Self-Combustion Synthesis of Novel Metastable Ternary Molybdenum Nitrides

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Supporting Information

ABSTRACT: Ternary metal nitrides are a promising class of functional materials, but their variety has been limited by the challenging nature of nitride synthesis. Here, we demonstrate a facile self-combustion synthesis route to novel ternary molybdenum nitrides. The room temperature mixing of NaNH2, MoCl4, and 3d transition metal chlorides, such as MnCl2, FeCl2, and CoCl2, initiates a highly exothermic metathesis reaction, which is thermodynamically driven by the formation of stable NaCl, N2, and NH3 byproducts. The rapid combustion reaction yields ternary rocksalt $\gamma$-TM$\times$Mo$_{1-x}$N$_{0.5}$ nanoparticles (TM = Mn, Fe, Co) in just a few seconds. We calculate from DFT that these disordered ternary molybdenum nitrides are thermodynamically stable under the high-temperatures at which they form but are remnant metastable when quenched to ambient conditions. Introduction of Mn, Fe, and Co into $\gamma$-Mo$_2$N is found to change its magnetic properties and to enhance its oxygen reduction catalytic activities. Our work demonstrates self-combustion synthesis as a simple but powerful route for the realization of novel ternary intermetallic nitrides with emergent functionality.

Ternary metal nitrides are an exciting class of functional materials, and have found applications as super hard materials, magnetic media, catalysts, semiconductor, and more. Mixed-transition metal (TM) nitrides have been reported, such as Fe$_2$WN$_2$, MnMoN$_2$, and others, but they are relatively rare compared to ternary alkali-TM-nitrides. Nevertheless, these early-TM nitrides, such as molybdenum nitrides, exhibit high chemical stability, which can be attributed to strong metal–nitrogen and metal–metal bonding. Of the known mixed-TM nitrides, many have been synthesized by ammonolysis of oxide precursors; however, this process often requires long-term heat treatment at a narrow temperature range and a large amount of toxic ammonia gas. Various other approaches have been developed for the synthesis of ternary nitrides, for example, thermal decomposition of a metal–hexamethylenetetramine complex, mechanochemical alloying, or solid-state reactions using NaN$_3$. Despite these great efforts to synthesize new nitride materials, materials exploration in this space remains a challenging issue. To facilitate the discovery of new nitride materials, novel synthetic approaches are desired.

Self-combustion synthesis involves combining an alkali or alkaline earth metal compound and a metal halide, which

Received: March 4, 2019
Accepted: May 10, 2019
Published: May 10, 2019
drives a highly exothermic reaction that results in nanomaterials, such as nanocrystals and porous materials. These double ion-exchange metathesis reactions are thermodynamically driven by the formation of stable byproducts, which can facilitate the synthesis of compounds with otherwise small formation energies. To illustrate this point, Table 1 compares the reaction thermodynamics between the ammonolysis of metal oxides to Mo$_3$N$_3$ versus the self-combustion synthesis of Mo$_3$N from NaH and MoCl$_4$ precursors. The oxide ammonolysis reaction is enthalpically unfavorable but can be entropically driven at high temperatures by the production of 1.75 mol of gas per Mo. On the other hand, the self-combustion metathesis reaction is highly exothermic and proceeds spontaneously even at room temperature. The resulting alkali halide salt byproducts can be removed by simply washing the reaction products with water or another polar solvent.

These self-combustion synthesis routes have been reported for several nitride compounds; for example, the reaction between ZrCl$_4$ and Li$_2$N produces ZrN with the formation of stable LiCl as a byproduct, and we recently reported the self-combustion synthesis of barium niobium perovskite oxide nitride from Ba(OH)$_2$, NbCl$_5$, and NaNH$_2$. For the most part, metathesis reactions in the nitrides space have primarily focused on binary nitrides or alkali ternary nitrides, such as Li$_2$SiN$_2$. Ternary mixed-transition metal ternary nitrides have not been explored as readily, despite their importance as superhard materials, superconductors, and catalysts. In this work, we report on the self-combustion synthesis of new ternary mixed-metal molybdenum nitrides in the rocksalt structure. We focus on molybdenum nitrides because molybdenum is the most effective transition metal for forming ternary metal nitrides and because of the excellent performance of molybdenum nitrides in catalytic applications. The reaction between molybdenum chloride, 3d transition metal chlorides, and sodium amide proceeded instantly, producing novel ternary molybdenum nitrides in just a few seconds. The temperature profiles of these combustion reactions exhibit rapid heating and quenching, which we demonstrate is able to produce metastable ternary TM$_x$Mo$_{1-x}$N$_y$ compounds isostuctural to the high-temperature γ-Mo$_3$N$_2$ polymorph. Nitrides are the most metastable class of inorganic materials, and our work here provides a simple but powerful route to this compelling class of functional materials.

