Kinetically Controlled Low-Temperature Solid-State Metathesis of Manganese Nitride Mn₃N₂

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ABSTRACT: The synthesis of inorganic metal nitrides poses a challenge due to the low reactivity of N₂ gas at low temperatures, yet entropy driven formation of N₂ gas at high temperatures. In contrast, synthetic approaches using more activated forms of nitrogen can be used to overcome the inertness of N₂, but increased exothermicity can also result in diminished stoichiometric control and the activation of deleterious competing pathways. Here, kinetically controlled solid-state metathesis reactions are used to prepare Mn₃N₂ without the use of experimental conditions that increase the chemical potential of nitrogen and are known to produce phase impurity (e.g., NH₃, N₂-based plasma, azides, or high pressure). The solid-state metathesis reaction between MnCl₂ and Mg₃NCl or Mg₃N₂ is shown to generate Mn₃N₂, a phase on the border of stability. Highly exothermic control reactions performed with Li₃N, Ca₃N₂, and Ca₃NCl yield poorly crystalline, nitrogen-deficient Mn-N phases and N₂ gas. The reactions with Mg₃NCl and Mg₃N₂ do not self-propagate and have the lowest predicted free energies of reaction. A series of reactions performed at different times and temperatures, as well as in situ synchrotron X-ray diffraction, illustrate the importance of kinetic competence, and the results implicate the mechanism for this competence: the formation of a solid-solution, Mg₃Mn₁₁−xCl₂, between the halide precursor (MnCl₂) and the halide product (MgCl₂) coupled to a mildly exothermic reaction. Kinetically controlled solid-state metathesis continues to provide an avenue toward the synthesis of materials that cannot be prepared under traditional, high-temperature ceramic methods.

INTRODUCTION

Transition metal nitrides have developed considerable interest in fields such as ceramics, photovoltaics, and batteries because of their unique bonding patterns, high hardness, photoactive band gap, and many more properties.¹,² Unfortunately, the development of these materials is limited by their difficult synthesis. The formation of nitrogen gas is often a kinetic (at low temperatures) and entropic (at high temperatures) competitor to the formation of metal nitrides.¹ Activated nitrogen, as found with nitrogen plasmas (N₂⁺), or unstable molecules (N₂⁻), has recently garnered increased interest in the synthesis of new binary² and ternary⁴−⁵ nitrides. However, the interdiffusion of nitride-containing precursors, as in solid-state metathesis (SSM),⁶ offers new opportunities to synthesize metal nitrides. SSM reactions provide a low activation temperature alternative to the solid-state synthesis of many materials, which includes nitrides.⁶−⁸ The SSM of metal nitrides has typically involved the combination of transition metal halides with alkali or alkaline earth nitrides. Many of these reactions are sufficiently exothermic as to be self-propagating (cf, 1300 °C for ZrN); however, upon self-heating, kinetic control may be lost and N₂(g) may be formed instead.⁶,⁹

Solid-state metathesis reactions need not be self-propagating due to the exothermic self-heating of the reaction. Our group has shown that solid-state metathesis reactions can be selected to enable kinetic control, as metastable products can be isolated from low-temperature, nonpropagating reactions.¹⁰−¹³ Furthermore, we recently recognized the role of kinetic competence in solid-state reactions, stipulating that the precursors have the necessary ability to perform the reaction at the given temperature, as it pertains to atomic transport and reactivity; this approach enables the synthesis of materials that are unstable at higher temperatures (e.g., orthorhombic YMnO₃+x).¹⁴

Manganese nitrides offer a platform for investigating controlled, stoichiometric nitride synthesis. At least four manganese nitride phases are known and include Mn₄N,
Mn$_2$N, MnN (i.e., Mn$_n$N$_{3-x}$), and Mn$_3$N$_2$. Of particular interest is the noninterstitial compound, Mn$_2$N$_2$, which has been sought after for catalysis and high-temperature antiferromagnetism ($T_N = 927$ K). While Mn$_2$N$_2$ can be prepared from reaction of Mn and N$_2$(g), and Mn$_3$N from reaction of Mn and NH$_3$(g), compounds with increased nitrogen composition, such as Mn$_2$N$_2$ and Mn$_3$N$_2$, have required an increased chemical potential of nitrogen, as enabled by plasma-enhanced sputtering, molecular beam epitaxy, high pressure (N$_2$ or NH$_3$), reaction with NaN$_2$, and via LiN$_2$ or NaNH$_2$ salt metathesis or flux. In many of the reported syntheses for Mn$_3$N$_2$, decomposition products include Mn$_2$N or MnN (with the necessary production of nitrogen gas). This contrasts the expected more thermodynamically favorable formation of “MnN” (Mn$_n$N$_2$) as a decomposition product based on the Mn–N phase diagram.

