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Introduction

Metathesis is a powerful synthetic tool used across a wide range of chemistries. In metathesis reactions, a desired product BQ is synthesized following the general form, AQ + BX \rightarrow BQ + AX, where the units A and B trade partners and AX is an (ideally separable) byproduct. Initial reports of metathesis reactions date back to 1925, where binary sulfides were synthesized *via* inorganic solid-state reactions: *e.g.*, ZnS + CdO \rightarrow CdS + ZnO.¹ Subsequently, catalyzed olefin metathesis was discovered in the 1950's, and decades of work led to deep mechanistic understanding, expansive synthetic control, and ultimately, to the

Low-temperature synthesis of cation-ordered bulk Zn₃WN₄ semiconductor *via* heterovalent solidstate metathesis†

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Metathesis reactions are widely used in synthetic chemistry. While state-of-the-art organic metathesis involves highly controlled processes where specific bonds are broken and formed, inorganic metathesis reactions are often extremely exothermic and, consequently, poorly controlled. Ternary nitrides offer a technologically relevant platform for expanding synthetic control of inorganic metathesis reactions. Here, we show that energy-controlled metathesis reactions involving a heterovalent exchange are possible in inorganic nitrides. We synthesized Zn_3WN_4 by swapping Zn^{2+} and Li⁺ between Li₆WN₄ and ZnX_2 (X = Br, Cl, F) precursors. The *in situ* synchrotron powder X-ray diffraction and differential scanning calorimetry show that the reaction onset is correlated with the ZnX₂ melting point and that product purity is inversely correlated with the reaction's exothermicity. Therefore, careful choice of the halide counterion (i.e., ZnBr₂) allows the synthesis to proceed in a swift but controlled manner at a surprisingly low temperature for an inorganic nitride (300 °C). High resolution synchrotron powder X-ray diffraction and diffuse reflectance spectroscopy confirm the synthesis of a cation-ordered Zn_3WN_4 semiconducting material. We hypothesize that this synthesis strategy is generalizable because many Li-M-N phases are known (where M is a metal) and could therefore serve as precursors for metathesis reactions targeting new ternary nitrides. This work expands the synthetic control of inorganic metathesis reactions in a way that will accelerate the discovery of novel functional ternary nitrides and other currently inaccessible materials.

2005 Nobel Prize in Chemistry.²⁻⁶ Presently, the technique enables synthetic precision for organic and organometallic chemistry,⁷⁻¹¹ metal–organic-frameworks,^{12–14} polymers,^{15–18} and beyond. In contrast, research on inorganic solid-state metathesis mostly focused on rapid, highly exothermic syntheses for binary compounds in the 1990's and early 2000's.¹⁹ Despite the historic head-start for inorganic solid-state metathesis, synthetic control is nascent.^{20,21}

Ternary nitrides provide a prime set of materials for expanding the synthetic control of metathesis reactions. Ternary nitrides are a promising class of semiconductors,²² yet relatively few are known. This dearth of nitrides is primarily due to the synthetic challenges of realizing these materials from elemental metal (or binary) precursors and dinitrogen gas.^{22–25} Molecular (di)nitrogen, N₂, is highly stable, and high temperatures are needed to break the strong N \equiv N triple bond (945 kJ mol⁻¹).²⁶ High temperatures (>800 °C) are also needed to drive diffusion, as nitrides tend to have high cohesive energies (*i.e.*, strong M–N bonds) and slow diffusion.^{27–29} Moreover, entropic penalties disfavor nitride incorporation in solids at high temperatures (*i.e.*, gaseous N₂ is favored). Finding a synthesis temperature that is hot enough for reactivity but cool enough to avoid decomposition is therefore challenging.

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Adding to the difficulty, O_2 is more reactive towards most metals than N_2 , so syntheses must be conducted in rigorously air-free conditions to avoid the formation of oxide impurities. Consequently, the number of known ternary nitrides lags behind the ternary oxides by an order of magnitude.^{22–25} Developing new synthesis methods (*e.g.*, controlled metathesis reactions) will help narrow this disparity, and in doing so, discover new materials upon which improved technologies can be built.

