Redox-Mediated Stabilization in Zinc Molybdenum Nitrides

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Supporting Information

ABSTRACT: We report on the theoretical prediction and experimental realization of new ternary zinc molybdenum nitride compounds. We used theory to identify previously unknown ternary compounds in the Zn–Mo–N systems, ZnMoN₄ and ZnMoN₂, and to analyze their bonding environment. Experiments show that Zn–Mo–N alloys can form in broad composition range from Zn₃MoN₄ to ZnMoN₂ in the wurtzite-derived structure, accommodating very large off-stoichiometry. Interestingly, the measured wurtzite-derived structure of the alloys is metastable for the ZnMoN₂ stoichiometry, in contrast to the Zn₃MoN₄ stoichiometry, where ordered wurtzite is predicted to be the ground state. The formation of Zn₃MoN₄−ZnMoN₂ alloy with wurtzite-derived crystal structure is enabled by the concomitant ability of Mo to change oxidation state from +VI in Zn₃MoN₄ to +IV in ZnMoN₂ and the capability of Zn to contribute to the bonding states of both compounds, an effect that we define as “redox-mediated stabilization”. The stabilization of Mo in both the +VI and +IV oxidation states is due to the intermediate electronegativity of Zn, which enables significant polar covalent bonding in both Zn₃MoN₄ and ZnMoN₂ compounds. The smooth change in the Mo oxidation state between Zn₃MoN₄ and ZnMoN₂ stoichiometries leads to a continuous change in optoelectronic properties—from resistive and semitransparent Zn₃MoN₄ to conductive and absorptive ZnMoN₂. The reported redox-mediated stabilization in zinc molybdenum nitrides suggests there might be many undiscovered ternary compounds with one metal having an intermediate electronegativity, enabling significant covalent bonding, and another metal capable of accommodating multiple oxidation states, enabling stoichiometric flexibility.

1. INTRODUCTION

The success of nitrides semiconductors in light-emitting devices has stimulated interest in the design and discovery of novel nitride materials for optoelectronic applications and other functionalities. The nitrides chemical space is much less explored than, for example, oxides, leaving considerable room for potential discovery of interesting new materials.¹ Experimental exploration of such broad chemical spaces is difficult and time-consuming, but it has recently been accelerated by high-throughput computations.² In addition to their potential application, nitrides are also interesting from the perspective of fundamental science: they are often metastable materials due to the inherent stability of the triple bond in the N₂ molecule and to the strength of the metal–nitrogen bonds.³,⁴

Despite the great scientific and technological interest, considerable challenges exist in synthesizing nitrides. Substantial progress has been made in designing nitride synthetic routes⁵−⁶ that address the difficulty of breaking the N₂ triple bond and also enable access to metastable compounds.³,⁵ These research efforts have led to discoveries of new binary (monometallic)⁷,⁸ and ternary (bimetallic) nitrides. Development of computational tools, in terms of both computational power and increasing accuracy, has been pivotal to accelerating materials’ discovery in many areas.⁹,¹⁰ Nitrides are no exception to this trend, with some examples including Zn-based ternary nitrides,¹¹ as well as nitrides with layered¹² or perovskite¹³ structures. Additionally, new classes of chemical compounds have been discovered (e.g., pernitrides¹⁴), and new functionalities have been reported (e.g., ultraincompressibility¹⁵). Nitrides have been demonstrated for a variety of applications, including catalysis,¹⁶ electrocatalysis,¹⁷ dichromism,¹⁸ plasmonics,¹⁸ and thermoelectrics.¹⁹

Of particular interest from both applied and basic perspectives are molybdenum-based nitrides. In solid-state chemistry, Mo-based nitrides can form covalent, ionic, or metallic compounds, depending on the Mo oxidation state. In ternary molybdenum nitrides, the latter depends on the...
electronegativity of the second cation, M. Highly electropositive elements (electronegativity EN ≤ 1) tend to form ionic nitridomolybdates with Mo formally in a + VI oxidation state, for example, M₂MoN₄ with M = Ca, Sr, Ba alkaline-earth metals. The electron donation from such electropositive elements stabilizes the [MoN₄]⁶⁻ units in monomeric, dimeric, or oligomeric forms. The less electropositive elements (1.55 ≤ EN ≤ 2.22) tend to form more covalent compounds with MMO₄ stoichiometry, where M = Fe, Co, or Mn, and Mo is formally in a + IV oxidation state. Transition-metal elements (Fe, Co, Ni) and Mo can also form M₂MoN₄ interstitial nitride compounds, which are metallic.

