

A New Conducting Ternary Nitride: $\text{Na}_x\text{Ta}_3\text{N}_5$ ($0 \leq x \leq 1.4$)

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Topotactic insertion of sodium into the channel structure of Ta_3N_5 has been accomplished by the reaction between Na and Ta_3N_5 at temperatures between 450 and 600°C in sealed Ni tubes. The limiting stoichiometry of $\text{Na}_x\text{Ta}_3\text{N}_5$ obtained is $x \approx 1.4$. The structure of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ has been refined using Rietveld full-profile refinement of X-ray powder diffraction data using the Ta_3N_5 structure as the starting model. The space group remains *Cmcm* (No. 63) with parameters $a = 3.995(1)$, $b = 10.197(2)$, and $c = 10.331(2)$ Å. The Na atoms are shown to occupy 7-coordinate sites in the holes present in the Ta_3N_5 framework. The weak temperature dependence of the magnetic susceptibility between 100 and 320 K of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ and its small value ($\chi_{\text{mol}}(300 \text{ K}) = 6.5 \times 10^{-4} \text{ emu mol}^{-1}$) suggest that the compound is a metallic conductor. This is supported by the moderate conduction of an unsintered pellet of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ powder. We also report the identification of the poorly crystalline disordered rock salt phase $\text{Na}_2\text{Ta}_3\text{N}_5$ ($a = 4.47(4)$ Å) which is obtained when the reaction temperature is between 600 and 800°C and a partly characterized hexagonal phase that results from nitrogen loss, $\text{Na}_{1-x}\text{Ta}_{3+x}\text{N}_4$ ($x \approx 0$), which forms at temperatures above 800°C. The latter compound crystallizes in *P6₃/mcm* (No. 193) with $a = 5.1784(1)$ and $c = 10.3650(3)$ Å and is analogous to previously reported Li and Mg compounds.

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INTRODUCTION

Many binary nitrides are commercially useful or technologically interesting. However, ternary nitrides have received very little attention until recently (1–3). The large energy required to stabilize the N^{3-} ion (1) means that the bonding in nitrides is usually much more covalent than bonding in oxides or sulfides, and this leads to unusual or unique structures. Ternary nitrides can be difficult to synthesize, are often air sensitive, and usually decompose upon heating with a loss of N_2 . Nitrides are thermodynamically less stable than the corresponding oxides, and their synthesis often requires forcing conditions.

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It is hoped that some ternary nitrides may prove to have useful technological properties. The most interesting materials from this point of view are those nitrides which have two- or three-dimensional metal–nitrogen covalent bonding networks and/or are metallic or close to the metal–insulator boundary.

Here we present the synthesis and partial characterization of a new ternary nitride obtained by the topotactic insertion of sodium into the channel structure of Ta_3N_5 at moderate temperatures with consequent reduction of the Ta(V) species.

Brick-red Ta_3N_5 (4, 5) has an orthorhombic structure which is very similar to that of the monoclinic pseudobrookite (Fe_2TiO_5) and the high temperature phase anosovite (Ti_3O_5). The structure is composed of irregular edge- and corner-sharing TaN_6 octahedra, consequently the N atoms are 3 or 4 coordinate. There are some short Ta–Ta distances of 3.00 Å, although these do not represent Ta–Ta bonds. This material is one of the few transition metal nitrides in which the metal is fully oxidized. Like many transition metal binary nitrides it is kinetically stable in air well above room temperature. The structure of Ta_3N_5 is complicated, but may be thought of as containing puckered layers in the *ac* plane which are linked when they approach closely. This framework gives rise to sizable channels running in the *c* direction into which ions may be inserted. The intercalation of Li has been accomplished at 600°C (6) in autoclaves by using Li, Li_3N or LiNH_2 as the Li source. This produces a black, air-stable product with the stoichiometry $\text{Li}_2\text{Ta}_3\text{N}_5$ which has a distorted Ta_3N_5 structure.

