X-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA) and i nfrared spectroscopy.

Introduction

Binary transition and main group metal chalcogenides, of the formulae ME or ME_2 (E = S, Se or Te), have varied technological uses. The most extensive use of metal chalcogenides stems from their wide range of semi-conducting properties.[1] Group 12 chalcogenides are classed as direct wide band-gap semiconductors, whilst tin(II) sulfide has a band gap (1.3 eV) between that of silicon (1.12 eV) and gallium arsenide (1.43 eV).

Many procedures exist for the synthesis of bulk metal chalcogenides. These include the decomposition of organometallic precursors,[2] electrodeposition from solution[3] and elemental combination at elevated temperatures.[4] Hydrogen sulfide and selenide have widely been employed in the synthesis of metal chalcogenides [5–8] through reactions with aqueous metal cations,[6] metal oxides, and sol–gel processing.[8] Most procedures to form metal chalcogenides require multiple steps with long processing times, carefully tailored precursors and/or the use of highly toxic reagents.[9]

One synthetic approach that circumvents these problems is the metathetical solid state reaction of metal halides with alkali metal chalcogenides.[10] Once initiated, these intimately mixed reagents undergo a rapid, self-propagating reaction to produce highly sintered metal chalcogenides and a co-produced salt such as LiCl. The reactions proceed by passage of a hot yellow-orange synthesis wave that progresses through the material as a solid flame. Kaner and co-workers have carried out some detailed mechanistic studies into the synthesis of ME_2 (M = Mo or W; E = S, Se or Te) from filament initiated solid state metathesis (SSM) reactions involving $MoCl_5$ and WCl_6.[11] They show that the reaction temperature is limited by the melting point of the co-produced salt. Product crystallinity and stoichiometry were optimised by the use of high oxidation state metal fluorides or chlorides. Consequent work resulted in the formation of crystalline NiS (vaesite) from the reaction of Na_2S with $K_2[NiF_6]$.[12] We have shown, through a wide range of survey work, that metathesis techniques can also be applied to the synthesis of both binary main-group, lanthanide and actinide chalcogenides, as well as to ternary Group I–lanthanide sulfides.[9,10,13]

In this paper we extend the scope of the solid state metathesis procedure to the synthesis of binary chalcogenides of manganese, iron, cobalt, nickel, silver and tin. We also show that solid state metathesis reactions can proceed without a solid flame, and that the use of low-oxidation state metal halide precursors gives a measure of stoichiometric control in the synthesis of crystalline mono- and di-chalcogenides.

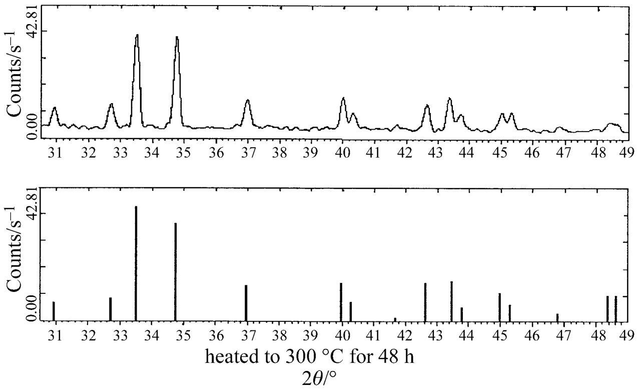

Fig. 1 XRD pattern of washed silver selenide synthesized by SSM reactions heated to 300 °C for 48 h.

Results and discussion

Synthesis and characterisation

The solid state metathesis reactions of metal halides and sodium chalcogenides (Na_2E, E = S, Se or Te, and Na_2S_2) in sealed evacuated ampoules at 300 °C for 48 h are described by eqns. (1)–(11) (Table 1). In terms of monochalcogenides, the reactions that afforded a single crystalline phase of desired stoichiometry are described by (1)–(4). Fig. 1 shows the XRD

$$2AgF + Na_2E \longrightarrow Ag_2E + 2NaF \quad (E = S, Se\ or\ Te) \quad (1)$$

$$SnBr_2 + Na_2E \longrightarrow SnE + 2NaBr \quad (E = Se\ or\ Te) \quad (2)$$

$$MnF_2 + Na_2S \longrightarrow MnS + 2NaF \quad (3)$$

$$FeBr_2 + Na_2Se \longrightarrow FeSe + 2NaBr \quad (4)$$

pattern obtained for silver selenide (Ag_2Se) formed from the SSM reaction after removal of the co-produced salt by washing with water.

