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Ambient Pressure Synthesis of Ternary Group(V) Nitrides

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We describe the ambient pressure synthesis of $M\mathrm{TaN}_2$ (M = Na or K), and the previously unreported, isostructural niobium analogs by the use of an ammonia flow system, starting with either Ta_3N_5 or tantalum metal, or either NbN or niobium metal, respectively, and an excess of the alkali metal amide at 500°C. The products are characterized by X-ray powder diffraction. In addition, we describe our attempts to deintercalate $NaTaN_2$ using NO_2PF_6. © 1992 Academic Press, Inc.

Introduction

Ternary nitrides are a relatively unexplored class of compounds. In most of the known ternary alkali metal nitrides, the alkali metal is lithium. Until recently the only examples of ternary alkali metal nitrides that do not contain lithium were $NaGe_2N_3$ (*1*), KMgN (*2*), KPN_2, and $NaPN_2$ (*3*). The first new examples of this rare class of compound are $M\mathrm{TaN}_2$, (M = Na, K, Rb, or Cs). They were synthesized by heating together a mixture the alkali metal amide and a tantalum(V) source (Ta_2O_5, $TaCl_5$, etc.), from 400 to 800°C in a bomb under an ammonia pressure of several kilobars (*4*). All of these new compounds have structures related to the β-crystobalite structure, except for Na TaN_2, which has the layered α-$NaFeO_2$ structure. Many compounds with layered structures show intercalation/deintercalation chemistry. For example, many of the transition metal dichalcogenides are easily intercalated by alkali metals; subsequently, these compounds are then easily deintercalated with simple oxidizing agents, such as iodine (*5, 6*). We have shown that more powerful oxidizing agents, such as NO_2PF_6 and MoF_6, can be used to deintercalate $LiCoO_2$. Not only does intercalation/deintercalation give rise to new compounds not easily prepared by other methods, but the physical properties of these new compounds are usually distinct from the parent compounds (*7*).

We report here a simple, ambient pressure route to synthesize the alkali tantalum nitrides, including the previously unreported niobium analogs of these compounds. In addition, we attempted deintercalation of $NaTaN_2$.

Experimental

All reagents and compounds were handled in an argon-filled glove box, unless otherwise noted. Reagents were used as received, unless otherwise noted. X-ray powder diffraction patterns were obtained using a Scintag XDS 2000 Powder Diffractometer (Cu K_α), with the contribution of the Cu $K_{\alpha 2}$ radiation mathematically removed using Scintag software. Thermogravimetric analysis was done on a Perkin–Elmer TGA 7 Thermogravimetric Analyzer.

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To synthesize Ta_3N_5, approximately 8 g of $TaCl_5$ (sublimed before use, Pressure Chemical Co., Pittsburgh, PA) was placed in an alumina boat, that was in turn placed into a quartz tube. The $TaCl_5$ was reacted with ammonia gas that had been dried as the liquid with sodium metal (flow rate of approximately 1-½ liter/min of gas). Under the flowing ammonia the temperature was then raised slowly (100°C per hr) to 225°C. Near 225°C, the $TaCl_5$ began to react vigorously with the ammonia. As the temperature was increased to 300–350°C, ammonium chloride began to sublime out of the boat. The temperature was then slowly increased to 700°C and kept there for 1 hr to complete the reaction (*8, 9*).

NbN was made in exactly the same way as Ta_3N_5, except $NbCl_5$ (sublimed before use, Strem Chemicals, Inc., 99+%) was used instead of $TaCl_5$. The NbN so obtained was black. Note that Nb_3N_5 has never been reported and we found no evidence of such a phase here.

To synthesize $NaTaN_2$, approximately 2–3 g of Ta_3N_5 was placed in an alumina boat. A 5- to 10-fold excess (1.5 to 3 g) of oil free sodium metal (washed with hexane) (Strem Chemicals, Inc., Newburyport, MA), that has had the oxide coat removed with a knife in a dry box, was also placed into the same alumina boat. Then the mixture was placed into a pyrex tube, and reacted with ammonia gas that had been dried as the liquid with sodium metal (flow rate of approximately 1-½ liter/min of gas). Under the flowing ammonia, the temperature was increased to 350°C at about 200°C/hr. As the furnace heated up, the sodium metal melted, and slowly began to react with the ammonia gas, forming sodium amide. In approximately 1 hr all of the sodium metal was converted to sodium amide. Next the temperature was raised to 500°C. At this temperature the sodium amide reacted with the Ta_3N_5 to form $NaTaN_2$ and the excess sodium amide slowly sublimed out of the boat. The reaction was allowed to continue for 5 to 10 hr, mostly to remove as much sodium amide as possible at this stage. After allowing the reaction mixture to cool, the reaction mixture was transferred to a quartz tube and the ammonia flow reestablished over the sample. The temperature was raised to 700°C for 10 to 12 hr. This removed all the unreacted sodium amide, as well as produced a very crystalline product. When $NaTaN_2$ was prepared by this method from Ta_3N_5, it was impurity-free by X-ray powder diffraction (*10*).