EXPERIMENTAL

Some of the starting materials were air sensitive and air sensitivity of the products was anticipated, so all manipulations were, unless stated, carried out in an argon-filled dry box with a combined atmospheric oxygen and water content reduced below 1 ppm. Ta_3N_5 was prepared in the following manner: approximately 5 g of white TaCl_5 (Alfa Chemicals 99.99%) was placed in an alumina boat which was inserted into a quartz tube equipped with stainless-steel end-caps each closed by a valve. The tube was placed in

a horizontal tube furnace and ammonia gas which had been dried as the liquid over sodium metal was passed through the tube at a rate of about $1 \text{ cm}^3 \text{ s}^{-1}$. The TaCl_5 was heated to 450°C over the course of a few hours at which point the tube was cooled quickly and removed to the glove box, where the brown charge was ground thoroughly and the NH_4Cl produced from the reaction was removed from the quartz tube to prevent blockage of the gas exit tube. The sample was then reheated under flowing ammonia for 18 h at 650°C , and the resulting brick-red powder was then removed from the boat. The change in mass of the charge indicated full conversion of TaCl_5 to Ta_3N_5 . Nitrogen analysis of the Ta_3N_5 was carried out using a modified Kjeldahl method in which 100 mg of sample was decomposed in molten KOH , and the ammonia so produced was dissolved in aqueous H_3BO_3 ; titration against acid reproducibly indicated a N-content within 1% of the theoretical value which indicates full conversion had taken place with little or no contamination by stray oxygen. Powder X-ray diffraction was carried out using a Scintag XDS 2000 diffractometer operating in Bragg–Brentano geometry with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). This confirmed the material to be single-phase Ta_3N_5 with peaks about 0.2° wide in 2θ which is about double the width of instrumentally resolved peaks and arises from the small particle size. There was no measurable contamination by TaN .

Reactions to produce Na–Ta–N phases were carried out in the following manner: approximately 0.2 g of Ta_3N_5 was placed in a mechanically cleaned Ni tube together with some freshly cut Na (Aldrich 99%). The Ni tube was sealed by arc welding under a clean Ar atmosphere then sealed inside a quartz tube to prevent aerial oxidation and heated in a resistance furnace. In some reactions there was an Na excess; this was removed anaerobically in an “H-cell” by condensing liquid ammonia onto the sample and pouring the liquid containing the Na away from the powder via a frit. The Na was then dissolved in ethanol and the solution titrated against HCl to determine the composition of the product.

The products were found to be air stable for many days once any excess Na had been removed, therefore, X-ray diffraction data were collected with the samples exposed to air.

RESULTS

Reactions carried out between 450 and 600°C for 6–8 days produced a black powder, and also some unreacted Na if the Na:Ta ratio of the starting materials was greater than 1:2. Titration of the excess Na present in these reactions indicated that the limiting composition of $\text{Na}_x\text{Ta}_3\text{N}_5$ is $x \approx 1.4$. The material produced by these reactions has a diffraction pattern very similar to Ta_3N_5 , but with shifted peaks. This indicates that the insertion is topotactic. When

Na is intercalated, the Ta_3N_5 framework expands but is essentially unchanged. The variation of the lattice parameters of samples with different Na-contents is presented in Fig. 1. The short a axis increases in length, the b axis also increases, but the c axis decreases slightly. This is indicative of a lengthening of the shortest Ta–Ta distance by about 1% in going from Ta_3N_5 to $\text{Na}_{1.4}\text{Ta}_3\text{N}_5$. At $x = 1.4$, the volume expansion of the unit cell, ΔV is 16.0 \AA^3 ($\Delta V/V = 3.9\%$).

