Title: Octahedral and Trigonal-Prismatic Coordination Preferences in Nb-, Mo-, Ta-, and W-based ABX$_2$ Layered Oxides, Oxynitrides, and Nitrides

Abstract: Crystallographic and electronic structures of Nb-, Mo-, Ta-, and W-based layered oxides, oxynitrides, and nitrides were analyzed to elucidate the structural relationship between layered oxides and nitrides consisting of octahedral and trigonal-prismatic layers. The electron density, as derived by synchrotron X-ray analysis of LiNbO$_2$ and Ta$_{5-x}$(O,N)$_6$, showed orbital overlaps between Nb–Nb and Ta–Ta metals in the trigonal layers. Computational calculations based on DFT exhibited that these overlaps stabilized these structures by lowering the hybridization states composed of the $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ orbitals below the Fermi level. The crystal structures and formation energies suggest that tuning the Fermi level through the substitutions and vacancies of the cation/anion sites determines the structural preferences of the coordination. The properties and syntheses of these compounds are briefly described. This study enhances the understanding of layered oxides, oxynitrides, and nitrides to further the development of new synthetic approaches, compounds, and applications.

Keywords: X-Ray diffraction, First-principles calculations, Maximum entropy method, Layered structure, Metal-metal bonding
1. Introduction

Layered oxides are attractive materials because of their anisotropic structures and properties. For instance, after the discovery of superconductive quaternary and higher oxides with layered structures, many studies have been performed on complicated layered oxides [1-5]. In these complicated materials, defects and substitution are the key routes to tuning their anisotropic properties, and many studies have focused on controlling the vacancies, coordination, and substitution of the cation and anion sites. Recently, the effects of the anion species, such as F\(^{-}\), O\(^{2-}\), S\(^{2-}\), N\(^{3-}\), P\(^{3-}\), and As\(^{3-}\), on the properties of inorganic materials have received significant attention [6-9]. Among them, the nitride anion (N\(^{3-}\)) is one of the most similar anions to the oxide anion (O\(^{2-}\)) in terms of ion size, polarization, and electronegativity. Thus, in a few decades, many ternary nitrides or oxynitrides with layered structures have been discovered [10-12]. The chemical and physical properties of these layered nitrides/oxynitrides have been examined for their potential applications, such as in lithium ion batteries, superconductors and photovoltaics, catalysts and thermoelectronics.

Some binary, ternary, and more complicated oxides and nitrides with early 4d and 5d transition metals adopt relatively simple layered ABX\(_2\) oxide, oxynitride, and nitride structures (A: Li, Na, Mg, Ca, Sc, Mn, Fe, Cu, Ag, Nb, Mo, Ta, W; B: Nb, Mo, Ta, W, X: O, N). For example, NaNbO\(_2\) has a layered structure consisting of octahedral Na–O and trigonal-prismatic Nb–O layers (Fig. 1) [13]. On the other hand, NaNbN\(_2\) contains both octahedral Nb–N and Na–N layers; this can be called a layered
rock-salt structure [14]. The structural difference between octahedral and trigonal-prismatic coordination has been theoretically studied in layered sulfides and selenides by Kertesz and Hoffmann:

They attributed the differences to variations in the electron count and overlap of the metal-metal orbitals [15]. Although some studies have computationally predicted this metal-metal overlap [16, 17], it has rarely been experimentally visualized. Compounds beyond layered ABX_2 oxides and nitrides have not been systematically studied, which is necessary for further investigation of related materials.

**Figure 1** Scheme of octahedral and trigonal coordination.

In this work, the crystal structures and bonding features of layered ABX_2 oxides, oxynitrides, and nitrides are examined. First, we focus on LiNbO_2 and Ta_5N_6 as examples of layered structures with octahedral and trigonal-prismatic layers. Analysis of their synchrotron X-ray powder diffraction patterns experimentally reveals the metal-metal bonding within the trigonal prism in real space, and computational calculations show that this orbital overlap stabilizes these layered structures. Next, we determine the relationship between the electron count and coordination by analyzing various related oxides, oxynitrides, and nitrides. In the final section, the properties of the related layered oxides,
oxynitrides, and nitrides are summarized to provide clues for exploring new synthetic approaches, unrevealed compounds, and novel applications.

