

The role of disorder in the synthesis of metastable ternary nitrides

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In materials science, it is often assumed that the most thermodynamically stable crystal structure is the easiest polymorph to synthesize. Ternary nitride materials, with many possible metastable polymorphs, provide a domain to test this assumption; for example, ZnZrN_2 is predicted to have an unusual layered “wurtzite” crystal structure and exciting optoelectronic properties, but can it be realized experimentally? Here, we synthesize hundreds of $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ thin film samples, and find metastable rocksalt-derived or boron-nitride-derived structures rather than the thermodynamically stable wurtzite structure. Computations show that this divergence is due to both entropic and enthalpic stabilization effects. Rocksalt- and boron-nitride-derived structures become the most stable polymorphs in the presence of disorder because of higher tolerances to cation cross-substitution and off-stoichiometry than the wurtzite structure. By understanding the role of disorder tolerance in the synthesis of metastable polymorphs, we can enable more accurate predictions of synthesizable crystal structures and their achievable material properties.

INTRODUCTION

Computational materials discovery is a rapidly progressing research field, with the potential to revolutionize how we design and scale up materials. However, determining whether a given predicted crystalline material is *actually experimentally synthesizable* remains a key challenge. One common assumption in research guided by density functional theory (DFT) is that the “true” DFT-predicted ground state structure, or structures with energies near the ground state energy, are the most likely to be experimentally realized. Conversely, another assumption is that increased energetic instability (i.e. formation energy farther away from the ground state energy) correlates with an increased difficulty to synthesize. However, neither of these assumptions necessarily hold, as demonstrated by multiple experimental and computational studies.[1] Recent work has emerged to further explore synthesizability in metastable materials,[2–5] but so far the research community still cannot definitively answer the simple question: “can I synthesize this material?”[6] Thus, as materials databases grow and structure predictions yield new predicted compounds for high-throughput screenings, it is increasingly pertinent that the materials discovery community develops comprehensive methods for assessing synthesizability so that we can avoid misleading false positives and negatives.

Nitride materials provide a compelling framework through which to examine synthesizability, in because they are more likely than any other anion class to crystallize in metastable phases.[3, 4, 7, 8] Recent computational predictions have yielded a multitude of new ternary nitride materials to explore,[9, 10] yet an understanding of which polymorphs are indeed synthesizable remains elusive. The

chemical and structural richness of this emerging class of materials, including their mixed ionic-covalent nature compared to oxides, provides new candidates for various applications such as hydrogen storage, photovoltaic (PV) devices, and light-emitting diodes (LEDs). One such emerging class of ternary nitrides is the II-IV- N_2 family, ternary analogs of GaN and promising candidate for PV absorbers and green LEDs. II-IV- N_2 materials are commonly studied in two prototype classes: (1) wurtzite-derived (WZ) structures, with four-fold coordinated cations (e.g. Zn-based ZnSnN_2 , ZnGeN_2 , ZnSnP_2 , ZnSiP_2),[11] and (2) rocksalt-derived structures (RS), with six-fold coordinated cations (e.g. MgTMN_2).[12] Some compounds (e.g. MgSnN_2) have been shown to co-crystallize in both of these configurations at certain growth conditions, such as at ambient temperature at Mg-rich stoichiometries or at increased synthesis temperature on GaN substrates.[7, 13, 14] However, these two structure classes are just a small subset of possible structure classes in the rich space of ternary nitrides; it remains unknown which other II-IV- N_2 polymorph structures and chemistries are stabilizable.

Of particular interest to this study is the experimentally empty region of phase space in the zinc zirconium nitride (Zn-Zr-N) material system, in particular at its II-IV- N_2 composition ZnZrN_2 , which serves as a case study to gain insight for ternary nitrides as a whole. In contrast to other II-IV- N_2 materials, ZnZrN_2 (as well as isoelectronic ZnHfN_2) has a predicted ground state $P3m1$ (156) space group structure—a layer of Zn atoms tetrahedrally coordinated by N (wurtzite-like), a layer of Zr atoms octahedrally coordinated by N (rocksalt-like), and alternating Zn and Zr layers (abab)—which has been corroborated by three different computational studies using three distinct structure prediction algorithms.[15–17] This structure is

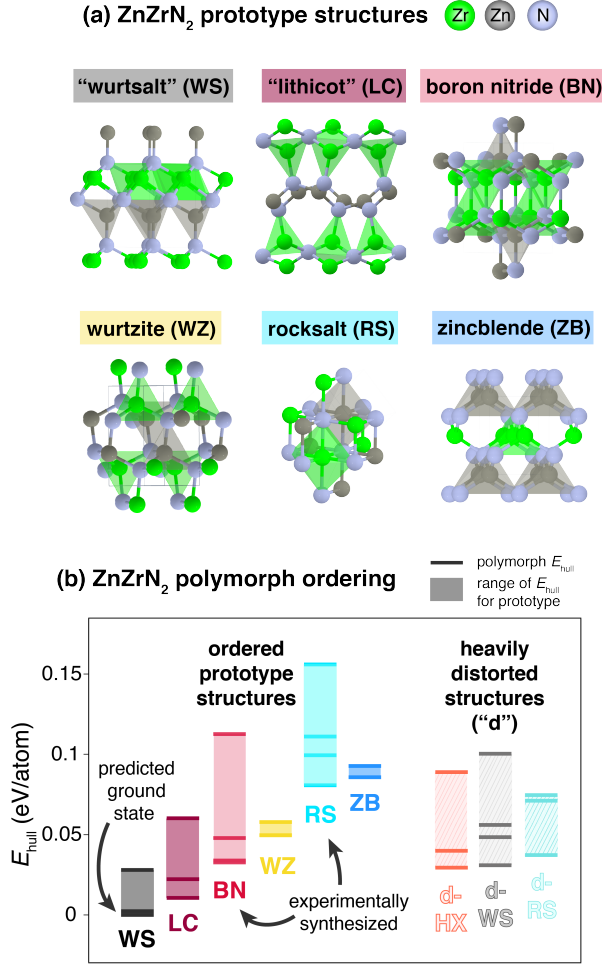


Figure 1: (a) Representative crystal structures for each of the six ordered structure prototype classes, and (b) energy ordering of the predicted ordered polymorphs, calculated by SCAN and grouped by structure prototype class, with labeled experimentally synthesized phases from this study. Horizontal solid lines in (b) correspond to calculated E_{hull} values of individual polymorphs, and shaded regions correspond to the range of E_{hull} for a given prototype class. Heavily distorted versions of the prototype structures, designated with a “d-” prefix, are plotted separately on the right of (b).

