A Novel Reaction between Physically Separated Solid Reactants†

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Ternary oxides were converted to ternary sulfides by a metathesis reaction with a sulfur source such as diyttrium trisulfide. Reactions took place between two physically separated solid reactants under vacuum in a sealed silica tube. Preparation of the alkali-metal niobium disulfides $ANbS_2$ (A = Li, Na, K, Rb or Cs) has been attempted with isolation of quality crystals of the materials Li_xNbS_2 [a = 3.3412(2) and c = 12.876(1) Å] and $Na_{0.41}NbS_2$ [a = 3.3424(8) and c = 14.664(4) Å] in the space group $P6_3/mmc$. Also considered has been the metathesis reaction of sodium metavanadate, alkaline-earth metal titanates and selected Group 6 ternary oxides with diyttrium trisulfide. The mechanism of these metathesis reactions has been studied, and in the course of these investigations the reduced hexagonal $LiNbO_2$ [a = 2.9070(6) and c = 10.457(3) Å] was characterised. Formation of binary nitrides and carbides has been possible by replacing the sulfur source, Y_2S_3, with a source of nitrogen (*e.g.* YN) or carbon (*e.g.* TiC).

Two methods are in general use for the preparation of solid-state sulfides, each using a gaseous sulfur source to overcome the inherent kinetic barrier associated with solid-state reactions. The first involves the introduction of either hydrogen sulfide or carbon disulfide vapour into an inert carrier gas at high temperatures over the corresponding oxide. A drawback of this method is that the sulfur source has a strong inherent reduction potential. The second method involves preparation from the elements in a sealed silica ampoule using elemental sulfur as a sulfur source. Owing to the high vapour pressure of elemental sulfur at high temperatures, large pressures are created inside the sealed tube, severely limiting the amount of material used for a safe reaction system. The method described in this study was designed to overcome the inherent problems with the preparation routes presently in use.

We considered an alternative method of achieving a metathesis reaction, in which oxygen and sulfur could be exchanged between two solids. The basic reaction scheme [equation (1)] can be described as a metathesis reaction with the

$$MO_x(s) + M'S_y(s) \rightarrow MS_y(s) + M'O_x(s) \qquad (1)$$

exchange of sulfur and oxygen between the materials MO_x and $M'S_y$. Thermodynamic considerations indicate that the free energy of reaction for the formation of $M'O_x$ from $M'S_y$ must be more favourable than the free energy of reaction for the oxidation of MS_y to MO_x. When these considerations are upheld, a favourable kinetic pathway must be available for the reaction to proceed.

The sulfur source initially chosen was diyttrium trisulfide owing to the high stability of the corresponding yttrium oxide Y_2O_3. In this reaction the thermodynamic driving force was expected to be the formation of Y_2O_3 from Y_2S_3 ($\Delta_r H_{298} \approx -617$ kJ mol^{-1}).[1,2]

Such a reaction is of little preparative value if the product is an intimate mixture of the target sulfide and Y_2O_3 which can never be separated. However, if the reactants can be physically separate throughout the reaction then isolation of a pure product may be possible. Under such conditions the exchange of the anions must take place *via* the gas phase. Such a mechanism would pose a kinetic constraint on the reaction due to the extremely low vapour pressure of oxygen over a solid ternary oxide. However the mobility of a gaseous species should still be greater than that of an ion diffusing through a solid lattice. It was hoped that this new preparative route would lead to some new materials, previously unattainable using the classical solid-state methods.

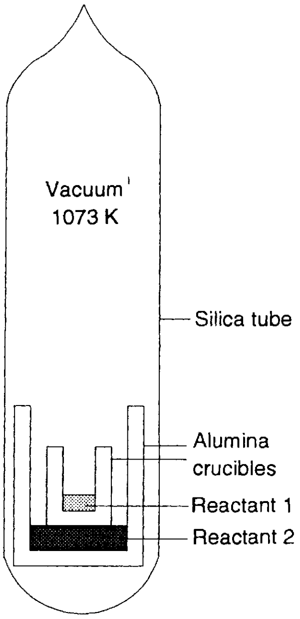

Fig. 1 Silica tube for metathesis reactions

This article describes the overall synthetic approach with extensive experimental details. Also included is a description of the variety of phases that have been observed, to give an indication of the range of materials which may be prepared by this method. It should however be noted that characterisation of some of these phases is not yet complete but they are included primarily to provide a clearer understanding of the synthetic approach.

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† Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Experimental and Results

The proposed metathesis reactions were carried out in evacuated silica tubes described in Fig. 1. The inner alumina crucible of diameter 10 mm was placed inside a larger alumina crucible of diameter 20 mm, containing an excess of the anion source (*eg.* Y_2S_3), and the smaller crucible was filled with the second reactant. The crucibles were placed in a silica tube of diameter 25 mm and the top of the tube drawn down to an approximate internal width of 5 mm. The tube was evacuated to approximately 10^{-4} Torr ($\approx 1.33 \times 10^{-2}$ Pa), heated overnight at 403 K to remove any moisture within the system and sealed under vacuum. The sealed tube was heated in either a muffle furnace (Carbolite EML 11/6) or a vertical tube furnace and manipulations of the products performed in a nitrogen-filled evacuable glove box.

