Two-Step Solid-State Synthesis of Ternary Nitride Materials

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ABSTRACT: Ternary nitride materials hold promise for many optical, electronic, and refractory applications; yet, their preparation via solid-state synthesis remains challenging. Often, high pressures or reactive gases are used to manipulate the effective chemical potential of nitrogen, yet these strategies require specialized equipment. Here, we report on a simple two-step synthesis using ion-exchange reactions that yield rocksalt-derived MgZrN2 and Mg2NbN3, as well as layered MgMoN2. All three compounds show almost temperature-independent and weak paramagnetic responses to an applied magnetic field at cryogenic temperatures, indicating phase-pure products. The key to synthesizing these ternary materials is an initial low-temperature step (300–450 °C) to promote Mg-M-N nucleation. The intermediates then are annealed (800–900 °C) to grow crystalline domains of the ternary product. Calorimetry experiments reveal that initial reaction temperatures are determined by phase transitions of reaction precursors, whereas heating directly to high temperatures results in decomposition. These two-step reactions provide a rational guide to material discovery of other bulk ternary nitrides.

Ternary metal nitrides remain under-explored as new functional inorganic materials,1,2 even though a large number of new nitride compositions and structure types have been recently predicted.3–6 The deficit in realized nitride products, compared to predicted materials, stems from their difficult synthesis, with few successful reactions that yield nitride products selectively.7 Furthermore, control over composition is limited when attempting to synthesize nitrogen-rich nitride semiconductors8 and mechanically ultrahard pernitrides,9 which have a tendency to be metastable, when compared to their metallic subnitride analogues.10 To access more nitrogen-rich phases, reactions must proceed at low temperatures, where dinitrogen (N2) formation is less thermodynamically favorable, or higher temperature reactions must change the effective chemical potential within the reaction system through use of high pressures or reactive gases, such as ammonia. Furthermore, a large number of potential binary metal nitride precursors are either refractory11,12 or energetic,13–17 which further reduces the number of useful reactions. Therefore, identifying sources of reactive nitrogen that yield desired products under mild conditions is imperative for advancement in nitride material discovery.

Various reactive nitrogen sources are used for ternary metal nitride synthesis. In bulk form, ternary nitrides have been synthesized by high-pressure metathesis,18,19 ammonothermally,20 within alkali-metal fluxes,22 self-combustion,21 and rarely from the elements under flowing N2.24 For thin film materials discovery and applications, an excited nitrogen plasma can be employed to deposit ternary metal nitrides ranging from rocksalt magnesium metal nitrides, such as MgZrN2 and Mg2NbN3,25,26 to wurtzite zinc metal nitrides, such as Zn2SbN3 and Zn3MoN4.27,28 For the ambient-pressure synthesis of bulk magnesium metal nitrides, precursors that react at low temperatures must be selected, since the loss of volatile elements, such as nitrogen, magnesium, or zinc, from the ternary product occurs at high temperatures. As a counterexample, reactions using Mg3N2 and refractory transition metals, such as zirconium or molybdenum, will not proceed before Mg3N2 decomposes, while metathetical preparations between Mg3N2 and transition-metal halides29 result in binary metal nitrides or reduced metals. To overcome these challenges, high-pressure autoclaves are used in...
control through careful precursor selection for other ternary nitride compositions.

Here, we describe the synthesis of three magnesium metal nitrides, where a transition-metal halide (ZrCl₄, NbCl₅, MoCl₅) reacts with magnesium chloride-nitride to yield each magnesium metal nitride product (MgZrN₂, Mg₂NbN₃, MgMoN₂) and equivalent amounts of MgCl₂ byproduct:

\[ n\text{Mg}_2\text{NCl} + \text{MCl}_2 \rightarrow \text{Mg}_{n-1}\text{MN}_n + (n + 1)\text{MgCl}_2 \]  

These ternary metal nitrides are synthesized close to ambient pressure via two-step reactions, where precursors are first heated at relatively low temperature (300–450 °C) to promote Mg–M–N nucleation, and then the temperature is increased (800–900 °C) to grow crystalline domains of the ternary metal nitride products. Differential scanning calorimetry (DSC) experiments reveal exothermic events that occur near the first low-temperature step for each composition, indicating intermediate reactions that likely yield magnesium metal nitride products. As a result of these two-step reactions, MgZrN₂ and Mg₂NbN₃ are observed in a rocksalt-derived structure while MgMoN₂ adopts a layered hexagonal structure. The ternary nitride products have close to stoichiometric cation compositions which are consistent with their weak paramagnetic behavior, as opposed to a strong diamagnetic response characteristic of the binary nitride impurities. These results demonstrate a low-temperature two-step solid-state synthesis approach to ternary nitride materials.

