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New synthetic routes to transition metal ternary nitrides and sulfides

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Abstract

Three new synthetic methods for the synthesis of ternary transition metal nitrides and sulfides, respectively, are described. The reactions of metals dissolved in liquid zinc with nitrogen gas are shown to produce both binary and ternary nitrides. The reactions of the Group 2 binary nitrides with transition metal foils has led to the formation of ternary nitrides as single crystals. The new nitrides $Ca_9Mo_2N_{10}$ and $Ca_{33}Mo_6N_{33}$ are briefly discussed and the preparation and structure of the first nitride chloride containing chromium, $Ba_4CrN_4Cl_2$, is described. The method of separated reactants has been shown to give several Group 2–transition metal–sulfides also in the form of single crystals. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Despite many years of intensive effort by several research groups the number of known ternary nitrides is trivial compared with the number of ternary oxides or sulfides [1]. This difference is clearly due to the fact that the synthesis of ternary nitrides containing transition metals presents several problems most of which stem from their instability with respect to oxides. Almost all the ternary nitrides prepared so far react rapidly with the smallest traces of oxygen and water. The synthesis of the Group 2–Transition metal–nitrides is also complicated by the unusual stoichiometries of the heavier Group 2 binary nitrides used as starting materials. Both strontium and barium do not form nitrides with the expected stoichiometry A_3N_2 but readily form subnitrides with the stoichiometry A_2N which are also extremely air sensitive. How all these problems come together can be seen by comparing the synthesis of the ternary oxide $SrCr_2O_4$ and the ternary nitride Sr_3CrN_3. The former could be prepared as a pure, single phase by simply heating a compressed pellet of the air stable $SrCO_3$ and Cr_2O_3 in air at high temperature for several hours according to the reaction

$$SrCO_3 + Cr_2O_3 \rightarrow SrCr_2O_4 + CO_2. \tag{1}$$

The ternary nitride reaction also requires heating a compressed mixture for several days at temperatures in excess of 1300 K but the pellet, wrapped in molybdenum foil, has to be sealed in a stainless steel crucible by argon-arc welding in a glove-box to avoid any contact with oxygen [2]. The reaction stoichiometry:

$$2Sr_2N + CrN \rightarrow Sr_3CrN_3 + Sr \tag{2}$$

can never be adjusted to give a single phase product because of the stoichiometry of Sr_2N and the fact that nitrogen added as flowing nitrogen gas is certain to lead to oxidation even if prepurified to ppm levels. The ternary nitride is therefore formed in these reactions wetted by strontium metal and is in the form of a powder requiring crystal structure determination by powder diffraction methods.

In this paper we will describe two alternative methods for the preparation of ternary nitrides. The first method lowers both the reaction temperature and the reaction time and enables stainless steel reaction vessels with removable lids to be used to contain the reaction mixture. The second method operates under the same conditions of temperature and time as in the conventional method but results in products in the form of single crystals. A further synthetic method described in this paper involves the reactants being contained in separate containers with the gas phase exchange of the anions of the two reactants being thermodynamically controlled. This method has been particularly

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successful for the production of ternary sulfides in the form of single crystals.

2. Experimental

2.1. Liquid metal reactions

Previously cleaned Group 2 element (2–5 g) was added to an excess of molten zinc contained in either a stainless steel or a boron nitride crucible in an argon filled glove box. The transition metal was added in powder form and stirred into the alloy mixture. The crucible was then sealed into a stainless steel vessel fitted with a cold finger attached to the lid which was sealed with viton O-ring seals. The steel vessel was heated to 900 K under a positive nitrogen pressure of about (1520 Torr) during this time the nitrogen pressure was monitored continuously by a pressure transducer and further nitrogen added through a magnetic valve controlled by a PC. When no further nitrogen was taken up by the alloy the vessel was cooled and then heated under vacuum at 550 K for 24 h to remove any excess zinc. Products were characterised by powder X-ray diffraction using a Philips X'PERT system.

2.2. Reactions of metal foils with Group 2 nitrides

Powdered Group 2 binary nitrides were placed inside a crucible formed from the appropriate metal foil before being placed into a stainless steel which was welded closed in an argon filled glove-box. These crucibles were heated in a tube furnace at 1400 K for a period of 4 days under flowing argon to minimise external oxidation. The crucibles were cooled, cut open in a nitrogen filled glove-box and the foil removed. The crystals adhering to the foil were removed for examination and selection under a microscope prior to crystal structure determination.

2.3. The method of separated reactants

Reactions were carried out in evacuated silica tubes as shown in Fig. 1. The inner alumina crucible (diameter 10 mm) was placed inside a larger alumina crucible (diameter 20 mm) containing an excess of the anion source (Y_2S_3) and the smaller crucible was filled with the second reactant (the appropriate ternary oxide). The crucibles were placed in a silica tube (diameter 25 mm) and the top of the tube drawn down to an approximate internal width of 5 mm. The tube was evacuated (10^{-4} Torr) and heated overnight at 500 K to remove any moisture within the system and sealed under vacuum. The sealed tube was heated in a muffle furnace (Carbolite EML 11/6) and manipulations of the products performed in a nitrogen-filled glove-box.

