Bulk synthesis, structure, and electronic properties of magnesium zirconium nitride solid solutions

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Abstract

Ternary nitride phase space holds great potential for new functional materials, as suggested by computational predictions of yet-to-be discovered stable phases. Here, we report a metathesis route to bulk powders of MgZrN₂ and the solid solutions $Mg_xZr_{2-x}N_2$ (0 < x < 1). These ternary phases only result when lower temperature reactions are used, in contrast to previous work using the similar Mg-based metathesis reactions that resulted in the formation of exclusively ZrN. Thermochemical calculations illustrate why lower-temperature metathesis reactions yield the incorporation of Mg, while higher temperature and ceramic reactions yield exclusively ZrN. Experimental *in situ* X-ray diffraction of metathesis reactions during heating reveals two stages in the reaction pathway: initial consumption of the precursors to make an amorphous product ($T_{rxn} > 350$ °C) followed by crystallization at higher temperatures ($T_{rxn} > 500$ °C). Changing the ratio of the metathesis precursors (Mg₂NCl and ZrCl₄) controllably varies the composition of Mg_xZr_{2-x}N₂, which crystallizes as a cation-disordered rock

salt, as evidenced by high-resolution synchrotron X-ray diffraction, electron microscopy, and bulk compositional analysis. Variation in composition leads to a gradual metal-to-insulator transition with increasing x, similar to other reports of analogous thin film specimens produced by combinatorial sputtering. Meanwhile, the optical behavior of these powders suggests nanoscale compositional inhomogeneity, as signatures of ZrN-like absorption are detectable even in Mg-rich samples. This metathesis approach appears to be generalizable to the synthesis of bulk ternary nitride materials.

Introduction

Nitride-based ceramics, with anionic nitrogen coordinating metals or metaloids, are an important but under-explored class of functional materials. Many binary early transition metal nitrides are mechanically hard metals that superconduct at cryogenic temperatures (e.g., ZrN, TiN).¹ Improved processing of GaN resulted in the widespread use of that binary nitride in inorganic light emitting diodes, as well as a Nobel prize.² In general, incorporating a third element to form ternary nitrides adds the possibility of tuning their functional properties.^{3,4} For example, the solid solution $In_xGa_{1-x}N$ has a tunable band gap ranging from 3.4 eV to 1.1 eV with *x*.⁵ Ternaries can also crystallize in distinct structures and properties relative to their binaries, as highlighted by the semiconducting perovskite LaWN₃ compared to metallic rock salts LaN and WN.⁶ In addition to functional optoelectronic materials, ternary nitrides are also of interest as catalysts,^{7,8} magnets,⁹ and battery materials.^{10,11} While technologically useful, relatively few ternary nitrides are known.⁴ For comparison, the phase space of ternary oxide-based compounds spans >4,000 unique crystal structures, whereas only approximately 400 ternary nitride crystal structures have been reported.¹² This dearth of known nitrides calls for improved synthetic methods to access this family of materials.

Computational mapping of the ternary nitride phase spaces has accelerated the synthesis of new materials. Data-mining-based structure prediction and density functional theory (DFT) calculations predicted 244 new thermodynamically stable ternaries, which is more than double the 213 known at the time.¹² Subsequently, some of these new ternary phases have been synthesized via



Figure 1: (a) The cation-disordered MgZrN₂ observed in this study adopts a cubic rock salt structure. This material and its solid solutions $Mg_xZr_{2-x}N_2$ (0 < x < 1) are isostructural with (b) binary ZrN, in contrast to (c) the predicted tetragonal cation-ordered structure of MgZrN₂. (d) Simulated SXRD patterns are shown in blue traces (top). SXRD data from 11-BM-B ($\lambda \approx 0.4579$ Å) of the washed reaction products from $nMg_2NCl + ZrCl_4$ heated to a 800 °C set point under vacuum in sealed ampules for 12 h show that increasing Mg₂NCl relative to ZrCl₄ leads to a smaller unit cell for the rock salt structure, broader peaks, and increasing *x*. No additional reflections that would be consistent with an ordered $I4_1/amd$ MgZrN₂ phase are observed. Trace MgO (*) and Zr₄N₂O₅ (†) are present in some of the samples. Data (black dots), calculated patterns from Rietveld analysis (orange trace), and difference curves (blue trace) are shown. The vertical axis is a linear scale. Full patterns are shown in Figure **??**.

combinatorial sputtering in a nitrogen-based plasma (e.g., LaWN₃, Mg₃SbN, Mg₂SbN₃),^{6,13} highpressure ceramic synthesis (e.g., $(Si_{1-x}Ti_x)_3N_4$),¹⁴ high-pressure metathesis (e.g., MgSnN₂),¹⁵ or self-combustion metathesis (e.g., $M_xMo_{1-x}N_{0.5}$ where M = Mn, Fe, Co).¹⁶ Sputtering methods have also been used to synthesize a set of ternary nitrides crystallizing with disordered rock salt structures (e.g., MgTiN₂, MgZrN₂, MgHfN₂, and Mg₂NbN₃).¹⁷ Circling back, these experimental synthesis results have revealed the importance of cation site disorder, which better informs predictive models.¹⁸

Of these new nitrides, MgZrN₂ has garnered particular interest due to the metal-to-insulator transition and compatibility of this rock salt structure with common electronic substrates like Si and MgO. As a thin film produced by sputtering, MgZrN₂ crystallizes with a disordered rock salt structure, isostructural with the binary superconductor ZrN (Figure 1a and b).^{17,19–21} In such studies, combinatorial sputtering was used to survey a broad range of stoichiometries around the targeted line compound MgZrN₂, with *x* in Mg_xZr_{2-x}N₂ between 0.5 and 1.6. The behavior transitions from metallic (10³ S/cm at *x* < 1.0) to semiconducting (10⁻³ S/cm at *x* ≥ 1.0) as Mg²⁺ replaces formally charged Zr³⁺, which is oxidized to Zr⁴⁺. An absorption onset of 2.2 eV appears with *x* ≈ 1 and shifts to 1.8 eV by *x* ≈ 1.6. There, they show that oxide incorporation charge balances the phase, resulting in Mg_xZr_{2-x}N_{4-2x}O_{2x-2} for 1 < *x* < 2.¹⁹ In addition to Mg-content, the degree of cation order is also expected to influence semiconducting properties, ^{3,22} but cation ordering has not yet been observed. Bulk samples with additional synthetic degrees of freedom are needed to further investigate these materials.

