This is the final report on a project funded for 3 years by ONR. The project was very successful; it resulted in the discovery of many new solid state ternary nitrides. Since there were so few ternary nitrides known, and since many of the binary nitrides, such as TiN, AlN and Si3N4, are so technologically useful, our aim was to explore the synthesis, structural chemistry and properties of ternary nitrides. Prior to our work very few ternary nitrides, other than those formed by alloying binaries and having simple binary like structures, were known. We have shown that there is indeed a very large class of such ternary nitrides.

We discovered that there is a very large class of ternary nitrides of general formula MxTyNz, where M is an electropositive metal (alkali or alkaline earth metal), T is a transition metal or post-transition main group metal, and N is nitrogen. Such compounds exist for example when M = Ca for all T, with only a few exceptions. These compounds have structures and properties quite unlike those of oxides, sulfides, phosphides or carbides - all those elements that are neighbors to nitrogen. In general when the compounds are in the highest oxidation state attainable in a N2 atmosphere, the coordination number of the T cation is small, generally 2 or 3. Sometimes oxidation states that are rare or non-existent in other compounds are produced; for example, Ni(I) is present in compounds such as CaNiN.
The reaction chemistry of nitrides also had to be developed. We prepared such phases by several methods including: reaction of pressed powders of binary nitrides in N$_2$ gas, reaction of metals or ternary oxides with NH$_3$, and the use of super critical NH$_3$ at high temperatures (up to 800°C). General thermodynamic principles were developed for the prediction of useful precursor solid state materials in NH$_3$ flow reactors. This predictive scheme is particularly useful for oxide precursors, since the thermodynamics of oxides is quite well explored. We predicted that in general oxide compounds containing electropositive metals (alkali, alkaline earth and rare earth metals) will NOT form ternary nitrides when reacted with NH$_3$, while all other oxides may well form such ternary phases.

We were the first scientists in the US to explore these materials, but two other chemists in Germany (H. Jacobs and R. Kniep) at the same time began research programs that are parallel to our program. Our work combined with their findings shows that there are indeed a huge number of ternary compounds of the type anticipated in our original proposal. More recently, several US research groups have begun research in this same area since it seems so ripe for discovery.

The research supported by ONR resulted in the publication of 18 research papers and was the main focus of the work reported in 4 PhD theses. The support of ONR in this research was greatly appreciated.

Publications Resulting from ONR Support:


**Theses Resulting from ONR Support:**