Below 450°C the reaction rate is very slow: after 12 days at 350°C there is very little or no change in the lattice parameters and the powder remains red. Not surprisingly, there is no reaction with sodium naphthalide in tetrahydrofuran at room temperature. When temperatures in excess of 600°C are used, a number of partially characterized products are produced, including other Na–Ta–N phases, which are briefly considered here, and Ta–N binaries. When the reaction is carried out at 700°C with a Na:Ta ratio of 2:3, the product is a black rock-salt phase with a lattice parameter of $4.47(4) \text{ \AA}$ in which the cations are completely disordered. The stoichiometry $\text{Na}_2\text{Ta}_3\text{N}_5$ is inferred from the apparent single-phase X-ray powder diffraction pattern, the fact that the mass of this product is equal to the mass of the reactants, and the fact that the product contains no free Na. This material has diffraction peaks about 1.0° wide in 2θ (about ten times the intrinsic resolution of the diffractometer). The fact that two metal ions of differing size and formal charge occupy the same octahedral site is one of the contrasts between nitride and oxide chemistry. The analogous disordered cation phases $\text{Li}_{2-x}\text{Ta}_{2+x}\text{N}_4$ ($0.2 < x < 1$) and $\text{Mg}_{2.6-x}\text{Ta}_{1.3+x}\text{N}_4$ ($0.3 < x < 1$) have been reported (7).

It proved impractical to anneal the rock-salt phase in order to try and narrow the diffraction peaks. Exposure to temperatures of 700°C or below for a few weeks did not alter the diffraction pattern. If temperatures near 900°C were used, a mixture of products was obtained including yellow NaTa_2N_2 (8,9), black Ta_5N_4 , and another black material,

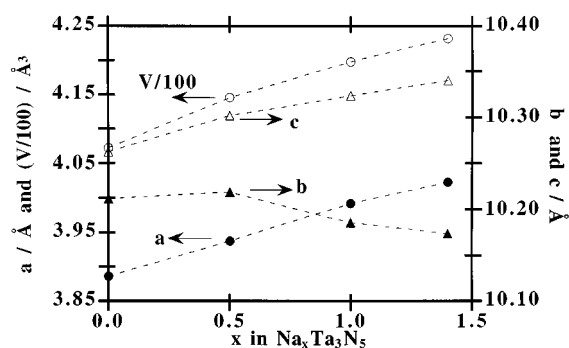


FIG. 1. The variation of the lattice parameters of $\text{Na}_x\text{Ta}_3\text{N}_5$ as a function of x . The lines are guides to the eye.

which by analogy with $\text{Li}_{1-x}\text{Ta}_{3+x}\text{N}_4$ ($0.0 \leq x \leq 0.02$) and $\text{Mg}_{1-x}\text{Ta}_{2+x}\text{N}_3$ ($0.0 \leq x \leq 0.06$) (7) appears to be $\text{Na}_{1-x}\text{Ta}_{3+x}\text{N}_4$ ($x \approx 0$). This latter material crystallizes in the space group $P6_3/mcm$ with the lattice parameters $a = 5.1784(1)$ and $c = 10.3650(3)$ Å. However, it was difficult to synthesize as a single phase and uncertainties in the composition prevented a very detailed Rietveld refinement from being carried out. A limited Rietveld analysis clearly showed that this material is isostructural with the Li and Mg analogues.

If excess N is included in the reaction by using a mixture of Na and NaN_3 as the source of Na, then the Ta is oxidized completely and NaTaN_2 (8, 9) is the product even at temperatures as low as 550°C .

Structural Analysis of $\text{Na}_x\text{Ta}_3\text{N}_5$ ($x = 1.0$)

Using Rietveld Refinement

Rietveld full-profile refinement was carried out on a sample of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ using the general structure analysis system (GSAS) (10). Nine hundred thirty-three points were measured for 60 s each in the range 14.0 to 70.0° in 2θ at intervals of 0.06° . The background was approximately flat in this region. The intrinsic broadness of the peaks coupled with some peak overlap caused severe correlation between the fitted background and peak profile parameters, so a fixed background was employed. Using this strategy, a reasonable refinement was obtained using the refined lattice parameters for $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ and the atomic positions and symmetry of Ta_3N_5 . In the Ta_3N_5 structure (4, 5), there are only two chemically sensible positions for Na (holes with Na–N distances ≥ 2.4 Å). The refinement was significantly better when the Na atoms filled the site at 0, 0.5, 3/4, rather than that at 0, 0.9, 1/4. Thus, the former position was adopted and further refinement yielded fairly large but sensible thermal parameters for the Na and thermal parameters for the Ta atoms which were very similar to those in Ta_3N_5 . The Ta–N bond lengths are very similar to those in Ta_3N_5 (4, 5). The refinement results are listed in Table 1, the structural parameters are listed in Table 2, and selected bond