In other areas of chemistry, the ability of Mo to switch between different oxidation states enables its participation in various catalytic processes, in contrast to other transition-metal elements such as Cr or W. For example, several organisms use a Mo-containing enzyme for the N₂ fixation process. Similarly, Mo active sites cycle from + IV to + VI oxidation states in the formate dehydrogenase (FDH) enzyme, relevant to the CO₂ reduction process. Mo-based nitrides have also been shown to have superior performance in both oxygen reduction reactions (ORRs) and hydrogen evolution reactions (HERs), with the Mo redox flexibility being pivotal for these electrocatalytic processes.

Here, we report on the discovery of nitrides in the Zn–Mo–N chemical space, whose synthesis was facilitated by the ability of Mo to accommodate different oxidation states and switch between them. Despite using readily available elements, the Zn–Mo–N ternary system has not been reported in the ICDD/ICDS databases or in literature. Ab-initio calculations resulted in the prediction two new compounds with ZnMoN₂ and Zn₂MoN₄ stoichiometries in this chemical space. Experiments show that these two compounds and the metastable alloys at intermediate compositions form in the wurtzite-derived crystal structure. Retaining the same wurtzite-derived crystal structure across the ZnMoN₂–Zn₂MoN₄ alloy composition is possible due to the ability of Mo to switch between + VI and + IV oxidation states and the stability of a covalent Zn–N framework. We also show that the optoelectronic properties of Zn–Mo–N vary dramatically as a function of composition: the Zn₂MoN₄ is resistive and has a relatively wide bandgap, whereas the ZnMoN₂ is a highly optically absorbing and electrically conductive material.

2. RESULTS AND DISCUSSION

2.1. Thermodynamic Stability. According to theoretical calculations, the Zn–Mo–N system should have two ternary compounds which are readily synthesizable: ZnMoN₂ (112-phase) with space group P6₃mc (Figure 1A), and Zn₂MoN₄ (314-phase) with space group Pmm2₁ (Figure 1B). The main difference between these two structures is the Mo coordination (4-fold in Pmm2₁ and 6-fold in P6₃mc). Neither phase has been reported so far in the ICDD/ICSD databases or in literature. The predicted orthorhombic Pmm2₁ structure of the 314-phase (Figure 1B) can be described by a supercell of a wurtzite structure with ordered Zn and Mo cations in a 3:1 ratio. The orthorhombic lattice vectors are a = 2a₁h₁, b = a₂h₂, c = c₀, where a₁ and c₀ are the hexagonal lattice vectors of the wurtzite lattice. Notably, the calculated ratio a/b = 1.1559 lies within 0.1% of the ideal wurtzite ratio of 2/√3 = 1.1547, so it would be experimentally difficult to detect such a small distortion. In the following, we use the term “wurtzite-derived” structure to describe either the ordered or disordered arrangements of Zn and Mo on the tetrahedrally coordinated cation sublattice of the underlying wurtzite structure.

The tetrahedral [MoN₄]⁶⁻ coordination of the Mo atoms in the wurtzite-derived Zn₆Mo₄N₁₂ structure (P6₃mc) is similar to that in nitridomolybdates, M₆Mo₄N₁₂ (P6m) of alkali-earth metals (M = Ca, Sr, Ba) and related materials. The Mo–N bond in Zn₆Mo₄N₁₂ is 1.87–1.89 Å, comparable to 1.87 Å in Mn₆Mo₄N₁₂. However, the coordination environment of the + II cation is quite different: Zn in Zn₆Mo₄N₁₂ is tetrahedrally coordinated by N atoms (Figure 1B), whereas the alkali-earth atoms in nitridomolybdates are often octahedrally coordinated. The Zn–N bond length is on average ~2.05 Å, which is substantially shorter than the 2.60–3.05 Å Ca–N and Ba–N bond lengths observed in these orthorhombic nitridomolybdates. In contrast to the tetrahedrally (Td)-coordinated Mo(+VI) in the Zn₆Mo₄N₁₂ crystal structure (Pmm2₁), the Zn₆Mo₄N₁₂ hexagonal (P6₃mc) structure has Mo(+IV) in a 6-fold trigonal prismatic coordination, similar to what is observed in MoS₃ or MnMoN₃. The Mo–N bond length is also very similar in these compounds: 2.09–2.17 Å for the predicted ZnMoN₂ structure compared to 2.12 Å in MnMoN₂. The Zn–N ions in Zn₂MoN₄ have tetrahedral coordination (Figure 1A), unlike the octahedral coordination of Mn in MnMoN₂. The Mo–N bond lengths in Zn–Mo–N compounds are as expected for the different size of the Mo(+VI) and Mo(+IV): 1.87–1.89 Å in Zn₆Mo₄N₁₂ and ~2.13 Å in Zn₂MoN₄.