Zn-containing ternary nitrides epitomize the promising applications and synthetic challenges of this class of materials. Fully nitridized compounds like $ZnSnN_2$ and Zn_3WN_4 (with metals in the highest oxidation state) are of interest as semiconductors for their high earth abundance and tunable bandgaps (spanning ca. 1 eV for ZnSnN2 to 4 eV for Zn3WN4).^{30,31} However, the bulk synthesis techniques that have been reported for Zn-M-N phases are limited to traditional ceramic methods (*i.e.*, metals $+ N_2$ or NH₃ at high temperatures) or high-pressure solid state metathesis reactions (e.g., 2 Li₃N + ZnF₂ + SnF₄ \rightarrow ZnSnN₂ + 6 LiF).^{32,33} These bulk methods have only produced fully nitridized phases when M is a main group element (i.e., LiZnN, Ca₂ZnN₂, Sr₂ZnN₂, Ba₂ZnN₂, ZnSiN₂, ZnGeN₂, ZnSnN₂).^{28,30-40} When transition metals are used in bulk syntheses, they tend to form sub-nitrides: e.g., Ti₃ZnN_{0.5}, V₃Zn₂N, Ti₂ZnN, Mn₃ZnN, and Fe₃ZnN.⁴¹⁻⁴⁶ The nitrogen-poor nature of these materials stems from the challenges described above (i.e., N2 stability, slow diffusion). Synthesizing fullynitridized Zn-M-N (where M is a transition metal) in bulk would advance technologies in which thin film nitrides have already shown promise, like photoelectrochemical energy conversion $(ZnTiN_2),^{47}$ transparent conducting oxides (ZnZrN₂),⁴⁸ and non-linear optics (Zn₃WN₄).⁴⁹

Synthesizing Zn-M-N ternary nitrides via traditional methods is difficult. Many transition metals are highly refractory, meaning high temperatures would likely be needed for interdiffusion of reactants. However, Zn has a low melting point (419 °C) and a relatively low boiling point (907 °C),⁵⁰ meaning that high temperatures would volatilize Zn away from the other metal unless special measures were taken (e.g., high pressure, closed vessels). Forming binary nitrides to use as precursors instead of metals is also challenging: Zn (like other latetransition metals) does not react with N2 at elevated temperatures, so Zn₃N₂ must be synthesized under ammonia.⁵¹ And as noted in thin film work, fully nitridized transition metal Zn-M-N phases have low decomposition temperatures on the order of 600-700 °C.24,47,48,52 These challenges mean that bulk synthesis of Zn-M-N from the elements or binaries would likely proceed only at low temperatures and extremely slowly, unless special high-pressure methods were employed (e.g., ammonothermal synthesis,33 diamond anvil cell synthesis,53 etc.).

Metathesis reactions are one promising way to circumvent the challenge of diffusion in the solid state.⁵⁴ To synthesize nitrides, this strategy starts with one nitrogen-containing precursor and one halide precursor, rather than elements or binary nitrides. The balanced reaction targets the desired phase along with a byproduct (often a halide salt). The formation of this byproduct provides a large thermodynamic driving force for the reaction and (ideally) can be washed away post-reaction. For example, Kaner *et al.* showed that mixing Li₃N with metal chlorides would produce LiCl in highly exothermic metathesis reactions that yielded a range of binary nitrides^{55–63} and some ternary nitrides.^{64,65} Alternatively, less exothermic reactions can be conducted with greater synthetic control,^{66–70} including low-temperature topotactic reactions (T_{rxn} *ca.* 200–400 °C).^{71–73} As for Zn–M–N compounds, ZnSnN₂ and ZnSiN₂ have been made using high pressure metathesis reactions, where the pressure is necessary to the loss of avoid gaseous N₂.^{32,40} Metathesis is well known for "turning down the heat" in solid-state synthesis⁷⁴ but is underutilized for synthesizing nitrides.

Here, we synthesize Zn₃WN₄ via a near-topotactic metathesis reaction between Li_6WN_4 and ZnX_2 (X = Br, Cl, F) at 300 °C and low pressure. In situ synchrotron powder X-ray diffraction (SPXRD) paired with differential scanning calorimetry (DSC) measurements reveal the reaction pathways and show that using a ZnBr₂ precursor is preferable over the fluoride or chloride analogs. High resolution SPXRD measurements indicate that the Zn₃WN₄ product is a mostly cation-ordered structure in space group Pmn2₁. We report some preliminary property characterizations for Zn₃WN₄, revealing optical absorption onsets near 2.5 eV and 4.0 eV, as well as paramagnetism consistent with some degree of disorder and off-stoichiometry. The reaction is near-topotactic, in that the structures of the Li₆WN₄ precursor and the Zn₃WN₄ product are related by a shift in anion layers but the [WN₄] tetrahedral unit is preserved. Using this synthesis approach, we also synthesized Zn₃MoN₄, albeit with lower levels of purity in our un-optimized reactions. This work demonstrates the viability of Li-M-N phases as metathesis precursors to synthesize other ternary nitride compounds, expanding the toolkit for materials discovery.

