A Novel Reaction between Physically Separated Solid Reactants

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Ternary oxides may be converted to ternary sulfides by a metathesis reaction with yttrium sulfide in a sealed, evacuated silica ampoule, even when the reactants are physically separated.

The conversion of ternary oxides to ternary sulfides is conventionally achieved by the reaction of the oxide with a sulfiding agent such as CS_2. This reaction, in the case of the alkali metal niobates, leads to the formation of a reduced phase of the type $ANbS_2$. In an effort to overcome the reduction potential of the system, we considered an alternative method of achieving a metathesis reaction in which oxygen and sulfur could be exchanged between two solids. The initial reaction which we considered was:

$$NaNbO_3 + Y_2S_3 \rightarrow NaNbS_3 + Y_2O_3$$

In this reaction the thermodynamic driving force was expected to be the large difference in the free energies of formation of yttrium oxide and yttrium sulfide, which has to be greater than the difference between the ternary oxide and ternary sulfide. Such a reaction is of little preparative value if the product is an intimate mixture of the ternary 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.

The proposed reaction was carried out by placing a small alumina crucible containing the alkali metal niobate inside a larger alumina crucible containing an excess of the yttrium sulfide. The two crucibles were sealed inside an evacuated silica capsule which was heated at 1073 K for 14 days. On opening the capsule in a nitrogen-filled glove box it was seen that the small inner crucible contained metallic, hexagonal single crystals which structure determination and EDX analysis showed to be $Na_{0.41}NbS_2$. Powder X-ray diffraction showed the outer crucible to contain a hexagonal phase with cell dimensions $a = 3.7817(5)$ and $c = 6.583(1)$ Å, corresponding well with the oxysulfide Y_2O_2S.[1] A minor phase present in the same crucible was also hexagonal with cell dimensions $a = 3.961(1)$ and $c = 19.866(8)$ Å, corresponding with the unit cell of $NaYS_2$.[2]

Clearly a metathesis reaction had taken place and the $NaNbO_3$ had been completely sulfided to Na_xNbS_2 which was formed as single crystals.

Modifying the conditions of the reaction showed that complete reaction was possible after only two days and at temperatures as low as 673 K. Measurement of the pressure in a modified reaction vessel indicated that pressures above atmospheric pressure were not reached during reaction.

A range of alkali metal niobium disulfides with the approximate stoichiometry $A_{0.5}NbS_2$ in the form of single crystals were isolated using this technique.[3] X-ray powder and single crystal diffraction studies indicated hexagonal materials with cell dimensions and alkali metal stoichiometries determined from EDX analysis as follows: Li_xNbS_2 $a = 3.412(2)$, $c = 12.876(1)$; $Na_{0.41}NbS_2$ $a = 3.424(8)$, $c = 14.664(4)$; $K_{0.59}NbS_2$ $a = 3.3564(9)$, $c = 16.142(3)$; $Rb_{0.5}NbS_2$ $a = 3.349(1)$, $c = 16.810(4)$; $Cs_{0.2}NbS_2$ $a = 3.352(2)$, $c = 17.485(9)$ Å. The cell dimensions determined corresponded well with the powdered materials prepared by Dahn,[4] Omloo[5] and Chen.[6] The Y_2O_2S phase described above was observed as the product for the full range of alkali metal niobium disulfide reactions, indicating the reaction to be independent of the alkali metal present.

The reason for the success of these reactions was clearly the thermodynamic driving force provided by the converson of Y_2S_3 to Y_2O_2S. This was demonstrated when the reaction of an alkali metal ternary niobate as described above was carried out in the presence of a third material acting as a sulfur 'sink'. The reaction between lithium niobate, $LiNbO_3$, and yttrium sulfide was repeated but with a third crucible containing stainless steel powder placed in the tube. It was hoped that some of the oxygen of the lithium niobate would be removed by the yttrium sulfide phase and the labile sulfur released on formation of Y_2O_2S would be trapped by the stainless steel due to the thermodynamically favourable formation of iron sulfide according to the following reaction scheme:

$$2LiNbO_3 + Y_2S_3 + 2Fe_{(ss)} \rightarrow 2LiNbO_2 + Y_2O_2S + 2FeS$$

Analysis of the reaction products showed the presence of the Y_2O_2S phase described earlier, the iron sulfide $Fe_{1-x}S$ and a mixture of $LiNbO_3$ [$a = 5.1510(7)$, $c = 6.9301(1)$ Å], $LiNbO_2$[7] [$a = 2.9070(6)$, $c = 10.457(3)$ Å] and $LiNbS_2$ [$a = 3.333(2)$, $c = 12.86(2)$ Å]. Although the reaction had not reached completion and the steel had not trapped all of the sulfur, the mechanism was as expected, with the removal of oxygen from lithium niobate being the initial reaction step. The formation of other, possibly novel, reduced products may be possible using this technique and control over the degree of reduction may be possible by changing the reaction components.

Metathesis reactions of other ternary transition metal oxides have been investigated, in particular the reaction between Y_2S_3 and $BaTiO_3$. It was hoped to prepare single crystals of the material $BaTiS_3$, previously isolated by sulfiding $BaTiO_3$ with carbon disulfide. The products of the metathesis reaction at 1073 K for 14 days were the yttrium oxysulfide Y_2O_2S and a mixture of orthorhombic Ba_2TiS_4 [$a = 12.288$, $b = 9.404(3)$, $c = 6.846(2)$ Å] and hexagonal $BaTiS_3$ [$a = 6.757(2)$, $c = 5.763(3)$ Å]. The temperature used in this metathesis reaction was 300 K below that required for the preparation of Ba_2TiS_4 by the sulfiding of $BaTiO_3$ with CS_2.[8]

The success of the metathesis reactions using Y_2S_3 as a sulfur source led us to attempt metathesis reactions for the exchange of different anions. The exchange of nitrogen and oxygen was the next obvious reaction; however, it was unclear whether this reaction would proceed due to the extremely stable nature of N_2. The reaction between YN and V_2O_3 was attempted in an analogous way to the sulfur reactions described above, with YN replacing Y_2S_3. Analysis of the products after reaction at 1073 K for 14 days revealed the phases Y_2O_3 and VN. This showed that complete reaction had occurred and indeed the preparation of nitrides using this novel technique is possible. Work is currently being carried out into the preparation of the more complex ternary nitrides.

A further investigation of these metathesis reactions involved the unlikely preparation of carbides. An identical reaction to those described above was carried out at 1073 K for 14 days between TiC and V_2O_3. The products found were principally unreacted TiC and vanadium(III) oxide; however, extra reflections were observed along with the X-ray powder pattern of V_2O_3. These reflections had a maximum relative intensity of approximately 15% and corresponded to the phase V_4C_3. This was unexpected as the kinetic barrier associated with the transport of carbon through the vapour phase at the temperatures used was thought to be substantial. Investigation into the preparation of other group four, five and six transition metal compounds is presently being undertaken, as well as the possibility of preparing selenides, tellurides and phosphides using this new procedure.

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