2. Material and methods

LiNbO$_2$ and Ta$_{5-x}$(N,O)$_6$ powders were synthesized following previously reported procedures [18, 19]. Briefly, LiNbO$_2$ was synthesized by heating NbO and Li$_3$NbO$_4$ in a vacuumed quartz tube [18]. Ta$_{5-x}$(N,O)$_6$ was synthesized by thermal ammonolysis of FeTaO$_4$ at 800 °C followed by washing with 1 M HCl aqueous solution to remove the iron byproducts [19]. Chemical analysis was performed by EDX, ICP, and combustion analysis. Synchrotron X-ray analysis was performed at the SPring-8 B02L beam line. Rietveld analysis was performed using RIETAN-FP [20], and the electron density was analyzed using a maximum entropy method (MEM) using Dysnomia [21]. The crystal structures and electron densities were visualized using VESTA [22]. Computational calculations based on density functional theory (DFT) were performed using the VASP package [23] with the GGA-PBE approach [24-26]. $k$-Point meshes of $12 \times 12 \times 3$ and $8 \times 8 \times 4$ were generated for LiNbO$_2$ and Ta$_3$N$_6$, respectively [27]. Relaxation of geometry optimization was performed, and a cutoff energy of 400 eV was used. Crystal orbital Hamilton population (COHP) analysis [28] was performed using the TB-LMTO-ASA package [29].

3. Results and Discussion

3.1 Structure and bonding of LiNbO$_2$
We shall start with LiNbO$_2$ consisting of alternate Nb–O trigonal-prismatic and Li–O octahedral layers (Figure 2). Isostructural compounds include many oxides and nitrides, such as Li$_x$NbO$_2$ [18], Na$_x$NbO$_2$ [30], and MgMoN$_2$ [31]. The Rietveld refinement profile of the X-ray diffraction of the synthesized LiNbO$_2$ powder showed the reported LiNbO$_2$ phase with approximately 1 mass% of NbO$_2$ [32] as an impurity. The lattice parameters ($a = 2.91267(2)$ Å and $c = 10.44871(8)$ Å) and atomic positions were close to those in previous reports [18, 33, 34]. The Li/Nb molar ratio was 0.97, as determined by ICP analysis; since it is close to unity, we performed the analysis with full occupancies for lithium and niobium. The $R_{wp}$ and $S$ values converged to 1.57% and 1.51, respectively.

**Figure 2** Crystal structure and Rietveld refinement profile of LiNbO$_2$. The structure shows the Nb–O trigonal-prismatic and Li–O octahedral layers. The small spheres represent oxygen atoms. Synchrotron XRD was measured at a wavelength of 0.49607 Å. The upper and lower tic marks represent the position of the allowed reflections for LiNbO$_2$ and NbO$_2$, respectively.

Experimental visualization of the charge density based on MEM analysis of the diffraction pattern showed good overlap of the orbitals between Nb and O and a localized Li orbital (Fig. 3(a)). As
expected, this electron density indicates a covalent Nb–O bond and a less covalent Li–O bond. The electron density in the Nb plane was clearly higher than that observed in the Li plane (Figs. 3(b) and (c)). Thus, the Nb orbitals overlapped in the trigonal-prismatic plane, while there was minimal overlap of the Li orbitals in the octahedral plane.

**Figure 3** Charge density of LiNbO$_2$ derived by MEM analysis of the synchrotron XRD data. (a) 3D charge density with an isosurface of 0.55 $e\cdot\text{Å}^{-3}$. (b) Nb plane parallel to the c-plane. (c) Li plane parallel to the c-plane.

Computational analysis using DFT supported the experimental MEM analysis (Fig. 4). Near the band gap, the Nb and O states were dominant and overlapped. The projected states of $d_{xz}$ and $d_{yz}$ spread over a wide range by interacting with oxygen orbitals in the trigonal prism. Additionally, the
projected $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ states also spread and formed relatively localized states just below the Fermi level. This calculated result is consistent with the previous report regarding Li$_x$NbO$_2$ [17] and similar trends can be seen in transition-metal dichalcogenites, such as NbS$_2$ [15].

![Density of states of LiNbO$_2$ calculated using the VASP code. (a) Total and partial DOS of LiNbO$_2$ and (b) projected DOS into the $d_{xz}+d_{yz}$, $d_{xz}+d_{x^2-y^2}$, and $d_{z^2}$ orbitals. Zero energy is set to the Fermi level.](image)

The overlaps between the Li–O, Nb–O, and Nb–Nb orbitals are shown in the COHP analysis (Fig. 5). A small overlapping population of Li–O bonding states is located around $-7$ eV, and more overlap between Nb–O and Nb–Nb occurs over a wide range. The state just below the Fermi level consists of
Nb–O anti-bonding interactions and Nb–Nb bonding interactions. Thus, the overlapped orbitals in the Nb plane, which were visualized as high electron density by MEM analysis, would stabilize this layered trigonal-prismatic structure.