analogous to sulfosalt ScCuS_2 , though we could not locate a name for this structure;[18, 19] thus, we herein refer to this structure type as “wurtsalt” (WS), an amalgam of *wurt*-zite and *rock*-salt, and depict this structure in the top left of **Figure 1**(a), alongside other polymorphs. Despite these predictions, no semiconducting nitride materials in the $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ ternary space have ever been confirmed experimentally, and it has not yet been confirmed whether any other polymorphs exist.

In this study, we demonstrate that certain polymorphs can be preferentially stabilized or destabilized due to their tolerance to disorder. To do so, we use combinatorial sputter synthesis to explore the full cation phase space of $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ alloys, focusing on the region where $y \approx 0$ and $x \approx 0$, and computationally investigate a set of 28 possible ZnZrN_2 polymorphs. Under our experimental conditions, the predicted WS ground state is *not* synthesizable; rather, a thermodynamically metastable rocksalt (RS) polymorph

Table I: Representative ordered polymorphs from each prototype class with the lowest E_{hull} , calculated with SCAN (see SI for full list of polymorphs and energies)

Prototype class	Space group	# of atoms [†]	E_{hull} (eV/at)	E_{G} (eV)	E_{G}^{d} (eV)	m_{e}^*	m_{h}^*
WS	$P3m1$	4	0.0	2.47	3.10	7.30	1.69
LC	$Pca2_1$	16	0.0106	1.63	1.63	1.33	1.87
d-HX	$P2_1/c$	16	0.0294	2.62	2.71	3.88	2.16
d-WS	Cm	32	0.0312	2.18	2.18	1.56	1.25
BN	Cm	16	0.0327	2.01	2.01	1.36	1.49
d-RS	Pc	16	0.0373	2.22	2.47	3.41	2.17
WZ	$Pmc2_1$	8	0.0496	2.53	3.23	0.62	3.62
RS	$I4_1/amd$	16	0.0807	1.15	1.87	0.83	1.96
ZB	$P4m2$	4	0.0857	2.04	3.03	0.52	1.59

[†] Number of atoms in primitive unit cell

is energetically stabilized, and a metastable hexagonal boron-nitride-derived (BN) phase is observed at higher Zn concentrations ($x \gtrsim 0.5$). We then use a series of computational methods to explain these findings, taking into account configurational entropy and enthalpy, as well as tolerance to off-stoichiometry. These results suggest that it is necessary to consider the effects of disorder tolerance on energetic stabilization in possible polymorphs when investigating new ternary nitrides and new computationally predicted materials in general.

RESULTS AND DISCUSSION

Identifying possible ZnZrN_2 polymorphs

Although only the WS phase is reported in the Materials Project database (ZrZnN_2 , mp-1014244),[20, 21] this unexplored Zn-Zr-N phase space could host a variety of different structures. Many methods exist to determine possible polymorphs and predict synthesizable compounds,[22] ranging from simple ionic substitution, to kinetically limited minimization (KLM)[23], random structure searches,[24] or more expensive evolutionary and genetic algorithms.[25] Since no single method is fully representative of configurational space, we use the combined methods of KLM,[23] the polymorph sampler method using random structure searching,[2] and ionic substitution of prototypes from other ternary nitrides[14] to predict 28 unique possible ordered ZnZrN_2 polymorphs and assess their relative phase stability. We classify these polymorphs into six distinct structure prototype classes, with representative crystals for each of these structure prototypes depicted in **Figure 1**(a), and adopt a naming convention from binary analogs as follows: rocksalt-derived (“RS”) is an fcc anion lattice with cations in O_h -coordinated voids, wurtzite-derived (“WZ”) exhibits a structurally face-centered tetragonal anion lattice with tetrahedral coordinated cations, zincblende-derived (“ZB”, i.e. chalcopyrite) is an fcc anion lattice with cations in every other tetrahedral void, wurtsalt (“WS”) presents alternating layers of octahedrally coordinated Zr and tetrahedrally coordinated

Zn (as discussed previously), and boron-nitride-derived (“BN”) exhibits hexagonal sheets of various stackings (similar to graphite, but a 3D structure with M -N bonds between c -axis layers). An additional compound, with alternating 2D layers corresponding to the mineral litharge (PbO, with a space group $P4/nmm$) and the mineral masicot (PbO, with a space group $P2_1ca$), we name with the amalgam “lithicot” (“LC”). We also separately categorize heavily distorted versions of three of these prototypes with the prefix “d-”, using a tolerance developed from a structure matching algorithm (see SI for classification scheme details). The structure class “d-HX” (HX = hexagonal) represents structures that are distortions between BN and WZ, which are commensurate to one another. We note that Zn_3N_2 crystallizes in an anti-bixbyite-derived phase (“BX”), which is observed experimentally, but this structure is not included in our set of prototypes since deriving an analogous topotactic ZnZrN_2 BX structure requires removing atoms and is not trivial.