Analysis of the products was carried out using energy dispersive analysis by X-rays (EDX) on a JEOL 6400 winsem scanning-electron microscope with the NORAN Tracor Series II analysis software package. X-Ray powder diffraction patterns were obtained using a Philips X-Pert 3710 diffractometer and indexed using the DICVOL software.[3]

Starting materials were purchased from commercial sources with the exception of Y_2S_3,[4] Al_2S_3[5] and YN. The sulfides were prepared by heating the oxides of either Al_2O_3 or Y_2O_3 at 1073 K under a carbon disulfide–argon gas flow for 18 h. Yttrium nitride was prepared using the method described by Kempter *et al.*[6] by the reaction of yttrium metal with hydrogen and nitrogen.

Preparation of Sulfides.—Preparation and crystal structure of Li_xNbS_2 ($0.5 < x < 1.0$). The metathesis reaction between Y_2S_3 and $LiNbO_3$ was carried out as described above and the sealed tube heated at approximately 1073 K for 14 days in a vertical furnace. There was a temperature gradient of 1 K cm^{-1} within the furnace, with the hot zone at the bottom. The reaction tube, after slow cooling, exhibited a thin layer of surface deposit. The exact nature of this deposit was unknown, however EDX analysis showed niobium and sulfur to be present.

In addition to this thin layer, large foil-like sheets were found with faces of up to 5 mm in diameter, bound to the top of the tube by their edges. An approximate thickness of 0.1–0.2 μm was determined using transmission electron microscopy (TEM), exhibiting the extreme anisotropy of this material. The TEM imaging also demonstrated the polycrystalline nature of this material with a randomly orientated layer structure. The EDX analysis of this material indicated a niobium : sulfur ratio of 1 : 1.92(9), which along with the appearance of layered crystallites implies the presence of either NbS_2 or a lithium-intercalated derivative of this material.

The material in the crucible originally containing $LiNbO_3$ consisted of hexagonal platelets with a high metallic lustre. X-Ray powder diffraction of this highly crystalline material illustrated a material with a high degree of preferred orientation, as expected for these anisotropic plates. Indexing of the powder pattern suggested a hexagonal structure with cell dimensions a = 3.3412(2) and c = 12.876(1) Å, corresponding well with the cell dimensions found for the powdered materials $Li_{(0.5-1.0)}NbS_2$ found by Omloo and Jellinek[7] and Dahn *et al.*,[8] however exact determination of the lithium content was not possible owing to the small changes in cell parameters over the range $0.5 < x < 1.0$.

Table 1 Atomic positional parameters for Li_xNbS_2

Atom	x	y	z
Li	0	0	0
Nb	0	0	$\frac{1}{4}$
S	$\frac{1}{3}$	$\frac{2}{3}$	0.1290(2)

Table 2 Selected bond lengths and angles for Li_xNbS_2

Nb–S	2.475(2)	S–Li	2.541(2)
S–Nb–S	77.9(1)	S–Li–S	81.99(7)
S–Nb–S	84.66(7)	S–Li–S	98.01(7)
S–Nb–S	134.24(3)	S–Li–S	180.0