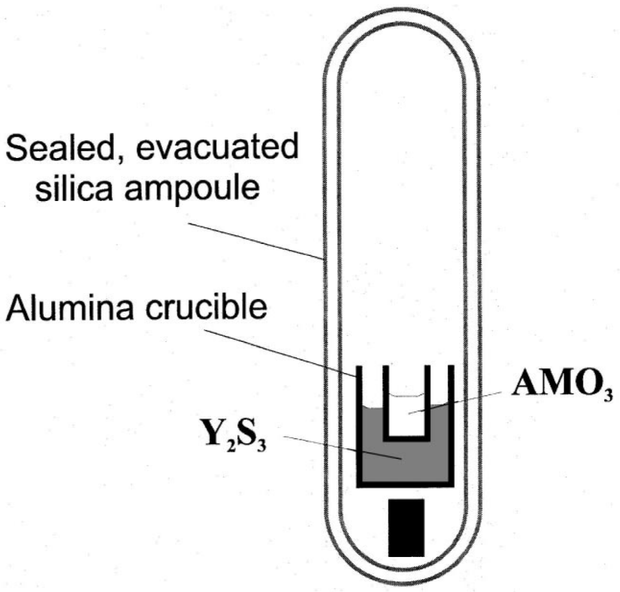

Fig. 1. Reactions of physically separated reactants.

3. Results and discussion

3.1. Liquid metals as solvents for nitride synthesis

The Group 2 binary nitrides may be prepared in a very pure state by reacting nitrogen gas with a liquid alloy of the Group 2 metal with sodium which acts as an inert solvent since sodium does not react with nitrogen [3]. The binary nitride precipitates from the sodium as a highly crystalline solid and complete reaction can be carried out at temperatures as low as 630 K. At the end of the reaction the excess sodium is removed by vacuum distillation. Replacement of sodium by a transition element such as zinc readily leads to the formation of the Group 2–zinc ternary nitrides Ca_2ZnN_2 and Sr_2ZnN_2. In the reaction of nitrogen with barium dissolved in zinc the expected ternary nitride Ba_2ZnN_2 was not found. Instead, the product was clearly identified by powder X-ray diffraction as the ternary nitride Ba_3FeN_3. The explanation for this unusual result was that iron from the stainless steel crucible used to contain the reactants had dissolved in the liquid zinc and the reaction of barium and nitrogen with the iron was more favourable than the formation of the barium zinc nitride. A survey of published phase diagrams indicates a range of transition metals are soluble in liquid zinc and we are currently investigating several potentially reactive systems for example molybdenum dissolved with barium in zinc reacts to give the ternary nitride Ba_3MoN_4 at 900 K and yttrium dissolved in zinc gives the binary nitride YN.

3.2. The reaction of metal foils with Group 2 nitrides

Clearly in this method there is no control over the stoichiometry of the final product and several compositions

Table 1
Crystals prepared by the reaction of Group 2 nitrides with transition metal foils

Compound	Space group	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)	Ref.
Ba_3WN_4	$P31c$	18.488	18.488	10.446	90	90	120	[5]
$Ca_{33}Mo_6N_{33}$	P-3	12.532	12.532	8.443	90	90	120	[5]
Sr_2NbN_3	$C2/c$	6.010	11.221	12.550	90	92.70	90	[5]
Sr_3WN_4	$C2/c$	17.815	10.318	9.911	90	97.98	90	[5]
Sr_4WN_4O	$P2_1/m$	8.943	14.742	10.723	90	102.00	90	[5]
$(Ca,Sr)_{51}[WN_4]_{12}N_8O_3$	$P\bar{1}$	10.633	15.203	16.080	102.658	95.658	109.839	[5]
Ba_3MoN_4	$Pbca$	10.839	10.3030	12.029	90	90	90	[5]
$Ca_{51}[WN_4]_{12}N_8O_3$	$P\bar{1}$	10.564	12.397	15.982	102.78	95.15	109.89	[5]
Sr_4MoN_4O	$P2_1/m$	8.951	14.694	10.715	90	102.08	90	[4]
Sr_3MoN_4	$C2/c$	17.76	10.29	9.881	90	97.76	90	[5]
$Ca_{18}Mo_4N_{20}$	$P\bar{1}$	6.8754	9.3319	10.384	85.352	89.828	79.436	[5]
Ba_3MoN_4	$P31c$	18.422	18.422	10.405	90	90	120	[6]
$Ba_4CrN_4Cl_2$	$P2_1/m$	8.334	5.989	10.533	90	98.645	90	[5]

may be present on a single foil but in every system so far studied single crystals have been formed. Using this method we have prepared for the first time two novel calcium–molybdenum nitrides $Ca_9Mo_2N_{10}$ and $Ca_{33}Mo_6N_{33}$. Both compounds contain isolated MoN_4 tetrahedral units with Mo–N distances between 1.837 and 1.916 Å for $Ca_9Mo_2N_{10}$ and 1.822–1.851 Å for $Ca_{33}Mo_6N_{33}$. The remaining nitrogen atoms in the structure are bonded only to calcium in a distorted octahedral coordination. The formulae of the two compounds can best be rationalised as being calcium nitride adducts of the parent compound Ca_3MoN_4 (which has not yet been prepared) giving formulae of $2Ca_3MoN_4 \cdot Ca_3N_2$ and $6Ca_3MoN_4 \cdot 3Ca_3N_2 \cdot 3Ca_2N$, respectively.

