Transition Metal Pnictide Synthesis: Self Propagating Reactions Involving Sodium Arsenide, Antimonide and Bismuthide

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Initiation of the reaction between Na_3E (E = As, Sb, Bi) and anhydrous metal halides at 25 to 550 °C produces metal arsenides M_xAs_y (M = Y, La, Ti, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Pt, Cu and Zn) and antimonides M_xSb_y (M = Ti, V, Nb, Ta, Cr, Fe, Co, Ni, Pt, Cu and Zn) *via* an exothermic selfpropagating reaction. The metal arsenides were characterized by X-ray powder diffraction, SEM/EDAX, microanalysis and FT-IR.

Introduction

Most metals form arsenides, antimonides and bismuthides, of which many have useful physical properties or interesting structures. A multitude of stoichiometries are known, for example metal arsenides have a compositional range from M_9As to M_3As_7 [1]. Industrial usage for metal pnictides includes semi-conductors, magnets, thermoelectric materials and hardeners for copper, lead and tin alloys [1,2]. These materials are conventionally made by high temperature combination of the elements (> 1000 °C) often requiring prolonged sintering [2]. Other routes to metal pnictides include reactions of the metal with EH_3 (E = As, Sb, Bi) [2].

Russian researchers first developed self-propagating high temperature synthesis (SHS) routes to binary materials [3]. This method involves initiating an exothermic elemental combination reaction within a compact disc of the material by means of an electric spark or hot oven and has been used as a route to a number of materials. Bonneau *et al.* [4] have extended the idea to solid state metathesis (SSM) reactions, which are extremely exothermic and often rapid (2–3 seconds), producing a brilliant flash of light and sublimed co-products. This technique has been used to synthesise a range of materials including layered transition metal dichalcogenides, refractory materials and Group III–V semiconductors.

We have applied SSM methods to the synthesis of transition metal and lanthanide oxides, nitrides and phosphides [5–8]. In this paper we investigate the applicability of these methods to the synthesis of transition metal arsenides, antimonides and bismuthides and show that transition metal arsenides and some antimonides can be made, with reasonable purity, with great saving in energy and time compared with traditional methods.

Experimental

All reactions and preparations were conducted under vacuum or in a nitrogen filled dry box. Ampoules were flame dried and evacuated prior to use. Methanol was distilled from Mg/I_2, stored over 3 Å molecular sieves and degassed with N_2 before use. Metal halides were purchased from Aldrich Chemical Co. and Strem Chemicals, pnictogens from Aldrich, sodium from BDH and K_2PtCl_4 on loan from Johnson Matthey. Sodium pnictides (Na_3E; E = As, Sb, Bi) were prepared by thermolysis of freshly cut sodium (to remove oxide contamination) with a stoichiometric amount of arsenic, antimony or bismuth in a sealed ampoule under vacuum at 550 °C for 10 h. Na_2As and Na_4As were made in the same way and used without further characterisation. X-ray powder diffraction (XRD) patterns were recorded on a Siemens D 5000 diffractometer using CuK_α radiation (λ = 1.5418 Å); scanning electron microscopy (SEM) and energy dispersive analysis with X-rays (EDAX) were obtained on a Jeol JSM 820 instru-

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ment equipped with Kevex detector and software [9] FT-IR as pressed KBr or CsI discs on a Nicolet 205 spectrometer. Thermolysis reactions were carried out in a Lenton Thermal Designs tube furnace. Microanalysis was performed by Medac Ltd, Brunel University.

Reactions of Na_3E with MX_n (E = As, Sb, Bi; M = Y, La, Ti, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, Pt, Cu, Zn and Hg)