Results and discussion

In situ SPXRD measurements

 Zn_3WN_4 was successfully synthesized *via* metathesis reactions. The net reaction is:

$$Li_6WN_4 + 3 ZnX_2 \rightarrow Zn_3WN_4 + 6 LiX (X = Br, Cl, F)$$

In situ SPXRD measurements reveal that Li_6WN_4 (synthesized by a ceramic method, Fig. S1[†]) directly converts to Zn_3WN_4 via metathesis without intermediate nitride phases or solid solution behavior as a function of temperature (Fig. 1, S2 and S3[†]). However, the halide precursor exerts an influence on the reaction kinetics and thermodynamics, which ultimately impact the reaction pathway and final product purity.

In situ SPXRD measurements reveal that the reaction pathway proceeds without intermediate nitrides between Li_6WN_4 and Zn_3WN_4 . Fig. 1a shows a heatmap for X = Br as an example; subsequent examination revealed that this anion leads to the most phase pure product. The reaction of Li_6WN_4 + $3 ZnBr_2 \rightarrow Zn_3WN_4$ + 6 LiBr initiates near 170 °C and proceeds to completion within the 14 minutes of ramp time up to 310 °C (Fig. 1b). Near 170 °C, the Bragg peaks arising from crystalline Li_6WN_4 and $ZnBr_2$ begin to gradually decline in intensity.



Fig. 1 (a) Heatmap of *in situ* SPXRD data upon heating a sealed capillary of $3 \text{ ZnBr}_2 + \text{Li}_6\text{WN}_4$ at $+10 \text{ °C min}^{-1}$. Reference patterns for the reactants and products/intermediates are simulated at the bottom and top, respectively (ICSD Col. Codes 30803 for ZnBr_2 , 66096 for Li_6WN_4 , 73223 for Li_2ZnBr_4 , and 53819 for LiBr).^{75–77} Analogous plots of the ZnCl_2 and ZnF_2 reactions are in Fig. S2 and S3.† Select patterns and fits are shown for ramp temperatures of (b) 311 °C, (c) 301 °C, and (d) 170 °C. Contributions from each phase (determined *via* Rietveld fitting) are displayed as colored lines. Difference traces are offset for clarity.

Shortly thereafter, new sets of Bragg peaks that can be indexed to LiBr, Li₂ZnBr₄, and Zn₃WN₄ begin growing in intensity (Fig. 1d). The Bragg peaks corresponding to Li₂ZnBr₄ gradually decrease in intensity between 210 °C and 270 °C, increase dramatically in intensity at 275 °C, and then disappear entirely at 305 °C (Fig. 1c). Such fluctuations may stem from crystal nucleation and growth within the capillary, especially given the small spot size of the synchrotron X-ray beam, possibly combined with crystallite motion in a liquid-like medium. Diffraction images show spotty diffraction patterns, consistent with crystallite growth. These data indicate that the synthesis proceeds directly via $Li_6WN_4 + 3 ZnBr_2 \rightarrow Zn_3WN_4 + 6 LiBr$. While this process occurs, the metal halides also react with one another: 2 LiBr + ZnBr₂ \rightarrow Li₂ZnBr₄. We do not observe signs of a crystalline theoretically-predicted LiZn₄W₂N₇ structure,⁷⁸ although this does not rule out the presence or synthesizability of such a phase. Similar trends are noted with the ZnCl₂ and ZnF₂ reactions (Fig. S2 and S3[†]), as shown by sequential Rietveld analysis (Fig. 2).

Sequential Rietveld analysis of *in situ* variable temperature SPXRD measurements of the $Li_6WN_4 + 3 ZnX_2$ reactions shows that the $ZnBr_2$ and $ZnCl_2$ reactions initiate at much lower temperatures than the ZnF_2 reaction (Fig. 2). For both the $ZnBr_2$ and $ZnCl_2$ reactions (Fig. 2a and b), the concentrations of the

precursor phases start decreasing near 170 °C, followed shortly thereafter by Zn₃WN₄ and LiX formation and growth. At the same time, ternary halides Li₂ZnBr₄ and Li₂ZnCl₄ form, and are then consumed or melt near 300 °C. In contrast, the precursors of the ZnF₂-based reaction do not begin declining until over 300 °C (Fig. 2c). The concomitant decrease in Li₆WN₄ and ZnF₂ suggests reactivity, but neither Zn₃WN₄ nor LiF are detected in our data at this temperature. Instead, very weak reflections for an unknown phase appear in the data (labeled as Unk*). This phase may be a Li-Zn-F ternary, but it does not index to any known ternary fluoride unit cells, including the reported Li₂ZnF₄ phase.⁷⁹ An amorphous phase is likely present in the 400 to 570 °C region, given the decrease in precursor peaks and lack of new intermediate peaks. Zn₃WN₄ and LiF crystallize above 570 °C, along with a rocksalt phase (fit with WN, but the material may be a $(Zn,W)N_r$ phase as observed with the Mobased system, Fig. S4[†]). We did not study the ZnF₂ reactions further, given that phase-pure Zn₃WN₄ did not crystallize and given the challenge associated with washing away LiF from the product. Instead, we focus on the ZnBr₂ and ZnCl₂ reactions.