$NaNbN_2$ was prepared in a similar manner to $NaTaN_2$, except NbN was used instead of Ta_3N_5. The Nb(III) in NbN is oxidized to Nb(V) in the reaction with $NaNH_2$ or NH_3, or with N_2 the decomposition product of both species. Also, no second heating of $NaNbN_2$ was performed; the remaining $NaNH_2$ was used as an X-ray standard. The X-ray powder diffraction pattern shows that $NaNbN_2$ is isostructural with $NaTaN_2$.

$KTaN_2$ was prepared in the same manner as $NaTaN_2$, except potassium metal (Alfa, Sticks, m3N5) was used in place of sodium metal.

$KNbN_2$ was also prepared in the same manner as $NaNbN_2$, except potassium metal was used in place of sodium metal. $KNbN_2$ again is found to be isostructural to $KTaN_2$ prepared at low pressures (vide infra).

For deintercalation reactions typically 0.5–1.0 g of $NaTaN_2$ was weighed into a shlenk flask. Eleven milliliters of acetonitrile (Burdik–Jackson) was added. A solution of NO_2PF_6 in acetonitrile was added, with stirring. The final volume of the reaction mixture was usually between 12 and 20 ml. Immediately upon addition of the NO_2PF_6 solution, the yellow slurry became orange to red, the depth of the color dependant upon the amount of NO_2PF_6 added. Also, a red-brown gas, NO_2, formed in and above the solution. After

TABLE 1

LATTICE PARAMETERS FOR SOME NITRIDES

Compound	Crystal system	Lattice parammeter (Å)	Color
$NaTaN_2$	Hexagonal	a = 3.131(1) c = 16.902(3)	Yellow
$NaNbN_2$	Hexagonal	a = 3.150(1) c = 16.939(3)	Red
$KTaN_2$	Cubic	a = 8.338(2)	Yellow
$KNbN_2$	Cubic	a = 8.312(2)	Purple
Nominal Na_0TaN_2	Hexagonal	a = 3.10 c = 14.84	Red
Ta_3N_5	Orthorhombic	a = 3.8862(1) b = 10.2118(2) c = 10.2624(3)	Brick red

Note. The lattice parameters obtained for $NaTaN_2$ are very close to those obtained in Ref. (*4*): a = 3.139(1)and c = 6.925(5). The lattice parameters for Ta_3N_5 are taken from a recent redetermination of the structure by neutron powder diffraction (*11*).

allowing the slurry to stir for 1 hr, the slurry was brought back into the dry box, filtered, and the precipitate was washed two times with acetonitrile, and allowed to dry. None of the products from these reactions appeared air-sensitive.

Results and Discussion

The lattice parameters and colors of $NaTaN_2$, $NaNbN_2$, $KTaN_2$, $KNbN_2$, deintercalated $NaTaN_2$, and Ta_3N_5 are listed in Table I. All of these compounds are colored insulators. The X-ray powder patterns of the potassium compounds could be completely indexed on a cubic unit cell. The unit cells of the same compounds prepared under 5 kbars of NH_3 pressure are slightly distorted from cubic to orthorhombic (*4*). However, $CsTaN_2$ prepared at high pressure is also cubic with a somewhat larger lattice parameter (8.7726 Å) than we find for KTaN2. The difference in the potassium structures may be due to the difference in synthesis pressure or small differences in stoichiometry.

Our ammonia flow furnace is a convenient way of synthesizing these group(V) alkali metal nitrides, as well as Ta_3N_5 and alkali metal amides. The system allows easy removal of unwanted volatile materials, such as the alkali metal amides. A pyrex outer tube was used instead of a quartz outer tube for the low-temperature reactions using alkali metal amides because the tubes are attacked by the subliming amide and the pyrex is less expensive. Once most of the amide had sublimed out of the reaction mixture, a quartz outer tube could be used several times for the higher temperature range (above 500°C) before amide attack became severe.