TABLE 1
The Results of Rietveld Refinement of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$

Formula	$\text{Na}_{1.0}\text{Ta}_3\text{N}_5$
Space group	$Cmcm$ (No. 63)
$a/\text{Å}$	3.995(1)
$b/\text{Å}$	10.197(2)
$c/\text{Å}$	10.331(2)
$V/\text{Å}^3$	420.8(1)
Z	4
R_{wp}	0.0518
R_{p}	0.0402
R_{exp}	0.0122

TABLE 2
The Atomic Parameters of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ Obtained by Rietveld Refinement of the Structure

Atom	Site	x	y	z	$U_{\text{iso}} \times 10^3$
Ta1	4c	0	0.2004(3)	1/4	4(1)
Ta2	8f	0	0.1384(2)	0.5523(3)	3(1)
Na	4c	0	0.501(3)	3/4	24(9)
N1	4c	0	0.754(6)	1/4	25 ^a
N2	8f	0	0.043(4)	0.129(3)	25 ^a
N3	8f	0	0.344(4)	0.076(4)	25 ^a

Note. All sites are fully occupied.

^aNot refined.

lengths are given in Table 3. The fit is shown in Fig. 2. The R factors for the refinement are $R_{\text{wp}} = 5.18$, $R_{\text{p}} = 4.02\%$, and $R_{\text{exp}} = 1.22\%$. R_{exp} is small because the data have a fairly small signal to noise ratio and the number of observables is small. Thus the goodness of fit defined by $(R_{\text{wp}}/R_{\text{exp}})^2$ is numerically poorer than Fig. 2 would suggest. The above considerations result in some parameter correlations, for example, between the thermal parameters of the Ta and the positions of the N atoms. Since N is a relatively poor X-ray scatterer, this is not surprising. In the refinement the fractional occupancy of the Na site was fixed equal to 1.0, as suggested by the synthesis, because this parameter was strongly correlated with the Na thermal parameter. The thermal parameters of the N atoms were also fixed during the refinement because their variation over a large range had a negligible effect on the quality of the fit. Recognizing the intrinsic difficulty in refining the data, it is nevertheless clear that the intercalated Na atoms have been located in the correct site. In the compound $\text{Li}_2\text{Ta}_3\text{N}_5$ (6) which has a similar framework, but which crystallizes in the lower symmetry space group $C2/m$, the two Li atoms are located at positions corresponding to 0, 0.37, 0.47 and 0, 0.42, 0.18 in the space group $Cmcm$. When the Na atom was placed in turn at each of these positions, the refinement routine moved the Na smoothly to the position at 0, 0.5, 3/4 which had previously been established. This is further evidence that the location of the Na is correct. The structure of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ is shown in Fig. 3 which shows the underlying Ta_3N_5 framework and the positions of the intercalated Na.

TABLE 3
Selected Bond Lengths (Å) for $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$

Ta1–2N1	2.06(1)	Ta2–N1	2.34(1)	Na1–N1	2.54(2)
Ta1–2N2	2.03(1)	Ta2–N2	2.02(1)	Na1–4N2	2.41(2)
Ta1–2N3	2.30(1)	Ta2–2N2	2.08(1)	Na1–2N3	2.42(2)
		Ta2–2N3	2.02(1)		

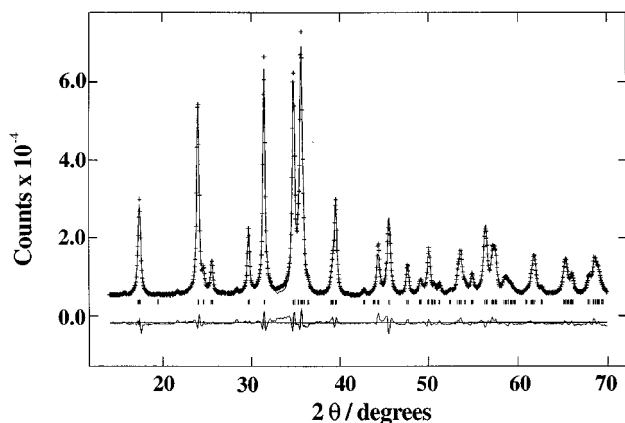


FIG. 2. A plot showing the Rietveld refinement of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$. Observed (crosses), calculated (continuous line), and difference profiles are shown.