Sodium pnictide (Na_3E; 200 mg) and anhydrous transition metal halide were ground together with an agate pestle and mortar in a nitrogen filled dry box (such that the ratio of sodium to halide was 1:1). The powder was added to a thick walled glass ampoule and sealed under vacuum. The ampoule was placed in a furnace at 550 °C for 4 h, during which time the solids invariably fused into a dark grey lump and a dark material coated the inner walls of the ampoule. The ampoule was removed from the oven, allowed to cool to room temperature and broken open in a dry box. Grinding followed by trituration of the fused solid with methanol (3×15 ml) produced a fine powder. Evaporation of the methanol produced sodium chloride. The fine powders were characterized by XRD, EDAX, microanalysis and FT-IR. Yields were typically greater than 70%, the main losses being mechanical ones during handling. Reactions involving $MoCl_5$, WCl_4, $TaCl_5$, $NbCl_5$, $FeCl_3$, $CoCl_2$, $NiCl_2$ and $HgCl_2$ were found to self initiate in the glove box at room temperature on light grinding with a pestle and mortar. These reactions were accompanied by a bright red/white flash and the sublimation of sodium chloride and pnictogen onto the walls of the box. Such reactions were invariably over in a few seconds and the products appeared identical to those that were initiated at 550 °C in glass ampoules.

Alternative procedure

I Most of the products could be freed of sodium halide by triturating with distilled water. YAs and LaAs readily decompose when washed with water, however the other arsenides display virtually no hydrolysis. All the antimonides investigated were sufficiently stable in water to allow purification.

II Attempts at producing mixed metal arsenides $M_xM'_yAs$ were performed in the same way as that described for the binary metal arsenides, except that equimolar quantities of the chosen metal halides were pre-ground together before addition of Na_3As.

Caution! The mixing of hydrated metal halides with sodium pnictides can result in a reaction without external initiation. Care should be taken to avoid such reactons which are extremely exothermic and uncontrollable and are likely to lead to oxide contamination.

Results and Discussion

Initiation, spontaneous or induced, of premixed powders of anhydrous metal halide and sodium pnictides resulted in a violently exothermic reaction. The crude product was contained in a fused black lump which showed a bloomed morphology by SEM, indicative of a coating of melted or sublimed NaX. EDAX showed sodium and chlorine, with lower intensity peaks for metal and pnictogen. Products were purified by washing with methanol and were subsequently characterized by XRD, EDAX, microanalysis and FT-IR.

The SEM profile of the methanol triturated products showed a rough, porous surface, whilst EDAX revealed only metal and arsenic with no sodium, halide or oxygen present, 0.5–1% estimated detection limit. Notably less than 0.2% sodium was detected by microanalysis in the triturated powders. FT-IR spectra were virtually featureless in the range 4000–200 cm^{-1}.

Reactions with sodium arsenide

The X-ray powder diffraction data for metal arsenides formed from reaction of Na_3As with metal halides are summarized in Table I. After reaction, whether self-initiating or thermolysed, a crystalline metal arsenide was formed [10]. The crystallite size, as determined by the Scherrer equation [11], based on the powder XRD line widths, varied from 250 Å to 450 Å. The metal arsenides, after trituration, had no crystalline sodium halide incorporated and showed the material as either one phase M_xAs_y or a mixture of metal arsenide phases. This is illustrated in Fig. 1 for YAs.

The products from the reaction of anhydrous metal halides with sodium arsenide are dependent on the metal used eq. 1–5.

$$MCl_3 + Na_3As \rightarrow MAs + 3\,NaCl \quad (M = Y, La, Ti, V, Cr, Fe) \qquad (1)$$

$$3\,CuI + Na_3As \rightarrow Cu_3As + 3\,NaI \qquad (2)$$

Table I. X-ray powder diffraction data for the materials obtained from reactions of MX_n with Na_3As.