Although we use Ta_3N_5 and NbN as our tantalum and niobium sources, respectively, for the synthesis of the corresponding alkali metal ternary nitrides, all of them could be made using pure tantalum metal or niobium metal. The advantage of using the nitrides is that they are very fine powders. When $NaTaN_2$, $NaNbN_2$, $KTaN_2$ or $KNbN_2$ were prepared from the group(V) metal rather than the group(V) metal nitride, there was always some unreacted group(V) metal left. It appears that the grains of metal are passivated from further reaction by the newly forming ternary nitride.

The $NaNbN_2$ and $KNbN_2$ resemble their tantalum analogs. The only differences are their colors and their slightly smaller lattice parameters. $NaNbN_2$ was slightly water-sensitive, decomposing slowly in air or water, while $NaTaN_2$ is not water- or air-sensitive. The alkali metal amides are pyrophoric, and they must be removed before either $NaTaN_2$ or $NaNbN_2$ are exposed to air. This removal is done by sublimation in the last steps of the reaction, but can also be done by reacting the amide with bis(trimethylsilyl)amine and washing out the product with toluene.

Figures 1–4 show X-ray diffraction patterns of $NaTaN_2$ as increasing amounts of sodium are removed to produce Na_xTaN_2, with $x < 1$. Figure 1 shows the pattern for $NaTaN_2$ as prepared. When $NaTaN_2$ is reacted with $\frac{1}{2}$ an equivalent of NO_2PF_6 we

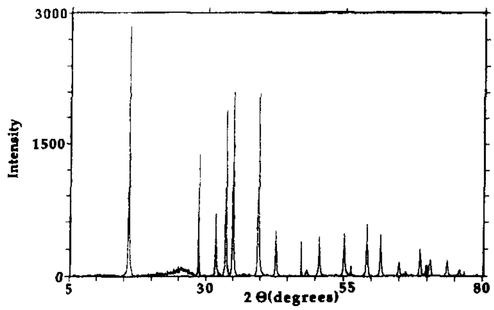

FIG. 1. The X-ray powder diffraction pattern of Na TaN_2. Note the peak intensities and the narrow linewidths.

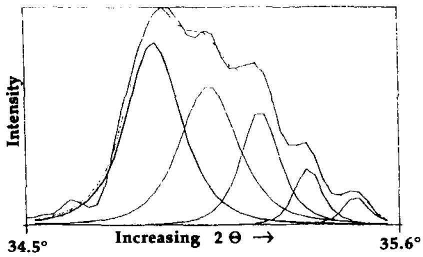

FIG. 3. A deconvolution of the (1 0 2) X-ray diffraction line of nominally $Na_{0.25}TaN_2$. The Cu $K_{\alpha2}$ radiation has been mathematically removed.

produce nominally $Na_{0.5}TaN_2$, presumably by oxidizing nitrogen, since tantalum is already Ta(V) in the parent material. The diffraction pattern for nominally $Na_{0.5}TaN_2$ is shown in Fig. 2. Note that the diffraction lines have all broadened and decreased in peak intensity from those seen in Fig. 1.

Figure 3 shows the (1 0 2) diffraction peak of nominally $Na_{0.25}TaN_2$. The peak is not only broad, but asymmetric, with a clear indication of being made up of several different peaks due to sample inhomogeneity. The low-angle edge of the peak is close to the position seen in $NaTaN_2$ (Fig. 1), indicating that some of the sample remains unreacted.

When $NaTaN_2$ is reacted with an excess of NO_2PF_6, the strongest peak after deintercalation in the X-ray powder diffraction is less than 10% as intense as it was before deintercalation. Figure 4 shows the diffraction pattern of nominally $Na_{0.0}TaN_2$. The diffraction intensities are quite low and the lines are broad; only five or six lines remain in the pattern, indicating considerable disorder in the resulting compound. It is not certain that the pattern represents the bulk of the sample, or if most of the sample is in fact amorphous. If the few remaining lines are indexed on a hexagonal cell the *a*-axis length remains about the same as in $NaTaN_2$ but the *c*-axis length has decreased considerably (see Table I).