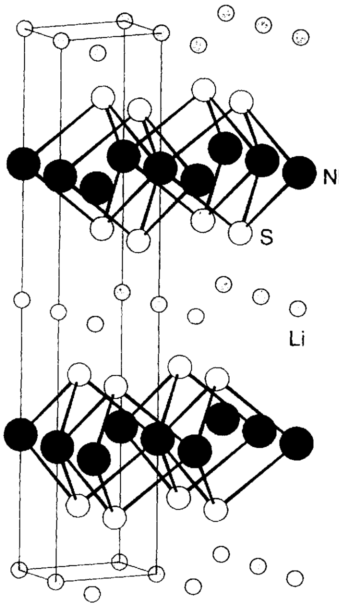

Fig. 2 Structure of Li_xNbS_2

Single crystals were isolated and loaded into Lindemann capillaries for data collection on a Hilger and Watts four-circle diffractometer in the range $1 < \theta < 30°$ ($0 < h < -1, 0 < k < 3, 0 < l < 14$) with 57 independent reflections of intensities $I > 3\sigma(I)$. Crystal data: Li_xNbS_2 (assuming $x = 1$), M = 163.97, space group $P6_3/mmc$, a = 3.3335(1) Å, c = 12.861(7) Å, U = 123.7 Å^3, Z = 2, D_c = 4.4 g cm^{-3}, $F(000)$ = 152, μ(Mo-Kα) = 58.9 cm^{-1}. Corrections were made for Lorentz and polarisation effects and an empirical absorption correction was applied using DIFABS.[9] (Minimum and maximum corrections of 0.789 and 1.247, average correction of 0.993.) Crystallographic calculations used the CRYSTALS programs[10] and scattering factors for neutral atoms.[11] The niobium and sulfur positions were obtained from a three-dimensional Patterson synthesis and the remaining lithium atom was revealed by a series of full-matrix least-squares refinements and Fourier-difference synthesis. Anisotropic thermal parameters were assigned and a three-coefficient Chebyshev weighting scheme was applied. Final convergence occurred at R = 0.0371 (R' = 0.0388) $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|,\ R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$, unit weighting scheme$\}$ for nine parameters (maximum shift: e.s.d. = 0.018, maximum and minimum residual electron densities −0.12 and 0.84 e A^{-3}). The final atomic coordinates are collected in Table 1 and selected bond lengths and angles in Table 2, and the structure is represented in Fig. 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and final bond lengths and angles.

Lithium niobium disulfide crystallises in the space group $P6_3/mmc$, with two NbS_2 layers within the unit cell. The lithium is in an octahedral site, distorted by elongation in the '*c*' direction as shown by the S–Li–S angles 81.99° (sulfur atoms of same layer) and 98.01° (sulfur atoms of adjacent layers). The NbS_2 layers consist of trigonal-prismatically co-ordinated niobium atoms surrounded by a hexagonal-close-packed array of sulfur atoms. The niobium–sulfur bond length of 2.475(2)Å is in excellent agreement with the bond length of 2.47Å found in non-intercalated NbS_2 indicating that the intercalation has only affected the layer separation and not the structure of the layers themselves. Using this method a crystal of high enough quality for single-crystal structure determination has enabled the first definitive solution of the structure of lithium-intercalated niobium disulfide.

The material in the crucible originally containing Y_2S_3 was a grey-white powder, for which indexing of the X-ray powder diffraction pattern suggested a single-phased, hexagonal structure with cell dimensions $a = 3.783(4)$ and $c = 6.5856(7)$ Å. These cell dimensions corresponded well with the previously reported material Y_2O_2S[12] ($a = 3.788$ and $c = 6.591$ Å), however EDX analysis showed a Y:S ratio of approximately 2:0.7. It is thought that this material is a sulfur-deficient form of Y_2O_2S and that the cell dimensions are minimally affected by the sulfur deficiency.

Although the very stable oxide Y_2O_3 was not formed it is apparent that the thermodynamic driving force gained with the production of $Y_2O_{2+x}S_{1-x}$ from diyttrium trisulfide was sufficient for the metathesis reaction to proceed to completion.

Preparation and crystal structure of $Na_{0.41}NbS_2$. An analogous experiment was carried out in the sodium niobate ($NaNbO_3$) and diyttrium trisulfide system, replacing $LiNbO_3$ with $NaNbO_3$ in the reaction described above. A highly crystalline product was again obtained, with a high metallic lustre, in the crucible originally containing $NaNbO_3$. The crystals produced were found on both the outer and inner walls of the small alumina crucible as shown in Fig. 3. It should be noted that the crystals were found on both the inner and outer walls of the crucible but crystals were not found on the crucible lip. This implies that formation of the crystals on the outer wall proceeded either *via* the gas phase or that material diffused through the porous alumina. Transport through the porous alumina is thought to be more likely as no other explanation could be found for the absence of crystals at the crucible lip.

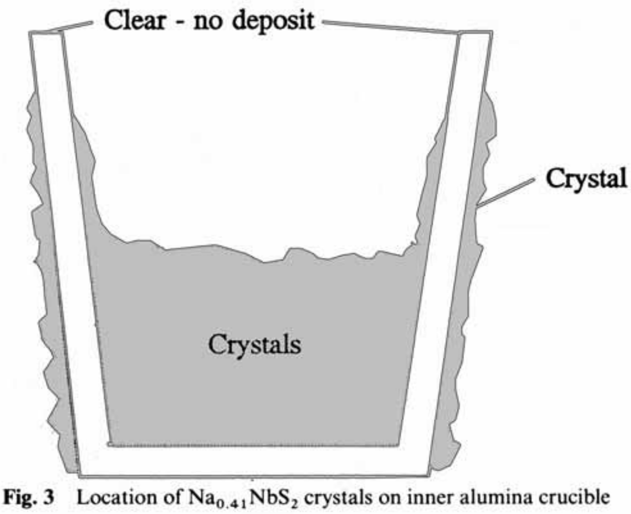

Fig. 3 Location of $Na_{0.41}NbS_2$ crystals on inner alumina crucible

A number of these crystals were loaded into Lindemann capillaries and data collection carried out over the range $1 < \theta < 30°$. Structure elucidation was performed on the 91 independent reflections observed with intensities $I > 3\sigma(I)$ with refinement converging at $R = 0.0266$, ($R' = 0.038$). The structure determined was effectively identical to that found for the material $Na_{0.5}NbS_2$, prepared in our group from a sodium sulfide melt.[13] The NbS_2 layers consisted of niobium in a trigonal prismatic co-ordination and were separated by a trigonal-prismatically co-ordinated sodium species.