For each ternary nitride synthesis performed at NREL, homogeneously mixed precursor powders were pelletized under argon and flame-sealed in evacuated quartz ampules. For reactions yielding MgZrN₂ and Mg₂NbN₃, ampules were heated in a muffle furnace to 450 °C for 24 h, followed by a subsequent anneal at 800 °C for 24 h. Similarly, reactions yielding MgMoN₂ were heated at 300 °C for 24 h, then at 900 °C for 24 h. Cation compositions were measured using energy-dispersive X-ray spectroscopy (EDX). Powder X-ray diffraction (PXRD) was used to characterize each product’s crystal structure and bulk magnetic susceptibility measurements using vibrating sample magnetometry (VSM) confirmed the product composition and purity. Temperature-dependent reaction profiles were determined from DSC experiments. More detailed accounts of synthesis methods and characterization techniques are provided in the Supporting Information.

Table 1. Refined Structural Parameters for the Magnesium Metal Nitride Products, compared to Reference Values and to Literature Data, and Phase Fraction of Binary Metal Nitride Impurity, as Measured from PXRD and VSM Measurements

| compound   | Structure (PXRD)      | Composition, \( x = \text{Mg}/(\text{Mg} + \text{M}) \) | Binary Nitride Phase Fraction |
|------------|-----------------------|---------------------------------------------------------|-------------------------------|
| MgZrN₂     | (Fm̅3m)               | EDX          | PXRD (mol % M₁N₂) | VSM (vol % SC M₁N₂) |
| present    | 4.54(2) – 93.67(1)    | 0.50         | 0.40 (0.48(8))  | –                  |
| ref 25     | 4.54 –                 | 0.49         | –                | –                  |
| Mg₂NbN₃    | (Fm̅3m)               | 0.67          | 0.67             | 0                  |
| present    | 4.38(3) – 84.39(2)    | 0.64         | 0.60(6)          | –                  |
| ref 25     | 4.37 –                 | 0.68         | –                | –                  |
| MgMoN₂     | (P6₃/mc)              | 0.50          | 0.50             | 0                  |
| present    | 2.92(4) – 10.4716(6)  | 0.46         | 0.53(4)          | 0.53(7)           |
| ref 24     | 2.91059(3) –          | 0.52         | 0.48             | –                  |

**Notes:** Measured chemical composition: \( x = \text{Mg}/(\text{Mg} + \text{M}) \) in \( \text{Mg}_x\text{M}_{1-x}\text{N}_2 \). EDX errors range from 5% to 10%.

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Using these two-step metathesis reactions, three magnesium metal nitrides were selectively prepared and confirmed through diffraction. Figure 1a depicts PXRD patterns of the reaction products—MgZrN₂, Mg₂NbN₃, and MgMoN₂—after washing with anhydrous methanol to remove MgCl₂ products. Quantitative crystallographic analysis using the Rietveld method reveals that the MgZrN₂ and Mg₂NbN₃ crystallize in the rocksalt (Fm3m) structure, as previously reported in thin-film products, whereas MgMoN₂ forms in the layered hexagonal crystal structure (P6₃/mmc), as previously reported in bulk form, and as illustrated in Figure 1c. The simulated XRD patterns are shown in Figure 1b for comparison, while structural parameters for each product are listed in Table 1 and compared to literature values.