These candidate polymorphs are relaxed using DFT, first with a GGA functional, then with GGA with a Hubbard +U correction of 3 eV/atom for Zr,[26] and then with the SCAN functional to verify polymorph ordering (see SI). SCAN is used herein, unless specified otherwise, because it has been demonstrated to more accurately predict polymorph orderings, with the trade-off of a higher computational cost.[27, 28] Figure 1(b) plots the resulting energy ordering of the 28 ordered structures, with each polymorph grouped and colored according to its prototype structure, “ E_{hull} ” indicating the computed formation energy above the convex hull, and only including structures with $E_{\text{hull}} < 0.160$ eV/atom. Individual polymorphs are designated with horizontal lines, and the range of E_{hull} for a given prototype class is shaded. With SCAN we confirm a predicted ground state WS ($P3m1$) that lies on the convex hull, corroborating the literature.[3, 15] Other WS polymorphs ($P6_3mc$, $P\bar{3}m1$) are low in energy, ranging from 0–0.025 eV/atom, and the LC structures ($Pca2_1$, $Iba2$) are the next-lowest in energy. RS polymorphs are the highest in energy, ranging from 0.080–0.155 eV/atom. GGA and GGA+U yield similar energy orderings (c.f. SI), though LC is the predicted ground state for GGA without a Hubbard U correction (see SI). The E_{hull} values of the lowest energy structure in each prototype class, as well as their calculated band gaps (E_G) and effective masses (m_e^* and m_h^*) from SCAN, are reported in **Table I**, with the full list in the SI. Optoelectronic properties vary significantly by structure. Most polymorphs have indirect gaps except for the LC structures, most of the BN, some distorted structures, and one RS. The WZ $Pna2_1$ polymorph exhibits the largest band gap ($E_G \approx 2.99$ eV with SCAN), followed by d-HX, WS, ZB, d-RS and d-WS with $E_G > 2$ eV, while RS has among the lowest band gaps (~ 0 –1.67 eV, depending on cation ordering). Notably, the lowest-energy WS $P3m1$ polymorph have exceptionally low hole effective mass m_h^* values (< 2) compared to m_e^* values (< 7) while retaining a wide direct band gap, $E_G^d > 3$ eV. This combination of electronic structure properties is unique among

all the considered polymorphs, and extremely rare for other chemistries outside of the ZnZrN_2 material system.

Synthesis of metastable phases

Surprisingly, despite the existence of at least 19 predicted polymorphs with lower formation energy (at $T = 0$), a RS phase with a high E_{hull} is experimentally synthesized at low growth temperatures and ZnZrN_2 stoichiometry. Using combinatorial sputter synthesis, we grow a set of approximately 400 samples in the $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ ternary alloy system, with cation concentration ranging across the full Zn–Zr composition space and growth temperature ranging from ambient to 500°C. Films are grown on amorphous fused silica substrates, with Zn and Zr metallic targets and N plasma, and the combinatorial method is used to induce composition and temperature gradients (see SI for details).[29] Rutherford backscattering spectrometry (RBS) corroborates the cation concentration measured by X-ray fluorescence spectroscopy for a set of representative samples grown at ambient temperature. As shown in **Figure 2(a)**, depicting anion composition, $y = (\text{N} + \text{O})/(\text{Zn} + \text{Zr})$, as a function of cation composition, $x = \text{Zn}/(\text{Zn} + \text{Zr})$, RBS indicates N-rich compositions at Zn-poor samples, N-poor compositions in Zn-rich samples, and approximately stoichiometric N at the ZnZrN_2 composition of interest. Additionally, a small but nonzero presence of oxygen likely substitutes for N and resides on the film surface (~ 0.3 at. % in Zn-poor samples, ~ 5 at. % in Zn-rich samples due to reaction of zinc nitride with ambient atmosphere; see SI). Figure 2(a) suggests our samples have crystallized along the Zn_3N_2 – Zr_3N_4 tieline, as indicated by the exponential fit to RBS referenced to the crossed markers, with an approximate stoichiometry of $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ where $y \approx (4 - 2x)/3$. We note this system could alternately be expressed as “ $\text{Zn}_{1+x}\text{Zr}_{1-x}\text{N}_{2+y}$ ” to emphasize off-stoichiometry from ZnZrN_2 (see SI discussion). For simplicity and generality we will refer to experimental alloys as “ $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ ” herein since multiple experimental phases are observed, and focus on varying x since we are not directly varying anion concentration.

Using high-throughput synchrotron X-ray diffraction (XRD) analysis, and referencing the XRD patterns from the set of predicted polymorphs, we map the crystalline phase space by linking the structure of each of the ~ 400 samples to its corresponding ternary composition and calibrated deposition temperature, T_{dep} . The resulting map is plotted in Figure 2(b) (see SI for details about patterns and T_{dep} calibration). Rather than crystallizing in its predicted ground state WS structure at and around the ZnZrN_2 ($x = 0.5$) composition (dotted vertical line), synchrotron diffraction demonstrates a range of alloys predominantly in an RS crystal structure, which is energetically unstable according to Figure 1. We also observe the transformation to a second phase at higher x compositions, a hexagonal structure likely BN or d-HX, and a third anti-bixbyite-derived phase (“BX”) at the highest x concentrations near Zn_3N_2 (again, simulating BX ZnZrN_2 is beyond our scope). At