To evaluate the relative stability of the Zn₆Mo₄N₁₂ and Zn₂MoN₄ materials, we calculated stability regions (Figure 2A) and their polymorph energies (Figure 2B). At the Zn₆Mo₄N₁₂ composition, the wurtzite-derived structure is 160 meV/atom higher in energy than the ground-state hexagonal P6₃mc structure; at the Zn₂MoN₄ composition, the P6₃mc (ZnMoN₂-like structure) is 250 meV/atom higher in energy than the Pmm2₁ structure. At the intermediate Zn₂MoN₄ composition, the wurtzite-derived structure is 80 meV/atom and the P6₃mc (Zn₂MoN₄-like structure) is 260 meV/atom above the Zn₂MoN₄–Zn₂MoN₄ convex-hull tie line (Figure 2B), so this Zn₂MoN₄ phase is higher in energy with respect to the ground-states for the two ends point (Figure 2A). As shown in Figure 2B, Zn₂MoN₄ has a wider stability region than ZnMoN₂ with respect to decomposition into binary competing phases, and hence, it should be easier to synthesize. Depending upon the chemical potentials of Zn and Mo, the required nitrogen chemical potential ΔµN ranges from the mild conditions typical of conventional synthesis (ΔµN down to −1 eV), up to highly

![Figure 1. Predicted crystal structures of the (A) Zn₆Mo₄N₁₂ with Mo in 6-fold coordination and (B) Zn₂MoN₄ compounds with Mo in 4-fold coordination. For Zn, 4-fold coordination is observed in both structures. The Mo coordination polyhedrons are magenta, and the Zn coordination polyhedrons are gray.](image-url)
reactive environments achievable when a nitrogen plasma source is used (Δμ ≤ 1 eV).

2.2. Crystal Structure. A representative X-ray diffraction (XRD) pattern for a Zn−Mo−N thin film with Zn/(Zn + Mo) = 0.68 (fZn = 0.68) composition deposited in 20 mTorr pressure without any intentional heating is shown in Figure 3A.

All the XRD peaks can be indexed to the wurtzite-derived structure, with good agreement between the simulated and measured peak positions. A slightly different peak-intensity ratio was observed for the measured XRD patterns, which is a common effect for thin-film samples. Additional studies employing bulk powders or single crystals, as well as more powerful diffraction sources (such as synchrotron X-ray or neutron diffraction sources), would be required for a full experimental assessment of the atoms’ position.

The XRD patterns of the Zn−Mo−N films deposited at higher temperature (200 °C, 20 mTorr) or lower pressure (25 °C, 10 mTorr) have strong 002 preferential orientation, as shown for one representative case in Figure 3B. More XRD patterns as a function of cation composition (fZn from 0.95−0.35) and deposition conditions (e.g., temperature and pressure) are presented in Figure S1 of Supporting Information. The position of the 002 peak progressively shifts to lower diffraction angles as the Zn content decreases from fZn ∼ 0.76 to fZn ∼ 0.55 (Figures 3B and S2), although it never reaches the position typical of the 002 reflection of the ZnMoN3 (P63mc) structure. At this Zn-poor fZn ∼ 0.55 composition, the crystal quality of the films degrades, as indicated by the lower intensity and higher full width at half-maximum (fwhm) of the 002 diffraction peak (Figure 3B).

The Raman spectra further corroborate the existence of the wurtzite-derived structure of the Zn3MoN6 material and its persistence as a function of composition (Figure 4). For the fZn = 0.75 composition, there is good agreement between the measured and calculated Raman spectra. As the composition changes between fZn = 0.75 and fZn = 0.55, the Raman spectra show a gradual change of peak intensities and a slight shift in peak positions. However, no new features appear that could be ascribed to a different structure. The Raman peaks characteristic of the wurtzite-derived structure disappear at Zn content of fZn < 0.5, consistent with the XRD results for the corresponding samples. For higher Mo content, the wurtzite-derived structure was not observed for the investigated synthesis conditions.