X-Ray powder diffraction of the crystals gave a pattern indexing in a hexagonal crystal system with cell dimensions $a = 3.3424(8)$ and $c = 14.664(4)$ Å. A comparison of the cell dimensions with those obtained by the high temperature conversion to the sulfide of Na_2CO_3–Nb_2O_5 under CS_2, described by Omloo and Jellinek[3] implied a low sodium stoichiometry of approximately $Na_{(0.3-0.4)}NbS_2$. The EDX analysis over a number of crystals indicated an average stoichiometry of $Na_{0.37(8)}NbS_{1.8(1)}$, in agreement with the sodium stoichiometry proposed by the comparison of the cell dimensions previously reported. These data are supported by the single-crystal structure determination, in which the stoichiometry was calculated by crystallographic refinement to be $Na_{0.41}NbS_2$. The amount of intercalated sodium in Na_xNbS_2 prepared by the sealed tube experiment described in this study was lower than for the material prepared in the sodium sulfide melt for which a stoichiometry of $Na_{(0.5-0.6)}NbS_2$ was found.

X-Ray powder diffraction of the material in the crucible, originally containing Y_2S_3, showed the presence of two phases. The major phase indexed in a hexagonal crystal system, with cell dimensions $a = 3.7817(5)$ and $c = 6.583(1)$ Å. These cell dimensions corresponded well with the previously published data for Y_2O_2S,[12] as found for the Li_xNbS_2 preparation described above. Also determined from the X-ray powder pattern was a secondary minor phase, which indexed in a hexagonal crystal system with cell dimensions $a = 3.961(1)$ and $c = 19.866(8)$ Å. This phase agreed well with the previously published data for $NaYS_2$[14] and the X-ray powder pattern for the mixed Y_2O_2S–$NaYS_2$ phase is shown in Fig. 4 with the reflection corresponding to $NaYS_2$ labelled. From this it is apparent that the alkali metals in this system have an appreciable vapour pressure and that the sodium had reacted with the diyttrium trisulfide phase, forming a minor product of $NaYS_2$. This is a possible explanation for the non-complete sodium intercalation found in the sodium niobium disulfide crystals described above. A thin film was found on the inside of the tube walls for which EDX analysis showed the presence of sodium, niobium and sulfur and mass spectroscopy showed the S_8 molecule of elemental sulfur to be present.

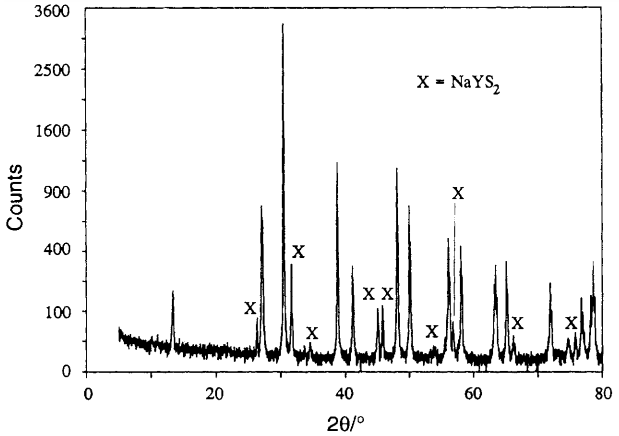

Fig. 4 X-Ray powder diffraction pattern of $NaYS_2$–Y_2O_2S mixed phase

Reaction of $ANbO_3$ *with diyttrium trisulfide* (A = K, Rb *or* Cs). Analogous preparations were carried out with the starting materials $KNbO_3$, $RbNbO_3$ and $CsNbO_3$ as above. In all reactions the material in the crucible originally containing Y_2S_3 was identified as Y_2O_2S with a sulfur deficiency as seen in the preparations of $ANbS_2$ (A = Li or Na). The isolation of single crystals of the products $ANbS_2$ (A = K, Rb or Cs) was attempted, however only severely twinned crystals were obtained and therefore single-crystal structure elucidation has not yet been possible. X-Ray powder diffraction and EDX analysis were used to determine the cell dimensions and alkali-metal stoichiometry of these hexagonal products $K_{0.59(5)}NbS_2$ [$a = 3.3564(9)$ and $c = 16.142(3)$ Å], $Rb_{0.51(5)}NbS_2$ [$a = 3.349(1)$ and $c = 16.810(4)$ Å] and $Cs_{0.22(4)}NbS_2$ [$a = 3.352(2)$ and $c = 17.485(9)$ Å].