In addition, a series of reactions (5), (6) afforded a single crystalline phase of non-stoichiometric metal chalcogenides.

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Table 1 XRD data of the products from the SSM reaction of metal halides with Na_2E and Na_2S_2 at 300 °C in sealed glass ampoules for 48 h

Reagents [a]	Initial products[b]	Product colour[c]	Washed and annealed material[d]	Lattice values/Å (±0.01) [e]	Lit.[15] lattice values/Å
$2AgF + Na_2S$	NaF	Black	Ag_2S (*acanthite*)	$a = c = 4.46$	$a = c = 4.46$
$2AgF + Na_2Se$	NaF	Black	Ag_2Se (*naumannite*)	$a = 4.33$	$a = 4.33$
				$b = 7.06$	$b = 7.06$
				$c = 7.76$	$c = 7.76$
$2AgF + Na_2Te$	NaF	Black	Ag_2Te (*hessite*)	$a = 8.09$	$a = 8.09$
				$b = 4.47$	$b = 4.47$
				$c = 8.96$	$c = 8.96$
$2MnF + Na_2S$	NaF	Black	MnS (*alabandite*)	$a = c = 5.24$	$a = c = 5.24$
$2MnF + Na_2S_2$	NaF	Black	MnS (*alabandite*)	$a = c = 5.24$	$a = c = 5.24$
$FeCl_2 + Na_2S$	NaCl	Black	$Fe_{1-x}S$ ($x = 0.04$)	$a = 3.43$	$a = 3.43$
				$c = 3.79$	$c = 3.79$
$FeCl_2 + Na_2S_2$	NaCl	Black	FeS_2 (*pyrite*)	$a = c = 5.41$	$a = c = 5.41$
$FeCl_2 + Na_2Se$	NaCl	Black	FeSe	$a = 3.77$	$a = 3.77$
				$c = 5.52$	$c = 5.52$
$FeCl_2 + Na_2Te$	NaCl	Black	$FeTe_2$	$a = 3.85$	$a = 3.85$
				$b = 5.34$	$b = 5.34$
				$c = 6.26$	$c = 6.26$
$CoCl_2 + Na_2S$	NaCl	Black	$Co_{1-x}S$ ($x = 0.05$)	$a = 3.38$	$a = 3.38$
				$c = 5.15$	$c = 5.15$
$CoCl_2 + Na_2S_2$	NaCl	Black	CoS_2	$a = c = 5.54$	$a = c = 5.54$
$CoCl_2 + Na_2Te$	NaCl	Black	$CoTe_2$	$a = 3.88$	$a = 3.88$
				$b = 5.30$	$b = 5.30$
				$c = 6.30$	$c = 6.30$
$NiCl_2 + Na_2S$	NaCl	Black	$Ni_{1-x}S$ ($x = 0.02$)	$a = c = 3.42$	$a = c = 3.42$
$NiCl_2 + Na_2S_2$	NaCl	Black	NiS_{2+x} ($x = 0.02$)	$a = c = 5.62$	$a = c = 5.62$
$NiCl_2 + Na_2Se$	NaCl	Black	$Ni_{1-x}Se$ ($x = 0.06$)	$a = 3.66$	$a = 3.66$
				$c = 5.33$	$c = 5.33$
$NiCl_2 + Na_2Te$	NaCl	Black	$Ni_{1-x}Te$ ($x = 0.45$)	$a = 3.78$	$a = 3.78$
				$c = 6.06$	$c = 6.06$
$SnBr_2 + Na_2S$	NaBr	Black	SnS	$a = 4.30$	$a = 4.30$
				$b = 11.20$	$b = 11.18$
				$c = 3.99$	$c = 3.98$

[a] Reagents shown with molar ratios. [b] Phases characterised by X-ray powder diffraction *prior* to work-up of product. [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 48 h. Values of x assessed by Vegard's law. [e] Unit cell parameters were determined for major phase binary material only.