This contribution describes how Mn$_n$N$_2$ is produced using kinetically competent Mg-based reactions, 2 MgNCl + 3 MnCl$_2$ → Mn$_n$N$_2$ + 4 MgCl$_2$ and MgN$_2$ + 3 MnCl$_2$ → Mn$_n$N$_2$ + 3 MgCl$_2$. Synthesis at higher temperatures loses stoichiometric control, as Mn$_n$N (and presumably N$_2$(g)) forms. From reactions quenched at lower temperatures, as well as in situ X-ray diffraction, solid-solution behavior for Mg$_x$Mn$_{1-x}$Cl$_2$ is observed, suggesting that this intermediate plays a role in enabling kinetic competence of the solid-state reaction. Control reactions with Li$_2$N, Ca$_3$N$_2$, and Ca$_3$NCl yield poorly crystalline, nitrogen-deficient Mn–N phases and N$_2$ formation; these control reactions are nearly twice as enthalpically favorable, and the halide salt byproducts are known to not form solid-solubilities with MnCl$_2$. By “turning down the heat,” the solid-state metathesis reactions of 2 MgNCl + 3 MnCl$_2$ and MgN$_2$ + 3 MnCl$_2$ yield stoichiometrically controlled reactions and formation of Mn$_n$N$_2$.

METHODS

All precursors were prepared and stored in an argon filled glovebox (O$_2 < 0.1$ ppm, H$_2$O < 0.5 ppm). MgNCl$_2$ was synthesized as previously reported with Mg$_2$N$_2$ (Alfa Aesar: 99.9% purity) and MgCl$_2$ (Sigma-Aldrich: 98% purity). Stoichiometric amounts of Mg$_n$N$_2$ and MgCl$_2$ were combined in an agate mortar and pestle and ground into a homogeneous tan powder. The powder was then pressed (P ≈ 1 ton) into a dense pellet and placed in a quartz ampule. This ampule was then brought out of the glovebox and quickly sealed under vacuum (P < 10 mTorr) using an oxygen/methane torch. The sealed ampule was then heated at 5 °C/min in a muffle furnace to a set point of 550 °C. The reaction was held at temperature for 7 days, and then allowed to cool to room temperature. The reactions reported here are sensitive to the precise temperature such that thermal gradients within the muffle furnaces influence reproducibility. Pelletized samples experienced temperatures approximately 20 to 40 °C below the temperature reported by the muffle furnace thermocouple, as probed by an external thermocouple. All temperatures reported are the nominal temperature set point, with estimates to the actual uncertainty described in the text.

The reactions of MnCl$_2$(Alfa Aesar: 97% purity) with Mg$_2$N$_2$ or Mg$_3$NCl to produce Mn$_n$N$_2$ were performed under a similar procedure. Stoichiometric amounts of reactants were combined with MnCl$_2$ in an agate mortar and pestle resulting in a homogenous pink powder. This powder was then pressed into a pellet (P ≈ 1 ton) and placed in a quartz glass ampule within an inert glovebox. Out of the glovebox, the ampule was quickly sealed under vacuum (P < 10 mTorr) with an oxygen/methane torch. Sealed ampules were heated in a conventional muffle furnace for various heating schedules described in the text; all reactions were performed with a ramp rate of 1 °C/min and furnace cool.

Control reactions were run with Li$_2$N (Alfa Aesar: 99.4% purity), Ca$_2$N$_2$ (Alfa Aesar: 99% purity), and Ca$_3$NCl. Ca$_3$NCl was synthesized from CaCl$_2$ and Ca$_3$N$_2$ as previously reported. The control reactions were performed under the same conditions as discussed above.

The products of all reactions were characterized by powder X-ray diffraction (PXRD) and Rietveld analysis. PXRD was performed using a Bruker D8 Vn diffractometer with CuK$_\alpha$ X-ray radiation. All samples were prepared for PXRD from within the glovebox by placing powder on “zero-background” silicon wafers and covered in polyimide tape to prevent exposure to the atmosphere. Some PXRD samples were prepared for quantitative Rietveld analyses by grinding known masses of silicon powder (as an internal standard) with known masses of the sample. Rietveld analyses were performed using the software TOPAS v6 (Bruker AXS) to obtain values for cell parameters, occupancies, and phase fractions.