![Figure 5 COHP analysis of (a) Li–O, (b) Nb–O, and (c) Nb–Nb bonding within LiNbO$_2$ performed using TB-LMTO-ASA code. Zero energy is set to the Fermi level.](image)

3.2 Structure and bonding of nitrogen-rich Ta$_{3-x}$(N,O)$_6$

The crystal structure of Ta$_3$N$_6$ consists of trigonal-prism and octahedral Ta–N layers with vacancies and slightly off-center Ta positions (Fig. 6) [19]. We can describe Ta$_3$N$_6$ as (Ta$_{0.67}$□$_{0.33}$)$_{oct}$N$_2$, in which the octahedral position comprises one third of the ordered vacancies, while the trigonal position is fully occupied. The trigonal position of Ta is slightly off-center in the trigonal
plane and forms Ta trimers. There are several related compounds, such as Nb$_5$(O,N)$_{6-x}$ [19], Ta$_5$(O,N)$_{6-x}$ [19], LiNb$_3$N$_4$ [35, 36], (Li$_{0.88}$□$_{0.12}$)Nb$_3$$_0$(O$_{0.13}$N$_{0.87}$)$_4$ [37], and Mo$_5$N$_6$ [38].

Figure 6 shows the Rietveld refinement of X-Ray diffraction pattern of Ta$_{5-x}$(O,N)$_6$ powder synthesized via thermal ammonolysis of FeTaO$_4$ followed by an acid wash. The major peaks were assigned as a hexagonal cell. Nonetheless, minor unindexed peaks were also observed. These may be assigned as the α-TaON phase with a hexagonal structure even though the electronic calculations do not support the existence of this phase [39]. EDX analysis showed that the ratio of Fe/Ta was semi-quantitatively less than 0.01. Combustion analysis showed 8.3 wt% nitrogen and 1.0 wt% oxygen. Assuming that the combustion residual was Ta, the Ta/N/O molar ratio was 1:1.20:0.13; this ratio is close to the theoretical value for Ta$_3$N$_6$, which indicates that the major phase should be close to Ta$_3$N$_6$. Fe and O may be present as impurity phases, as an amorphous oxidized layer, or incorporated into Ta or N sites in Ta$_3$N$_6$. Since partial incorporation of oxygen cannot be disproven, we shall describe the major phase as Ta$_{5-x}$(O,N)$_6$, i.e., a nitrogen-rich layered tantalum oxynitride with trigonal-prismatic layers.
Figure 6 Crystal structure and Rietveld refinement profile of Ta$_{5-x}$(O,N)$_6$ ($x \approx 0.18$). The structure shows a Ta–(O,N) trigonal-prismatic layer and octahedral layer with ordered vacancies. The small spheres represent oxygen/nitrogen atoms. Synchrotron XRD was measured at a wavelength of 0.41365 Å. The tic marks and line below the pattern represent the positions of the allowed reflections for Ta$_{5-x}$(O,N)$_6$ and difference between the observed and calculated profiles, respectively. The asterisk indicates an impurity phase(s).

Rietveld refinement showed lattice parameters ($a = 5.18369$ (4) Å and $c = 10.36567(8)$ Å) and atomic positions similar to those reported previously for Ta$_5$N$_6$ and Ta$_5$(O,N)$_6$ [19]. Refinement of the occupation of the trigonal Ta site revealed that it was unity and formed triangle trimers by a slight shift parallel to the c-plane [19]. The distances of the shorter Ta–Ta bonds in the trimers and longer bonds between the trimers were 2.9072(6) and 3.0365(6) Å, respectively. The octahedral sites were found to have ordered and disordered vacancies; the ordered vacancies comprised one third of the octahedral sites (2a site) [19], while the disordered vacancies comprised ~9% of the 4d site, which had not been reported previously. The Ta–Ta distance in the octahedral layer was 2.9928(3) Å. The equivalent isotropic atomic displacement parameter, $B_{eq}$, of the octahedral site (0.543(12) Å$^2$) was
much higher than that of the trigonal site (0.056(6) Å²), which could be related to the vacancies and decreased metal-metal overlap in the octahedra, as described below. The final \( R_{wp} \) and \( S \) values were 4.88% and 4.35, respectively.

The electron density derived from MEM analysis of the diffraction peaks is shown in Fig. 7. Both the trigonal and octahedral layers showed connected electron density between the Ta and (N,O) atoms. The electron densities in the trigonal and octahedral planes parallel to the \( xy \) plane were different. The trigonal sites showed a high electron density between Ta sites within the trigonal trimer. The minimum electron densities of Ta–Ta for the shorter bond in the trimers and longer bond between trimers were 0.51 and 0.26 \( e^{-} \text{Å}^{-3} \), respectively. In contrast, the electron density between the Ta atoms in the octahedral layer was 0.29 \( e^{-} \text{Å}^{-3} \). Thus, the Ta–Ta interactions in Ta trimers in the trigonal prism would have more covalent characteristics than those in the octahedral layer.
Figure 7 Charge density of $\text{Tas}_{5-x}(\text{O,N})_6$ derived by MEM analysis of synchrotron XRD data. (a) 3D charge density with an isosurface of 0.55 Å⁻³. (b) Ta trigonal plane parallel to the c-plane. (c) Ta octahedral plane parallel to the c-plane.