Self-combustion synthesis of ternary molybdenum nitrides is initiated from a reaction between MoCl$_4$, NaNH$_2$, and 3d transition metal chlorides. Preliminary experiments in optimizing Mo–Cl precursors found that the reaction of MoCl$_4$ (Wako, 99.5%) with NaNH$_2$ at room temperature formed γ-Mo$_3$N$_2$ and δ-MoN (Figure S1). On the other hand, a reaction with MoCl$_3$ precursors (Aldrich, 99.95%) did not initiate at room temperature. However, MoCl$_4$ was found to be an effective starting precursor for the combustion synthesis of single-phase ternary molybdenum nitrides. Note that MoCl$_4$, MoCl$_3$, and NaNH$_2$ powders are moisture-sensitive and should be handled in a glove box with inert atmosphere.

To synthesize MoCl$_4$, MoCl$_3$, and MoCl$_2$ were mixed in Ar-filled glove box. The mixture was then heated at 543 K for 12 h in a vacuum sealed glass tube and was subsequently heated at 433 K for 30 min under vacuum, resulting in MoCl$_4$. The Teflon-lined autoclave with an inner volume of 70 mL (Yanako, AD-70) was heated at 493 K overnight to remove any water before the synthesis reaction of molybdenum nitrides. Binary molybdenum nitrides were synthesized by reaction of 1 mmol of MoCl$_4$ and 10 mmol of NaNH$_2$ (Aldrich, 98%) in argon-filled glove box. For the synthesis of ternary manganese molybdenum nitride, 0.3–1.5 mmol of MnCl$_2$ (Sterm, 97%) and MoCl$_4$ was mixed in an argon-filled glove box, and placed into autoclave with 10 mmol of NaNH$_2$. Thereafter, the same procedure as described above was performed. The synthesis of molybdenum nitride with other metals was attempted in the same way employing 0.3 mmol of CoCl$_2$ (Kanto, 95%) or FeCl$_2$ (Sterm, 98%).

For the combustion synthesis reaction, black transition metal chloride powders and a magnetic stirrer were put in the autoclave, and then white NaNH$_2$ powder was added. The total mass of these powders was less than 700 mg. The mixing of MoCl$_4$, MnCl$_2$, and NaNH$_2$ initiated the combustion reaction, resulting in the formation of black powder. Caution! An intense exothermic reaction occurs suddenly by mixing these powders. Synthesis using a large amount of the starting materials may cause a serious accident. In the Supporting Information, we include a movie demonstrating this self-combustion reaction; although for reader’s reference, the movie shows the combustion reaction in an open reaction vessel, whereas in practice, the reactions were performed in a closed autoclave. Under ambient atmosphere, the resulting products were washed with ethanol and distilled water to remove the NaCl byproducts and unreacted starting materials and, then, filtered. Then, the samples were further washed with approximately 10 mL of acetic acid (~20 vol %; diluted aqueous solution from commercial acetic acid (Kanto, 99.7 %)) and, then, washed again with ethanol and water.

Upon washing with distilled water, excess NaNH$_2$ converts into NaOH and is dissolved and washed away from the product, along with NaCl. The subsequent acetic acid treatment should dissolve residual binary manganese nitrides, which are not stable in acid. The reaction yields of the target ternary nitride materials were 20–30% mass based on molybdenum. Although this yield is lower than the corresponding ammonolysis reactions, the self-combustion synthesis reaction has the advantage of proceeding quickly, being relatively simple to prepare, and as we will demonstrate later, also being able to form metastable ternary nitrides.

