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Synthesis of the New Ternary Transition Metal Nitride $FeWN_2$ via Ammonolysis of a Solid State Oxide Precursor

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A new ternary nitride, $FeWN_2$, was prepared via ammonolysis of the solid state oxide precursor $FeWO_4$ at 800°C. The powder diffraction data were indexed as a hexagonal structure with lattice parameters $a = 2.867(2)$ Å and $c = 16.458(9)$ Å. The successful preparation of $FeWN_2$ demonstrates that the inductive effect is not necessary for preparing some ternary transition metal nitrides.

Solid state nitrides are of interest because they exhibit technologically useful properties. For example, some transition metal nitrides are extremely hard and strong, yet are good conductors of heat and electricity. Because of the diverse properties exhibited by nitrides, they have found utility as packaging materials, as structural materials, and as catalysts (*1*, *2*). Nonetheless, relatively few nitrides have been synthesized and fully characterized, in part because nitrides have low decomposition temperatures due to the high bond energy of N_2 (941 kJ/mole) (*1–3*). A recent synthetic strategy for synthesizing ternary nitrides involves the stabilization of late transition metals via the inductive effect (*1*, *4*). This approach has been very successful; however, it limits the number of potential new ternary nitrides to those containing highly electropositive elements. In this letter we describe the simple synthesis of the new single-phased ternary nitride $FeWN_2$, which is not stabilized by an inductive effect.

Nitride research has become more active recently, with several groups pursuing the synthesis and characterization of new compounds (*5–11*). Synthetic approaches for ternary nitrides include the reaction of a metal nitride with an alkali, alkaline, or rare earth metal, or the reaction of alkali, alkaline, or rare earth nitrides with a transition metal under N_2 or NH_3. Another approach has been the use of mixed metal precursors. For example, the ternary nitride $LiMoN_2$ can be synthesized by the reaction between Li_2MoO_4 and NH_3 (g) (*12*).

There are few known and well characterized ternary nitrides that do not contain highly electropositive elements. Often, nitrides are not synthesized directly, but rather one nitride is converted into another. For example, recently $CuTaN_2$ was synthesized via an ion-exchange reaction between $CuCl_2$ and $NaTaN_2$ (*13*). We are currently investigating the use of transition series metalates as precursors to ternary transition metal nitrides in single-step reactions. Our successful preparation of $FeWN_2$ demonstrates that the inductive effect is not necessary for preparing some ternary transition metal nitrides and suggests that a large number of other ternary transition metal nitrides can also be prepared directly.

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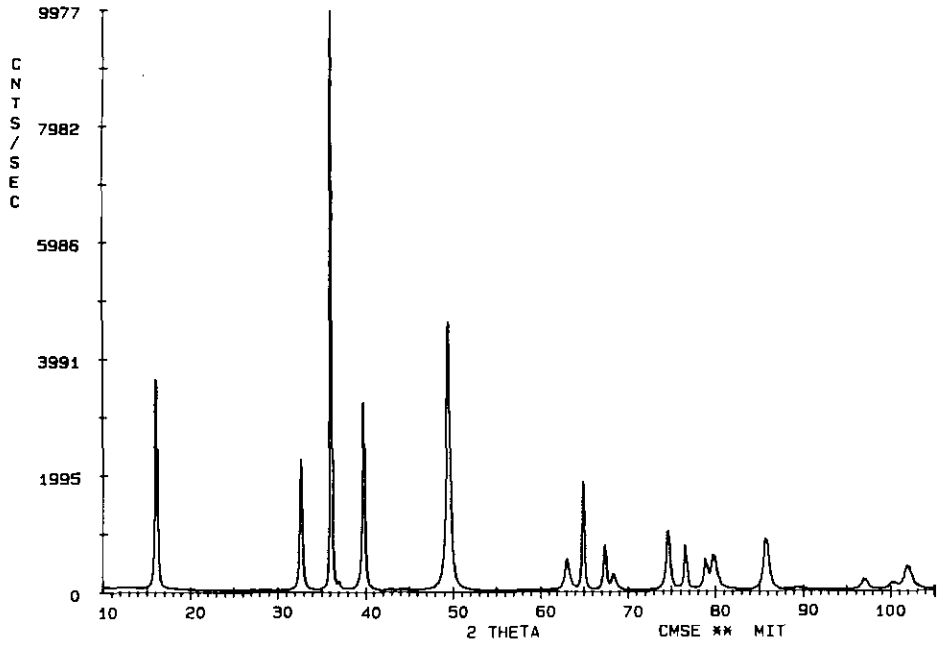

FIG. 1. Powder X-ray diffraction pattern of $FeWN_2$.

$FeWN_2$ is prepared via the ammonolysis of the transition metal tungstate $FeWO_4$. The hydrated iron tungstate was prepared by dropwise addition of a 40-ml (0.25 *M*) aqueous solution of metal chloride, $FeCl_2$ (Cerac, 99.99%), to a 15-ml (0.67 *M*) solution of $Na_2WO_4 \cdot (H_2O)_2$ (Aldrich 99%). A brown solid product was isolated by vacuum filtration and rinsed with two washings in water followed by a single washing in ethanol. The solid was air-dried overnight followed by further drying at 150°C for 24 hr. The product was a brown powder which was characterized by powder X-ray diffraction as $FeWO_4$. The metal tungstate precursor was placed in an alumina boat which was inserted into a quartz flow-through reactor located in a hinged tube furnace. The sample was heated under flowing ammonia gas (160 cm^3/min) at 5°/min to 800°C. The sample was held at the reaction temperature for 12 hr and then quenched to room temperature by turning off and opening the furnace. The black product, $FeWN_2$, was pure by X-ray powder diffraction (Fig. 1) and was indexed as hexagonal, $a = 2.867(2)$ Å and $c = 16.458(9)$ Å (Table I). The hexagonal structure is similar to the known nitrides $LiMoN_2$ ($a = 2.8674$Å, $c = 15.801$Å) (*12*) and Cu TaN_2 ($a = 3.136$Å, $c = 17.438$Å) (*13*).

TABLE I

D-SPACINGS AND INDEXING OF $FeWN_2$

d-Spacing	*h k l*
5.4683	0 0 3
2.7370	0 0 6
2.4818	1 0 0
2.2609	1 0 3
1.8387	1 0 6
1.4733	1 0 9
1.4343	1 1 0
1.3882	1 1 3
1.3707	0 0 12
1.2706	1 1 6
1.2421	2 0 0
1.2095	2 0 3
1.1999	1 0 12
1.1315	2 0 6
1.0277	2 0 9
0.9908	1 1 12

The nitrogen content of the sample was determined by thermogravimetric analysis (Cahn 121 TGA). The sample $FeWN_2$ was heated 5°C/min to 900°C under O_2. After 3 hr at 900°C, the oxygen was shut off and the forming gas ($5\%H_2:95\%N_2$) was switched on. The sample had a weight gain of 14.26% when heated under the oxygen and a subsequent weight loss of 23.47% under the forming gas. This weight change is consistent with the formula $FeWN_{1.94}$. The results of C, H, N combustion analysis (Oneida N = 10.18 wt% or $FeWN_{1.95}$) are in good agreement with the nitrogen content determined by thermogravimetric analysis.

$FeWN_2$ is a new ternary transition metal nitride that was prepared in a single-step synthesis. Rietveld refinements of its structure and measurements of its magnetic and electronic properties are in progress.

Acknowledgments

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