Reaction of sodium vanadate and yttrium sulfide. Following the success of the alkali-metal niobate reactions described above, it was decided to investigate the $NaVO_3$–Y_2S_3 system. The reaction was identical to that of the alkali-metal niobate reactions with $NaVO_3$ in place of the $ANbO_3$.

After reaction at 1073 K for 14 days, the product found in the crucible originally containing $NaVO_3$ was highly crystalline, having a dark purple metallic tinge. Isolation of single crystals of this material was attempted, however it was not possible to obtain crystals which were not severely twinned and thus single-crystal structure determination has not been possible. X-Ray powder diffraction gave a good pattern which appeared to be single phased. Indexing of the powder pattern revealed distinct $00l$ reflections, associated with the layered material $NaVS_2$.[15] It was not possible to determine the positions of any non-$00l$ reflections thus the 'a' cell parameter is unknown. The $00l$ reflections ($l = 3n$) yielded a 'c' cell dimension of approximately 21.3 Å, agreeing with the value of 21.21 Å found for $NaVS_2$.

Low temperature measurements using a superconducting quantum interference device (SQUID) were carried out for this material and it was found that a transition at approximately 18 K occurred with a sharp increase in paramagnetism, as shown in Fig. 5. This is in contrast to previous work by Weigers and van Bruggen,[16] where a transition temperature of 50 K was found for the semiconducting type II $NaVS_2$, in which a sharp decrease in magnetic susceptibility was observed. It is clear that complete identification of this material is necessary before any conclusions can be drawn from the magnetic measurements and further work is in progress.

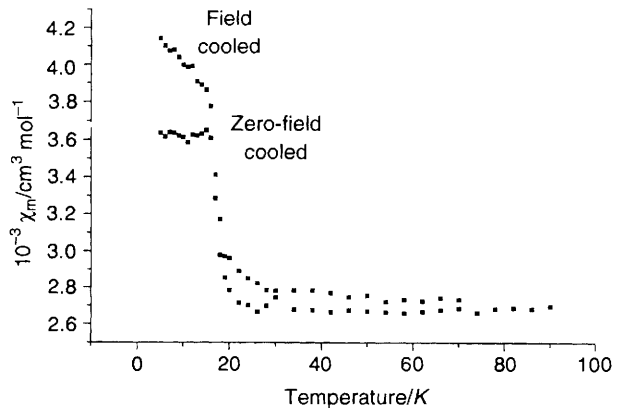

Fig. 5 Magnetic susceptibility *vs.* temperature of proposed $NaVS_2$ material

The material in the crucible originally containing Y_2S_3 gave an X-ray powder pattern which indexed in a hexagonal crystal system with cell dimensions $a = 3.7846(5)$ and $c = 6.5871(9)$ Å, corresponding well with the familiar yttrium oxide sulfide, Y_2O_2S.

The inside walls of the silica tube exhibited coloured bands of surface deposit. A green band formed at a height corresponding to the top of the large alumina crucible, which was seen to consist of many small rod-shaped crystals for which EDX analysis resulted in a stoichiometry of $V_{2.0(1)}Si$ with very small amounts of sodium and sulfur also being present. Formation of this phase necessitates the transport of vanadium through the gas phase. The vanadium species was clearly very reactive due to the formation of this green band, exclusively in close proximity to the top of the alumina crucible.

A red deposit was seen at the top of the crucible and analysis revealed the presence of randomly distributed hexagonal platelet crystals, which were found to have a stoichiometry of $Na_{0.70(6)}VS_{2.51(7)}$ from EDX analysis. Further analysis of these crystals was impossible due to the inability to remove them from the silica wall. The presence of vanadium in an average oxidation state between four and five indicated the non-reducing capabilities of this metathesis reaction.

In summary the sodium vanadium oxide reaction with Y_2S_3 appears to have a complicated reaction scheme with a variety of vanadium species being present in the gas phase.

Further work is being carried out which will hopefully reveal some more information about the products and the mechanism of this interesting reaction.

Metathesis reaction between $BaTiO_3$ *and* Y_2S_3. The barium titanium sulfide system has been extensively studied by Green[17] who investigated the reaction of $BaTiO_3$ under a CS_2 atmosphere at a variety of temperatures. It was found that sulfur-deficient $BaTiS_{3-x}$ was formed below 1373 K, whilst above this temperature Ba_2TiS_4 was the product together with other unknown phases.

The reaction described in this study was analogous to the previous silica-tube reactions described above, with the alkali-metal niobates being replaced by barium titanate. The reaction was carried out at 1073 K (300 K below the transition temperature in the carbon disulfide method) and left for 14 days.