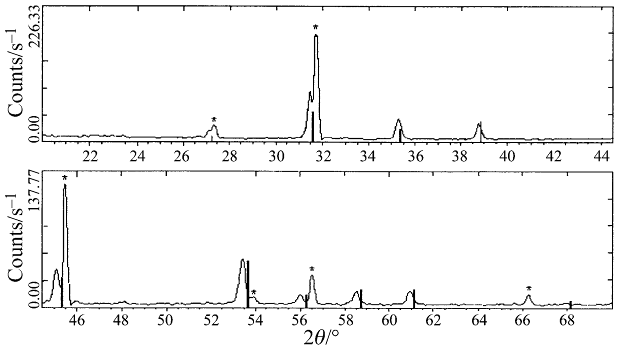

Fig. 2 XRD of unwashed nickel disulfide ($NiS_{2.02}$) synthesized by SSM reactions heated to 300 °C for 48 h. Stick pattern is for stoichiometric NiS_2.

$$NiCl_2 + Na_2E \longrightarrow Ni_{(1-x)}E + 2NaCl \quad (E = S, Se\ or\ Te) \quad (5)$$

$$MX_2 + Na_2S \longrightarrow M_{(1-x)}S + 2NaCl \quad (MX_2 = FeBr_2\ or\ CoCl_2) \quad (6)$$

The stoichiometries were derived from application of Vegard's law. The results are shown in Table 1, and represent an average stoichiometric value derived from the four most intense peaks in the range $20 \leq 2\theta \leq 70°$. Application of Vegard's law to the XRD spectrum of the $Ni_{(1-x)}S$ product showed it to be a slightly metal deficient phase (with an empirical formula of $NiS_{1.02}$).[14] By changing the sulfide precursor to Na_2S_2, eqn. (7), the *vaesite* structure was obtained, NiS_2. However, upon close examination of the XRD spectrum (Fig. 2) 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 $NiS_{(2+x)}$. This phase was not observed in Kaner's reactions employing $K_2[NiF_6]$ where NiS was formed.[12]

The reactions that afforded a single phase of crystalline metal dichalcogenides are described in eqns. (7) and (8). Fig. 2 shows

$$MX_2 + Na_2S_2 \longrightarrow MS_2 + 2NaX \quad (MX_2 = FeBr_2, CoCl_2\ or\ NiCl_2) \quad (7)$$

$$MX_2 + Na_2Te \longrightarrow 0.5MTe_2 + 0.5M + 2NaX \quad (MX_2 = FeBr_2\ or\ CoCl_2) \quad (8)$$

the XRD pattern of the initial reaction product from the reaction of Na_2S_2 with $NiCl_2$, showing both the formation of co-produced salt (NaCl) and a slightly sulfur deficient phase of nickel disulfide, $NiS_{(2+x)}$. The telluride reactions, (8), showed that elemental metal was produced in the process. The elemental metal could not be seen in the X-ray powder diffraction pattern probably as it was amorphous. It was, however, readily seen in the back-scattered electron micrographs from SEM and by EDAX (energy dispersive X-ray analysis) which showed regions of phase segregated metal and metal ditelluride.