Finally, although accurate lattice parame-

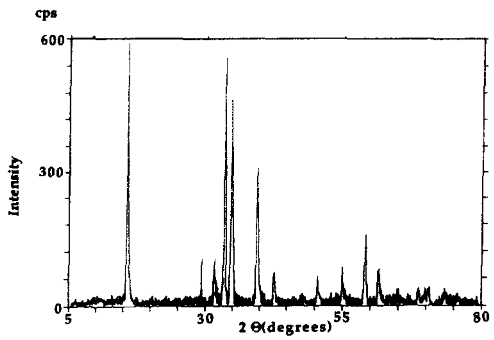

FIG. 2. The X-ray powder diffraction pattern for nominally $Na_{0.5}TaN_2$.

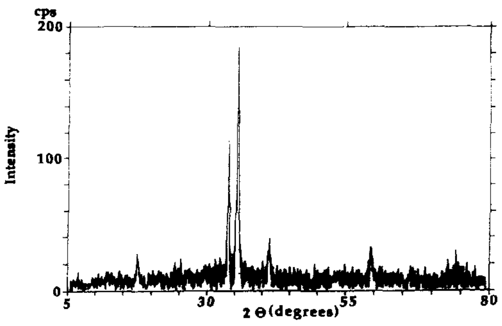

FIG. 4. The X-ray powder diffraction pattern for nominally $Na_{0.0}TaN_2$. Note the intensity of the first diffraction peak has decreased almost into the background.

ters cannot be obtained for samples with $x < 1$ due to the inhomogeneous nature of the samples, it is clear that the lattice contracts along the *c* direction as Na is removed. This is quite consistent with observations of deintercalation products of many layered compounds (*6, 7, 12, 13*).

We have tried a variety of nitrogen analysis techniques on these materials, all with ambiguous results. Like the parent compound, these deintercalated materials are resistant to most mineral acids, dissolving only slowly in hydrofluoric acid or boiling phosphoric acid, making wet chemical analysis almost impossible. The only technique that has given reproducible information on the nitrogen content of Na_xTaN_2 is thermogravimetric analysis (TGA). By reacting the nominally $Na_{0.0}TaN_2$ ($NaTaN_2$ that has been reacted with a small excess of NO_2^+) with oxygen in the TGA we found a weight gain of 6.9%, and therefore know that no more than 8% of the original nitrogen has been lost. The reaction is

$$Na_{1-x}TaN_{2-y} + [(3/2) - x/4]O_2 \Rightarrow \text{“}Na_{1-x}TaO_{3-x/2}.\text{”}$$

The product is given in quotes to show that it may not be single phase, but that all elements are present in their maximum oxidation states. Since there is a weight gain of 6.9%, we calculate from the above formula that y must be equal to $x(0.43) - (0.27)$; this gives a maximum nitrogen loss of $y = 0.16$, or 7.9%, assuming that all the sodium is removed. Otherwise, even less nitrogen is lost from the deintercalated phases.) In addition, from X-ray power diffraction of nominally $Na_{0.0}TaN_2$ that has been heated to 900°C in air, we know that not all the sodium has been removed, because small amounts (approx. 20%) of $Na_2Ta_4O_{11}$ are seen in the pattern along with the majority phase, Ta_2O_5. We therefore believe the composition of this final product to be about $Na_{0.1}TaN_{1.9}$. We take this as crude evidence that little, if any, of the nitrogen has been lost during the deintercalation reaction.

Attempts to reintroduce sodium in to $Na_{0.1}TaN_2$ at room tempertaure with sodium naphthalide in THF were unsuccessful. This may be due to the disordered nature of the material.

Since the nominally $Na_{0.1}TaN_2$ is a colored insulator, and the maximum oxidation state of tantalum is Ta(V), then either nitrogen–nitrogen bonds form, or unpaired electrons remain on nitrogen atoms. Unfortunately, we have not been able to find any direct evidence for either of these.

Conclusion

We have described a simple and easy method for the synthesis the alkali metal, group(V) metal nitrides. We have also synthesized $NaNbN_2$ and $KNbN_2$, two new alkali metal nitrides that do not contain lithium. Finally, we have made some metastable disordered nitrides by deintercalation of layered $NaTaN_2$ using NO_2PF_6. In a subsequent report we will show how this general system can be used to synthesize another class of alkali metal nitrides (*14*).

Acknowledgment

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