Here, we describe the synthesis of bulk $Mg_xZr_{2-x}N_2$ powders (0 < x < 1) via metathesis (i.e., double-displacement) reactions between $ZrCl_4$ and Mg_2NCl or Mg_3N_2 . In situ powder X-ray diffraction (PXRD) measurements along the reaction pathway identify reactivity differences between these two Mg-based precursors. Thermochemical calculations rationalize why the metathesis route produces $Mg_xZr_{2-x}N_2$, yet traditional ceramic reactions yield only ZrN. Solid solution behavior in a disordered rock salt crystal structure is observed by high-resolution synchrotron powder X-ray diffraction (SXRD); no evidence for cation ordering is observed. The ratio of Mg

to Zr in the reaction products were studied by Rietveld analysis of synchrotron X-ray diffraction data, energy dispersive X-ray spectroscopy (EDS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES). Electronic measurements show metallic behavior in Mg-poor phases and semiconducting behavior in near-stoichiometric MgZrN₂ phases ($x \approx 1$ in Mg_xZr_{2-x}N₂). Optical measurements suggest the presence of small ZrN domains within Mg-rich Mg_xZr_{2-x}N₂. This metathesis synthesis yields a ternary nitride where traditional ceramic techniques fail, offering a route to other predicted (but not yet synthesized) ternary nitrides.

Methods

Synthesis

Caution: Solid-state metathesis reactions can be highly exothermic and can yield gaseous byproducts (e.g., N_2). These properties pose explosion and fire hazards, particularly when sealing reagents in closed containers and when scaling up reactions. Keep nitride precursors away from flammable materials and under inert conditions to avoid fires. Calculate the expected pressure in a closed system prior to heating to ensure the pressure does not exceed safe limits. Exercise caution when cleaning nitride-contaminated materials once removed from the glovebox.

All precursors were prepared and stored in an argon filled glovebox ($O_2 < 0.1$ ppm, $H_2O < 0.5$ ppm, unless explicitly mentioned). Mg₂NCl was synthesized as previously reported with Mg₃N₂ (Alfa Aesar, 99% purity) and MgCl₂ (Sigma Aldrich, 98% purity).²³ Stoichiometric amounts of Mg₃N₂ (~3 g) and MgCl₂ (~3 g) were combined in an agate mortar and pestle and ground into a homogeneous tan powder. The powder was then cold pressed (P ~ 80 MPa) into a dense pellet (diameter = 0.5 in) and placed in a quartz ampule (14 mm inner diameter, 16 mm outer diameter). This ampule was then brought out of the glovebox and quickly sealed under vacuum (≤ 20 mTorr, as determined by a Pirani gauge) using an oxygen/methane torch. The sealed ampule (~15 cm³ internal volume) was then heated at 10 °C/min in a muffle furnace to a set point of 550 °C. The reaction was held at temperature for 5 days, and then allowed to cool to room temperature before

opening the ampule in the glovebox. $ZrCl_4$ (Acros, 98%) was purified by heating approximately 4 g in a sealed quartz ampule (~30 cm long) in a 3-zone horizontal tube furnace to transport $ZrCl_4$ from the hot zone (400 °C set point) to the colder zone (300 °C set point), leaving behind less volatile, oxide-based impurities (e.g., ZrO_2).

Throughout this manuscript, reaction temperatures are described as either set point temperatures or as the recorded temperature during *in situ* experiments. Temperatures experienced by the sample may be as much as 40 °C lower than the specified furnace set point due to thermal gradients within furnaces. Furnace temperatures were ramped at a nominal rate of 10 °C/min and cooled by turning off power to the heating elements, unless otherwise specified. *In situ* reaction temperatures have been calibrated against reference samples by monitoring the thermal expansion via X-ray diffraction and are accurate within ± 10 °C.

Syntheses of $Mg_xZr_{2-x}N_2$ powders were conducted by grinding $ZrCl_4$ (200 mg–500 mg) with either Mg_2NCl (200 mg–500 mg) or Mg_3N_2 (100 mg–300 mg) in various ratios. The ratio between magnesium and zirconium precursors is represented by the molar coefficient *n* (i.e., $nMg_2NCl +$ $ZrCl_4$ indicates a mol ratio of $ZrCl_4:Mg_2NCl::1:n$). The mixtures were loaded into quartz ampules (either as 0.25 in diameter pellets cold pressed at 300 MPa or loose powders, 300 mg–1000 mg), sealed under vacuum (≤ 20 mTorr, approximately 10 cm³ internal volume), and heated in muffle or tube furnaces. Reactivity was induced by heating samples at a 500 °C set point in a box furnace for 12 hours, followed by annealing at a 800 °C set point for 12 hours to crystallize the $Mg_xZr_{2-x}N_2$ material. To remove byproduct $MgCl_2$ from the target compound, samples were washed with anhydrous methanol (dried over molecular sieves for at least five days)²⁴ in a N₂ glovebox. The products are moisture sensitive (Figure **??**), so all steps of the process were conducted under inert conditions unless otherwise specified.