DSC measurements

DSC was employed to study the ZnBr₂- and ZnCl₂-based reactions, with reaction mixtures sealed in aluminum pans under



Fig. 2 Sequential Rietveld analysis of *in situ* SPXRD patterns yields the weighted scale factors (W.S.F.), which are plotted as a function of temperature. The W.S.F. indicates the relative phase concentrations for the crystalline phases during reactions between Li_6WN_4 and (a) ZnBr₂, (b) ZnCl₂, and (c) ZnF₂. One unknown phase (Unk*, likely a Li–Zn–F phase) is modeled using a peak fit to the most intense reflection, rather than full-pattern Rietveld analysis.

argon for the measurements. The lower exothermicity of the ZnBr₂-based reaction leads to a more controlled release of heat and greater product purity, compared to the ZnCl₂-based reaction. DSC measurements show that the ZnBr₂ reaction has three small exotherms (Fig. 3a). A gradual exotherm starts near 190 °C (a-i), followed by two exotherms near 305 °C (a-ii) and 334 °C (aiii). Peak a-i is likely a slow, solid-solid reaction of $Li_6WN_4 + 3$ $ZnBr_2 \rightarrow Zn_3WN_4 + 6$ LiBr, consistent with the *in situ* SPXRD measurement. Peak a-ii may be the reaction 2 LiBr + $ZrBr_2 \rightarrow$ Li₂ZnBr₄. Li₂ZnBr₄ melts at 326 °C,⁷⁷ so peak a-iii is likely a rapid completion of the Zn₃WN₄ formation facilitated by the presence of a liquid phase. This kind of rapid exothermic event is common in metathesis reactions; once a liquid phase forms, reaction kinetics accelerate and the heat release selfpropagates.57

The ZnCl₂ reaction (Fig. 3b) starts similarly, with a gradual exotherm between 190 °C and 280 °C (b-i), a solid–solid reaction yielding Zn₃WN₄ and LiCl. Then at ~280 °C, a massive exotherm (b-ii) initiates just below the melting point of ZnCl₂ (325 °C). This event likely corresponds to the formation of a liquid phase, such as a LiCl–ZnCl₂ eutectic (275 °C at 78% ZnCl₂ and 287 °C at 91% ZnCl₂).⁸⁰ Peak b-ii has curvature because this event releases heat so quickly that the DSC stage increases in temperature by approximately 15 °C, after which the DSC pan cools slightly (Fig. S5†). Lastly, a small endotherm is observed at 336 °C (b-iii), consistent with the melting of Li₂ZnCl₄. These results are broadly consistent with the *in situ* SPXRD results, albeit shifted slightly in temperature owing to differences in experimental configuration.



Fig. 3 DSC measurements of $\rm Li_6WN_4$ reacting with (a) 3 $ZnBr_2$ and (b) 3 $ZnCl_2.$ Inset photos show the products from reactions heated at 300 °C for 1 h.

These DSC results show why the ZnBr₂ reaction yields the purest product while the ZnCl₂ reaction exhibits a small Zn impurity. The rapid release of heat in the ZnCl₂ reaction causes small portions of the material to decompose: Zn₃WN₄ \rightarrow W + 3 Zn + 2 N₂ or Zn₃WN₄ \rightarrow WN + 3 Zn + 3/2 N₂ (Fig. S6†). In contrast, the washed product of the ZnBr₂ synthesis yielded a PXRD pattern with all Bragg peaks indexed to *Pmn2*₁ Zn₃WN₄. These differences can easily be seen in the color of the material (see insets, Fig. 3), where Zn impurities in the ZnCl₂ reaction led to a grey color. The Zn₃WN₄ sample produced by the ZnBr₂ reaction is light brown and was phase pure (as discussed subsequently). These differences stem from both thermodynamic and kinetic factors.

