Preparation of Some New Ternary Nitrides

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WE now report the syntheses of some ternary nitrides of the type $A_xM_yN_z$ where A = Ba or Sr and M = Re, Os, Mo, and W. These compounds were prepared by the reaction of the alkaline-earth nitride and the appropriate transition metal with purified nitrogen at atmospheric pressure and elevated temperatures.

One series of compounds has been prepared which has the general formula $A_9M_3N_{10}$. Examples of compounds with this composition are $Ba_9Re_3N_{10}$ and $Ba_9Os_3N_{10}$. In both examples, the formal oxidation state of the transition metal is presumably tetravalent. Both compounds are thermally stable under atmospheric pressure of nitrogen; $Ba_9Os_3N_{10}$ to 900°C, and $Ba_9Re_3N_{10}$ to 1000°C. They are also stable in liquid ammonia under acid conditions (*i.e.* low concentrations of NH_4NO_3). However, they are hydrolytically unstable and therefore must be handled under dry nitrogen.

X-Ray powder diffraction patterns of these products both could be indexed on the basis of a pseudo-tetragonal unit cell. For $Ba_9Re_3N_{10}$, $a = 7{\cdot}43$ Å, $c = 32{\cdot}2$ Å, and for $Ba_9Os_3N_{10}$, $a = 7{\cdot}42$ Å, $c = 31{\cdot}8$ Å. A complete chemical analysis has been carried out for $Ba_9Re_3N_{10}$. The analysis gave barium (as sulphate) 62·61%; Re (precipitated as nitron per-rhenate) 28·88%; and nitrogen (Kjeldahl) 7·20% (calculated for $Ba_9Re_3N_{10}$, Ba = 63·89%, Re = 28·87%, N = 7·24%. For $Ba_9Os_3N_{10}$, only nitrogen was determined. This was done by measuring nitrogen absorption, and gave for nitrogen 6·96% (calculated for $Ba_9Os_3N_{10}$, N = 7·19%).

Attempts have been made to make the strontium analogues of the above compounds. In the case of the rhenium system, there is some evidence for $Sr_9Re_3N_{10}$, and several other phases with high Sr/Re ratios. No strontium analogue of $Ba_9Os_3N_{10}$ has yet been found. High-pressure synthesis is being used in an attempt to prepare this compound. Both Sr_3N_2 and Ba_3N_2 intimately mixed with either molybdenum or tungsten metal powders absorb nitrogen under atmospheric

pressure at elevated temperatures. The products are voluminous yellow to yellow-green powders. The *X*-ray patterns are complex and it is possible that more than one phase is being formed.

The characterization and details of the preparation of these new ternary nitrides will be described later.

It is interesting that rhenium and osmium which do not form binary nitrides directly are so readily converted to ternary nitrides by reaction wish elemental nitrogen.

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