For the two rocksalt structures, MgZrN₂ and Mg₂NbN₃, the observed PXRD patterns support magnesium inclusion into the rocksalt structure by a change in the (111) peak intensity, which is indicative of less electron density of the cation. Rietveld analysis permits refinement of the site occupancies of the 4a Wyckoff position in the rocksalt structure, which accounts for the change in relative peak intensity in Figure 1a, with the x = Mg/(Mg + M) values reported in Table 1. For Mg₂Zr₁₋ₓNₓ and Mg₂Nb₁₋ₓNₓ, the cation concentrations fall within the limits that have been previously reported for these cation-disordered solid solutions. However, MgZr₁₋ₓNₓ (x = 0.48) and Mg₂Nb₁₋ₓNₓ (x = 0.60) reported here reveal a deficiency of magnesium, compared to ideal values (x = 0.50 and x = 0.67, respectively). Furthermore, the peak width for these rocksalt phases broadens with increasing cation site disorder, which has been previously observed for the solid-solution MgZr₁₋ₓNₓ.

Fitting the layered hexagonal structure of MgMoN₂ using Rietveld refinement reveals an absence in intensity in the (00\text{\text{1}}) family of reflections, relative to peaks associated with atoms in the (h0\text{\text{1}}) family, as similarly observed for structurally analogous MnMoN₂. This observation can be explained by either disorder in the (00\text{\text{1}}) direction of the MgMoN₂ layers or preferred orientation of crystallites in the (10\text{\text{1}}) direction. During the Rietveld analysis, applying preferred orientation in the (10\text{\text{1}}) direction accounts for the increase in intensity of these reflections, relative to the (10\text{\text{1}}) family of peaks. Furthermore, there is a contraction of the c-axis (Table 1), which could indicate the presence of smaller Mo⁹⁹⁹ cations in the nominally Mo⁴⁺ site, likely due excess magnesium incorporation. Free refinement of each cation site in the P6₃/mmc lattice (Table 1) supports greater magnesium content than molybdenum in Mg₃Mo₁₋ₓNₓ (refined x = 0.53, compared to x = 0.50 reference value), along with some cation deficiency on the molybdenum site with (Mg + Mo)/ (Mg + Mo + N) = 0.85, compared to the 1.00 reference value.

The relative cation composition in these Mg₂Zr₁₋ₓNₓ, Mg₂Nb₁₋ₓNₓ, and Mg₂Mo₁₋ₓNₓ materials, where x = Mg/(Mg + M), was confirmed by EDX analysis. For these metals, the EDX peak intensities are high enough to provide reasonable error. The nitrogen and oxygen differentiation is not as facile, because of low signal-to-noise ratio in the low-energy part of the spectrum, as well as high background oxygen counts from the substrate. As presented in Table 1, the EDX results show magnesium and transition-metal compositions that fall within the limits determined from XRD refinement and previously reported in other publications, although, for the rocksalt products, this ratio is substoichiometric, with regard to magnesium. Therefore, it is likely that some magnesium is lost during the reaction, because of the thermal decomposition of MgCl₂ at higher temperatures, despite intentional excess of this precursor in the reactions. In all reactions, a metal deposit is present on the quartz ampule, supporting the reduction of magnesium and the formation of N₂.

To further evaluate the phase purity of our Mg-M-N products, magnetic susceptibility measurements were performed at CSU. The results in Figure 2 exhibit weak paramagnetic behavior ($\chi > 0$), which supports the compositions presented in Table 1. For each of these ternary Mg-M-N products, a binary metal nitride or oxynitride impurity (ZrN, NbN, Mo₂N) should produce a diamagnetic response from a superconducting transition, which is virtually absent in Figure 2 for the samples reported in Table 1. To illustrate the effect of even small fractions of binary nitride impurities, reaction products were treated with 1 M nitric acid, leading to binary transition-metal nitride impurities with clear superconducting transitions. DC magnetization data were collected using a measurement field of $H = 20$ Oe.

![Figure 2. Temperature-dependent magnetic susceptibility of magnesium metal nitride ternary products: (a) MgZrN₂, (b) Mg₂NbN₃, and (c) MgMoN₂. The phase-pure products washed with dry methanol are shown in contrast to samples with magnesium leached out by 1 M nitric acid, leading to binary transition-metal nitride impurities with clear superconducting transitions. DC magnetization data were collected using a measurement field of $H = 20$ Oe.](https://doi.org/10.1021/acsmaterialslett.1c00656)