In situ PXRD studies were conducted at 17-BM-B of the Advanced Photon Source at Argonne National Laboratory (λ = 0.24125 Å). Precursors were packed in extruded borosilicate capillaries and flame-sealed under vacuum (<10 mTorr). The tip of a thermocouple was placed against the capillary, within 3 mm of the X-ray beam, and two parallel resistive heaters controlled the sample temperature during the measurements with much greater accuracy than the muffle furnaces. Data collection was carried out with a 2048 × 2048 PerkinElmer 2D plate detector at a distance of 70 cm from the sample. The 2D diffraction patterns were then radially integrated with GSAS-II. Sequential Rietveld refinements were conducted using TOPAS v6 (Bruker AXS) to identify phase fraction, the occupancy (x) of Mg$_n$Mn$_{1-x}$Cl$_2$ and lattice parameters. Strain was also refined. The Mn$_n$ phase was only refined for the dwell scans to prevent poor convergence of the calculation, although small peaks can be qualitatively observed for data collected above T = 385 °C.

The thermochemistry of manganese nitride stability and metathesis reaction energetics were computationally evaluated at finite temperatures using quantum chemical calculations. All atomic structure and total energy calculations were performed using the projector augmented-wave method within the VASP code and in accordance with our previous calculation parameters used for computing binary nitride phase diagrams and evaluating stability. In brief, the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation exchange-correlation functional was employed for all calculations, with a plane-wave energy cutoff of 520 eV, and Γ-centered Monkhorst–Pack k-point grid. The energy cutoff, k-point density, and related convergence settings were sufficient to achieve total energy convergence of <0.5 meV/atom for all calculations. These computational parameters were selected to enable the direct evaluation of thermodynamic stability and reactions energetics involving all potential competing compounds and formation enthalpies computed within this work and those reported within the Materials Project database. We note that our predicted Mn–N convex hull phase diagram is consistent with the results reported using the meta-GGA SCAN functional was employed for all calculations, with a plane-wave energy cutoff of 520 eV, and Γ-centered Monkhorst–Pack k-point grid. The energy cutoff, k-point density, and related convergence settings were sufficient to achieve total energy convergence of <0.5 meV/atom for all calculations. These computational parameters were selected to enable the direct evaluation of thermodynamic stability and reactions energetics involving all potential competing compounds and formation enthalpies computed within this work and those reported within the Materials Project database. We note that our predicted Mn–N convex hull phase diagram is consistent with the results reported using the meta-GGA SCAN functional was employed for all calculations, with a plane-wave energy cutoff of 520 eV, and Γ-centered Monkhorst–Pack k-point grid. The energy cutoff, k-point density, and related convergence settings were sufficient to achieve total energy convergence of <0.5 meV/atom for all calculations. These computational parameters were selected to enable the direct evaluation of thermodynamic stability and reactions energetics involving all potential competing compounds and formation enthalpies computed within this work and those reported within the Materials Project database. We note that our predicted Mn–N convex hull phase diagram is consistent with the results reported using the meta-GGA SCAN functional was employed for all calculations, with a plane-wave energy cutoff of 520 eV, and Γ-centered Monkhorst–Pack k-point grid. The energy cutoff, k-point density, and related convergence settings were sufficient to achieve total energy convergence of <0.5 meV/atom for all calculations.
RESULTS

The structure of manganese nitride, Mn$_3$N$_2$, adopts a body-centered tetragonal unit cell and is pictured in Figure 1.

Nitrogen atoms occupy two-thirds of the octahedral sites allowing for two distinct manganese atom locations. One manganese atom is linearly coordinated to the interstitial nitrogens, while the other atom is coordinated in a square pyramidal fashion to five nitrogen atoms. The unit cell parameters of synthesized Mn$_3$N$_2$ are within uncertainty (evaluated from PXRD) of those found in the literature; $a = 2.974$ Å and $c = 12.126$ Å (14/mmm).  

Stoichiometric control of the reaction of 2 Mg$_2$NCl + 3 MnCl$_2$ → Mn$_3$N$_2$ + 4MgCl$_2$ is optimized at muffle furnace set points of 400 °C. PXRD patterns of the reaction products over a temperature set point range from 300 to 500 °C are shown in Figure 2, and the respective quantitative phase analysis is tabulated in Table S1 of the Supporting Information (S1). At lower temperatures, solid-solution Mg$_{1-x}$Mn$_x$Cl$_2$ phases are also observed. Set points above 400 °C lead to the decomposition of Mn$_3$N$_2$ to the nitrogen deficient phase, Mn$_2$N. Similar trends are noted for the reaction Mg$_2$N$_2$ + 3 MnCl$_2$ → Mn$_2$N + 3 MgCl$_2$ (Figure S1).