Control reactions followed traditional ceramic synthetic methods, exemplified by the synthesis of MgMoN₂.¹⁰ Mg₃N₂ (~400 mg) and 3/2 molar equivalents of Zr powder (~500 mg) were ground together (i.e., excess Mg₃N₂), pelletized (~300 mg pellets), placed in an alumina crucible with a Zr foil cap (to reduce Mg₃N₂ loss by evaporation and to react with adventitious oxygen) and

heated in a tube furnace under flowing purified N_2 . The N_2 gas was purified by flowing through a Supelco high capacity gas purifier (Model # 29542-U) prior to flowing into a quartz reaction tube fitted with custom endcaps that permit disconnection from the gas line without air exposure. Samples were recovered directly into an Ar glovebox at room temperature for further analysis.

X-ray diffraction experiments

The products of all reactions were characterized by powder X-ray diffraction (PXRD) and analyzed by the Rietveld method. PXRD measurements were performed using a Bruker DaVinci diffractometer with CuKα X-ray radiation. All samples were prepared for PXRD from within the glovebox by placing powder on off-axis cut silicon single crystal wafers to reduce the background, and then covered with polyimide tape to slow exposure to the atmosphere.

Select samples were sent to Argonne National Laboratory for synchrotron powder X-ray diffraction data (SXRD). Washed samples were flame sealed under vacuum in quartz capillaries (0.5 mm inner diameter, 0.6 mm outer diameter) under Ar (g). SXRD measurements were collected on the high-resolution diffractometer at beamline 11-BM-B with a wavelength of either 0.457879 Å or 0.457900 Å.²⁵ SXRD patterns are shown in *Q*-space to account for this small difference in wavelength ($Q = 4\pi \sin(\theta)/\lambda$).

In situ PXRD measurements at elevated temperatures were made on capillary-held samples in a Panalytical Empyrean diffractometer in Debye-Scherrer geometry using a well insulated Anton Parr HTK1200N high temperature sample environment. AgK α X-ray radiation and focusing Xray optics were used, and data sets were collected from 2 θ scans of the GaliPIX 2D detector. Capillaries of the reagents were heated at a rate of 10 °C/min between scans and held isothermally for 7 minutes during collection of each diffraction pattern. A temperature correction was applied to the measurements via a calibration curve determined from the temperature dependence of MgO and Al₂O₃ lattice parameters measured under the same heating conditions.

X-ray diffraction analysis

Quantitative phase analysis of the PXRD, SXRD, and *in situ* PXRD data and structural refinement of previously-reported crystal structures (e.g., lattice parameters, cation occupancies) were performed using the Rietveld method as implemented in TOPAS v6 (Bruker AXS). To determine lattice parameters, Si powder was added to aliquots of the reaction products, gently homogenized in an agate mortar, and used as an internal standard in the PXRD experiments. The Si powder was sourced from a single crystal wafer, pulverized in a glovebox to minimize the presence of surface oxide.

To compare the relative amounts of phases in the *in situ* PXRD data sets, a weighted scale factor (Q_p) was calculated such that $Q_p = S_p \times V_p \times M_p$. S_p is the scale factor calculated from Rietveld for phase p, V_p is the volume of the unit cell for phase p, and M_p is the atomic mass of the unit cell for phase p. These experiments did not include a Si internal standard. Amorphous, liquid, and gaseous phases are not detected by this method.

For Rietveld analysis of the rock salt phase, cubic $(Fm\bar{3}m)$ ZrN was used as a starting model, with both Mg²⁺ and Zr⁴⁺ occupying the cation site. Cation occupancy (*x*) was constrained to equal anion occupancy (i.e., Mg + Zr = N). The anion site was fixed at fully occupancy. The atomic displacement parameters were refined isotropically. Lattice parameter, crystallite size (Lorentzian) and microstrain (Gaussian) were also refined. The background was fit independently for each pattern with a six-term polynomial. An impurity phase of MgO or Zr₄N₂O₅ was fit to each pattern if observed, although only the unit cell and crystallite size parameters were refined. To better estimate error in metal occupancy, sequential refinements were carried out by fixing the Mg occupancy parameter between x = 0.0 to x = 2.0 in increments of 0.1, and refining all other parameters as described above. Mg occupancy uncertainties were estimated from a 1% increase in the refinement Goodness of Fit parameter relative to the best fit. Total μR for samples range from 1.5 (MgZrN₂) to 3.0 (ZrN), assuming a 0.5 packing fraction, which suggests that absorption corrections should be applied. However, control refinements accounting for absorption using the calculated, nominal absorption do not lead to meaningful changes in the refined occupancies or their calculated uncertainty.

Additional Characterization

Scanning electron microscopy (SEM) measurements were made using a JEOL JSM-6500F instrument. Energy dispersive X-ray spectroscopy (EDS) measurements were made with the attached Oxford 80 X-MAX silicon drift detector and analyzed using AZtec software (Oxford Instruments). Samples for SEM-EDS analysis were pelletized in an Ar glovebox, adhered to SEM stubs with double-sided carbon tape, and quickly transferred from the glovebox to the instrument (< 5 min air exposure). SEM imaging and mapping was conducted at 15 kV. A 5 kV accelerating voltage was used for quantitative EDS measurements. Averages of the elemental composition were calculated from point-defined EDS measurements made at six different locations on each pellet.

Inductively coupled plasma atomic absorption spectroscopy (ICP-AES) analysis of the metal compositional ratios were conducted by Huffman Hazen Laboratories (Golden, CO) following digestion of the samples using nitric, perchloric and hydrofluoric acids. The error in the Mg results are ± 0.1 % w/w and the error in the Zr results are ± 0.5 % w/w.