Starting metal halide	Self initiated reaction	Crystalline phase detected	lattice **a** parameter/Å	Ref. [10] **a** parameter/Å
YCl_3	N	YAs	5.81	5.79
$LaCl_3$	N	LaAs	6.17	6.14
$TiCl_3$	N	TiAs	3.64	3.64
$HfCl_4$	N	HfAs	3.74	3.76
VCl_3	N	VAs, [V_5As_3]	6.33, [9.50]	6.32, [9.51]
$NbCl_5$	Y	NbAs, $NbAs_2$	3.46, 9.34	3.45, 9.35
$TaCl_5$	Y	TaAs, [$TaAs_2$]	3.44, [9.32]	3.44, [9.35]
$CrCl_3$	N	CrAs	3.46	3.49
$MoCl_3$	N	Mo_5As_4, MoAs	9.62, 5.97	9.60, 5.99
WCl_4	Y	WAs_2	9.07	9,08
$MnCl_2$	N	MnAs, [Mn]	3.72, [8.87]	3.72, [8.91]
$FeCl_3$	Y	$FeAs_2$	5.32	5.30
$CoCl_2$	Y	CoAs, Co_2As	3.48, 5.97	3.46, 5.97
$NiCl_2$	Y	$Ni_{11}As_8$, Ni_5As_2	6.85, 6.86	6.85, 6.82
K_2PtCl_4	Y	Pt, $PtAs_2$	3.90, 5.92	3.92, 5.97
CuI	N	Cu_3As, Cu	7.11, 3.62	7.11, 3.62
$ZnCl_2$	N	Zn_3As_2	11.77	11.79

Parentheses indicate minor phases.

$$27\,NiCl_2 + 18\,Na_3As \rightarrow 2\,Ni_{11}As_8 + Ni_5As_2 + 54\,NaCl \quad (3)$$

$$6\,MCl_5 + 10\,Na_3As \rightarrow 5\,MAs_2 + 30\,NaCl + M \quad (M = Nb, Ta) \quad (4)$$

$$3\,ZnCl_2 + 2\,Na_3As \rightarrow Zn_3As_2 + 6\,NaCl \quad (5)$$

With MCl_3 (M = Y, La, Ti, V, Cr), CuI and $ZnCl_2$ no change of oxidation state for the metal is observed and only phases corresponding to M_xAs_y and NaCl are produced. The other metals underwent changes in formal oxidation state and usually yielded more than one phase and sometimes some elemental arsenic. All the transition metal halides studied react with Na_3As to form metal arsenides, whereas analogous studies of Li_3N and MCl_x found that a dividing line in reactivity was observed with the early transition metal halides forming metal nitrides and the later transition metal halides being reduced to the metal [6]. This difference could be due to the greater thermal stability of arsenides compared with nitrides of the latter transition metals.

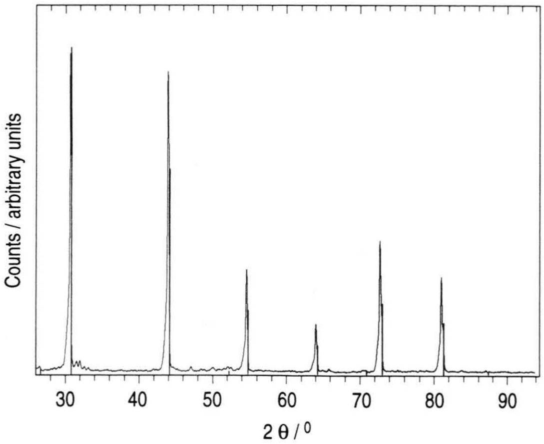

Fig. 1. X-ray powder diffraction pattern obtained from reaction of YCl_3 with Na_3As and standard trace [10] for TiAs.

Reactions of hafnium chloride with other stoichiometries of sodium arsenide (Na_xAs; x = 2, 3, 4) were found to yield different products. Na_4As gave almost entirely HfAs; Na_3As gave HfAs and some As; Na_2As gave mostly $HfAs_2$ and some HfAs. Some control of product stoichiometry may, thus, be possible through the use of sodium pnictides of varying composition to yield the desired transition metal arsenide phase. The Na_4As reaction was found to self-initiate upon grinding. Na_2As and Na_3As reactions required hot filament initiation. The reaction of Na_3As with $HfCl_4$ could also be initiated by addition of a small amount of finely divided sodium metal. This could indicate that free sodium in the sodium arsenide is responsible for initiation in the Na_4As reaction.

Hess' law calculations [12] for the reaction of metal halide with sodium arsenide indicate that the reaction is exothermic with $\Delta H_r \approx -200$ to -700 kJ mol^{-1}. The primary driving force for the reaction is the large lattice energy of the co-product NaX which accounts for up to 80% of the reaction enthalphy. The exothermicity of the reaction explains the sublimation of material during reaction.