An interesting extension of this method is that microscopic leaks in the welds of the stainless steel crucible have led to the fortuitous formation of ternary nitride oxides. Replacement of the binary nitride with the precursors of a nitride halide such as Ba_2NCl led to the formation of the novel ternary nitride halide $Ba_4CrN_4Cl_2$ on the stainless steel foil used to contain the Ba_2N and $BaCl_2$ reactants. Crystals were only formed when the reaction temperature exceeded 1020 K at which temperature the Ba_2NCl was molten. This nitride halide is the first to be reported for chromium and is the first nitride of a Group 2 metal with chromium to have the transition metal in its maximum oxidation state. Like most of the Group 6 ternary nitrides prepared so far it contains MN_4 tetrahedra with Cr–N bond lengths in the range 1.701–1.761 Å. All the nitrogen atoms are bonded to the chromium atom but the chlorine atom is only bonded to the barium giving a representative formula of $Ba_3CrN_4 \cdot BaCl_2$.

Some of the crystal structures determined from crystals grown by this method are given in Table 1.

3.3. The method of separated reactants

The method is of general application but is particularly useful for the preparation of ternary sulfides. The driving force in these reactions is the extremely favourable reaction for the conversion of Y_2S_3 to Y_2O_3 even though the final product in many cases is observed to be the oxysulfide Y_2O_2S. In an earlier publication [7] we showed that the method could be used for the rapid synthesis of many alkali metal–transition metal–sulfides and we have now demonstrated that the ternary sulfides of the Group 2 elements with transition metals can also be prepared in the form of single crystals growing in the inner crucible. A selection of the compounds prepared by this method are shown in Table 2.

Table 2
Compounds prepared as single crystals by the method of separated reactants

Compound	Space group	*a* (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
$BaTiS_3$	$P\bar{3}c1$	11.709	11.709	5.782	90	90	120
Ba_2TiS_4	$Pnma$	9.035	6.830	12.282	90	90	90
$SrTiS_3$	$P321$	11.511	11.511	20.936	90	90	120
$CaNb_2S_5$ [a]	$P63/mmc$	3.3037	3.3037	14.286	90	90	120
$SrTa_2S_5$ [a]	$P6322$	3.305	3.305	24.296	90	90	120
$SrNb_2S_5$ [a]	$P\bar{6}2c$	3.368	3.368	24.103	90	90	120
$BaNb_2S_5$ [a]	$P\bar{6}2c$	3.333	3.333	25.201	90	90	120
$BaTa_2S_5$ [a]	$P\bar{6}2c$	3.314	3.314	25.21	90	90	120
$Sr_{17}Ta_{10}S_{42}$	$R3$	18.146	18.146	18.676	90	90	120

[a] Crystallographic data from powder data.

Of particular interest is the formation of single crystals of the ternary sulfides $BaTiS_3$ Ba_2TiS_4 and $SrTiS_3$. Crystal structure determination showed that $BaTiS_3$ has a supercell caused by the slight rotation of the TiS_6 octahedra up the *c*-axis, Ba_2TiS_4 contains isolated TiS_4 tetrahedra and $SrTiS_3$ may be considered as having either a very large supercell of dimensions $a=11.511$ Å and $c=20.936$ Å or to be incommensurate [8] with $a=11.501$, $c_1=2.991$ and $c_2=5.186$ both solutions giving very similar *R* values.

Of current interest are phases of the general formula AM_2S_5 where A is a Group 2 element and M a Group 5 element. These compounds have been shown to have a wide range of electrical conductivities from insulating to superconducting [9] but recent work [10] has cast doubt on the composition of the SrV_2S_5 phase suggesting that the actual formula is $Sr_6V_9S_{22}O_2$. We have recently prepared single crystals of several of these phases by metathesis reactions between Y_2S_3 and the oxides AM_2O_6 using the separated reactions method and single crystal structure determinations are now being undertaken.

4. Conclusions

The reaction of nitrogen gas with solutions of group two metals in liquid zinc has been shown to produce ternary nitrides such as Ca_2ZnN_2 at temperatures well below those required by conventional solid state methods. In some cases unexpected reactions took place between transition metals dissolved by the zinc from the reaction container and the dissolved group two elements, again leading to the formation of ternary nitrides.

The reaction of transition metal foils with group two element nitrides has been remarkably successful for the preparation of new ternary nitrides in the form of single crystals. Two new calcium–molybdenum–nitrides have been prepared using this route. The use of group two nitride halides in place of the binary nitride gave rise to the formation of ternary nitride halides in single crystal form.

The method of separated reactants has been extended to the reactions of ternary oxides of group two elements and transition metals and again metathesis reactions were observed resulting in the formation of crystalline ternary sulfides.

Acknowledgements

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