2.3. Chemical Composition. The results of the crystal structure analysis presented above suggest that Zn−Mo−N films crystallize in a wurtzite-derived structure in a broad range of X-ray fluorescence (XRF)-measured cation compositions, from fZn = 0.8 to fZn = 0.5. The N and O content of these thin films was determined by Rutherford backscattering (RBS) (see Figure S3 for raw data and fitting results). As the films get progressively Mo-rich, the nitrogen content measured by RBS decreases from Zn94MoN67 to Zn90MoN53 (Figure S5) to maintain a cation/anion ratio of ∼1. Assuming a charge-neutrality condition, these results would imply the lowering of the Mo oxidation state from +VI to +IV. Comparing these results to the XRD results, we determined that the most Mo-rich composition at which films are still crystalline, i.e. they display well-defined RDX peaks, is Zn91MoN19.

To rule out the possibility of any amorphous phases, which could account for a large change in stoichiometry determined by XRF and RBS on the macroscopic scale, we performed microscopic analysis on the Zn−Mo−N film having fZn = 0.75 and fZn = 0.55 compositions. The scanning transmission electron microscopy—high-angle annular dark-field (STEM-HAADF) and EDS results in Figure 6 show a homogeneous distribution of elements at the nanoscale: the modulation of the cations is only ∼2% in amplitude and ∼15 nm in period. These results indicate that all the elements measured by XRF and RBS are incorporated into the crystalline structure, confirming that this material is capable of accommodating large off-
stoichiometry without amorphization or phase separation. We also note that oxygen is present in both films at levels higher than those determined from RBS (for $f_{\text{Zn}} = 0.75$, the oxygen content as determined by glancing angle RBS was found to be $\sim 11\%$ at. %), which is likely due to the exposure of the TEM lamellae to air while outside vacuum.

At larger scale, bright-field and dark-field TEM images of both stoichiometric and off-stoichiometric Zn−Mo−N films show columnar grain structure throughout the thickness of the film (Figure S4), as expected for samples prepared by physical vapor deposition. Also, no major impurity phases have been detected in the SAED patterns (Figures S5 and S6), consistent with the STEM-HAADF and EDS results in Figure 6. However, a very weak diffraction ring is present in a few of the raw SAED patterns, corresponding to a $d$-spacing of 1.16 Å. Since this ring cannot be assigned to any known binary or ternary compounds made of Zn, Mo, N, and O, we conclude that it may be attributed to an outside contamination, possibly during the measurement. The integrated SAED patterns (Figure S5) show no sign of other diffraction peaks besides those characteristic of the Zn$_3$MoN$_4$ phase, suggesting that this outside contamination is very small.

2.4. Oxidation States. The results of composition and structure measurements indicate that crystalline Zn−Mo−N thin films retain their wurtzite-derived structure in a broad range of stoichiometries. This is possible due to the ability of Mo to assume several oxidation states, which change from +VI to +IV to maintain the charge neutrality between Zn$_3$MoN$_4$ and ZnMoN$_2$ compositions. To gain insights into the Mo oxidation state at the surfaces of Zn−Mo−N thin films, we performed X-ray photoelectron spectroscopy (XPS) measurements as a function of compositions from $f_{\text{Zn}} = 0.77$ to $f_{\text{Zn}} = 0.55$ (Figures S7 and S8). A continuous shift of all XPS peaks, i.e., Mo, N and Zn core-levels, to lower binding energies was noticed as the Zn cation fraction decreased from $f_{\text{Zn}} = 0.77$ to $f_{\text{Zn}} = 0.55$. This is consistent with a change in Fermi level position in the material as a function of composition. In addition, the shape of the Mo 3d peak changed as a function of composition.

For a more quantitative description of the Mo oxidation states, as determined at the surface, the XPS peaks were spectrally decomposed following the procedure outlined in the Supporting Information. The results are shown in Figure 7 for $f_{\text{Zn}} = 0.74$ and in Figure S8 for other compositions. For the film having $f_{\text{Zn}} = 0.74$, the main component is at $230.85 \pm 0.05$ eV, which is $0.85$ eV higher than the value normally attributed to Mo (+IV). However, this value of binding energy is still lower compared to the 231.5 $\pm$ 0.2 eV that is often attributed to the formal +V oxidation state on the surface of MoO$_2$ or MoO$_3$ (Table SI in the Supporting Information). In addition, a shoulder at higher binding energy (232.50 $\pm$ 0.05 eV) is present, which is usually attributed to the presence of Mo in the +VI oxidation state in oxides.

As the composition is progressively increased toward Mo-rich, another component appears at binding energy of 229.3 eV.

Figure 5. N stoichiometry as a function of Zn stoichiometry for Mo stoichiometry equal to 1. The N content in the films decrease as the Zn content decreases in a manner that maintains the cation/anion = 1 ratio of the wurtzite structure. This change is consistent with lowering the Mo oxidation state from +VI in Zn$_3$MoN$_4$ to +IV in ZnMoN$_2$.