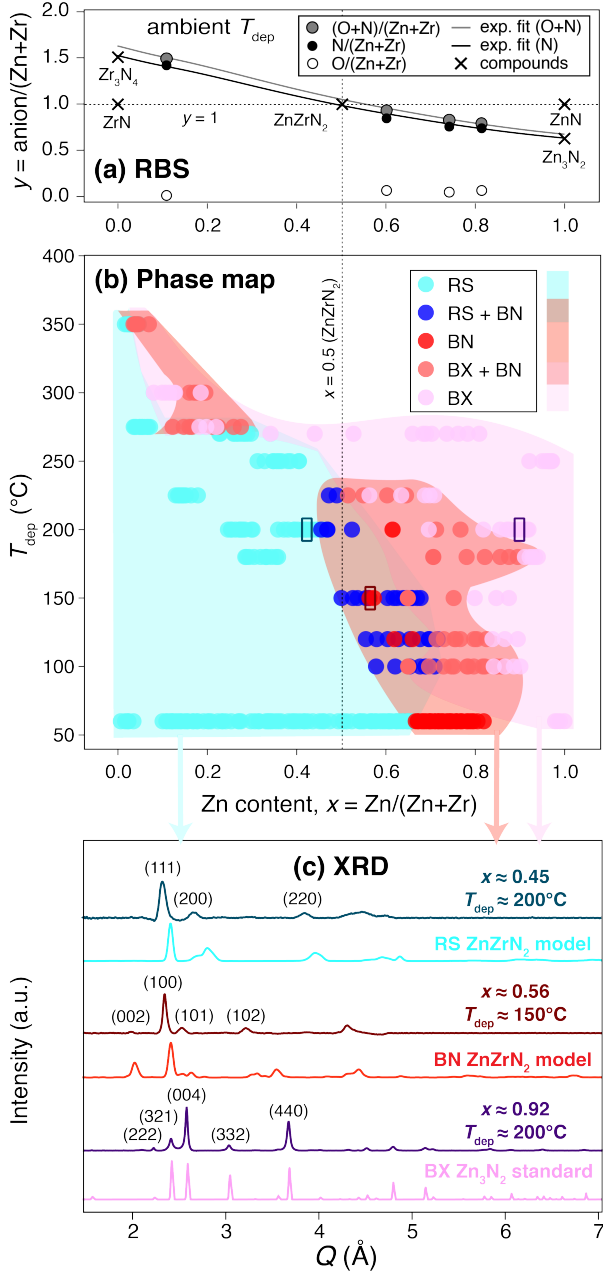


Figure 2: (a) RBS measurements of anion composition as a function of cation composition, and extrapolated with the black line. (b) Map of over 400 samples in Zn-Zr-N experimental phase space, with cation composition $x = \text{Zn}/(\text{Zn}+\text{Zr})$ on the x-axis and calibrated deposition temperature on the y-axis. (c) Representative diffraction patterns for 3 samples marked with rectangles in (b), with “modeled” ZnZrN_2 RS and BN from ensemble averages of XRD patterns from the polymorph sampler method for ZnZrN_2 compositions, and “standard” Zn_3N_2 anti-bixbyite (BX) from the Materials Project database with smearing bandwidth of 0.05.

higher temperatures, there are regions of mixed phases of these three polymorphs, perhaps due to miscibility or Zn volatility. We note that we attempted to synthesize high-temperature Zn-rich samples, but no such samples were realized due to the high vapor pressure of Zn under our growth conditions (see SI).

Figures 2(b) and (c) represent the key structural observations in $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$, where x is the cation ratio

$\text{Zn}/(\text{Zn}+\text{Zr})$. First, a RS-derived phase dominates from $x = 0$ (Zr_3N_4) up to a threshold x value, which is approximately $x \approx 0.66$ at ambient temperature growth conditions ($T_{\text{dep}} \approx 65^\circ\text{C}$, bottom of figure) and which drops as T_{dep} increases. A diffraction pattern for a representative RS sample of $x \approx 0.45$ is depicted in (c) in dark teal, compared to a modeled RS diffraction pattern in light teal, simulated as ensemble-averages from the polymorph sampler (see next section and SI for more details). As Zn increases, the XRD peaks around $Q = 2.3$ and 2.65 \AA , corresponding to RS (111) and (200), respectively (indices from the ZrN RS structure; see SI), shift to higher Q values, with the former strengthening and the latter weakening (see SI). This trade-off is likely due to shifts in texturing, as also commonly observed in other ternary nitrides.[30]

At the threshold x value ($x \approx 0.66$ at ambient temperature), there is a phase-change to a hexagonal BN-derived structure. Figure 2(c) depicts a representative BN diffraction pattern for a sample with $x \approx 0.56$ in dark red, with diffraction peaks at Q values of $\sim 2.10, 2.45$, and 2.55 \AA corresponding to BN (001), (100), and (101) reflections, respectively (with the modeled BN pattern also from the polymorph sampler, and indices from the BN structure; see SI). This transformation occurs at lower x values for samples grown in the approximately range $100^\circ\text{C} \lesssim T_{\text{dep}} \lesssim 225^\circ\text{C}$, with a large region of mixed phase RS and BN (“RS + BN”). At a second threshold composition ($x \gtrsim 0.8$ at ambient temperature, and at lower values for high temperatures) and up to 100% Zn at a stoichiometry of approximately Zn_3N_2 , a second phase transition occurs to the BX phase. The presence of a BX phase in Zn_3N_2 corroborates literature reports,[31] and may be enabled by Zr_{Zn} stabilization across phase space as indicated by a shifts to higher Q with increasing x . There are several regions of phase-segregated BX phases as well, in particular at high temperatures ($T_{\text{dep}} > 250^\circ\text{C}$) where films are likely completely phase-separating into binaries of RS Zr_3N_4 and BX Zn_3N_2 .

Overall, the measured and simulated XRD patterns correspond very well, except for the offsets in Q that are a consequence of errors in DFT lattice constants and/or experimental artifacts (e.g. off-stoichiometry, possible residual strain in the films, sample misalignment in XRD etc.). This work warrants follow-up in-depth study of this abundant alloy space and associated materials properties, but for this analysis we focus primarily on the near-stoichiometric regime around ZnZrN_2 , i.e. $x = 0.5$ (dotted vertical line in Figure 2b), which can be most easily probed computationally due to its simple stoichiometry and II-IV- V_2 chemistry.