In situ PXRD patterns reveal direct conversion of Mg$_2$NCl and MnCl$_2$ to MgCl$_2$ and Mn$_3$N$_2$, with a trace quantity of Mn$_2$N detected at higher temperatures after isothermal dwell (Figure 3). No other crystalline intermediates are detected. In addition to the observation of thermal expansion during heating, the peaks from Mg$_2$NCl decrease in intensity over time, while Mn$_2$N is detectable after 35 min ($T = 370$ °C). As the reaction proceeds, the (210) peak of Mg$_{1-x}$Mn$_x$Cl$_2$ decreases in Q (due to contraction along the a axis) and decreases in intensity, while the (108) peak grows in intensity, suggesting Mg substitution at Mn sites. Mn$_3$N formation is observable at 400 °C (38 min). These data reveal a narrow temperature window in which Mg$_2$NCl is a kinetically competent precursor for formation of Mn$_3$N$_2$, but above which formation of Mn$_3$N competes and Mn$_2$N$_2$ decomposes (Figure S4). Within this window, however, Mn$_2$N formation is not detectable by ex situ PXRD, even at reaction dwell times as long as 1 month (Figure S3).

Solid-solution behavior of the MnCl$_2$ precursor with the MgCl$_2$ product is observed through Rietveld analysis of the in situ PXRD data (Figure 4). The increase in Mg occupancy during the dwell (Figure 4b) mirrors the decrease in the a lattice parameter for the Mg$_{1-x}$Mn$_x$Cl$_2$ phase (Figure 4c), as the phase shifts from predominantly MnCl$_2$ ($\alpha_{298}$ K = 3.711 Å) to MgCl$_2$ ($\alpha_{298}$ K = 3.636 Å). These data are consistent with ex situ PXRD data under various reaction conditions (Figures S5 and S6). However, the in situ data illustrate that the rate of increasing phase fraction of Mn$_2$N$_2$ is more gradual in time than are the changes to Mg$_{1-x}$Mn$_x$Cl$_2$.

Several control reactions were attempted with other nitrogen-containing precursors to understand the thermochemical factors responsible for Mn$_3$N$_2$ formation. The
Figure 4. Summary of Rietveld analysis results from the in situ PXRD experiment of 2MgNCl + 3MnCl₂ ramped from room temperature to 400 °C at a rate of 10 °C/min (Figure 3). (a) The phase fraction of MgNCl decreases as manganese nitride phases form, which corresponds with (b) a change in occupancy and (c) a contraction in the a lattice parameter of MgMn₁₋ₓCl₃. (d) The c lattice parameter of MgMn₁₋ₓCl₃ expands slightly.

reaction, 2 Li₃N + 3 MnCl₂ → Mn₃N₂+6 LiCl, instead produces nitrogen deficient manganese nitrides: MnₓN and MnN. The reaction mixture self-propagated under mild heat (CAUTION! e.g., while flame sealing; Figure 5a). The reaction, Ca₃N₂ + 3 MnCl₂ → MnₓN₂ + 3 CaCl₂ also yields nitrogen-deficient Mn–N phases, MnₓN (11.51 mol %) and MnN (19.90 mol %), as well as CaCl₂ (68.58 mol %; Figure 5b). The reaction, 2 Ca₃NCl + 3 MnCl₂ → MnₓN₂ + 4 CaCl₂ produces a mixture of the nitrides MnₓN₂ (2.75 mol %), MnN (6.76 mol %), and MnN (19.00 mol %), as well as CaCl₂ (71.49 mol %; Figure 5c).

**DISCUSSION**

The reactions, 2 MgNCl + 3 MnCl₂ → MnₓN₂ + 4 MgCl₂ and MgₓN₂ + 3 MnCl₂ → MnₓN₂ + 3 MgCl₂ proceed stoichiometrically to yield crystalline MnₓN₂. These reactions contrast previous efforts, which rely on conditions aimed at increasing the chemical potential of nitrogen, often through pressure or highly reactive precursors. The reaction here instead proceeds at relatively low temperature (~370 °C) via the interdiffusion of magnesium-based nitride precursors.