After we washed the reaction products with distilled water and treated them with acetic acid, we characterized the black powder. Figure 1 shows the X-ray diffraction patterns of the products synthesized with various molar ratio of MoCl$_4$/MnCl$_2$, where the molar ratio of MnCl$_2$/MoCl$_4$ in the starting materials is defined as x. In all products, the main peaks could

<table>
<thead>
<tr>
<th>reaction type</th>
<th>balanced reaction</th>
<th>$\Delta H_f$ (kJ/MoN$_{0.5}$)</th>
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</thead>
<tbody>
<tr>
<td>ammonolysis of metal oxides</td>
<td>MoO$_3$ + 2NH$<em>3$(g)$^+$ $\rightarrow$ MoN$</em>{0.5}$ + 3H$_2$O(g) + 3/4N$_2$(g)</td>
<td>50</td>
</tr>
<tr>
<td>combustion</td>
<td>MoCl$_4$ + 4NaNH$<em>2$ $\rightarrow$ MoN$</em>{0.5}$ + 4NaCl + 8/3NH$_3$(g) + 5/12N$_2$(g)</td>
<td>-285</td>
</tr>
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</table>
be indexed as cubic $\gamma$-Mo$_2$N. No diffraction peaks corresponding to $\beta$-Mo$_2$N, MnMoN$_x$, and Mn$_2$N were observed. At $x=0$, cubic $\gamma$-Mo$_2$N and impurities, MoN, and Mo metal, were detected. The lattice parameters of cubic $\gamma$-Mo$_2$N increased linearly from the precursor ratios of $x=0$ to $0.6$ but did not change within the error bar between $x=0.6$ and $1.5$. The Mn-composition of the products, as shown as the Mn/(Mn + Mo) ratio in Figure 1, were semi-quantitatively determined by EDX; the ratios determined by SEM-EDX agreed with those by STEM-EDX. The composition varied linearly with the lattice parameters. This linear relationship between lattice parameter and composition was further confirmed by comparing the DFT-relaxed average volume of disordered $\gamma$-Mo$_{0.875}$Mn$_{0.125}$N$_{0.5}$ against the linear interpolation between the isostructural Mo$_2$N and Mn$_2$N binaries (details in Supporting Information). This linear change in lattice parameters with composition suggests random Mn substitution for the Mo site in $\gamma$-Mo$_2$N at $x=0.3$ and $0.6$. Hereafter, these products with $x=0$, $0.3$, and $0.6$ are expressed as $\text{Mn}_{y}\text{Mo}_{1-y}\text{N}_{0.5}$ ($y=0$, $0.06$, and $0.12$), respectively, according to the EDX analysis. We note that the Mn/(Mn + Mo) ratios in the product phase were lower than MnCl$_2$/MoCl$_4$ ratio in starting precursor mixtures, suggesting that there may have been unreacted manganese byproducts in the reaction, which were removed after washing with distilled water and acid treatment.

On the basis of the broad diffraction peaks, the crystalline size estimated from the Scherrer equation using the strongest peaks were 5–6 nm, although broad diffraction peaks could also arise from structural disorder in the synthesized nitrides. For $x \geq 0.9$, we observe several additional broad diffraction peaks, which cannot be assigned to the cubic phase. These diffraction peaks for $x \geq 0.9$ might possibly be attributed to the partial ordering of Mn and Mo, since the angles of unindexed peaks are close to peaks corresponding to layered MnMoN$_x$, where Mn and Mo layers stack alternatively.

The scanning transmission electron microscopy (STEM) images of Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$ products ($x=0$, $0.06$, and $0.12$) are shown in Figure 2a–f, taken on a Hitachi HD-2000. The size of primary particles, which formed aggregates, increased with an increase in the molar ratio of MnCl$_2$/MoCl$_4$. These approximate particle sizes were estimated to be 20 nm for MoN$_{0.5}$, 30–40 nm for Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$, and 50 nm for Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$, respectively. Figure 2b shows the energy dispersive X-ray spectrometry (EDX) spectrum of products. The EDX peaks of Mo ($L_\alpha=2.293$ keV) and Mn ($K_\alpha=5.894$ keV) were detected for Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$ sample. On the other hand, no manganese was detected for MoN$_{0.5}$. STEM-EDX mapping images of manganese molybdenum nitrides are shown in Figure 2c–e for Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$ sample. Mn and Mo layers stack alternatively.

![Figure 1](image1.png)

**Figure 1.** (a) XRD patterns of synthesized manganese molybdenum nitrides with various molar ratio of MnCl$_2$/MoCl$_4$, in the starting materials represented as $x$: The MnCl$_2$/MoCl$_4$/NaNH$_2$ ratio was 0–1.5:1:10. (b) The lattice parameters and Mn content of synthesized products from the molar ratio of MnCl$_2$/MoCl$_4$. The atomic ratios of the product determined by EDX, $y$, were shown as bars. (c) Crystal structure of synthesized Mn$_y$Mo$_{1-y}$N$_{0.5}$

![Figure 2](image2.png)