A refinement in the monoclinic space group $C2/m$, appropriate to $\text{Li}_2\text{Ta}_3\text{N}_5$ (6) was attempted using the result of $Cmcm$ refinement as the starting model. However, this refinement was much less stable and did not suggest that the symmetry was lower than $Cmcm$.

The Na position is 7-coordinate by N. Six N atoms are about 2.4 Å distant from the Na and the seventh is slightly further away at 2.54(2) Å. These distances are similar to the Na–N distance in NaTa_2N_2 (2.50 Å) (8, 9). The geometry of the site is shown in Fig. 4. It may be thought of as an octahedron which has had the atom at one apex replaced by two and has then been severely distorted. The geometry of the site is dictated by the Ta_3N_5 framework which is hardly disrupted when the intercalation is carried out below 600°C.

Rietveld refinement of the most Na-rich phase $\text{Na}_{1.4}\text{Ta}_3\text{N}_5$ was attempted, but as the peaks were broader than those

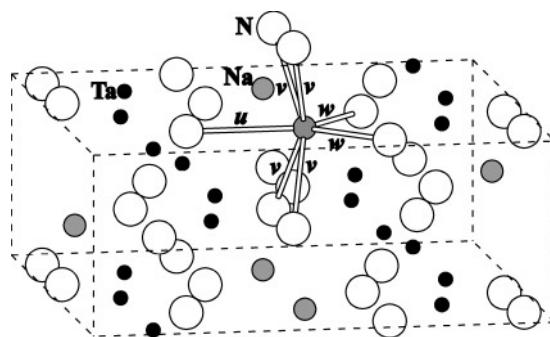


FIG. 4. The Na coordination in $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ as determined by Rietveld refinement. The symmetry inequivalent Na–N bond distances are: $u = 2.54(2)$, $v = 2.41(2)$, and $w = 2.41(2)$ Å.

in $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ and there was possibly some contamination by impurity phases, determination of the site for the extra Na was not possible.

Magnetic susceptibility measurements were carried out using a homemade Faraday balance. The susceptibility of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ was determined in a field of 0.6 T between 4.7 and 320 K. A plot of the susceptibility as a function of temperature is shown in Fig. 5. A reasonable fit to the susceptibility may be obtained using $\chi_{\text{mol}} = \chi_0 + C/T$; with $\chi_0 = 6.5(1) \times 10^{-4}$ emu mol⁻¹ per formula unit and $C = 3.4(1) \times 10^{-3}$ emu mol⁻¹ K. The hump at about 65 K was not present when the sample was measured in that temperature region using a Quantum Design MPMS-2 SQUID magnetometer and is probably due to the condensation of some O_2 on the sample in the Faraday balance. Condensed O_2 only makes a contribution between about 40 and 65 K, and this region of data has been left out of the fit. The value of χ_0 is unchanged if only the data above 65 K are used in the fit. The very small value of the Curie constant