The described synthesis conditions in eq 1 require two-step temperature profiles where an initial temperature ($T_{\text{init}}$) nucleates metal nitride products, followed by a higher crystallite growth temperature ($T_g$). Figure S2 in the Supporting Information depicts PXRD patterns of the unwashed products observed when using these two-step heating profiles, compared to directly heating to $T_g$. When
heated directly to 800 °C, the rocksalt MgZrN2 product observes a clear shift in lattice parameter (see Figure S2a in the Supporting Information) toward ZrN paired with an increase in the relative intensity of the (1 1 1) peak, supporting a loss of Mg. For Mg2NbN3 products, heating directly to 800 °C results in broad peaks in the PXRD pattern (Figure S2b in the Supporting Information) with a shift toward a smaller lattice parameters than the reaction product via two-step heating schedule. The calculated ground-state lattice parameter of 4.42 Å is larger than that of binary NbN, yet thin-film Mg2NbN3 reports a lattice parameter of 4.37 Å. For reactions yielding MgMoN2 directly heating above 800 °C yields more Mo2N than MgMoN2, whereas the described two-step heating profile increases the yield of MgMoN2 as seen in Figure S2c in the Supporting Information. 

To gain insight into the low-temperature reaction pathway, we performed DSC experiments presented in Figure 3. These DSC results reveal new low-temperature exothermic reactions paired with known endothermic phase transitions of the respective transition-metal halide precursors. Mg(NCl) does not have a phase transition below 600 °C, suggesting that observed exotherms are attributed to the formation of MgCl2, Mg-M-N products, or unknown intermediate species. For the reactions yielding MgZrN2 (Figure 3a), there is an exotherm observed after the sublimation temperature of ZrCl4 at 331 °C (ZrI: 366 °C). At 411 °C, a large endothermic inflection is observed, which we attribute to the pressure-induced melting of ZrCl4 from the gaseous state near 437 °C. For reactions yielding Mg2NbN3 (Figure 3b), a similar exothermic peak is observed after the melting point of NbCl5 at 205 °C (NbI: 208 °C; Nb2: 216 °C), with two additional exotherms—Nb3: 450 °C and Nb4: 513 °C—also observed. For the MgMoN2 reaction in Figure 3c), no phase transition endotherm is observed for MoCl5 at the expected melting point of 194 °C, yet a triplet of exothermic peaks is observed near this transition temperature (Mo1: 174 °C, Mo2: 200 °C, and Mo3: 233 °C). Furthermore, there are two additional broad exotherms at higher temperatures (Mo4: 465 °C and Mo5: 550 °C).

Using the measured temperatures of relevant exothermic peaks in Figure 3, control reactions were performed, targeting three Tnuc values (300, 450, and 600 °C) and two Tgr values (800 and 900 °C) to evaluate the effect of temperature on the reaction products. Figure S4a in the Supporting Information depict the changes in hexagonal lattice parameters, as a function of heating schedule for MgMoN2 products. Here, the proposed Tnuc of 300 °C yields lattice parameters most similar to MgMoN2. As Tnuc increases, the a-axis lattice parameter remains constant, whereas the c-axis lattice parameter decreases. In addition, Figure S4a further supports increased MgMoN2 yields at a lower Tnuc values, whereas higher initial temperatures result in greater Mo2N yields. Contrary to the lower Tgr value of the rocksalt-yielding reactions, MgMoN2 product yields increase at 900 °C, albeit only with a two-step temperature profile.

For rocksalt Mg2ZrN and Mg2NbN products from these control reactions, Rietveld analysis was used to quantify changes in lattice parameter (Figure S4a), as well as the changes in peak intensity relative to the (1 1 1) by allowing the magnesium:transition-metal ratio to openly refine (see Figure S3). For Mg2ZrN, the proposed heating schedule results in the smallest lattice parameter and largest Mg concentration in Figure S5a in the Supporting Information. In addition, the lower Tgr results in peak broadening, as calculated in Figure S5b in the Supporting Information, which also supports increased cation disorder in these rocksalt structures. For Mg2NbN, the change in lattice parameter in Figure S5a is less indicative of increased Mg content; yet, changes in peak shape in Figure S5b support a similar trend of increased magnesium content with broadened peak shape, which requires a lower Tgr value.