Eqns. (9)–(11) show those reactions that did not produce single phase metal chalcogenide products after trituration.

$$ZnCl_2 + Na_2S_2 \longrightarrow ZnS^* + 2NaCl + S \quad (9)$$

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

$$SnBr_2 + Na_2S \longrightarrow SnS + Sn_2S_3^* + Sn_3S_4^* + 2NaBr \quad (10)$$

(* These are minor phases less than 10%)

$$2CrCl_3 + 3Na_2S \longrightarrow NaCl + \text{‘amorphous material’} \quad (11)$$

The yield of metal chalcogenide obtained for each reaction as described in eqns. (1)–(10) was typically greater than 90% . All products were black, and after washing with water, showed characteristic IR absorptions for binary metal chalcogenides with broad bands between 600 and 300 cm^{-1}.

All reactions of metal halides with sodium chalcogenides at 300 °C for 48 h gave products of sufficient crystallinity to be characterised by XRD. The metal chalcogenide phases produced correlated well with literature values (cell parameters within 0.02 Å, Table 1).[15] The XRD pattern of each product, as formed, also showed the presence of crystalline sodium halide. This was easily removed by trituration with distilled water without decomposition of the crystalline metal chalcogenide. In each case, analysis of the washed product by SEM showed it 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 detection limits). The notable exception to this was reaction (10) that formed tin sulfide. Evaporation of the water washings left colourless co-produced salt, which was confirmed by X-ray powder diffraction.

The product from the SSM reaction of $SnBr_2$ with Na_2S (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_2S_3). Increasing the annealing temperature to 500–550 °C produced predominantly SnS with a 2–5% trace of Sn_2S_3. This is consistent with the formation of tin sulfide thin films from the APCVD of $SnCl_4$ with H_2S,[16] where Sn_2S_3 predominates at low temperatures and SnS predominates at 525 °C and above.

The reaction of $CrCl_3$ with Na_2S, (11) shows the formation of a co-produced salt suggesting that a metathesis reaction has occurred. However, the chromium product was amorphous to X-rays, even after annealing at 300 °C for 48 h. 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. This suggests either the existence of different chromium sulfide phases or impurities resulting from oxygen contamination. The origin of the impurities is unknown, although contamination from the reaction vessel has been observed in SSM reactions.[10,13] The Cr–S system has six discrete phases in the composition range $Cr_{0.95}S$ to $Cr_{1.5}S$, each of which may also be encountered in a non-stoichiometric form,[17] so definitive elucidation proved problematic.

Whilst it was not possible to synthesize ZnS_2 from the reaction of $ZnCl_2$ with Na_2S_2, the resultant metathesis afforded both cubic and hexagonal structures of ZnS with the formation of free sulfur, eqn. (9). Interestingly, previous studies have shown that the reaction of $ZnCl_2$ with Na_2S results only in the more thermodynamically stable hexagonal phase,[9] suggesting that the reactions studied here may follow a less energetic route.

Role of chalcogenide precursor

Previous studies[9] have shown that metathetical reactions between solid alkali metal chalcogenide and metal halide occur very rapidly, with a large evolution of heat. In virtually all cases this gives rise to a characteristic thermal flash or solid flame, with temperatures in excess of 1000 °C being reported.[9] For solid-state metathesis reactions it has been suggested that propagation will only occur once the heat of reaction is sufficient to melt the co-produced salt. In so doing, the reaction can proceed through successive layers and hence propagate through the solid. In the reactions observed here, however, a dark wave passes through the reagents (rather than a solid flame) once the surroundings reach approximately 200 °C, irrespective of which metal halides are used. In addition, the calculated heats of reaction (200–250 kJ mol^{-1}) are insufficiently exothermic to support a solid flame synthesis wave.[18] It is likely that the intimate mix of reagents allows neighbouring grains to react *via* close contact. This could be triggered by decomposition of the sodium chalcogenide. This gives rise to an observed dark wave front that progresses through the material. Hence, propagation is accomplished without the massive evolution of heat and resultant thermal flash associated with conventional SSM reactions. It should be noted that the dark wave is an exothermic phenomenon, just insufficiently exothermic to promote a solid flame.