Thermodynamic and kinetic factors

Zn₃WN₄ is calculated to be thermodynamically stable at moderate temperatures, so differences in product purity reflect differences in kinetic control for the ZnX₂ reactions. For each halide, the reactions are calculated to be enthalpically driven (*i.e.*, negative $\Delta H_{\rm rxn}$, Fig. 4). Furthermore, chemical potential diagrams show that Li₆WN₄ and Zn₃WN₄ share a border in chemical potential space (Fig. S7[†]), indicating that diffusion can occur between these phases without nucleating an intermediate phase at the interface,⁸¹ as previously shown for metathesis reactions towards ternary oxides and nitrides.^{70,82} However, Zn₃WN₄ is only stable down to a nitrogen chemical potential of $\mu_{\rm N} = -0.26$ eV when at 300 °C (Fig. S7a and b⁺), whereas these reactions were conducted in evacuated ampules $(p < 0.03 \text{ torr}, \mu_N < -0.5 \text{ eV})$. This means thermodynamics favor some N_2 (g) evolution from the reaction (with Zn and W as decomposition products). Therefore, the fact that the ZnBr₂ reaction proceeds without detectable decomposition means the reaction is fully under kinetic control, while the ZnCl₂ and ZnF₂ reactions are not.

Fig. 4 The initial formation of Zn₃WN₄ (as detected by in situ SPXRD) is correlated with the melting point of the halide salt (from CRC values)⁵⁰ but is not correlated with calculated reaction enthalpy (ΔH_{rxn} , color, from the materials project).⁸⁴ The dashed line shows where melting point would equal onset temperature.

The magnitude of the exothermicity combined with the melting points of the halide salts affect the degree of kinetic control. The lowest melting point we can identify in the LiBr-ZnBr₂ system is 326 °C for Li₂ZnBr₄,⁷⁷ meaning the reaction may be controlled by solid-state diffusion below this point. Additionally, the ΔH_{rxn} of the ZnBr₂ reaction (-0.20 eV per atom) is less exothermic than the $ZnCl_2$ reaction (-0.25 eV per atom), which may limit local self-heating and avoid decomposition (Fig. 3a). In contrast, the liquidus line in the LiCl-ZnCl₂ system extends as low as 275 °C,80 at which point diffusion accelerates rapidly (Fig. 3b, peak b-ii). Even if the temperature is kept lower (e.g., 250 °C), partial Zn₃WN₄ decomposition is observed in the ZnCl₂ system (Fig. S6[†]). This decomposition indicates a loss of kinetic control. The ZnF₂ reaction is worse. The high melting point of ZnF₂ (872 °C)⁵⁰ means the kinetics are sluggish until the reaction is perilously close to the decomposition temperature (estimated near 700 °C, Fig. S7c and d†), at which point the selfheating from the high exothermicity ($\Delta H_{\rm rxn} = -0.40$ eV per atom)83 likely drives substantial decomposition (Fig. 2c). In contrast, the ZnBr2-based reaction retains kinetic control as the moderate melting point of Li-Zn-Br phases enable diffusion near 300 °C while the low $\Delta H_{\rm rxn}$ prevents excessive self-heating, thereby avoiding decomposition.

This type of reaction control has been explored in oxides but is less well studied for ternary nitrides. "Spectator ions" that are not incorporated into the final product still have substantial influence over reaction pathways and polymorph formation, as demonstrated for syntheses of Y-Mn-O phases.21,82,85-88 In particular, work on "co-metathesis" identified that when eutectic halide mixtures form in situ, these liquids decrease reaction onset temperatures relative to systems without eutectics.85,86 Similar eutectics are likely forming between ZnX2 and LiX in our syntheses of Zn₃WN₄. This thermodynamic analysis, along with in situ SPXRD and DSC measurements, guided our optimization of the synthesis for Zn₃WN₄.

Structural and composition analysis of Zn₃WN₄

The best conditions we found for the synthesis of Zn₃WN₄ were heating ZnBr₂ with Li₆WN₄ at a ramp of +5 °C min⁻¹ to 300 °C for a 1 h dwell, followed by natural cooling in the furnace. This reaction was scaled up to ca. 1 g of reactant mix for ex situ analysis. Washing with anhydrous methanol successfully removed byproduct LiBr and excess ZnBr₂ while preserving the targeted phase. We subsequently learned that Zn₃WN₄ does not appear to be moisture or air sensitive, so washing with water may be viable in future work. We used a slight excess of ZnBr₂ $(3.1 \text{ ZnBr}_2 + \text{Li}_6 \text{WN}_4)$ to ensure complete conversion and minimize reaction temperature by acting as a heat sink. XRF measurements show a Zn : W ratio of 3.165(3): 1, slightly higher than the expected 3:1 ratio of Zn₃WN₄ (representative XRF spectrum shown in Fig. S8[†]), which may be a result of the excess ZnBr₂. PXRD techniques confirmed that this synthesis of Zn₃WN₄ proceeded without the formation of decomposition products (*i.e.*, Zn, $(Zn,W)N_x$ phases).