Statistical and thermodynamic influences on polymorph stabilization

Why are the RS-derived and BN-derived ZnZrN_2 structures synthesized rather than wurtzite (WS), which is the predicted ground state at 0 K? To examine this and contextualize our experimental findings, we apply a series of

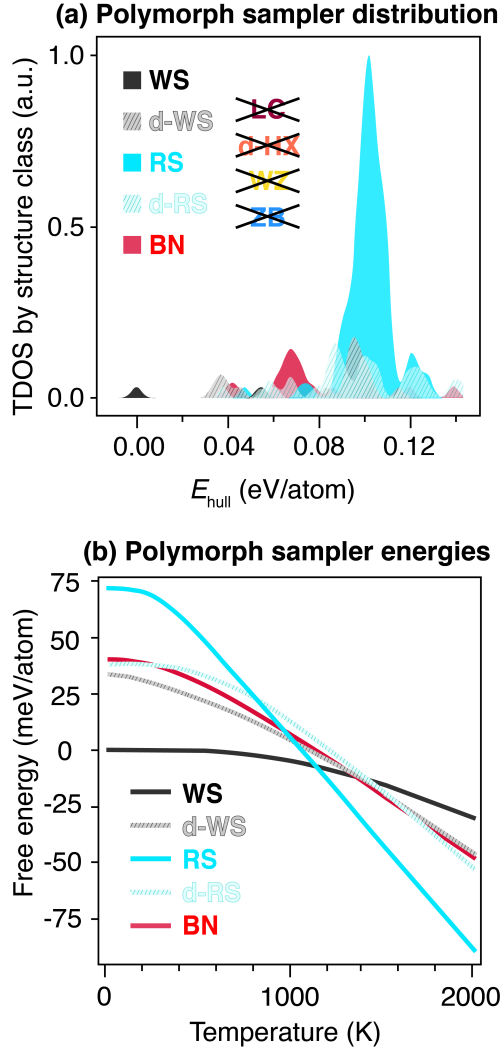


Figure 3: (a) Thermodynamic density of states (TDOS) distribution of polymorphs from the polymorph sampler using random structure searching, demonstrating a dominant RS peak, with the crossed-out phases depicting the absence of several predicted polymorph phases from (a). (b) Free energy as a function of temperature, calculated from the polymorph sampler in (a).

high- to medium-throughput computational methods to investigate the role of cation disorder and free energy on polymorph ordering. Figure 1(a) indicates that the structures with lowest formation energies exhibit unique cation coordination environments for Zr and Zn (WS, LC), while higher energy structures have similar coordination environments for all cation sites (RS, BN, WZ, ZB). Our hypothesis is that cation disordering during synthesis—enabled by rapid condensation from the vapor state to the solid state in physical vapor deposition (PVD)—favors structures with similar cation coordination environments, thus lowering the probability of the formation of WS. To assess this hypothesis, we (1) apply a polymorph sampler method to treat configurational degrees of freedom, (2) develop a random disorder descriptor to explain and understand the results of the polymorph sampler, and (3) estimate formation energies of alloys with varied cation ratios to assess the effects of off-stoichiometry.

Statistical treatment of configurational degrees of freedom

To account for the configurational degrees of freedom and the associated entropy contributions to the free energy in various ZnZrN_2 polymorph structures, we apply the “polymorph sampler” statistical approach developed by Stevanović and coworkers.[2, 32, 33] It has previously been shown that treating the spectrum of structures generated by *ab-initio* random structure sampling[24] as a proper statistical ensemble makes it possible to understand the experimental realizability of metastable crystalline polymorphs phases[2, 32] as well as the structural features of glasses.[33] Namely, crystalline structures with high ensemble probabilities — that is, high enough occurrence in random sampling and low enough energies — were shown to correlate with synthetically realized polymorphs in the chemical systems of MgO , ZnO , SnO_2 , Si , and others. Experimental enthalpies, powder X-ray diffraction patterns, and radial distribution functions of amorphous Si were also all reproduced with high accuracy when compared to the corresponding computed ensemble-averaged quantities.

Herein, the original approach is modified to include cation (lattice) disorder in the ZnZrN_2 system, the suspected phenomenon behind experimentally observed structures. The modification pertains mainly to structure classification and the statistical treatment (see SI for details). Specifically, we generate a set of 5,000 random superlattice (RSL) ZnZrN_2 structures with 24-atom cells and relax them to the closest local minimum using DFT with the GGA+U functional (note that SCAN is too computationally expensive for this many structures). The resulting spectrum of polymorph structures is split into prototype classes with the same underlying space group (see SI). Next, the ensemble probability P_k of every individual class is evaluated as:

$$P_k = \frac{\sum_{n=m}^{m+n_k} \omega_n e^{-\frac{\epsilon_n}{k_B T}}}{\Xi} = \frac{\Xi_k}{\Xi} \quad (1)$$

where k represents different prototype classes, n counts different polymorph structures within a given prototype class, ω_n is the frequency of occurrence of a structure n belonging to the class k , and ϵ_n is the total energy normalized per atom evaluated relative to the ground state structure. Lastly, Ξ_k and Ξ are the partial and the full partition functions respectively; the former pertaining only to the k -class of structures with the same underlying space group, while the latter is evaluated for the entire set of structures obtained from the random sampling.

The thermodynamics density of states (TDOS, i.e. number of structures per energy unit) resulting from the random structure sampling, normalized and resolved by the underlying structure class, is shown in **Figure 3(a)**. Two features become immediately apparent. First, consistent with the KLM algorithm and literature reports, the ground state WS structure is correctly identified, but the corresponding frequency of occurrence of this structure and the associated TDOS are very small. Second, random sampling indicates that the class of RS structures has the

largest TDOS peak (blue), indicating the flexibility of this structure class to accommodate cation disorder in a relatively narrow energy interval. While their energies span $\sim 0.04 - \sim 0.15$ eV/atom range, the largest fraction of structures is concentrated in the narrow window of 0.08–0.12 eV/atom, giving rise to the large peak shown in Figure 3(a). Additional classes of disordered structures with more significant occurrence in the random polymorph sampling are the BN (red) and the two highly distorted d-RS and d-WS classes (striped patterns), with the latter also including structures with more than one tetrahedral layer sandwiched between the octahedrally-coordinated layers of the WS structures. It is also important to note that none of the other previously discussed structure types appear in the random sampling, including the LC and WZ structure classes with $T = 0$ enthalpies lower than that of RS. This indicates that all these possible structures exhibit very “narrow” local minima in configurational energy space, leading to the very low probability of occurrence. The same is true for a relatively large number of very low symmetry structures (space groups $P1$ and $P\bar{1}$) typically obtained in random structure sampling, but since none of these structures occur in large numbers they become statistically insignificant compared to those depicted in Figure 3.