Kinetic products and reaction mechanism

The relatively low temperatures at which these SSM reactions proceed allow some degree of stoichiometric control in the reaction simply by varying the sulfur content of the precursor. Thus it is possible to form single phases of both $M_{(1-x)}S$ and MS_2 (M = Fe, Co or Ni) by using Na_2S and Na_2S_2 respectively. In addition, the low reaction temperature may allow the formation of kinetic products, and so the formation of mixed phases of tin sulfide.

Solid state metathetical reactions are believed to proceed *via* reductive recombination or ionic metathesis pathways.[11,19] Ionic metathesis involves the exchange of ions within a salt melt. Reductive recombination involves reduction to the elements followed by recombination to form the metal chalcogenide. The reactions resulting in metal monochalcogenides, (1)–(4), are likely to proceeded *via* partial reduction of the reagents to the elements, followed by their recombination to form the product, eqns. (12), (13). Moreover, the lack of a solid flame raises serious doubts as to the free mobility of ions within the reaction mixture required for efficient ‘ionic exchange’. The nickel arsenide structure adopted by many of the metal products infers a high degree of covalency (close approach of dipositive metal atoms, 2.60–2.68 Å for FeS, CoS and FeS). This taken in conjunction with the covalent nature of the metal precursors, and the common crystal structure,[20] infers that an ionic intermediate is unlikely.

$$MX_2(s) + Na_2E(s) \longrightarrow [M + E + 2NaX] \longrightarrow ME(s) + 2NaX(s) \quad (12)$$

$$MX_2(s) + Na_2S_2(s) \longrightarrow [M + 2S + 2NaX] \longrightarrow MS_2(s) + 2NaX(s) \quad (13)$$

In addition, elemental metal was produced in the synthesis of the metal ditellurides, eqn. (8), indicating reductive recombination.

By considering the comparative heats of formation of M–Te, M–M and Te–Te, it is apparent that for the low temperatures at which these SSM reactions proceeded the most favorable product is MTe_2. Increasing the reaction temperature would favour the reverse reaction, and so the synthesis of MTe.

Conclusion

Solid state metathesis reactions of low oxidation state metal halides with sodium chalcogenides at 300 °C for 48 h offer a convenient route to the synthesis of a range of crystalline transition metal chalcogenides in high yield (> 90%). In the majority of cases a single 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 SSM reactions of metal halides with alkali metal chalcogenides. Once initiated, these intimately mixed reagents undergo reaction to produce highly sintered metal chalcogenides and a co-produced salt. The reaction is not self-propagating in the sense that no solid flame is observed, however a dark wave was observed promoting transformation of products into reactants. The alkali metal halide co-produced salt is easily removed by trituration, affording pure metal chalcogenide. In comparison to conventional elemental combination reactions, SSM occurs at significantly lower temperatures with shorter reaction times and fewer preparative steps. 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 di-chalcogenides with, for the most part, preservation of the oxidation state of the metal.

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. Clarification of reaction mechanisms is not, however, forthcoming, although in these reactions the reductive recombination route is favoured.

Experimental

All reagents used were of 99.9% purity, or better, purchased from Aldrich Chemical Company and used without further purification. Ammonia was purchased from BOC and used without drying. Na_2E ($E = S$, Se or Te) and Na_2S_2 were prepared by the direct combination of stoichiometric quantities of sodium metal and elemental chalcogen in liquid ammonia. These reactions were carried out 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 without annealing or exposure to atmospheric conditions. 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 ($\lambda = 1.5405$ Å). They were indexed using either TREOR or METRIC-LS programs[14] (lattice parameters matched to within 0.02 Å with literature[15]). The SEM/EDXA measurements were made 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 instrument, using polished samples, and compared to those of metal and chalcogen standards. FT-IR spectra were recorded using a Nicolet 205 FT-IR spectrometer, as pressed KBr discs.

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

Reaction of sodium chalcogenide with metal halide

The same general reaction scale and procedure was adopted for all these reactions, as exemplified here for FeS_2.

Disodium disulfide (100 mg, 0.91 mmol) and iron(II) bromide (196 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^{-1}) in a tube furnace. For each reaction, 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 it was triturated with 3 × 20 cm^3 of 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.

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