Self-initiating reactions

Reactions of sodium arsenide with $NbCl_5$, $TaCl_5$, $MoCl_5$, WCl_4, $FeCl_3$, $CoCl_2$ and $NiCl_2$ self initiated on grinding or in some cases just mixing the reagents at room temperature producing a red/white flash, sublimed material and the products left in a fused lump. The other metal halides, including $MoCl_3$, did not lead to self-initiation with Na_3As despite vigorous grinding. The reactions that did self-initiate included the metals in high formal oxidation states. Such reactions are more exothermic than comparable reactions of the lower oxidation state metal halides as more NaCl is produced, however this does not explain the low initiation temperatures. It has been postulated [4] that the reactions of metal halides with sodium chalcogenides self initiate if the metal halides are volatile. Indeed this partially matches the pattern observed here as $MoCl_5$, $NbCl_5$ and $TaCl_5$ have boiling points below 280 °C. However reactions involving $NiCl_2$ (948 °C) and $CoCl_2$ (1049 °C) with Na_3As also self-initiated on light grinding at variance with the volatility arguments.

The addition of LiCl up to 1000 mol% to the reaction of $NbCl_5$ or $MoCl_5$ with Na_3As did not prevent the self-initiation although it did limit the spread of material and the reaction appeared visibly less violent. If 1500 mol% LiCl was added, the reaction failed to self initiate on vigorous grinding but did initiate on gentle warming with a hair dryer. The products from the reaction with $NbCl_5$ varied with the quantity of LiCl added; with increasing amounts of LiCl, less of the NbAs phase was detected and more $NbAs_2$ and As. The LiCl would reduce the voracity of the reaction by acting as a packing agent. The greater presence of arsenic in the products is presumably due to the degree of sublimation of this relatively volatile component being reduced by the action of LiCl as a heat sink. The number of phases produced using $MoCl_5$ was too great to draw any useful conclusions.

Reactions using mixtures of halides

Reactions of mixtures of metal halides with sodium arsenide were studied analogously to those which produced binary M_xAs_y materials. The X-ray powder diffraction patterns of the mixed metal reactions normally showed the individual arsenide lattices, but broadened relative to the single reactions and shifted to an intermediate position. For example the reaction of YCl_3 and $LaCl_3$ with Na_3As yielded an intermediate pattern between the YAs and LaAs lattices. Broadening of the reflections associated with this material relative to those of the binary materials is indicative of an incomplete solid solution. Similar behaviour was observed for reactions of mixtures of $NbCl_5$ with $TaCl_5$ and $TiCl_3$ with $MnCl_2$. The potential for forming mixed metal arsenides exists *via* the self-propagating method but requires high temperature annealing to form completely intermixed materials.

Reactions with sodium antimonide and bismuthide

These reactions were performed as per those with sodium arsenide. The use of sodium antimonide generally yielded metal antimonides, although there was a noticeably greater tendency toward mixtures of products. Table II shows XRD data for these materials. Reactions involving molybdenum, tungsten and mercury yielded the elements. Reactions of sodium bismuthide were found to yield the metal and bismuth, although in the case of platinum, PtBi (hexagonal NiAs structure, **a** = 4.33, lit. [13] **a** = 4.32) was observed as well as metal and bismuth. Where reactions of sodium antimonide or bismuthide were found to self-initiate, they were noticeably less voracious than those of sodium arsenide.

Table II. X-ray powder diffraction data for the materials obtained from reactions of MX_n with Na_3Sb.