Resistivity measurements were conducted on pelletized samples enclosed in Swagelok® cells with PTFE bodies and PTFE compression fittings around the stainless steel current collectors (0.25 inch diameter, 0.317 cm² surface area). Samples were prepared in an Ar (g) glovebox but were removed from the box for measurement after being sealed within the measurement cells. A cold-pressed pellet (P ~ 300 MPa) with mass of approximately 0.1 g was loaded into each cell. Sample thicknesses were calculated from the difference in length between empty and loaded cells as measured by calipers (\pm 0.01 mm). The cells were removed from the glovebox and connected to a Gamry Reference 3000 potentiostat. Electrochemical Impedance Spectroscopy (EIS) measurements were conducted at room temperature (24 °C) by applying a 50 mV excitation voltage relative to open circuit potential across a frequency range from 3 × 10⁵ Hz to 3 × 10⁻¹ Hz. The samples all exhibited electronically conductive behavior (Figure ??), and resistance (*R*) was taken as the low frequency limit of the impedance magnitude (e.g., Z at 300 mHz). Resistance of the contacts

 $(0.05 \ \Omega)$ was determined by measuring blank cells (e.g., stainless steel electrodes in direct contact with one another) and subtracted out to determine sample resistance (R_s) . Sample conductivity (σ) was calculated from $\sigma = (t)/(R_s A)$ where t is pellet thickness and A is cross-sectional area (0.317 cm^2) . Pellets were recovered post-measurement and analyzed by PXRD to confirm that no chemical changes occurred.

Optical spectroscopy measurements were made using an Ocean Optics tungsten-halogen light source (HL-2000-FHSA) and an Ocean Insight Flame Spectrometer with an integrating sphere. A fiber optic cable was used to illuminate the flat base of a borosilicate glass vial covered by loose powder of the sample. A photograph of this setup is shown in Figure **??**. A vial with BaSO₄ was used as a white reflectance standard. Samples were prepared by homogeneously mixing a small portion of sample into BaSO₄ using an agate mortar and pestle in an argon glovebox (~ 7 wt% sample in BaSO₄). Mixtures were then loaded into vials (containing an inert Ar atmosphere in the headspace) and were sealed with electrical tape before removing the vials from the glovebox for measurement. The Kubelka-Munk transform was calculated via $k/s = ((1 - R)^2)/(2R)$ where k is the absorption coefficient, s is the scattering coefficient, and R is the diffuse reflectance.

Thermodynamic calculations

Thermochemical equilibrium calculations were made using a method described by Bartel et al.²⁶ Briefly, the Gibbs free energy of formation as a function of temperature, $\Delta G_f(T)$, is calculated from the sum of density functional theory formation energy ΔH_f , tabulated elemental chemical potentials $G_i(T)$, and a machine-learning calculated correction factor $G^{\delta}(T)$ that largely corrects for vibrational entropy. The tabulated elemental chemical potentials are referenced to the FactSage database.²⁷ These calculations source crystal structures, unit cell volumes, and DFT-computed ΔH_f from the Materials Project²⁸ or our prior work in the case of Mg₂NCl.²⁹ The calculations are implemented using open source code.²⁶ From the estimated Gibbs free energies of each phase, reaction energies are calculated by summing formation energies multiplied by molar coefficients ($\Delta G_{rxn} = \Sigma n \Delta G_f$). Calculated (T = 0 K) ternary isopleths of the quaternary phase diagram are shown in Figure ??. Relevant phase formation energies are tabulated in Table ??. Temperaturedependent reaction energies are plotted in Figure ??.

Results and Discussion

Synthesis pathways to $Mg_xZr_{2-x}N_2$



Mg3N2 v Mg2NCl XRD.png

Figure 2: PXRD patterns of reaction products from syntheses targeting $MgZrN_2$ via Equations 1 and 2 show complete reactivity after annealing at a 800 °C set point for 12 h. Data (black dots), calculated patterns from Rietveld analysis (orange trace), and difference curves (blue trace) are shown. Silicon powder (denoted by the grey *) was mixed into the sample post-reaction to serve as an internal standard against which the lattice parameters were refined. Simulated patterns of the products, $MgCl_2$ and cation disordered rock salt $MgZrN_2$, are shown for reference (top boxes).

Bulk $Mg_xZr_{2-x}N_2$ powders are synthesized via metathesis reactions between $ZrCl_4$ and Mg_3N_2 or Mg_2NCl . The ideal stoichiometric reactions to produce $MgZrN_2$ from these precursors are:

$$Mg_{3}N_{2} + ZrCl_{4} \longrightarrow MgZrN_{2} + 2MgCl_{2} (\Delta G_{rxn}(1100 \text{ K}) = -0.378 \text{ eV/atom}), \qquad (1)$$

$$2 \operatorname{Mg}_2 \operatorname{NCl} + \operatorname{ZrCl}_4 \longrightarrow \operatorname{MgZrN}_2 + 3 \operatorname{MgCl}_2 (\Delta G_{rxn}(1100 \text{ K}) = -0.324 \text{ eV/atom}).$$
(2)



Figure 3: Weighted scale factor of each phase from Rietveld refinements of *in situ* PXRD data as a function of temperature. This quantitative phase analysis reveals that Mg_2NCl reacts more readily than Mg_3N_2 . In both reactions, $MgZrCl_6$ forms near 300 °C, indicating reactivity of the Mg-based reactant. However, the reaction of $2Mg_2NCl + ZrCl_4$ (bottom plot) yields $MgCl_2$ by 350 °C. In contrast, $Mg_3N_2 + ZrCl_4$ (top plot) does not yield $MgCl_2$ until $T_{rxn} = 420$ °C. Therefore, Mg_2NCl is more reactive at lower temperatures than Mg_3N_2 . Capillaries of the reagents were heated at a rate of 10 °C/min between scans and held isothermally for 7 minutes during collection of each diffraction pattern. Measurements were carried out inside a high temperature stage of a laboratory diffractometer with a Ag K α source and focusing optics. Selected PXRD patterns are shown in Figure **??**.