Figure 6. STEM-HAADF and EDS analysis of two Zn−Mo−N thin films having (a) $f_{\text{Zn}} = 0.75$ and (b) $f_{\text{Zn}} = 0.55$. The results show a columnar grain structure and quite homogeneous distribution of elements.
The trend has an analogy in the MoO density of states at the top of the Valence Band, corresponding to a formal +3.5 oxidation state. Another interesting aspect, comparing the COHP analysis results to the chemically related Sr compounds, we performed a Crystal Orbital Hamilton Population (COHP) and density-derived bond energy (see Supporting Information) analysis to understand the role of Zn in the stabilization of these new nitridomolybdates.

For Figure 8, the bonding states are qualitatively similar between the Zn$_3$Mo$_2$N$_6$ in $P6/mmc$ structure and ZnMoN$_2$ in $P6_3/mmc$ structure, with substantial bonding present for both Mo−N and Zn−N at similar energies. While the covalent bonding is deeper for both Zn−N and Mo−N in ZnMoN$_2$ compared with Zn$_3$Mo$_2$N$_6$, the extent of the covalent bonding (net bonding area (Σ)) is greater in Zn$_3$Mo$_2$N$_6$ primarily due to increased covalency of Zn−N interactions. The layered tetrahedra $[\text{ZnN}_4]$/$[\text{MoN}_4]$ of Zn$_3$Mo$_2$N$_6$ thus enable increased overall covalency for Zn−N and increased chemical hardness compared with the alternating $[\text{ZnN}_4]$ tetrahedra and $[\text{MoN}_4]$ octahedra of the ZnMoN$_2$ arrangement. Zn$_3$Mo$_2$N$_6$ also exhibits increased charge transfer between cations and nitrogen anions compared with the metallic ZnMoN$_2$, which we quantify by analyzing the ratio of summed bond-orders to density derived electrostatic charges. This is to be expected as the density-derived charge increases by ∼1 eV for Mo in Zn$_3$Mo$_2$N$_6$ compared with ZnMoN$_2$, aligning with the increase in oxidation state from +IV to +VI (Figure S8). The favorable mixed covalency bonding arrangement of the Zn$_3$Mo$_2$N$_6$ structure leads to a significant bandgap (compared with the electrically conductive ZnMoN$_2$) and retention of the wurtzite-derived structure even as $f_{\text{Zn}}$ is decreased.

The structural transition from $P6/mmc$ to $P6_3/mmc$ would require significant rearrangement: from $[\text{ZnN}_4]$ and $[\text{MoN}_4]$ tetrahedra in $Zn_3Mo_2N_6$ ($Pmn2_1$), to layered $[\text{ZnN}_4]$ tetrahedra and $[\text{MoN}_4]$ octahedra in ZnMoN$_2$ ($P6_3/mmc$). Thus, as $f_{\text{Zn}}$ is decreased from 0.75 to 0.50 and the thermodynamic driving force for forming Mo octahedra is increasing, the metastable wurtzite-derived structure remains favorable for Zn bonding and is kinetically preserved due to the reconstructive barrier toward forming the ordered layers of the 112 structure.

2.6. Optoelectronic Properties. The influence of the changing Mo oxidation state on the optoelectronic properties of the Zn−Mo−N material is dramatic. As shown in Figure 9A, stochiometric Zn$_3$Mo$_2$N$_6$ samples are quite resistive ($10^4$−$10^5$ Ωcm). The resistivity decreases with decreasing $f_{\text{Zn}}$, down to $10^{-1}$−$10^0$ Ω cm at the ZnMoN$_2$ composition. Thus, the resistivity of the films varies over 5 orders of magnitude for compositions where the material is crystalline and isostructural. This is remarkable because doping control in nitrides is usually quite challenging and requires careful tuning of processing conditions. A small dependence of resistivity on the deposition conditions was noticed, as well. For the samples having the
same cation composition in the $f_{\text{Zn}} = 0.5-0.7$ range, 10X lower resistivity is achieved when the films are grown at 25 °C and 10 mTorr, compared to 200 °C and 20 mTorr. It is also interesting to note that ZnMoN$_2$ films display temperature-activated conductivity in the 150–350 K region (Figure S10A), unlike the previously known metallic ternary molybdenum nitrides. Hall measurements were attempted on the ZnMoN$_2$ thin films but were not successful, which implies that the carrier mobility is less than 0.1 cm$^2$/V·s$^{-1}$ for these polycrystalline samples.