High resolution SPXRD measurements confirm the successful synthesis of Zn₃WN₄ (Fig. 5). Rietveld analysis of the SPXRD data (Fig. 5a) shows that Zn₃WN₄ crystallizes in space group $Pmn2_1$ with lattice parameters a = 6.5602(8) Å, b =5.6813(7) Å, and c = 5.3235(2) Å. The presence of intensity at the (010), (110), (101), and (011) Bragg positions indicates a substantial degree of cation ordering (Fig. 5c and f). The peaks for the (210), (002), and (211) reflections are characteristic of wurtzite-derived structures; these correspond to the (100), (002), and (101) reflections in the prototypical wurtzite structure $(P6_3mc)$, respectively (Fig. 5b and e). Rietveld-refined occupancies suggest a Zn:W ratio of 3.8:1, a higher ratio than that measured by XRF (3.2:1), with partial occupancy of Zn on the W site (Table S1[†]), indicating a composition of Zn_{3.17}W_{0.83}N₄ (Fig. 5d). The occupancies of the N atoms refined to 1 within error and so were fixed at unity. Alternative structural models were also considered, as discussed further in the ESI (Table S2 and Fig. S9-S11).[†] We selected the single-phase model shown in Fig. 5 as it is the simplest model that effectively describes both the diffraction data (presented here) and the optical data (discussed subsequently).

Our metathesis approach yielded a different polytype for Zn₃WN₄ compared to prior thin film syntheses. Metathesis between Li₆WN₄ and ZnBr₂ successfully synthesized Zn₃WN₄ in space group Pmn2₁ (Fig. 5). In contrast, prior thin film sputtering work produced cation-disordered P63mc structures.23,52,89 While both the $Pmn2_1$ and $P6_3mc$ structures are wurtzitederived, the cation-ordered structure is expected to be the thermodynamic ground state.^{23,48} In thin film sputtering, highenergy plasma precursors deposit onto a substrate and quench rapidly in a local energy minimum, thus locking in the disordered cation arrangement.48 While bulk syntheses can sometimes lead to cation-disordered structures, 28,32,66,67,70 the high

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Fig. 5 (a) High resolution SPXRD data (black dots) and Rietveld refinement (orange trace) of Zn_3WN_4 powder. Simulated patterns are shown for reference: (b) the cation-disordered $P6_3mc$ model and (c) the fully ordered $Pmn2_1$ model. Visualizations of (d) the $Pmn2_1$ structure of Zn_3WN_4 refined from the SPXRD data, (e) the cation-disordered $P6_3mc$ model, and (f) the fully ordered $Pmn2_1$ model.

charge on W(6+) likely encourages ordering to maximize the spacing between the hexavalent cations. The reaction pathway here proceeds in a way that avoids the local energy minimum of the disordered structure, instead forming a (mostly) ordered structure. This aspect of the bulk synthesis may be due to the ordered nature of W⁶⁺ in the Li₆WN₄ precursor. Further work is needed to assess the influence of reaction conditions (*e.g.*, precursor ratios, halide choice, heating profiles, *etc.*) on cation ordering, as the degree of cation ordering affects the optical properties of the material.

Property measurements

Diffuse reflectance spectroscopy measurements reveal two absorption onsets for Zn_3WN_4 : one near 2.5 eV and another near 4.0 eV (Fig. 6). The absorption feature near 4.0 eV is consistent with the expected bandgap for long-range cationordered Zn_3WN_4 (*i.e.*, the *Pmn2*₁ space group). The GWcalculated indirect band gap for this phase is 3.96 eV, with a direct bandgap of 4.20 eV (NREL MatDB ID 287103; blue trace in Fig. 6).^{90,91} Other researchers using a hybrid functional, HSE06, calculated the bandgap to be 3.60 eV.⁴⁹ The absorption feature near 2.5 eV is similar to the 2.0 eV to 2.4 eV absorption onset reported for cation disordered Zn_3MON_4 and Zn_3WN_4 synthesized as thin films.^{52,89} Computational work on similar materials has shown that localized, mid-gap electronic states arise when N atoms have Zn-rich coordination.⁹² These two optical features are consistent with the Rietveld analysis of our Zn_3WN_4 powder sample (Fig. 5): long-range cation order is present (leading to the 4.0 eV absorption) along with some Zn anti-site defects on the W position (which lead to Zn-rich



Fig. 6 Diffuse reflectance spectrum of Zn_3WN_4 (solid brown trace) compared with GW-calculated absorbance (dashed blue trace).

coordination for N and the 2.5 eV absorption). Magnetic susceptibility measurements are consistent with the presence of a paramagnetic impurity, as the material does not exhibit purely diamagnetic behavior (Fig. S12†). We note that the same batch of Zn_3WN_4 was used for the diffuse reflectance optical spectroscopy, magnetometry, XRF, and the high resolution SPXRD measurements.