The computed convex hull phase diagram depicting the 0 K and finite temperature thermochemical stability of MnₓN₂ illustrates the challenge toward formation of MnₓN₂ under standard synthesis conditions (Figure 6). The free energy of formation falls within the ∼35 meV/atom MAE uncertainty of the density functional calculations in resolving the on or near hull stability of MnₓN₂ at 0 K, and it remains within this range of uncertainty for all finite temperatures evaluated. Note that neglecting zero point energies and heat capacity contributions to the enthalpy introduces only a modest source of error, 7 meV/atom on average, and that the MAE of the finite temperature predictions using the statistical-descriptor for evaluating free energies is of similar magnitude as the uncertainty in the DFT methods, ∼40 meV/atom. From Figure 6, we can see that if the MnₓN₂ phase decomposes to release N₂ as an expected kinetic product in vacuum, MnN should be observed, as consistent with our observations for reactions performed above 400 °C (Figure S4).

The role of controlled interdiffusion is substantiated by the observation of the solid-solution behavior of MgₓMn₁₋ₓCl₂, MgCl₂ and MnCl₂ are isostriuctural and the ionic size of Mg²⁺ and Mn²⁺ are highly similar, thus the solubility (enthalpy of mixing) between these two compounds is high (low) and they are thermodynamically miscible at the moderate temperatures

Figure 5. (a) PXRD of products from the reaction of 2 Li₃N + 3 MnCl₂ after self-propagation during mild heating from flame sealing the reaction ampule. The reaction products were exposed to air, resulting in deliquescence of the LiCl to reveal only crystalline MnₓN₂ and MnN. (b) Products from Ca₃N₂ + 3 MnCl₂ at 400 °C (muffle furnace set point) for 12 h detectable by PXRD. The reaction produced CaCl₂ (68.58 mol %), as well as the nitrogen deficient manganese nitrides; MnₓN (11.51 mol %) and MnN (19.90 mol %). This suggests loss of nitrogen in the form of N₂(g). (c) Products from 2 Ca₃NCl + 3 MnCl₂ at 400 °C (muffle furnace set point) for 12 h detectable by PXRD. Three manganese nitride compounds were formed including MnₓN (6.76 mol %), MnN (19.00 mol %), and MnN (2.75 mol %) along with CaCl₂ (71.49 mol %).

Figure 6. Convex hull phase diagram of binary manganese nitride compounds at 0, 300, 600, and 900 K. Δ𝐺ₓ(T) is the Gibb's formation energy at the specified temperature, x is the fraction of nitrogen in the compound, and the shaded regions indicate the energetic resolution of the computational approach in evaluating the hull stability. The predicted formation energy of MnₓN₂ relative to MnN and MnN places it near the border of stability and being metastable toward decomposition into these compounds, which is consistent with the experimentally observed challenge of readily synthesizing MnₓN₂ using reactive nitrogen sources.
employed in our metathesis synthesis reactions. Rietveld analysis of PXRD data shown in Figure 2 permits extraction of the unit cell parameters and metal site occupancy of the (Mg/Mn)Cl phases, which generally agree with the data collected in situ (summarized in Figures S5 and S6). The reaction product, MgMn₁₋₃Cl₃, converges to MgCl₂ (a = 3.636 Å and c = 17.666 Å) as temperature increases. Given the X-ray scattering contrast between Mg (Z = 12) and Mn (Z = 25), the refined occupancy of Mg²⁺ in the salt phase also increases as a function of temperature, converging to complete Mg²⁺ occupancy as a function of temperature and time with both precursors. Effectively, the salt solution affords the ions in the reaction mixture a transient place for diffusion to occur.

Analysis of the in situ PXRD data shows that the MgCl₂ forms faster than Mn₃N₂ can be detected. This is reflected in the different slopes of Figure 4a during the isothermal dwell at 400 °C. This transient stoichiometric imbalance strongly hints at the presence of an amorphous phase generated in this low-temperature reaction. As a control, a known mass fraction of crystalline Si (<2 wt % amorphous component) was added into the mixture of reaction products after the reaction was completed but before collecting PXRD data. Quantitative phase analysis relative to the known amount of Si reveals the presence of an amorphous component in the mixture (Figure S3). A comparison with the initial composition suggests that the amorphous component is predominantly composed of MgCl₂. The formation of an amorphous precursor during a kinetically controlled reaction has previously been observed by us in solid-state metathesis reactions and warrants further future study, as it may provide access to the most metastable polymorphs that can be synthesized. We do not detect the exact intermediate containing the nitrogen, although we infer that it must contain Mn and N₂ otherwise the nitrogen would escape the solid product as N₂(g). We do not see evidence for solid-solution behavior as Mgₓ−ₓMnₓN₂; therefore, we must speculate the MnₓN₂ forms by itself a second phase.