**Figure 2.** (a) STEM image of MoN$_{0.5}$. (b) EDX spectra of products. (c) STEM image and EDX mapping of (d) Mo and (e) Mn for Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$ sample. (f) STEM image and EDX mapping of (g) Mo and (h) Mn for Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$ sample.
During combustion, the temperature rises quickly and is then quenched rapidly. Thus, there is the compelling possibility that any high-temperature phases formed during combustion synthesis can be retained in a metastable state at ambient conditions. γ-Mo₄N is the high-temperature polymorph of Mo₂N, and so, the formation of the γ-phase instead of the β- or δ-phases suggests that the temperature of the self-combustion synthesis reaction exceeds 673–1123 K. The presence of manganese could change the order/disorder transition temperature, but this effect is likely small, because of the relatively small fraction of Mn in solid-solution. Although MnMoN₂ is a stable phase in the predicted Mo-N phase diagram, high-temperatures promote metal reduction by evolution of gaseous N₂, driving phase equilibrium towards the nitrogen-poor intermetallic subnitrides, such as MoN₀.₅. It is possible that metathesis reactions carried out under high-pressures may facilitate the formation of nitrogen-rich nitrates, which could enable interesting semiconducting properties in these ternary mixed-transition metal nitrates.

To determine the thermodynamic (meta)stability of Mn-substituted Mo₄N, we used density functional theory (DFT) to model the formation energies of disordered γ-Mn₀.₁₂M₀₀.₈₈N₀.₅ structures. We sampled 100 randomly ordered Mn₀₁₂Mo₀₈₈N₀₅ structures on a 2 × 2 × 2 primitive rock salt structure, with a 1:7 ratio of Mn:Mo on the cation sublattice, and a 1:1 ratio of N:Vacancy on the anion sublattice. We assume that these 100 calculations statistically sample the structural density of states of the disordered structure. Because the 2 × 2 × 2 primitive lattice represents small unit cells, we compute the total energy of the disordered γ-Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ as a microcanonical ensemble formed from a sum of smaller canonical ensembles, given by the equation

\[ \langle E \rangle = \sum_i \exp(-E_i/k_B T) \]

where \( \langle E \rangle \) is the energy of the microcanonical γ-Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ phase, \( i \) represents a single ordered γ-Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ configuration on a 2 × 2 × 2 primitive cell, and \( E_i \) is the energy of that configuration.

Total energies were calculated in DFT using the Vienna ab initio software package (VASP), using the projector augmented-wave method with the GGA-PBE functional. Plane-wave basis cut-off energies are set to 520 eV. The k-point densities were distributed within the Brillouin zone in a Monkhorst-Pack grid and used default k-point densities in compliance with Materials Project calculation standards, which were calibrated to achieve total energy convergence of better than 0.5 meV/atom. Each structure is initiated in ferromagnetic spin configurations. Phase stability calculations are then computed using the phase diagram analysis package in pymatgen, calculated with respect to known nitride phases from the Materials Project.

The Mo–Mn–N phase diagram and a Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ structural density of states is shown in Figure 3. The canonical ensemble-averaged formation enthalpy of Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ is metastable by \( \Delta H_{\text{form}} = 11.7 \text{ kJ/mol} \) at room temperature with respect to Mn₄N + MoN + Mo, and metastable by \( \Delta H_{\text{form}} = 13.6 \text{ kJ/mol} \) at 1000 K. By the ideal solution model, the maximal configurational entropy of Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ is \( S_{\text{config}} = S_{\text{cation}} + S_{\text{anion}} = 13.4 \text{ J/(mol K)} \). This means that disordered Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅ can be stabilized at temperatures >1000 K through its Gibbs free-energy, but it is metastable if quenched to ambient conditions, consistent with a concept of Remnant Metastability.

To compute the reaction thermodynamics of the self-combustion reactions, we used the DFT-calculated formation energy of γ-Mn₀.₁₂₅Mo₀.₈₇₅N₀.₅ as well as the DFT formation energies for the known competing phases from the Materials Project database, and with formation energies of gaseous H₂O, NH₃, and N₂ referenced to experimental nitride formation energies, using the energy referencing scheme by Wang et al. In the Supporting Information, we show benchmarked ammonolysis reactions, showing good agreement with calculated reaction energies and calorimetry results.

From the previously determined formation enthalpy of Mo₀.₈₇₅Mn₀.₁₂₅N₀.₅, we compute the solid-state metathesis reaction conducted here to be highly exothermic (\( \Delta H = -253 \text{ kJ/mol} \)), as shown in Table 2, enabling it to proceed spontaneously at room temperature. On the other hand, the reaction enthalpy of the corresponding ammonolysis of oxides would be endothermic (\( \Delta H = 49 \text{ kJ/mol} \)) but could
To these novel ternary nitride compounds.