Optical properties of Zn–Mo–N also change as a function of composition. Progressive enrichment in Mo and the change of its oxidation state led to an increase in the absorption coefficient (Figure 9B) and a substantial reduction of the transmittance of the films (Figure S11B). The optical bandgap, estimated from the kink in the slope of the square value of the optical absorption spectrum, is in the order of 2.4 eV for $f_{\text{Zn}} = 0.75$ (Figure S11). Also, the overall absorption coefficient increases as a function of increasing Mo content. The resulting pale-yellow coloration for the ZnMoN$_2$ thin films coincides with the yellow color of the single crystals of both Sr$_3$MoN$_4$ and Ba$_3$MoN$_4$ nitromolybdates reported in literature. In comparison with the 2.4 eV optical bandgap of Zn$_2$MoN$_4$ thin films, the GW-calculated indirect and direct bandgaps for the Zn$_2$MoN$_4$ in cation-ordered orthorhombic structure are 3.82 and 3.98 eV, respectively. The difference between the experimental optical absorption onset and the theoretical band gap determined by GW calculations, could be due to Zn/Mo cation disorder and/or oxygen contamination in experimental samples. Atomic disorder has been widely studied in several materials systems and shown to play an active role in affecting the band gap of the material, and thus its optical properties.

Preliminary results on the Zn$_2$MoN$_4$ material show that disorder can induce a substantial reduction of the band gap, to values comparable to the experimental results.

3. DISCUSSION

Two new compounds with Zn$_4$MoN$_8$ and ZnMoN$_3$ stoichiometries have been synthesized and characterized, following the theoretical predictions. The calculations suggest that new ternary nitrides are likely to be observed in the Zn–Mo–N ternary system (Figure 1) and predict thermodynamic stability regions of these Zn$_4$MoN$_8$ ($Pmn_2$) and ZnMoN$_3$ ($P6_3mc$) compounds (Figure 2). Structural measurements indicate that both nitrides crystallize in the wurtzite-derived structure in the 0.75 < $f_{\text{Zn}}$ ≤ 0.50 composition range (Figures 3 and 4). As the material becomes Mo-rich, the measured anion/cation ratio remains constant (Figures 5 and 6) and the Mo oxidation state varies (Figures 5 and 7). The theoretical COHP analysis results (Figure 8) corroborate these experimental observations, and also suggest significant Zn–N bonding in both Zn$_4$MoN$_8$ ($Pmn_2$) and ZnMoN$_3$ ($P6_3mc$) compounds, in contrast to Sr$_3$MoN$_4$ ($Pbca$) which is predominantly stabilized by Mo–N bonding. The optical absorption coefficient at 2 eV increases by 10X, and the electrical conductivity increases by 10$^5$, going from Zn$_4$MoN$_8$ to ZnMoN$_3$ end-member points of the alloy (Figure 9).

Experimental XRD results (Figures 3 and 4) indicate the formation of a Zn$_4$MoN$_8$–Zn$_2$MoN$_4$ alloy with wurtzite-derived structure. On the other hand, according to theoretical calculations, the wurtzite-derived structure at Zn$_2$MoN$_4$ composition is 160 meV/atom higher in energy compared to the hexagonal $P6_3mc$ structure (Figure 2). However, even higher mixing enthalpies (∼400 meV/atom) have recently been observed in (Sn/Ti)$_3$N$_4$ typical for metastable heterostructural alloys. Additionally, in the wurtzite-derived structure, DFT calculations predict a contraction of the ZnMoN$_2$ lattice parameters compared to Zn$_2$MoN$_4$ lattice parameters. In contrast, the closest agreement with the measured XRD and selected-area electron diffraction (SAED) patterns is achieved for a simulated wurtzite-derived structure with lattice parameters expanded by 1.5%. Thus, further theoretical studies making use of cluster expansion or Monte Carlo methods would be required to assess if lower-energy configurations of wurtzite-derived structures exist at ZnMoN$_2$ composition.

The RBS composition analysis (Figure 6), combined with the XPS results (Figure 7), suggest a rather complex situation for the Mo oxidation state in Zn–Mo–N thin films. The bulk RBS analysis implies that the Mo oxidation state shifts from nominally +VI to +IV as the stoichiometry changes from Zn$_2$MoN$_4$ to ZnMoN$_3$, based on formal charge count with Zn in +II oxidation state and N in -III oxidation state. From more surface-sensitive XPS analysis, it appears that some Mo peak components have binding energies characteristic of the +VI and +V oxidation state for the stoichiometric Zn$_2$MoN$_4$ phase and an increasing concentration of +3.5 for the more Mo-rich compositions. For this Mo-rich composition, alongside the Mo +3.5 components, at least two other components are present, which could be attributed to the +V and +VI oxidation state. The presence of multiple oxidation states suggests that the nature of the Mo–N bond in Zn$_2$MoN$_4$ is not completely ionic. This is also supported by the presence of significant covalent bonding states for Mo–N (Figure 8).