Upon completion of the reaction, MgCl₂ is washed away with dry methanol in an argon glovebox, leaving one crystalline phase remaining as shown by SXRD (Figures 1, ??). All of the reflections of this phase are indexed to a $Fm\bar{3}m$ phase of a disordered rock salt structure type (Figures 1, 2, ??). Diffraction peaks indicative of the cation ordered $I4_1/amd$ MgZrN₂ phase are not observed. Thin film work in the Mg-Zr-N phase space similarly finds no evidence for cation-ordered MgZrN₂, only the disordered rock salt Mg_xZr_{2-x}N₂.^{17,19–21} This finding is consistent with recent exploration of the Zn-Zr-N phase space with combinatorial sputtering, which found that the disordered rock salt structure was entropically stabilized compared to the cation ordered structure.¹⁸ While both the Mg₃N₂ and Mg₂NCl precursors react with ZrCl₄ to form the cation disordered rock salt MgZrN₂, the reactivities of these precursors differ.

In situ PXRD data show subtle differences between the two different Mg-containing precursors (Figure 3). Most prominently, the Mg₂NCl reaction yields MgCl₂ at a lower temperature (350 °C) than Mg₃N₂ (420 °C). While both reactions produce MgZrCl₆ near 300 °C, indicating some degree of reactivity, when using Mg₂NCl, the intermediate MgZrCl₆ fully reacts below 400 °C, while MgZrCl₆ persists until 420 °C in the Mg₃N₂ reaction. In both cases, the rock salt product, MgZrN₂, does not crystallize until heated above 600 °C. The ZrCl₄ phase fraction decrease is also attributed to volatization in addition to reactivity. The differences revealed by *in situ* PXRD are corroborated by *ex situ* PXRD from longer timepoint experiments.

Ex situ PXRD data show that reactions with Mg_2NCl proceed to completion within 12 h of heating at a 500 °C set point, while those beginning with Mg_3N_2 are still incomplete under identical conditions (Figure ??). This difference is not attributable to the increased reactivity of smaller particles, as the Mg_2NCl precursor used is composed of larger particle sizes than the Mg_3N_2 precursor (Figure ??). This finding is consistent with our prior study using metathesis to synthesize Mn_3N_2 , where we identify Mg_2NCl as a more kinetically competent precursor relative to Mg_3N_2 (i.e., Mg_2NCl reacts quickly and specifically).²⁹ Therefore, we used Mg_2NCl for most of our synthetic work reported here. This kinetic competence allows the metathesis routes to be selective³⁰ by accessing the $Mg_xZr_{2-x}N_2$ phase, while traditional "ceramic" reactions yield only ZrN.

Previous metathesis reactions targeting ZrN using Mg_3N_2 overlooked the possibility of ternary formation. For example, reactions between Mg_3N_2 and ZrO₂ at 1000 °C produced ZrN nanoparticles (along with MgO and N₂ byproducts).³¹ Additionally, that procedure involved washing with water, removing any of the MgZrN₂ that may have formed (which we have found to be moisture sensitive, Figure **??**). Reactions between Mg_3N_2 and various transition metal chlorides yielded binary nitrides and subnitrides (e.g., TiN, HfN, VN, V₂N, TaN, Ta₂N, CrN, Cr₂N) and reduced metals (e.g., Mo, W).^{32,33} These metathesis reactions therefore missed ternary phases that have subsequently been synthesized by other methods (e.g., MgTiN₂, MgMoN₂, MgTa₂N₃, and Mg₂Ta₂N₄).^{10,11,17} The results reported here emphasize that careful control of the reaction conditions is needed to yield ternary phases.

Control reactions following a ceramic route fail to yield the ternary MgZrN₂ target (Figure 4). The ceramic reaction should nominally proceed via:

$$Mg_{3}N_{2} + 3Zr + 2N_{2} \longrightarrow 3MgZrN_{2} \qquad (\Delta G_{rxn}(1100 \text{ K}) = -0.829 \text{ eV/atom}), \qquad (3)$$

by analogy to the synthesis of MgMoN₂.¹⁰ Analysis of diffraction data show that, rather than yielding the ternary, the product rock salt phase was ZrN with negligible Mg incorporation ($x \le 0.05$ for Mg_xZr_{2-x}N₂ after 100 h of heating at 800 °C, Figure ??). Therefore, the first reaction step is likely $2Zr + N_2 \longrightarrow 2ZrN$ ($\Delta G_{rxn}(1100 \text{ K}) = -1.363 \text{ eV/atom}$), followed by negligibly slow incorporation of Mg. Although thermodynamics predict both ceramic and metathesis routes should yield MgZrN₂, differing intermediates suggest that kinetics allow metathesis reactions succeed where the ceramic route fails.

Thermodynamic and kinetic rationale for metathesis

Although MgZrN₂ is thermodynamically stable at the synthesis temperature, this phase is impractically slow to form via the ceramic route. Gibbs free energy calculations show that at the synthesis temperature (~ 1000 °C), ZrN formation provides the most exergonic reaction per atom



Figure 4: PXRD patterns of control reactions showing that traditional bulk syntheses fail to produce $Mg_xZr_{2-x}N_2$. Mg_3N_2 and 3 equivalents of Zr powder were ground together, pelletized, placed in an alumina crucible with a Zr foil cap (to reduce Mg_3N_2 loss by evaporation and to remove adventitious oxygen) and heated in a tube furnace under flowing, purified, N_2 . Diffraction patterns from the recovered samples show ZrN and unreacted Mg_3N_2 . Rietveld analysis of the rock salt phase indicates negligible incorporation of Mg (i.e., $x \le 0.05$ for $Mg_xZr_{2-x}N_2$; Figure ??).