Structural relation of precursor and product

The transformation from Li₆WN₄ to Zn₃WN₄ involves slight structural rearrangements (Fig. 7). The W⁶⁺ retains its tetrahedral coordination and (for the most part) its oxidation state through the process, but the orientations of the polyhedra change. The fcc anion lattice of Li₆WN₄ converts to the hcp anion lattice of Zn₃WN₄. Visual inspection of the structures using VESTA software93 shows that one likely path for this transformation is for half of the W⁶⁺ ions in Li₆WN₄ to migrate through an octahedral site to a new tetrahedral site in Zn₃WN₄ (red annotations). However, various migration pathways may be occurring during the synthesis (e.g., W-migration between anion layers). Zn₃WN₄ has broader peaks in SPXRD data than Li₆WN₄ (Fig. 1 and 5), indicating shorter crystalline domain lengths. That difference may arise from the W in different sections of the Li₆WN₄ crystallites migrating in alternative directions (Fig. 7a, dashed orange arrow). The anion packing layers also decrease in spacing from 2.767(1) Å in Li₆WN₄ to 2.662(1) Å in Zn₃WN₄. The shortest W-W distance decreases from 4.927(1) Å to 4.646(1) Å. Lastly, the centrosymmetric structure of Li_6WN_4 (P4₂/nmc) converts to a polar structure of Zn_3WN_4 (*Pmn2*₁). We did not observe any signs of solid solution behavior (*i.e.*, $Li_{6-x}Zn_{x/2}WN_4$) in the *in situ* SPXRD studies. However, solid solution behavior may be present but undetected by the *in situ* SPXRD data if it occurs on short timescales (<30 s) or small length scales (*ca.* 10 nm).

The synthesis reported here is distinct from literature on prior metathesis syntheses of nitrides in that the ions undergoing exchange have different formal charges. All prior reports on nitride metathesis reactions have exchanged ions of the same charge (*e.g.*, displacing Na⁺ with Cu⁺ in ATaN₂, or Ca²⁺ with Mg²⁺ in A₂Si₅N₈; where A represents the exchangeable cations).^{68,71,72} Here, we replace a monovalent cation (Li⁺) with a divalent cation (Zn²⁺). While such exchange has been conducted in oxides^{86,87,94,95} and sulfides (*e.g.*, 2 NaCrS₂ + MgCl₂ \rightarrow MgCr₂S₄ + 2 NaCl),⁹⁶ to the best of our knowledge this is the first report of such an exchange in nitrides. The resulting decrease in the cation : anion ratio (from 7:4 to 4:4) means that a truly topotactic replacement is unlikely to occur. However, the transformation appears to be near-topotactic.

Generalizability to other materials

There are numerous Zn–M–N phases that have been demonstrated to be synthesizable *via* thin film sputtering but that have not yet been made in bulk. In addition to Zn_3WN_4 ,^{23,89} sputtering has been used to synthesize fully nitridized transition metal ternaries: ZnTiN₂, ZnZrN₂, Zn₂VN₃, Zn₂NbN₃, Zn₂TaN₃, and Zn₃MoN₄.^{23,24,47,48,52} Although computational predictions for these thin film materials find that cation-ordered structures are the thermodynamic ground state (Fig. 5f), these sputtered films