The material in the crucible originally containing the white $BaTiO_3$ was black and gave an X-ray powder pattern with a major phase indexing in an orthorhombic crystal system with cell dimensions $a = 12.288(3)$, $b = 9.040(3)$ and $c = 6.846(2)$ Å. This corresponded very well with the cell dimensions found by Green by single-crystal structure determination for Ba_2TiS_4 of $a = 12.282(3)$, $b = 9.035(5)$ and $c = 6.835(8)$ Å in the orthorhombic space group *Pnma*. A second phase with a maximum relative intensity of 53.7% indexed in a hexagonal crystal system with cell dimensions $a = 6.757(2)$ and $c = 5.763(3)$ Å, agreeing well with the cell dimensions of the single crystal of $BaTiS_3$ [$a = 6.757(3)$ and $c = 5.759(8)$ Å].[17] A small number of residual reflections were also found and were attributed to a phase containing the residual titanium atoms. This phase, however, was not identified.

The overall reaction scheme is thus as in equation (2). The

$$3BaTiO_3(s) + S(g)(Y_2S_3) \longrightarrow Ba_2TiS_4(s) + BaTiS_3(s) + Ti? \quad (2)$$

nature of the sulfur in the gas phase is unknown, as is the form of the excess titanium. The EDX analysis of the material in the crucible originally containing Y_2S_3 gave a Y:S ratio of 2:0.79(3) in agreement with the findings of the alkali-metal niobium disulfide systems above.

Metathesis reaction between $BaCrO_4$ *and* Y_2S_3. The sulfur metathesis reaction described above was utilised in an attempt to prepare a barium chromium tetrasulfide. Barium chromate was prepared by the aqueous coprecipitation of stoichiometric amounts of barium chloride and potassium dichromate and the product, $BaCrO_4$, used as a starting material with yttrium sulfide for the sealed silica-tube reaction at 1073 K for 14 days.

A globular yellow precipitate was found on the inside walls of the crucible after the reaction, which analysed as elemental sulfur. This implied, as for the barium titanate reaction described above, that elemental sulfur was present in the gas phase during reaction.

The X-ray powder pattern of the material in the crucible originally containing barium chromate showed a major phase of tetragonal BaS_3. Previous preparation of this polysulfide involved the high pressure reaction at 50 kBar ($\approx 10^8$ Pa) at 1073 K between BaS and elemental sulfur.[18] These extreme pressures are not thought to be reproduced in the reaction performed in this study.

Residual reflections with maximum intensities of about 40% were seen, however these could not be indexed with a satisfactory solution. The nature of this secondary phase is hitherto unknown.

Metathesis reaction between WO_3 *and* Y_2S_3. The reaction between tungsten trioxide and diyttrium trisulfide in an evacuated sealed silica tube was carried out as for the sealed-tube reactions described above, at 1073 K for 14 days.

The tungsten oxide phase turned from white to black and the yellow-green yttrium sulfide became grey. No deposits were seen on the wall of the silica tube.

The X-ray powder diffraction pattern of the black material in the crucible originally containing WO_3 showed the exclusive presence of WS_2, as expected from this reaction. The formation of the familiar phase Y_2O_2S, was determined from the powder pattern of the material in the second crucible.

Mechanistic Studies of the Sulfur Metathesis Reaction.—Reduction of lithium niobate. It was postulated that if the metathesis reactions described above were driven by the formation of Y_2O_2S, then the initial reaction step would be the loss of oxygen from the oxygen source (*e.g.* $LiNbO_3$) and the formation of Y_2O_2S [equation (3)]. The next step for the preparation of $LiNbS_2$ would be the uptake of the free sulfur into the reactive oxygen-deficient lithium niobate. A third phase was introduced into the system which would remove this free sulfur and thus prevent the reduced oxygen-deficient material, $LiNbO_{(3-2x)}$, from further reaction. The sulfur 'sink' chosen was powdered 316 stainless steel in molar excess. Analysis of the reaction products indicated the formation of the familiar Y_2O_2S phase described above, a mixture of 316 stainless steel and a phase corresponding to $Fe_{0.95}S$[19] and finally a mixture of $LiNbO_3$, $LiNbO_2$ and $LiNbS_2$. Clearly the reaction was partially successful with the formation of hexagonal $LiNbO_2$ [$a = 2.9070(6)$ Å, $c = 10.457(3)$ Å] and $Fe_{0.95}S$, however unreacted $LiNbO_3$ and $LiNbS_2$ were also found. The amount of $LiNbS_2$ produced was substantially less than either of the lithium niobates. The reason for the large proportion of unreacted $LiNbO_3$ is unclear but further reaction at elevated temperatures is expected to drive the reaction to completion. This result indicated that the reduction of oxides *via* this metathesis route was indeed possible, and with careful selection of reactants and sulfur sinks, control over the degree of reduction may be possible.

$$xY_2S_3 + LiNbO_3 \xrightarrow{\text{Vacuum 1073 K}} xY_2O_2S + LiNbO_{(3-2x)} + 2xS \quad (3)$$

Heating of Y_2S_3 *alone.* A reaction was set up with both the $LiNbO_3$ phase and the sulfur sink omitted, to investigate the stability of Y_2S_3 alone under the same reaction conditions and no change was found for this phase after reaction. This indicated that the formation of the yttrium oxide sulfide is only possible when in the presence of an oxygen source (such as lithium niobate) and that oxygen remaining in the system due to a non-perfect vacuum did not affect the reaction.