Starting metal halide	Self initiated reaction	Crystalline phase detected	lattice **a** parameter/Å	Ref. [10] **a** parameter/Å
$TiCl_3$	N	$TiSb_2$, TiSb	6.67, 4.06	6.67, 4.07
VCl_3	N	VSb_2, $[V_3Sb_2]$	6.55, 5.57	6.56, 5.55
$NbCl_5$	Y	$NbSb_2$	10.24	10.24
$TaCl_5$	Y	$TaSb_2$, $[Ta_5Sb_4]$	10.23, 10.22	10.22, 10.25
$MoCl_3$	N	Mo, Mo_3Sb_7	3.14, 9.55	3.15, 9.57
WCl_4	Y	W, Sb	3.16, 4.30	3.17, 4.31
$FeCl_3$	Y	$FeSb_2$, [FeSb], [Sb]	5.80, 4.09, 2.97	5.82, 4.09, 2.96
$CoCl_2$	N	CoSb, $[CoSb_2]$	3.90, 6.51	3.88, 6.51
$NiCl_2$	N	NiSb, $NiSb_2$	3.94, 5.18	3.95, 5.18
K_2PtCl_4	N	PtSb, Pt_3Sb_2, [Pt]	4.14, 6.42, 3.93	4.14, 6.45, 3.92
$ZnCl_2$	N	Zn_4Sb_3, Sb	12.22, 4.30	12.23, 4.31
$HgCl_2$	Y	Hg, Sb	obs. droplets, 4.31	–, 4.31

Parentheses indicate minor phases.

Relevance to reaction mechanism

The reactions of transition metal halides with alkali metal pnictides can be considered as following two mechanistic extremes, from reductive recombination (reduction to the elements followed by recombination) to a direct ionic metathetical exchange. A trend is observed down the pnictogen group toward a reductive recombination type reaction mechanism rather than metathesis. The use of Li_3N with MCl_x to yield metal nitrides [6, 14] cannot involve recombination of the elements as nitrogen would not tend to remain in the reaction mixture and the N_2 pressures reached would not be sufficient to favour nitride formation. This and previous [6, 7, 14, 15] work has indicated that nitrides, phosphides and arsenides form readily, whilst antimonides and especially bismuthides have a greater tendency to yield metal and pnictogen. The exception to this rule is with nitrides, where the low thermal stability of some nitrides results in thermal decomposition to metal and nitrogen [6].

Reactions to form metal pnictides are more exothermic than those to form metal and pnictogen if ΔH_f of the metal pnictide is negative. Equations 6–8, for previously reported reactions involving $TiCl_4$, [15] illustrate this point.

$$TiCl_4 + {}^4/_3 Na_3As \rightarrow TiAs + 4NaCl + {}^1/_3 As \quad \Delta H = -715\ \mathrm{kJ\ mol^{-1}} \tag{6}$$

$$TiCl_4 + {}^4/_3 Na_3Sb \rightarrow TiSb + 4NaCl + {}^1/_3 Sb \quad \Delta H = -847\ \mathrm{kJ\ mol^{-1}} \tag{7}$$

$$TiCl_4 + {}^4/_3 Na_3E \rightarrow Ti + {}^4/_3 E + 4NaCl\ (E = As, Sb) \quad \Delta H = -565\ \mathrm{kJ\ mol^{-1}} \tag{8}$$

These values, calculated from Hess' law [12], demonstrate that some factors other than thermodynamic ones must apply, as the materials isolated from the reaction of $TiCl_4$ and Na_3E are TiAs or Ti + Sb despite TiSb formation being more exothermic than TiAs. Na_3E (E = As, Sb, Bi) are essentially metallic, but it could be argued that Na_3As has the most ionic character. Na_3As and Na_3Sb hydrolyse readily in water to yield arsine and stibine, in this they ar "saltlike" [2], displaying essentially ionic behaviour. The metathesis mechanism is more probable if ions are available. The reactions are all self-propagating, therefore, the most likely first step would be alkali metal halide formation as this is the most exothermic step, leaving metal cations and pnictide anions. Thus, a more ionic Na_3E could favour an ionic metathesis mechanism, whereas a more metallic Na_3E could make some mechanism involving uncharged species preferable.

Conclusions

Solid state metathesis reactions offer a route to crystalline transition metal arsenides and antimonides and mixed metal arsenides. The reactions are initiated at low temperatures (25–500 °C), are rapid compared with conventional preparations and are self-propagating. The purity of the metal arsenide is high with the by-product sodium halide being easily removed by methanol trituration. To some extent, initiation temperatures can be modified by use of an inert heat sink and product stoichiometry altered by variation of the alkali metal pnictide composition. Metal arsenides are probably formed by a metathetical reaction, whilst formation of metal antimonides is more likely to proceed *via* a reductive recombination mechanism.

Acknowledgements

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