The TDOS from Figure 3(a) allows evaluating ensemble probabilities per Equation 1 and associated partial partition functions Ξ_k . These can then be used to evaluate the “configurational” free energies F_k of the corresponding structure types using the standard statistical mechanics equation:

$$F_k = -k_B T \ln \Xi_k \quad (2)$$

where k_B is the Boltzmann constant and T is the temperature. The temperature dependence of the free energies displayed in Figure 3(b) clearly shows that at low T the lowest free energy structure is the ground state WS structure, consistent with Figure 1; at $T \approx 1100$ K the disordered RS becomes the most favorable structure due to the large gain in configurational entropy at higher temperatures.[34] In the temperature range 1300–1600 K, the WS structure gives way to the disordered BN as the second most favorable structure, the order that perseveres, while at higher temperatures the d-RS takes over. This structure, if mixed with RS, would be virtually experimentally undetectable from RS because of their very similar XRD patterns. In summary, at higher temperatures the polymorph sampler procedure and the ensemble treatment suggest the following ordering of structures according to their free energies: (1) disordered RS, (2) distorted RS (d-RS), (3) BN, and (4) distorted WS (d-WS). This is consistent with experimentally observed XRD patterns that are compared with the ensemble-averaged patterns in Figure 2(c). Since previous studies have suggested that sputter deposition occurs at *effective* temperatures greater than 1150 K in ternary nitrides (note that this is *not* equivalent to synthesis temperature T_{dep} , which scales inversely with effective temperature for $T_{\text{dep}} \lesssim 600^\circ\text{C}$; see SI),[35, 36] these ensemble

probabilities and free energies support the observed behavior, i.e. the stabilization of the RS phase and the destabilization of the WS phase.

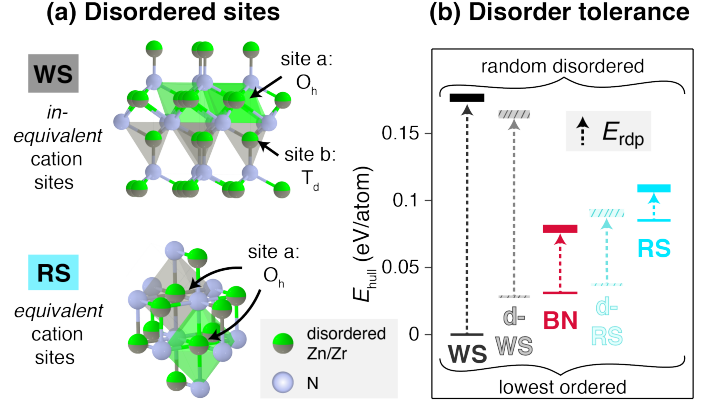


Figure 4: (a) Schematic of the WS and RS derived structures with cation site disorder. WS is an example of a structure with in-equivalent cation sites, while RS is an example of a structure with equivalent cation sites. (b) Comparison of formation energies of the lowest ordered polymorph structure and the random disordered structure, derived from special quasirandom structure (SQS) calculations, for each prototype class that emerged from the polymorph sampler (see Figure 3). The E_{rdp} descriptor is denoted by the magnitude of the dashed arrow, depicting the lower disorder tolerance for the BN and RS structures that are observed experimentally (see SI for all structure energies and details).

Configurational enthalpy of random disorder

What is the physical rationale behind the higher cation disorder tolerance in RS ZnZrN_2 , and why do we also observe BN experimentally in the Zn-Zr-N phase space? In practice, cation disorder is ubiquitous in ternary nitrides,[36–38] especially in materials synthesized at high effective temperatures (as present in sputtering). Thus, modeling small ordered unit cells may not adequately capture energetic information in these systems. Here, we explicitly consider the energetic effects of random disorder in ZnZrN_2 polymorph structures. One common method to simulate disorder is the special quasirandom structures (SQS) method, which models random atomic decorations on a lattice in relatively small unit cells.[39] This is achieved by searching for unit cells that reproduce or approximate pair (or higher order) correlation functions up to a cutoff distance by minimizing an objective function (a metric to assess the “goodness” of the disordered structure with respect to the correlation functions). Here, we calculate a set of SQS structures with 64 atoms for each structure class using the ATAT package,[40, 41] selecting only structures with the lowest objective functions (see SI and the python module `pymatgen.command_line.mcsqs_caller` for equations and details). Each SQS structure is relaxed, its formation enthalpy is computed with GGA and then SCAN, and it is assigned to its closest structure prototype class via a

structure-matching algorithm (see SI) to account for any SQS structures that relaxed to a different geometry. For each structure class k , the resulting SQS formation energies all are within ~ 10 eV of one another; these energies are then ensemble-averaged to best represent the random disorder formation energy, $\Delta H_k^{\text{disordered}}$.

Formation energies of random disordered structures are presented in **Figure 4(b)** with thick bar markers, in comparison to those of the lowest energy ordered structures of each prototype (thin bar markers), plotting only the five structure classes that emerge from the polymorph sampler (see SI for other structure classes). We find that the random disordered WS and d-WS structures have significantly higher formation energies than their ordered counterparts, with the disordered WS energy increasing drastically to over 0.170 eV/atom. In contrast, the BN random disordered structure has the lowest formation energy of all disordered structures. Although RS does not have the lowest random energy disordered structure, it is significant is that the formation energy of the RS disordered structure is very low (within 25 meV/atom) compared to that of the RS ordered structure. To assess this disorder tolerance for each class k , we introduce a new descriptor, the “random disordered polymorph energy” $E_{\text{rdp},k}$:

$$E_{\text{rdp},k} = \Delta H_k^{\text{disordered}} - \Delta H_k^{\text{ordered}} \quad (3)$$

which is the difference between the random disordered SQS structure’s energy and the energy of the lowest energy ordered structure $\Delta H_k^{\text{ordered}}$, for a given structure class. RS and BN, which are the structures that have been experimentally synthesized, have the lowest E_{rdp} values. Physically, since the $T = 0$ DFT formation energy is an approximation of formation enthalpy, the E_{rdp} corresponds to the additional *configurational enthalpy* that is introduced for each structure as a result of cation disorder. Thus, we have shown that in the ZnZrN_2 polymorph structures with inequivalent cation sites (WS, LC), disordering significantly increases enthalpy, whereas in the ZnZrN_2 structures with equivalent cation sites (RS, BN) disordering only negligibly increases enthalpy.