Figure 5: Gibbs free energy calculations show that MgZrN₂ is on the thermodynamic convex hull when Mg₃N₂ and Zr are combined with an open nitrogen atmosphere (p = 1 atm) at 1300 K (1023 °C). However, ZrN formation is much more energetically favorable than MgZrN₂ formation on a per-atom basis. Experimental results show ZrN forms first, and subsequent interdiffusion to form MgZrN₂ is negligibly slow (Figure 4). In contrast, MgMoN₂ can successfully be synthesized via the ceramic route¹⁰ because formation of the binary (MoN) is less exergonic than formation of the ternary. $\Delta G_{rxn}(1300 \text{ K})$ calculations used $\Delta G_f(1300 \text{ K})$ values determined via the method described by Bartel et al.²⁶

(Figure 5). Experimentally, the first phase to form in the ceramic synthesis is ZrN (Figure 4; $2Zr + N_2 \longrightarrow 2ZrN$; $\Delta G_{rxn}(1300 \text{ K}) = -1.271 \text{ eV/atom}$), consistent with literature showing that ceramic syntheses proceed through sequential pairwise reactions and that the most exothermic reaction tends to occur first.^{34,35} Although the subsequent reaction to yield MgZrN₂ is still exergonic (Mg₃N₂ + 3ZrN + 0.5N₂ \longrightarrow 3MgZrN₂; $\Delta G_{rxn}(1300 \text{ K}) = -0.142 \text{ eV/atom}$), we observe the process to be negligibly slow. ZrN is a refractory ceramic, often used as a diffusion barrier in microelectronics to inhibit atom migration.³⁶ Consequently, the interdiffusion of Mg into the ZrN lattice is not observed. Figure 5 also shows the differing thermodynamic landscapes for a successful ceramic synthesis, MgMoN₂, which Verrelli et al. made via Mg₃N₂ + 3Mo + 2N₂ \longrightarrow 3MgMoN₂.¹⁰ In the Mg-Mo-N system, binary formation (MoN) is less exergonic than ternary formation (MgMoN₂), and therefore MgMoN₂ synthesis is not inhibited by a refractory intermediate. Circumventing the formation of a refractory binary is key to ternary formation.

While the metathesis reaction is less exothermic than the ceramic route, this route successfully synthesizes $MgZrN_2$ by largely bypassing ZrN formation. This finding is analogous to recent work targeting the ternary sulfide, $MgCr_2S_4$.³⁷ Examining reaction enthalpies show that three stoichiometric reactions are thermodynamically competitive in a narrow composition space:

$$Mg_2NCl + ZrCl_4 \longrightarrow ZrNCl + 2MgCl_2 (\Delta G_{rxn}(1100 \text{ K}) = -0.340 \text{ eV/atom}), \quad (4)$$

$$\frac{4}{3}Mg_2NCl + ZrCl_4 \longrightarrow ZrN + \frac{1}{6}N_2 + \frac{8}{3}MgCl_2 (\Delta G_{rxn}(1100 \text{ K}) = -0.337 \text{ eV/atom}), \quad (5)$$

$$2 \operatorname{Mg}_2 \operatorname{NCl} + \operatorname{ZrCl}_4 \longrightarrow \operatorname{MgZrN}_2 + 3 \operatorname{MgCl}_2 (\Delta G_{rxn}(1100 \text{ K}) = -0.324 \text{ eV/atom}).$$
(6)

Our *in situ* PXRD data show that MgCl₂ begins forming by 350 °C when Mg₂NCl is used as a precursor and 420 °C when Mg₃N₂ is used (Figure 3). However, we are not able to detect other crystalline products at low reaction temperatures (350–500 °C), so we cannot distinguish which of these reactions (Equations 4, 5, or 6) is occurring by diffraction alone.

We hypothesize that both Equations 4 and 6 occur to some degree at low temperatures (\sim 350 °C to 500 °C) to yield intermediate nitride species undetected by XRD. ZrNCl formation is

supported by the presence of yellow-green coatings that form on the side of the ampules near 500 °C. Although these deposits are too scant for PXRD characterization, ZrNCl is known to be pale yellow-green in color and is susceptible to vapor transport.^{38,39} The entropically-favored release of N₂(g) in Equation 5 makes ZrN formation increasingly favorable at high temperatures (Figure 6). The relative stability of ZrN at T = 1100 K could yield the irreversible formation of ZrN and N₂ as the composition various during the course of the reaction (Figure ??). Therefore low temperature reactivity (~ 500 °C) is critical for the preferential formation of MgZrN₂.



Figure 6: Gibbs free energy calculations show that MgZrN₂ is on the thermodynamic hull of the Mg₂NClZrCl₄ phase space, along with ZrNCl, at each temperature calculated. At high temperatures (≥ 1100 K), ZrN production also becomes favorable. $\Delta G_{rxn}(T)$ calculations used $\Delta G_f(T)$ values determined via the method described by Bartel et al.²⁶ At low temperatures (e.g., 527 °C), the reaction producing ZrN (with N₂ gas loss) is not thermodynamically favored relative to the other two reactions. The full compositional range of the convex hull is shown in Figure **??**.

At elevated temperatures (~ 800 °C), Gibbs free energy calculations show that MgZrN₂, ZrN, and ZrNCl are stable metathesis products in the Mg-Zr-N-Cl phase space, depending on the composition. MgZrN₂ + 3MgCl₂ is the most thermodynamically stable product combination given reactants $2Mg_2NCl + ZrCl_4$ (Equation 6, Figure 6). At $ZrCl_4:Mg_2NCl :: 1:n$ ratios near n = 1.33, $ZrN + \frac{1}{6}N_2 + \frac{8}{3}MgCl_2$ is thermodynamically competitive (Equation 5), followed by $ZrNCl + 2MgCl_2$ near n = 1.0 (Equation 4). We have experimentally observed crystalline ZrNCl formation at n = 1.16 ($T_{rxn} = 950$ °C, Figure ??). While these calculations consider line compounds (e.g., MgZrN₂) rather than non-stoichiometric compounds like Mg_xZr_{2-x}N₂, the fact that both ZrN and MgZrN₂ are thermodynamically stable and structurally similar supports the mixing of those two phases at the atomic level (i.e., as a solid solution), as biphasic mixtures, or somewhere in between.