Dependence upon physical conditions. Variations of the $NaNbO_3$–Y_2S_3 crucible reaction were carried out to investigate the time necessary for reaction, the temperatures required and the pressures reached during reaction.

Reactions at 1073 K for 2 and 4 days were carried out, with all products showing the same basic structures found in the 14-day experiment described above. A reaction at 673 K for seven days was also performed. The cell dimensions of the products of these reactions showed variations in the a and c cell parameters which could be related to the sodium stoichiometry when compared with the values obtained for the Na_xNbS_2 system investigated by Omloo and Jellinek.[7]

The X-ray powder pattern of the product from the four-day preparation at 1073 K exhibited cell dimensions approximating to a stoichiometry of $Na_{0.65}NbS_2$. The cell dimensions obtained for the reaction at 1073 K for two days did not give a good stoichiometry approximation as the a and c values gave conflicting values for x in Na_xNbS_2; however x was thought to fall between 0.4 and 0.7. The preparation at 1073 K for 14 days gave a good approximation to a stoichiometry of $Na_{0.4}NbS_2$, clearly below the values obtained for the 2- and 4-day experiments. An explanation for this is possibly that with extended reaction times the sodium in the system may equilibrate throughout the different phases in the silica tube. Thus for the reaction under the most extreme conditions, at 1073 K for 14 days, the sodium stoichiometry was the lowest found. The reaction at 673 K gave a product corresponding to the material $Na_{0.65}NbS_2$, again showing how less extreme reaction conditions resulted in materials with higher sodium stoichiometries. It was surprising that any reaction occurred at this temperature, indicating the relatively low kinetic barrier associated with the transport of the anions through the gas phase in this system.

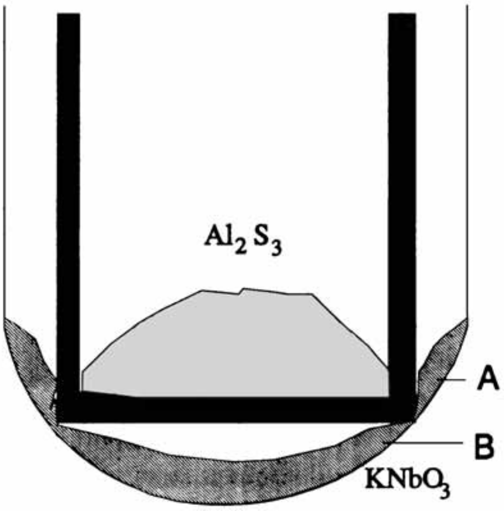

Fig. 6 Location of reactants for the $KNbO_3$–Al_2S_3 reaction

A crude experiment was set up in which the pressure reached during the reaction could be investigated. The reaction was carried out in an evacuated silica tube, sealed with a heavily greased stopper. The glass stopper remained intact on the tube throughout the reaction, implying that the pressure inside the silica tube did not rise above atmospheric pressure. This pressure was thought to be controlled by the rate of reaction of the diyttrium trisulfide. This was a distinct advantage over the silica-tube reactions using elemental sulfur as a sulfur source, in which high pressures were formed during reaction.

Metathesis reaction between $KNbO_3$ *and* Al_2S_3. Preparation of $KNbS_2$ was attempted by replacing diyttrium trisulfide with dialuminium trisulfide. The thermodynamic driving force associated with the oxidation of Al_2S_3 to Al_2O_3 ($\Delta_rH_{298} \approx -960$ kJ mol^{-1})[1] is higher than for the oxidation of Y_2S_3, and the ability of a different sulfur source to drive the metathesis reaction was investigated.

The crucible was prepared in an analogous way to the previous silica-tube experiments; however a single alumina crucible was used, containing Al_2S_3, and the $KNbO_3$ was placed at the bottom of the silica tube as described in Fig. 6 and the tube heated to 1073 K for 14 days. Examination of the products revealed only partial conversion of the $KNbO_3$ phase to $KNbS_2$. The potassium niobate above the base of the alumina crucible (area A) had turned black, with the material below the crucible (area B) remaining off white. The X-ray powder pattern of these phases showed reflections corresponding to $KNbS_2$, as expected for the metathesis reactions described, and also a secondary phase with reflections corresponding well with KNb_3O_8. These results indicated that the desired metathesis reaction yielding potassium niobium disulfide had occurred with the thermodynamically favourable sulfur source Al_2S_3. An effect limiting the reaction was observed where the material at the bottom of the crucible had not been converted to $KNbS_2$, but had actually lost oxygen and potassium resulting in the phase KNb_3O_8. This is thought to be due to the removal of the oxygen in the initial step forming Al_2O_3, however the kinetic barrier associated with the proximity of the powder is sufficient to prevent reaction with sulfur. The product in this area of the crucible was the stable material KNb_3O_8, in which potassium was lost to the system in a form not identified.