The collective results presented in this letter reveal a synthesis approach to ternary magnesium metal nitrides at low temperatures and ambient pressures (Figure 1). A key to this two-step process is the dependence on a low-temperature reaction Tnuc. We suggest that Tnuc yields Mg-M-N nucleation, as evidenced by the numerous exothermic events from DSC (Figure 3), and the absence of ternary products from direct heating (Figure S2 in the Supporting Information). This low-temperature reaction step at Tnuc ensures that solid-state diffusion can proceed below the temperature where product decomposition is observed, because of the overall small changes in formation energies and the increasing entropic driving force for N2 formation.5,10 This low-temperature reaction pathway is facilitated by the low melting points of the transition-metal halide precursors, according to the DSC measurements in Figure 3. These transition-metal halides form monomeric or dimeric species as they melt,37-39 which reduces diffusion lengths at the reaction interface, thus ensuring that necessary ion exchange yields Mg-M-N intermediate phases or poorly crystalline products. Heating to higher Tgr temperatures too quickly results in deleterious sublimation and decomposition of these halide precursors. Thus, a higher Tgr temperature may be required to increase the crystallinity of the products, yet the Tnuc reaction temperature is the most likely “rate-limiting” step in this two-step reaction pathway.

The presented reaction conditions are benign and can be performed in a traditional solid-state chemistry laboratory, thus increasing their utility in targeting other metal nitride
compositions by multiple research groups. Previous studies on
the synthesis of magnesium metal nitrides have employed
custom high-pressure reactors,28 or specialized deposition
chambers.3,32 By starting with the mixed anion Mg,NCl as a
precursor, the reaction pathway does not proceed via a rapid
propagation, as observed when starting with more energetic
precursors, such as alkali azides or alkali-earth nitrides.29,30
Furthermore, diffusion-limited products and binary metal
nitrides observed in some metathesis reactions31,32 are avoided.
The presented reactions avoid toxic environments, such as
ammonia or amide-based mineralizers,31,32 that decompose
under elevated temperatures and require careful safety
considerations and custom equipment. Similar to the
abundance of metal halide precursors, numerous metal
chloride-nitride phases exist and are easily synthesized.44

For example, Zn2NX (X = Cl, Br, I) precursors may provide a
low-temperature route to zinc metal nitrides, such as Zn,N,NbN3
and ZnZrN2, which exhibit a loss of zinc at elevated
temperatures.47−50

The degree of precursor interchangeability in eq 1 provides a
design space for discovering new ternary metal nitrides and
controlling their properties. Optoelectronic property
measurements on bulk32 and thin-film25,33 Mg,N,NbN3, samples exhibit
tunable metal to semiconductor electronic properties as the
magnesium content increases with band gaps and effective
masses that exhibit remarkable tolerance to structural
disorder.25 Similar behavior has also been observed in
Mg,N,Nb,Ni,N, thin films,28 while MgMoN3s is calculated to be metallic.51
Bulk MgZrN2, Mg,NbN3, and MgMoN2 materials reported here are expected to exhibit similar
optoelectronic properties based on the stoichiometric
composition range observed (Table 1) and the absence of
binary metal nitride impurities (Figure 2). As a next step, synthesizing new zinc metal nitride compositions, as well as
potential Mg/Zn alloyed quaternary phases could lead to
precise tuning of these optoelectronic properties.

In summary, we report on the bulk solid-state synthesis of
classical magnesium metal nitrides—MgMoN3 with layered
hexagonal structure, and MgZrN2, Mg,NbN3 with rocksalt-derived structure—using two-step low-temperature ion-exchange
reactions. An initial low-temperature reaction of the
precursors nucleates the magnesium metal nitride product, and
that is followed by a high-temperature step to grow the
product crystalline domains. The products are measured by
PXRD, with cation stoichiometry confirmed by EDX, and
phase purity supported by magnetic susceptibility
measurements. Characterizing this reaction pathway using DSC reveals
multistep crystallization that occurs at low temperatures, which
we attribute to the formation of an intermediate ternary
product with short-range ternary metal nitride bonds but
without long-range crystallographic order. In contrast, by
heating the precursors too rapidly, before they can successfully
nucleate the magnesium metal nitride products, results in a net
loss of Mg and N at high temperature. The results presented
here indicate that this low-temperature ambient-pressure
approach can be used to synthesize other ternary nitride
materials.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at
https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00656.

■ EXPERIMENTAL METHODS AND ADDITIONAL RESULTS FROM
CONTROL REACTIONS (PDF)

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