Furthermore, since random disordered SQS structures effectively represent high temperature structures, by qualitatively comparing the formation energies $\Delta H_k^{\text{disordered}}$ of the random disordered structures in Figure 4(b) to the statistical ensemble free energies F_k from Figure 3(b), we observe that the relative polymorph ordering changes: the RS phase is far lower in free energy F_k at high temperatures ($T \gtrsim 1000$ K), while the disordered BN phase is lowest in $\Delta H_k^{\text{disordered}}$ in Figure 4(b). Since F_k inherently includes configurational enthalpy and configurational entropy, and $\Delta H_k^{\text{disordered}}$ includes only configurational enthalpy, this suggests that the WS phase is *enthalpically destabilized*, while the RS phase is *entropically stabilized* compared to the BN and other phases. We acknowledge that these SQS disordered structures are estimates (a cluster expansion should be fit to rigorously account for local effects of cation ordering), but ultimately these estimates

support the hypothesis that disorder tolerance stabilizes the RS and BN phases over other considered polymorphs, due to both configurational enthalpy and configurational entropy.

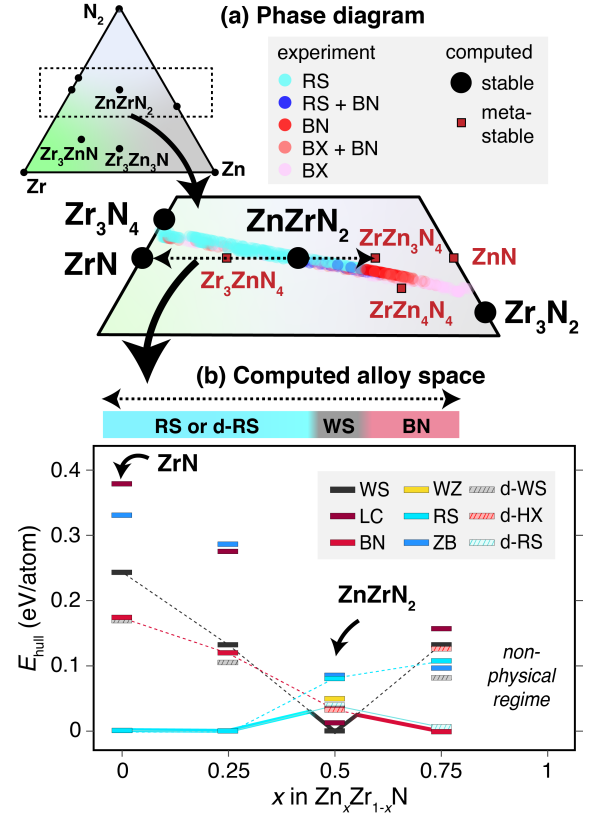


Figure 5: (a) Ternary phase diagram of Zn-Zr-N and a close-up of the $\text{Zn}_x\text{Zr}_{1-x}\text{N}$ region, with computed stable and unstable compounds from the Materials Project designated. The colored circle depict the approximate composition and associated phases of experimental data from this work. (b) Computed phase space across the alloy tie-line ZrN – Zn_3ZrN_4 , with lowest energies plotted for each computed structure. Similar structure prototypes are connected with dotted lines for the lowest energy structures. The thick line on the bottom indicates the approximate hull.

Off-stoichiometry tolerance

Lastly, we have thus far suggested why RS and BN are stabilized, but why is RS generally synthesized at Zr-rich compositions and BN at Zn-rich compositions? Another plausible explanation for the absence of WS ZnZrN_2 is that it is a *line compound*, i.e. stable only in a very narrow region of ternary phase space (see **Figure 5(a)**) and configurational energy space that we may have missed with combinatorial growth. To address this, we use a simplified alloy model. We perform cation substitution in each of the ordered ZnZrN_2 polymorph structures from Figure 1 to create a set of ordered prototypes across the ZrN – ZnN tie-line (i.e. $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ where $y = 1$ and $x = 0, 0.25, 0.50$, and 0.75), and then relax the structures and calculate their formation energies (with SCAN). We note that this is a very rough approximation, since films are N-rich

for $x < 0.5$ and N-poor for $x > 0.5$; the experimental alloy is closer to the Zr_3N_4 – Zn_3N_2 tie-line, but this heterovalent alloy is far trickier to model due to defect compensation and is beyond the scope here. Figure 5(b) plots the relative phase stability for four values of x across this tie-line, normalized to the E_{hull} for a given composition, with horizontal bar markers denoting the lowest energy polymorph of a given prototype and dotted lines connecting such values (note some absent phases, since d-RS and d-HX both relax into RS for $x = 0, 0.25$, and WZ relaxes into BN for $x \neq 0.5$). This indeed suggests a narrow window of x in which WS has the lowest E_{hull} , with RS the lowest energy polymorph for a wide window of approximately $0 < x \lesssim 0.45$, and BN (or d-RS) the lowest energy polymorph at approximately $x \gtrsim 0.55$. Removing WS and LC, following the polymorph sampler results, would suggest a phase change from RS to BN somewhere within approximately $0.45 < x < 0.55$. We do not plot $x > 0.75$ (labeled “non-physical regime”), as ZnN is a non-physical unstable compound since Zn is not stable in a +3 oxidation state, yet another phase change at high Zn content is plausible since we observe Zn_3N_2 experimentally. We note that in our alloy system $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$, the presence of a lower density hexagonal phase (BN, here) located between two higher density cubic phases (RS and BX, here) is indicative of a phenomenon in heterovalent heterostructural alloys called “negative pressure” alloys.[42, 43] Additionally, these calculations use the nominal valence of the cations, namely, Zn^{2+} and Zr^{4+} ; we do not perform defect calculations nor vary cation oxidation states. Rigorous examination of alloy phase space would require an in-depth calculation of a temperature phase diagram, which is beyond our scope, but this approximation supports our experimental observation of a phase change from RS to BN as x increases in $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$.