Preparation of Nitrides.—It was thought that as the sulfur metathesis reactions described above were successful, it might also be possible to prepare nitrides in a similar way. The reactions were carried out in basically the same manner as for the sulfides, replacing the sulfur source, Y_2S_3, with a binary nitride of a metal having a stable oxide.

Metathesis reaction between V_2O_3 *and* YN. Hydrogen reduction and the subsequent reaction of yttrium oxide produced a mixture of the nitride and some unreacted oxide. An excess of this mixture was placed in an alumina crucible for the metathesis reaction with vanadium(III) oxide at 1073 K for 14 days.

X-Ray powder patterns of the products showed the complete reaction of V_2O_3 to VN as was originally anticipated. The YN phase showed a relative decrease in the intensities for the YN reflections, between the initial starting mixture of YN and Y_2O_3 and the mixture after reaction. This was evidence for the replacement of YN with yttrium oxide, indicating that reaction had occurred *via* the removal of oxygen from V_2O_3 as expected.

The thermodynamic restriction on the reaction was apparent with this system when aluminium nitride was used as a nitrogen source. Complete conversion of V_2O_3 to VN was not observed under identical conditions to the YN–V_2O_3 metathesis reaction described above [Δ_rH_{298} (3AlN $\rightarrow$ Al_2O_3) = -724, Δ_rH_{298} (3YN $\rightarrow$ Y_2O_3) = -1011 kJ mol^{-1}].[1]

Preparation of Carbides.—Finally, an experiment to investigate the metathesis reaction involving the transport of carbon was attempted. This reaction was not expected to proceed owing to the kinetic barriers associated with the carbon transport.

It was decided after analysis of the thermodynamics of the binary carbides to react titanium carbide (TiC) with divanadium trioxide. The reaction was set up as previously described for all of the metathesis reactions and left for 14 days at 1073 K. No deposits were seen on the walls of the tube and both black starting materials remained black after reaction. The X-ray powder pattern of the titanium carbide showed no sign of reaction, which was thought to be due to the large excess of this material used. The vanadium(III) oxide was predominantly unchanged, however reflections were seen in the X-ray pattern with a maximum relative intensity of 14.7% which corresponded to V_4C_3, however slight shifts in the peak positions were seen, implying a degree of non-stoichiometry. The X-ray powder pattern is shown in Fig. 7 with the non-labelled peaks corresponding to V_2O_3 and the V_4C_3 reflections asterisked.

Energy dispersive analysis by X-rays was employed to ensure that the material TiO, of similar structure to V_4C_3, was not present as an impurity in this material. The sample used for the X-ray powder measurement was analysed and was found to contain at least 99% vanadium and only approximately 1% titanium. The titanium present may have crossed crucibles when the vacuum was applied and small particles of titanium carbide were disturbed by the air flow. It was felt that 1% of titanium in the sample would not give rise to reflections of up to 15% relative intensity in the powder pattern and thus it was assumed that the reflections were due to the vanadium carbide reported.

This result was quite unexpected and shows the capability and possibilities of the metathesis reactions under investigation.

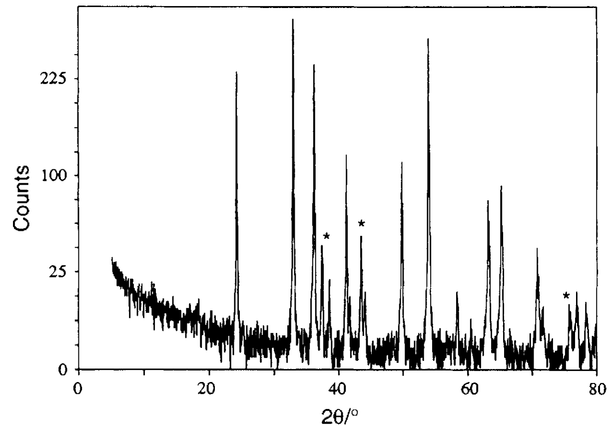

Fig. 7 X-Ray powder diffraction pattern of the V_2O_3–V_4C_3 mixture produced from the metathesis of TiC and V_2O_3

Conclusion

The new technique employed in this study, using the thermodynamics of compounds of metals with very stable oxides, has proven to be a good experimental route for the preparation of solid-state materials.

This class of metathesis reaction is completely new and has many unexplained phenomena connected with it. Many preparations of existing and possibly new materials are expected in the future, giving a further insight into the mechanisms of these fascinating reactions.

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