Fig. 7 Arrangement of $[WN_4]$ tetrahedral units when looking down (a) on one layer of Li_6WN_4 ($P4_2/nmc$) in the (201) plane, and (b) on a layer of Zn_3WN_4 ($Pmn2_1$) in the (001) plane. Red annotations in (a) show the likely displacement undergone by some W^{6+} ions in the transition to Zn_3WN_4 ($Pan2_1$) in the (001) plane. Red annotations in (a) show the likely displacement undergone by some W^{6+} ions in the transition to Zn_3WN_4 (Pa_2/nmc) in the (001) plane. Red annotations in (a) show the likely displacement undergone by some W^{6+} ions in the transition to Zn_3WN_4 via a tetrahedral (1) to octahedral (2) to tetrahedral (3) sequence, while the orange dashed arrow shows an alternative migration direction. Side views of three layers of (c) Li_6WN_4 and (d) Zn_3WN_4 stacked along the [201] and [001] directions, respectively. The shading of the [WN_4] units in (c) indicates depth. Li and Zn are omitted for clarity; they are shown in Fig. S13.[†]

tend to form in cation-disordered structure variants (Fig. 5e).^{23,24} This disorder tends to decrease the bandgap of the material by creating localized electronic states.^{29,92} Bulk syntheses could advance the development of these new semiconductors by studying the effect of structure (*e.g.*, ordering) on optoelectronic properties of these new materials.

The synthesis of Zn₃WN₄ from Li₆WN₄ and ZnX₂ suggests a promising strategy for future materials discovery of cationordered heterovalent ternary nitrides via metathesis from lithium-based ternary nitride precursors. Lithium-based ternary nitrides are the most well-studied subset of ternary nitrides,23 suggesting that many Li-M-N phases exist that could be used to synthesize additional A-M-N phases via exchange with AX_n (where A and M are metals and X is a halide). Following our results here, X should be selected to minimize reaction energy and thus minimize the risk of decomposing the target phase via gaseous N₂ loss. To demonstrate this point, we also synthesized Zn₃MoN₄ from Li₆MoN₄ and ZnBr₂ (Fig. S4[†]). Zn₃MoN₄ was the main product, but some decomposition products were also observed, indicating that additional reaction optimization is needed. Unlike in Zn₃WN₄, the ZnBr₂-based reaction was not sufficiently lowenergy to fully avoid this decomposition for Zn₃MoN₄. While we did not synthesize phase-pure Zn₃MoN₄ here, further reaction engineering, like adding NH4Cl to manage heat flow,⁶²⁻⁶⁵ may be able to produce phase-pure Zn₃MoN₄. As we found that the reaction onset temperature is correlated with AX₂ melting point, phases with high-melting temperature precursors may be difficult to synthesize below the decomposition point of the targeted ternary. Therefore, future work should consider ways to decouple the reaction onset from the AX₂ melting point. In sum, this work shows how Li-M-N phases can be promising precursors for accelerating the discovery of new ternary nitrides.

Conclusions

Here, we report the bulk synthesis of cation-ordered Zn₃WN₄, through metathesis reactions beginning from a Li-based ternary nitride precursor: $\text{Li}_6\text{WN}_4 + \text{ZnX}_2 \rightarrow \text{Zn}_3\text{WN}_4 + 6 \text{LiX} (X = \text{Br, Cl},$ F). These reactions proceed directly (*i.e.*, without nitride intermediates), as measured by in situ synchrotron powder X-ray diffraction and differential scanning calorimetry. The reaction onset temperature correlates with the melting point of the ZnX₂ precursor, allowing ZnCl2- and ZnBr2-based reactions to proceed at \leq 300 °C. The more exothermic reactions lead to greater degrees of Zn₃WN₄ decomposition, meaning that the least exothermic reaction (with $ZnBr_2$) is the most favorable for synthesis. The high resolution synchrotron powder X-ray diffraction data are consistent with cation-ordered Zn₃WN₄ (*Pmn2*₁). This finding is distinct from prior thin film syntheses, which yielded cation-disordered P63mc Zn3WN4. Diffuse reflectance spectroscopy shows that Zn₃WN₄ powders exhibit absorption onsets near 2.5 eV and 4.0 eV, consistent with a small degree of cation disorder in the mostly long-range ordered Pmn2₁ phase. Preliminary work targeting Zn₃MoN₄ from Li₆MoN₄ and ZnBr₂ suggests this synthesis approach may

Data availability

Density functional theory calculations can be found at the NREL MatDB (https://materials.nrel.gov/). The ESI† contains additional data on experimental conditions, additional PXRD patterns, *in situ* variable temperature SPXRD measurements, DSC measurements, compositional characterization, structural models, and magnetic susceptibility measurements.

Author contributions

Christopher L. Rom: conceptualization, investigation, formal analysis, visualization, writing – original draft preparation, writing – reviewing and editing Shaun O'Donnell: investigation Kayla Huang: investigation Ryan A. Klein: investigation, formal analysis Morgan J. Kramer: investigation, formal analysis Rebecca W. Smaha: investigation, writing – reviewing and editing Andriy Zakutayev: conceptualization, funding acquisition, supervision, writing – reviewing and editing.

Conflicts of interest

There are no conflicts to declare.

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