Other effects and implications

In principle, it is also necessary to acknowledge the role of dynamic and kinetic effects in this ternary phase space. Dynamic instabilities could be assessed by phonon calculations. As has been demonstrated in other II-IV- N_2 systems, spurious oxygen incorporation from the growth chamber can influence phase stability and result in impurity phases phases,[14] though our values below 1% from Figure 2(a) suggest that a phase-segregated oxide is not observed here. Additionally, it is important to note that the elemental Zr used in synthesis contains ~ 10 at. % Hf, which could influence relative phase stability. Finally, surface morphology, templating during growth, and kinetic effects could be assisting in restricting the formation of WS, and in enabling the preferential formation of RS. Even though these films are grown on amorphous fused silica, we also acknowledge the possibility of preferential nucleation.

As a thought experiment to assess the role of disorder tolerance in other new ternary pnictide systems, we can consider the set of II-IV- V_2 pnictide semiconductors where II = Ba, Mg, Ca, Be, Sr, Zn, Cd, IV = Si, Ge, Sn, Pb, Ti,

Zr, Hf, and V = N, P, As. Theoretically, this set includes 147 unique compositions, though only 31 of these compositions have been confirmed experimentally and only 43 other predicted compositions are in the Materials Project (MP) database, leaving 73 II-IV- V_2 compositions not on MP. Within the set of predicted but not-yet-synthesized compounds, six other systems other than ZnZrN_2 have computed ground states where cations occupy symmetrically in-equivalent lattice sites: SrGeN_2 , CaTiN_2 , ZnHfN_2 , SrZrN_2 , SrHfN_2 , and CdGeN_2 . Thus, it is feasible that higher-enthalpy polymorphs of these compounds, as well as the 73 empty compositions, could be synthesized, leading to the experimental realizability of new metastable compounds with promising properties to be explored.

CONCLUSION

In summary, we have grown the first $\text{Zn}_x\text{Zr}_{1-x}\text{N}_y$ alloys (a set of approximately 400 samples), demonstrating the crystallization of metastable rocksalt-derived (RS) and boron-nitride-derived (BN) phases rather than the predicted “wurtsalt” (WS) ground state phase. We explain these findings using a series of first-principles computational methods. First, through a statistically rigorous polymorph sampler approach, we demonstrate energetic destabilization of the predicted ground state at high temperatures, and stabilization of RS and BN phases that support our experimental results. Second, we propose that this stabilization is attributed to the increased disorder tolerance in the RS and BN phases due to only minor gains in configurational enthalpy, and suggest that the RS phase is more entropically stabilized than BN. Third, ordered alloy calculations suggest that RS and BN have a higher tolerance to cation off-stoichiometries compared to WS, and we predict a phase transformation from RS to BN as x increases that corroborates our experimental findings. We acknowledge that growth conditions matter significantly in phase stabilization, and have demonstrated the advantages of combinatorial sputtering in accessing high effective temperatures and quenching metastable states. Although WS is energetically destabilized here, its realizability is not ruled out, and this case study could provide a framework to target synthesis for WS phases (e.g. low effective temperature, epitaxial, on-stoichiometry synthesis). The optoelectronic properties of the synthesizable polymorphs in this system remain to be investigated, and Table I indicates promising properties for device applications such as contact materials, solar cell absorbers, photocatalysts, piezoelectric and ferroelectric materials.[16, 44] In particular, the synthesized BN-derived polymorph has >2 eV band gap and low (<1.5) well-matched electron and hole effective masses, making it interesting for electronic devices that can operate at elevated temperatures. Additionally, this non-polar BN polymorph is the transition state between two variants of the polar WZ structure, suggesting a pathway to tuning its predicted and measured ferroelectric response.[45, 46]

A fundamental goal of materials discovery is to bridge

the gap between computationally predicted materials and materials that can actually be grown in the laboratory with desired properties. Thus, these results are interesting beyond this specific material system; this study points to the fact that there may be many accessible energetic states that neither we nor nature have realized yet, suggests that some of these accessible states may be thermodynamically “metastable” (at $T = 0$), and offers possible routes to synthesis. Many high-throughput materials discovery studies discard materials that have an E_{hull} above a certain cut-off. However, since we have demonstrated synthesis of a polymorph phase with $E_{\text{hull}} > 0.080$ eV/atom using a common physical vapor deposition technique, we must question what other metastable phases we have been discarding. In the Zn-Zr-N system, we have suggested tolerance to disorder and off-stoichiometry are responsible for the realization of metastable phases, and have introduced a new descriptor to assess disorder tolerance, but in other systems there may be different physical mechanisms enabling synthesis of high-energy polymorphs. In general, the materials discovery community needs to continue to redefine the metrics by which we computationally assess phase stability in order to yield experimentally realizable predictions that enable new functional materials.

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SUPPLEMENTARY MATERIALS

The following supporting information is included:

- S1 Synthesis details
- S2 Composition and structural characterization
- S3 Polymorph and DFT ordering
- S4 Computational methods

AUTHOR CONTRIBUTIONS

Conceptualization, R.W.R., A.Z., K.A.P.; Methodology, R.W.R., V.S., S.L., K.H.; Computational investigation, R.W.R., V.S., S.L.; Experimental investigation, R.W.R., K.H., A.Z.; Writing, R.W.R., V.S.; Funding Acquisition, R.W.R., A.Z., V.S., K.A.P.; Supervision, A.Z., V.S., K.A.P.

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