There are several likely reasons for the formation of the metastable alloys with wurtzite structure in the composition range from Zn$_2$MoN$_4$ to ZnMoN$_2$. First, according to the combination of RBS and XPS measurements, the ability of Mo to adopt different oxidation states from +VI to +IV helps to accommodate a range of Zn/Mo stoichiometries. Second, this range can be accommodated by the ability of Zn to contribute to the bonding states of both Zn$_2$MoN$_4$ and ZnMoN$_3$ materials, as shown by the COHP analysis (Figure 8). The wide stoichiometry range in Zn–Mo–N materials is different than the fixed M$_x$MoN$_4$ stoichiometry of the previously reported nitromolybdates based on highly electropositive M = Ca, Sr, and Ba elements. Thus, it appears that the propensity for Zn to contribute to the bonding states, coupled with the ability of Mo to stabilize both +VI and +IV oxidation states, together enable the formation of Zn–Mo–N alloys with a wide range of stoichiometry.

Based on the results and discussion presented above, we propose the concept of “redox-mediated stabilization” to describe the formation of Zn–Mo–N materials with wurtzite-derived structure in a broad range of chemical compositions, enabled by change in the oxidation state of Mo. This concept is expected to extend beyond the Zn–Mo–N family and be applicable to other solid-state materials. In pnictides, other possible materials classes that could show redox-mediated stabilization include II–IV–P$_2$N$_5$, III–V–P$_2$N$_5$, and II–VI–P$_4$N$_4$ compounds, where II is a relatively electropositive element that contributes to the bonding states; IV, V, and VI are transition metals that can access higher or lower oxidation states; and Pn is an element belonging to the pnictides family (e.g., N, P, As). One past example of chalcogenide materials showing a similar redox-mediated stabilization in the Cu$_4$Sn$_2$S$_5$–Cu$_2$Sn$_3$S$_4$ system, where the stoichiometry variation is accommodated by the change in Cu from I+ to II+ oxidation states without...
altering the zincblende-derived crystal structure. A few examples in oxides that we are aware of include Cr$_3$MnO$_4$–CrMn$_2$O$_4$ and Fe$_3$MnO$_4$–FeMn$_2$O$_4$, both with spinel-derived crystal structures.

4. CONCLUSIONS

Redox-mediated stabilization of the crystal structure has been demonstrated in the newly discovered Zn–Mo–N ternary material system. Experimentally, we have shown that it is possible to tune the stoichiometry from Zn$_2$MoN$_2$ to ZnMoN$_2$ while retaining the wurtzite-derived crystal structure. Theoretical calculations suggest that the cation-ordered wurtzite with Pmn2$_1$ symmetry has the lowest energy only for the Zn$_2$MoN$_2$ composition, whereas the ZnMoN$_2$ composition should crystallize in the hexagonal structure with P6$_3$mc symmetry. The results of the combined theoretical and experimental analysis suggest that the formation of the metastable wurtzite Zn$_2$MoN$_2$–ZnMoN$_2$ alloy is possible because (1) Mo can accommodate multiple oxidation states, from +IV to +VI, allowing this smooth transition; and (2) Zn has an intermediate electronegativity and contributes to the bonding character of both Zn$_2$MoN$_2$ and ZnMoN$_2$ phases. The impact of the tunable composition on the optoelectronic properties is dramatic: Zn$_2$MoN$_2$ is a semitransparent and relatively resistive, whereas ZnMoN$_2$ is an electrically conductive and optically absorbing material. The demonstration of redox-mediated stabilization in the Zn–Mo–N system opens up the possibility to tune the properties by the concurrent change in chemical composition and oxidation state in many other materials with wurtzite and other crystal structures. Additional theoretical and synthetic efforts are currently underway to show the redox-mediated stabilization in other material systems.