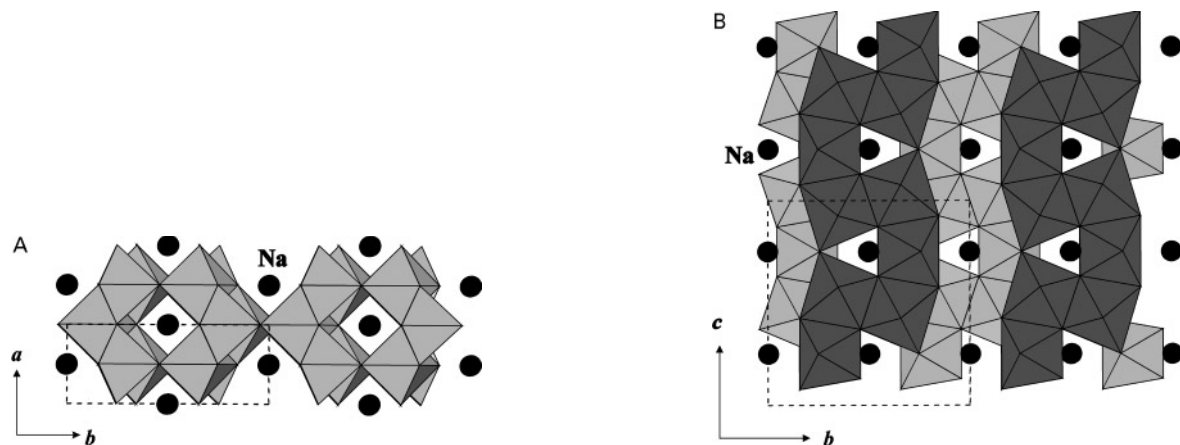


FIG. 3. The structure of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ showing the position of the intercalated Na as determined by Rietveld refinement. TaN_6 octahedra are shown: (a) projection along c axis and (b) projection along a axis.

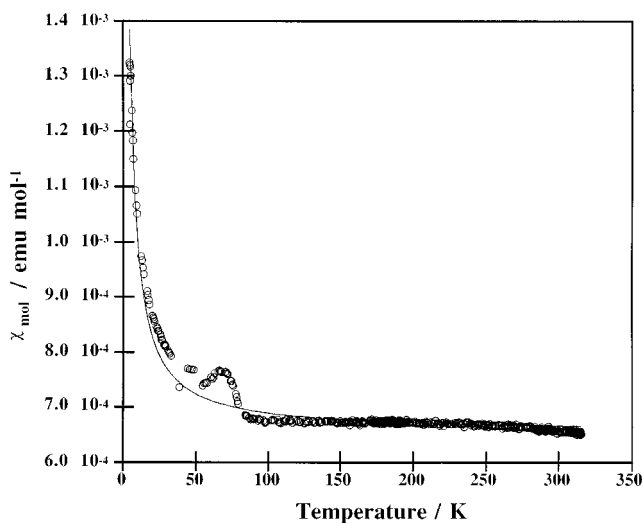


FIG. 5. A graph of the magnetic susceptibility of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ as a function of temperature. The line is a fit of the susceptibility to $\chi_{\text{mol}} = \chi_0 + C/T$. The hump at about 65 K is ascribed to O_2 condensing on the sample.

suggests that the Curie tail is due to a small amount of a paramagnetic impurity since it corresponds to about 1% of the Ta atoms having a spin of 1/2, or, more likely, 0.12% Fe impurities with $S = 2$. The positive χ_0 suggests that the material is a Pauli paramagnet. The slight temperature dependence of the susceptibility above 250 K may be due to the presence of some structure in the density of states near the Fermi level.

Because the material decomposes above 600°C , and because no crystals were available, electrical conductivity was measured at room temperature on an unsintered pressed pellet of $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ powder 3.0 mm in length and 4.8 mm in diameter. The measured resistivity is $2.7(1) \Omega\text{cm}$, a value considerably above that of good metals (10^{-6} to $10^{-4} \Omega\text{cm}$). However, the $\text{Na}_{1.0}\text{Ta}_3\text{N}_5$ used was a very fine powder, so we suspect that the measured resistivity of the pellet is dominated by interparticle contacts. Thus the measured

value is an upper limit on the intrinsic value of the bulk resistivity. We cannot be certain from resistivity measurements of this nature that the material is metallic, but the small resistivity coupled with the small, positive, temperature independent χ_0 is suggestive of metallic behavior.

SUMMARY

We have synthesized a new conducting ternary transition metal nitride, $\text{Na}_x\text{Ta}_3\text{N}_5$, by reducing the transition metal with intercalated Na in the absence of nitrogen gas. This may be an appropriate route for the synthesis of some other ternary or quaternary transition metal nitrides.

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