Solid solution behavior of $Mg_x Zr_{2-x}N_2$

Figure 7: SXRD, EDS, and ICP-AES show similar trends in cation composition in the metathesis product as a function of precursor ratios. As Mg_2NCl increases relative to $ZrCl_4$, Mg-content in $Mg_xZr_{2-x}N_2$ increases systematically. However, the amount of Mg into the rock salt structure is less than predicted by the balanced equation (x = (6n - 8)/(3n - 2) for $4/3 \le n \le 2$, black dashed trace, Equation 7). Shaded regions show uncertainty, as defined by a 1% increase in the goodness of fit parameter (SXRD), or one standard deviation about the mean from replicate measurements (ICP-AES, EDS). Sources of uncertainty are discussed in the text.

 $Mg_xZr_{2-x}N_2$ exhibits solid solution behavior in the rock salt structure. SXRD data shown in Figure 1 were analyzed with the Rietveld method to show that Mg content in the rock salt increases as the amount of Mg_2NCl increases relative to $ZrCl_4$ in the precursor mix (Figure 7). This trend is also correlated with a shift in diffraction peaks to higher angles with increasing Mg content (Figure 1d). This lattice shift tracks with Vegard's law (Figure 9a). The lack of additional diffraction peaks, the shift in lattice parameter, and the variable Mg/Zr site occupancy is consistent with solid solution behavior, $Mg_xZr_{2-x}N_2$. However, Rietveld analysis alone exhibited a high degree of uncertainty, so complementary methods were used to confirm the elemental composition of the material. Uncertainty in the Rietveld analysis (shown by the grey shading in Figure 7) stems from the fact that the Goodness of Fit (χ^2) is relatively insensitive to *x* (Figure ??). EDS and ICP-AES measurements corroborate the trend in the SXRD data.



Figure 8: (a) A representative SEM-derived EDS map of a powdered n = 2.02 sample shows that Mg, Zr, and N are colocalized in the same particles. Oxygen is also present both in the particles and on the carbon tape. Mapping suggests chlorine persists in the sample, but (b) a representative EDS spectrum from a pelletized sample (n = 2.02) shows only a weak signal from this element, likely due to residual MgCl₂. Carbon and oxygen signals may be from adventitious carbon or from the carbon tape used to mount the pellet. Relative atomic fractions are shown in Figure **??**.

Equation 7 relates the stoichiometry of the precursors to the expected solid solution behavior of $Mg_xZr_{2-x}N_2$. Due to the N₂-based redox, the overall balanced reaction is shown by Equation 7 and visualized in Figure ??. We use *n* to describe the ratio of precursors (ZrCl₄:Mg₂NCl :: 1:*n*). That ratio relates to magnesium content of the rock salt product (*x* in Mg_xZr_{2-x}N₂) by n = (8 - 2x)/(6 - 3x), which shows how magnesium content in the rock salt is controlled by the precursor ratio:

$$\frac{8-2x}{6-3x}Mg_2NCl + ZrCl_4 \longrightarrow \frac{1}{2-x}Mg_xZr_{2-x}N_2 + \frac{1-x}{6-3x}N_2 + \frac{16-7x}{6-3x}MgCl_2$$
(7)

This equation is valid for $\frac{4}{3} \le n \le 2$, which allows for $0 \le x \le 1$. Plotting this equation along with experimental measurements of *x* as a function of *n* (black dashed trace, Figure 7) shows that reactions systematically yield Mg-deficient Mg_xZr_{2-x}N₂ compared to the expected Mg content. A deficiency in Mg is consistent with the hypothesis that the Mg_xZr_{2-x}N₂ is an inhomogeneous mixture of Mg-rich domains with ZrN-like domains, which is discussed below in light of the optical properties. In our reactions, we observe brown deposits on the side of the quartz ampules for $T_{rxn} \sim 800$ °C, consistent with loss of Mg from the reaction.



Figure 9: (a) Rietveld analysis of PXRD data (referenced to a silicon internal standard) shows that the lattice parameter (*a*) decreases with increasing Mg content in the rock salt $Mg_xZr_{2-x}N_2$. For reference, Vegard's law between single crystal ZrN (a = 4.585 Å)⁴⁰ and thin film MgZrN₂ (a = 4.537 Å)¹⁹ is shown by the grey dashed line. The error bar around ZrN approximates the lattice parameter variation with nitrogen off-stoichiometry and oxygen incorporation.⁴¹ Increasing Mg content is correlated with broader PXRD peaks, which are best modeled by (b) decreasing crystallite size and (c) increasing strain. Crystallite size refers to the average diameter of ordered domains.⁴² The dotted lines connect the dots through the reaction precursor ratios of $nMg_2NCl + ZrCl_4$, with n = 1.36 on the left going to n = 2.19 on the right.

Diffraction peak broadness can also be explained by nanoscale inhomogeneity within $Mg_x Zr_{2-x}N_2$.

When the precursor mixture is near $\frac{4}{3}$ Mg₂NCl+ZrCl₄ in composition, sharp rock salt peaks are observed (Figure 1d), consistent with large crystallites of pure ZrN forming via Equation 5. However, with a higher Mg₂NCl concentration, peak broadness increases, which we model as decreasing crystallite size and increasing strain (Figure 9b, c). This peak broadness was modeled as double-Voigt functions for size and strain, after convolving with instrument broadening.⁴² This strain may arise at interfaces between ZrN-like domains ($a \sim 4.58$ Å) and MgZrN₂-like domains ($a \sim 4.54$ Å). Strain (e) between two such structures is on the same order of magnitude as the strain modeled here (e = (4.58 - 4.54)/(4.54) = 0.9%; Figure 9c). This microstrain analysis is consistent with both Equations 5 and 6 proceeding with precursor ratios of 2Mg₂NCl + ZrCl₄.