Solid-solution behavior is not observed between LiCl and MnCl₂ or between CaCl₂ and MnCl₂. In those cases, the cation size differences are likely large enough to increase mixing enthalpies, and the phases have distinct structures; such a structural discontinuity precludes facile pathways for itinerant ions. This factor may contribute to the observation of nitrogen-poor Mn₃N₂ phase formation in the corresponding reactions, rather than stoichiometric reaction. Without a pathway for ion intercalation, it is possible that random assortment of ions within the reaction mixture occurs, and the formation of nitrogen gas can readily take place. Upon formation of N₂, the chemical activity of nitrogen is reduced to ineffective levels.

Thermochemistry provides a counterintuitive perspective on the experimental observations, in that the least exergic reactions are those which yield the targeted phase. Free energies of reaction derived from first-principles calculations (Figure 7), illustrate that the Mg₃NCl and Mg₃N₂ sourced reactions are about half as exergic as the analogous Ca₃NCl and Ca₃N₂ reactions, as loosely attributable to the lower ΔG.solve(T) of the CaCl₂ relative to MgCl₂, even at typical synthesis conditions (T = 600–900 K). One possible explanation is that the formation of the respective salts in these reactions generate enough heat locally that even if Mn₃N₂ forms, it will decompose into the reduced nitrdes, metal, and nitrogen gas, as previously observed. Crystal Orbital Hamilton Population (COHP) calculations show that Mg₃N₂ is more covalent than Ca₃N₂ (Figure S7), which may also kinetically inhibit N₂ formation by having both a higher Mg–N bond dissociation energy and bond directionality, inhibiting off-stoichiometry from the liberation and transport of ions allowing the Mg₃N₂ to produce the targeted phase while Ca₃N₂ produces subnitrdes. Alternatively, for highly exergic reactions (e.g., with Ca₃N₂, Ca₃NCl, and Li₃N), the systems appear to form compounds that would produce the fastest change in free energy (∆G/∆t), as observed in thin film metallurgical junctions; the rapid formation of N₂(g) as a kinetic product does not require a concerted nucleation and growth process. This may be why Mn₃N₂ is observed instead of forming a more thermodynamically favorable MnN phase. However, this rapid free energy change refers to the local reaction zone, as rapid heating of 2 Mg₃NCl + 3 MnCl₂ still produces Mn₃N₂ (Figure S8).

**CONCLUSIONS**

Manganese nitride (Mn₃N₂) is formed stoichiometrically via a kinetically controlled solid-state metathesis reaction between 2 Mg₃NCl and 3 MnCl₂, and between Mg₃N₂ and 3 MnCl₂. The reaction proceeds without loss of nitrogen and yields crystalline products. The controlled reaction is afforded by a low heat of reaction (<400 kJ mol⁻¹) and the solid solution between the reactants and products (Mg₃NCl and MnCl₂) enables the reaction to proceed at a relatively low temperature. Free energy calculations suggest Mn₃N₂ is thermodynamically stable up to 900 K, although experiments show N₂ formation competes as the reaction temperature increases above ~380 °C. Control reactions using other nitride binaries reveal that a small free energy change in time (∆G/∆t) is required in synthesizing materials that decompose at elevated temperatures, such as Mn₃N₂. Using precursors with a reasonably high nitrogen bond dissociation energy also appears to prevent loss of nitrogen to N₂ during the reaction (e.g., Mg₃N₂ vs Ca₃N₂). The use of kinetically controlled reactions to prescribe synthesis reactions for nominally refractory solids (e.g., nitrides) will continue to increase the diversity of nitride-based materials available for study.
ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.9b01565.

This content provides additional details about: Products from Mg\textsubscript{5}N\textsubscript{2} + 3 MnCl\textsubscript{2} and 2 Mg\textsubscript{3}N\textsubscript{2}Cl + 3 MnCl\textsubscript{2} determined by ex situ powder X-ray diffraction at various temperatures and times, as well as variations in the crystallographic parameters; an expanded view of in situ powder X-ray diffraction data; and results from DFT calculations (tables of free energies and Crystal Orbital Hamilton Population calculations) (PDF)

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The authors declare no competing financial interest.

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