5. METHODS

5.1. Experimental Methods. Experimental synthesis of Zn–Mo–N thin-film sample libraries was performed using combinatorial cosputtering of Mo and Zn metals in the presence of N$_2$ plasma on glass substrates in a deposition chamber with $<1 \times 10^{-6}$ Torr base pressure. Two sputtering guns were loaded with 2"-diameter Mo and Zn metal targets and positioned at 45° with respect to the substrate normal to achieve a cation compositional gradient; the N$_2$ plasma source was aligned to the normal. To access a broad range of Zn/Mo ratios, we used gun powers in the range of 25–45 W. Before the deposition, the 2" × 2" Eagle-XG glass substrates were cleaned by degreasing in water and soap, followed by ultrasonic cleaning in acetone and isopropanol baths. Depositions were performed at ambient substrate temperature to maximize the N-chemical potential, or on the heated substrate (200 °C) to improve the crystallinity. The flow of the gases was set to 10 and 30 sccm for Ar and N$_2$, respectively. The sputtering pressure was adjusted between 20 and 10 mTorr, to $\sim$4001/cm$^2$. The resulting data are available at [insert URL].

For a few selected locations on each sample library, additional detailed characterization experiments were performed. X-ray photoelectron spectroscopy measurements were performed on a Kratos Axis Nova instrument with Al Kα X-ray source. The effects of surface oxidation on the measurement results were minimized by analyzing samples on the same library and by quickly transferring the samples between deposition and characterization chambers. Rutherford backscattering was performed using a model 3S-MR10 RBS system from National Electrostatics Corporation, with either high (160°, RBS) or low (110°, RBG) scattering angles. Microscopy was performed on an FEI Co. Talsos F200X instrument in transmission electron microscopy, selected-area electron diffractions, and energy-dispersive spectroscopy modes, on specimens prepared using the focused ion beam (FIB) lift-out method. More RBS and TEM characterization details are provided in Supporting Information.

5.2. Computational Methods. The initial computational search for novel ternary metal nitrides was performed by starting from the known ternary nitrides and applying rational chemical substitutions to them, so as to extend the sampling to previously unreported compounds (DMSF algorithm). The stability of these new candidate crystal structures was evaluated by comparing their density functional theory (DFT) formation energies to those of all potential competing phases. Such a search was performed in 942 ternary metal-nitride chemical spaces (M$_i$-M$_j$-N) leading to hundreds of novel compounds found to be stable. In the previously unexplored Zn–Mo–N space Zn$_2$MoN$_2$ was identified to be stable (negative formation energy).

To sample more comprehensively the Zn–Mo–N ternary space for possible compositions and their structures, we used a modified version of the Kinetically Limited Minimization (KLM) algorithm, originally designed to sample amorphous structures, so to obtain a wider range of possible stoichiometries and their structures. This search was performed for many Zn$_2$Mo$_2$N$_2$ stoichiometries ($ijk = 112, 146, 414, 213, 124, 326, 338, 313$) chosen to accommodate the Zn$_2^+$, Mo$_{4+/5+/6+}$, and N$^{3-}$ oxidation states. However, only the Zn$_2$Mo$_2$N$_2$ and Zn$_2$Mo$_2$N$_4$ compositions were found to be stable against the binary competing phases. As the competing phases, we considered known materials Zn$_2$N$_2$ (space group SG 206), Mo$_3$N$_4$ (SG 11), MoN (SG 186), as well as KLM-predicted materials Mo$_2$N$_4$ (SG 9), and a recently reported Mo$_3$N$_4$ (SG160) pernitride. The symmetry analysis for all structures was performed with the FINDSYM software. The Crystallographic Information Files (CIF) were loaded into the MAUDUS software to simulate the reference XRD pattern. More details of the KLM calculations and the CIF files for all new stable structures are provided as Supporting Information.

The first-principles calculations in DFT and in the GW approximation were performed with the VASP code, using the PBE+U functional with U = 3 eV for Mo–O. Final total energies were calculated with an energy cutoff of 520 eV and a number of approximately 4000/k-points in the full Brillouin zone, where $n_{\text{k}}$ is the number of atoms in the unit cell. To calculate accurate lattice parameters, we performed van der Waals-corrected DFT calculations employing the optB86b-vDW functional. Within the KLM search, we successively increased the convergence criteria for samples that are likely to be accepted in the KLM sequence, while more quickly discarding unlikely high-energy structures. For evaluating the formation enthalpies and thermodynamic stability ranges of the charge-balanced compounds, we used the fitted elemental reference energies $\mu_{\text{Fe}}$. For noncharge-balanced materials such as Mo$_3$N$_4$, we use a weighted average between $\mu_{\text{Fe}}$ (Mo) and the DFT energy of metallic Mo. All electronic structure calculations reported here rely on band gap corrected many body perturbation theory (GW approximation) and do not depend significantly of computational parameters like U. Crystal Orbital Hamilton Population (COHP) analysis was performed with the LOBSTER code whereas density-derived charges...
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