Optoelectronic properties of $Mg_x Zr_{2-x}N_2$



Figure 10: Conductivity values as a function of Mg-content (x, as quantified by ICP-AES) in pressed pellets of Mg_xZr_{2-x}N₂, compared to thin films synthesized and measured by Kim et al.²¹ The conductivity decreases as Mg content (x) increases. The bulk samples in this work are approximately two orders of magnitude less conductive than the films.

EIS measurements show a conducting to semiconducting transition with increasing *x* in Mg_{*x*}Zr_{2-*x*}N₂ (Figure 10). Although the magnitude of conductivity differs from the thin films deposited by Kim

et al., the correlation between magnesium content and electronic properties is consistent.²¹ The lower conductivity of the measurements here is attributable to grain- and particle-boundary resistance, porosity, or oxide incorporation.



Figure 11: Kubelka-Munk transformations of diffuse reflectance optical spectroscopy data show that the $Mg_xZr_{2-x}N_2$ do not match the expected absorption profile for a pure semiconductor. Rather, absorption maxima suggest the presence of plasmonic ZrN nanoparticles and oxygen-substituted ZrN, as discussed in the text. All samples appear mostly black, although the Mg-rich phase (n = 2.0; $Mg_{1.0}Zr_{1.0}N_2$) has a slightly blue tint. Inset images show the measured samples. These samples were annealed at a 800 °C set point for 12 h, washed with methanol, and diluted to 7 wt% in BaSO₄. Reflectance spectra are shown in Figure **??**.

Diffuse reflectance optical spectroscopy data do not show evidence of a semiconducting optical absorption onset, but they are instead consistent with the hypothesis that ZrN domains are present in otherwise Mg-rich Mg_xZr_{2-x}N₂ (Figure 11). These bulk samples appear black or black with a hint of dark blue, and are absorbing across the visible spectrum at all values of x. Similarly, the absorption profile previously reported for thin films of Mg_xZr_{2-x}N₂ show high absorption coefficients for metallic compositions (i.e., x < 0.8).^{19,21} In contrast, Mg-rich thin films, with Mg_xZr_{2-x}N₂ having x > 0.8, show an absorption onset of 1.8-2.2 eV, with high absorption coefficients (~ 10⁵ cm⁻¹) above the bandgap and low absorption coefficients below the bandgap

(~ 10^4 cm^{-1}). The bulk powders here show peaks in the optical spectra (as opposed to plateaus). Nanoparticles of ZrN are known to exhibit plasmon resonances, with absorption peaks in the range of 1.9 eV to 2.1 eV (653 nm to 585 nm).^{31,43,44} These absorption peaks vary in energy with particle size, shape, and surrounding dielectric media.⁴⁵ Small degrees of Mg incorporation may further change the absorption energy in ways that go beyond the scope of this study.⁴⁶ Small ZrN nanoparticles included within Mg_xZr_{2-x}N₂ may explain the absorption peak observed for (Mg_{1.0}Zr_{1.0}N₂). While bulk ZrN typically appears golden in color (due to surface plasmon resonance), oxide incorporation turns the material black.⁴⁷ Therefore, it is possible that our Mg-poor samples (e.g. $x \le 0.5$) contain some amount of oxygen, likely from the commercially sourced Mg₃N₂ used to make Mg₂NCl. Furthermore, the low conductivity of Mg-rich samples suggests that any ZrN-domains that formed are electrically isolated, and therefore are a minor phase.

Conclusions

Metathesis reactions, between $nMg_2NCl + ZrCl_4$, yield bulk powders of the ternary rock salt $Mg_xZr_{2-x}N_2$ (0 < x < 1), where the resulting composition (*x*) depends on the input composition (*n*). The reaction proceeds first to a poorly-crystalline product at low temperatures (350 °C– 500 °C), and annealing above 600 °C increases the crystallinity of the ternary. Together, SXRD, EDS, and ICP-AES show that a solid solution forms between ZrN and MgZrN₂. *In situ* PXRD shows how Mg₂NCl is a more kinetically competent precursor than Mg₃N₂. However, thermodynamic calculations and microstructure analysis suggest inhomogeneity in the product phase, even with a more kinetically competent precursor. Gibbs free energy calculations suggest both ZrN and MgZrN₂ are likely to form via metathesis. Therefore, ZrN domains are likely mixed in with Mg_xZr_{2-x}N₂. Optical absorption measurements support this hypothesis, with absorption features likely due to ZrN nanoparticle plasmon resonance. Measurements of bulk electronic properties show a transition from metallic to semiconducting behavior with increasing Mg-content, consistent with thin-film literature on $Mg_xZr_{2-x}N_2$.^{17,19–21}

Low-temperature metathesis may provide a generalizable approach for targeting additional ternary nitrides. Analogous nitride halide precursors (e.g., Ca_2NCl , Zn_2NCl)^{48,49} could be paired with the appropriate transition metal chloride to target a variety of ternary transition metal nitrides. While prior work using Mg₃N₂ and Ca₃N₂ as metathesis precursors often yielded binary transition metal nitrides, subnitrides, or reduced metals,^{31,32} we suspect that more kinetically competent nitride halide precursors may permit even lower temperature routes to new phases. This work therefore illustrates a promising strategy for future success in synthesizing ternary nitrides.

Author Contributions

C.L.R. and J.R.N. conceived the project. M.J.F. and A.W. assisted with *in situ* X-ray diffraction experiments and analysis. C.L.R. performed the experiments and wrote the manuscript with guidance of A.L.P. and J.R.N.

Acknowledgements

This work was supported by the National Science Foundation (DMR-1653863). The authors thank the Analytical Resources Core, Center for Materials and Molecular Analysis at Colorado State University for instrument access and training. We thank Matthew McDermott for assistance with the Gibbs Free Energy calculations. We thank Leslie Kraynak for helpful discussions and preliminary data. Use of the Advanced Photon Source at Argonne National Laboratory was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. JRN acknowledges partial support from a Sloan Research Fellowship.

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