Nevertheless, between these two synthesis methods, combustion synthesis appears to be the simpler and more facile route to these novel ternary nitride compounds.

To examine the effect of Mn-substitution on the electronic structure of MoN0.5, magnetic properties of the products were investigated by a vibrating sample magnetometer (VSM). Figure 4 shows the temperature dependence of the magnetic moment of synthesized manganese molybdenum nitride Mn$_{y}$Mo$_{1-y}$N$_{0.5}$ $(y = 0, 0.06, 0.12)$. The sample with MnN$_{0.5}$ showed diamagnetic signal at approximately 5 K, suggesting the appearance of superconductivity.

This further evidence of γ-Mo$_{2}$N with a random occupation of nitrogen. On the other hand, Mn$_{0.06}$Mo$_{0.94}$N$_{0.5}$ and Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$ did not show diamagnetic signal, indicating the disappearance of superconductivity. This change in magnetic moment indicates a modification of the electronic structure in Mn-substituted MoN$_{0.5}$.

Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$ was also demonstrated, potentially be initiated at high-temperature by the production of H$_2$O and N$_2$ gases, providing entropy on the product side of the reaction to drive the formation of Mo$_{0.875}$Mn$_{0.125}$N$_{0.5}$. Nevertheless, between these two synthesis methods, combustion synthesis appears to be the simpler and more facile route to these novel ternary nitride compounds.

In summary, rapid materials preparatory methods are in great demand for scalable and sustainable materials synthesis. In this Letter, we demonstrated a facile self-combustion synthesis method for the realization of new ternary molybdenum nitrides. These reactions initiate at room temperature but rapidly reach high temperatures, and are then quenched shortly thereafter. The non-equilibrium nature of this process enables the formation of metastable disordered nitrides with emergent properties. Notably, introduction of manganese into molybdenum nitrides was found to enhance catalytic activity, and its activity was enhanced by introducing Fe into γ-Mo$_{2}$N. Catalytic activity improved with increasing Mn content, and Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$ showed the lowest overpotential and the highest current density, even though it had the largest nanoparticle size (Mo$_2$N ~ 20 nm, Mn$_{0.12}$Mo$_{0.88}$N$_{0.5}$ ~ 50 nm). Although these catalytic activities are not as high as commercial Pt/C, we demonstrate here that substitution of 3d transition metals improves the catalytic performance of γ-Mo$_{2}$N, which is likely due to modification of the electronic structure via these transition metal substitutions on the Mo site. By extending the known binary metal nitrides into ternary compositions, we can access a broader structure–property design space for enhanced materials functionality.

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Finally, we explored the potential electrocatalytic applications of our ternary molybdenum nitrides for the oxygen reduction reaction (ORR). The ternary molybdenum nitrides synthesized in this study have <50 nm particle size and appear kinetically resistant against corrosion in alkaline solutions. Figure 5 shows the oxygen reduction reaction activity of MoN$_{0.5}$ and its Mn-, Co-, and Fe-substituted ternaries in a 1 M KOH aqueous solution and also includes for reader’s reference a dashed line for 20 wt % Pt/C. γ-Mo$_{2}$N exhibited the lowest catalytic activity, and its activity was enhanced by introducing Fe into γ-Mo$_{2}$N (Figure 5).
yielded thermochemical insights into this highly exothermic reaction, and can be generally applied to screen for and identify similar self-combustion metathesis reactions. Finally, the combined experimental and computational investigation here offers a general paradigm for the predictive synthesis of novel functional materials.

■ ASSOCIATED CONTENT

5 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmaterialslett.9b00057.

Detailed characterization details and computational methods (PDF)

Movie of the combustion reaction (MP4)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was partially supported by KAKENHI Grant Numbers 17H04950 and 17H03382, and Nissan Chemical Corporation and through the EIG CONCERT-Japan 4th Call under the Strategic International Collaborative Research Program (SICORP) of the Japan Science and Technology Agency (JST). Funding for W.S. and G.C. was provided by the US Department of Energy, Office of Science, Basic Energy Sciences, under Contract no. UGA-0-41029-16/ER392000, as a part of the DOE Energy Frontier Research Center “Center for Next Generation of Materials Design: Incorporating Metastability”. STEM observation was supported by Hokkaido University microstructural characterization platform as a program of “Nanotechnology Platform” of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan.

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