$\text{Tas}_5\text{N}_6$ was further analyzed by computational calculations: Its trigonal site was fully occupied, and only ordered octahedral vacancies formed in the octahedral layer. Figure 8 shows the pDOS of $\text{Tas}_5\text{N}_6$. The Ta 5d and N 2p orbitals overlapped well and formed states within a wide range. The pDOS of the octahedral and trigonal Ta states showed characteristic features of their trigonal and octahedral coordination spheres; in both, the $d_{xz} + d_{yz}$ orbitals were separated, similar to in $\text{LiNbO}_2$. The states that were mainly composed of $d_{xy} + d_{z^2}$ and $d_{z^2}$ orbitals near the Fermi level were significantly different in the trigonal and octahedral layers: The trigonal layer formed these states around $-$3 and 4 eV while those in the octahedral layer formed at $-$0.5–3 eV. The greater separation of the states in the trigonal layer could be explained by the greater overlap between Ta–Ta orbitals, which was experimentally visualized by MEM analysis.
Figure 8 DOS of Ta$_5$N$_6$ calculated using the VASP code. (a) Total and partial DOS of Ta$_5$N$_6$ projections into the $d_{xz}+d_{yz}$, $d_{xz}+d_{x^2−y^2}$, and $d_{z^2}$ orbitals of Ta in the (b) octahedral and (c) trigonal sites. Zero energy is set to the Fermi level.

Figure 9 shows the COHP analysis of Ta$_5$N$_6$, which exhibited similar trends for the Ta–N bonds in the octahedral and trigonal coordination sites, but different features for the Ta–Ta bonds. The Ta–N bonds in both coordination show bonding and anti-bonding interactions below and above the Fermi level, respectively. For the Ta–Ta bonds in the octahedral site, there was only slight electron occupation of the states from bonding interactions. In the trigonal site, two different Ta–Ta bonds formed because of the slightly off-center position of the Ta atom. As expected, shorter bonds resulted in greater overlap of the Ta–Ta orbitals (solid line) and vice versa (dotted line). These bonding populations were located below the Fermi level; thus, the interactions between Ta–Ta orbitals in the trigonal trimer would stabilize this layered structure.
Figure 9 COHP analysis using TB-LMTO-ASA code of (a) Ta–N and (b) Ta–Ta bonds in the octahedral layer and (c) Ta–N and (d) Ta–Ta bonds in the trigonal-prismatic layer within Ta₅N₆. The solid and dotted lines indicate the shorter bonds that form the trimers and longer bonds between trimers due to the slightly off-centered Ta in the trigonal prism, respectively. Zero energy is set to the Fermi level.

To understand the effects of the vacancies, the formation energies of TaₓN₆ with different vacancies were calculated (Fig. 10): Ta₆N₆ is the structure with no vacancies, while Ta₃N₆ has full vacancies of either the octahedral or trigonal sites. Our results showed that TaₓN₆ became increasingly unstable with increasing concentration of trigonal vacancies and more stable upon the introduction of one third of the vacancies in the octahedral site, as was exhibited experimentally. This can be explained by the fully filled states formed via bonding interactions between Ta atoms in the trigonal layer, as
described. Thus, a one third vacancy in the octahedral sites is preferable to that in the trigonal sites in this layered structure.

**Figure 10** Formation energies of Ta$_x$N$_6$ with (a) fully occupied trigonal sites with octahedral vacancies and (b) fully occupied octahedral sites with trigonal vacancies calculated by the VASP code.

3.3 Electron count and structure of ABX$_2$ compounds

Structural study of LiNbO$_2$ and Ta$_{5-x}$(O,N)$_6$ revealed that the trigonal prism formed from metal-metal bonds. The metal-metal bonds placed the hybridized states of the $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ orbitals below the Fermi level; thus, these layered structures were stabilized. Similar explanation have been reported regarding calcogenides, such as NbS$_2$ and NbSe$_2$, using a computational approach [15]. It has been found that hybridization of the $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ orbitals is enhanced by the formation of trigonal prisms when their electron count is well below the Fermi level [15]. We may expect that similar trends may occur in ABX$_2$ oxides, oxynitrides, and nitrides with different cations and anions.
Table 1 Reported ABX$_2$ oxides, oxinitrides, and nitrides with d electron counts and BX$_2$ coordination assuming a charge transfer from the alkali/alkali-earth metals/Sc$^{3+}$ and O$^{2-}$/N$^{3-}$ ions to Nb/Mo/Ta/W.

<table>
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<th>Formula</th>
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<td>Octahedral</td>
<td>[14]</td>
</tr>
<tr>
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<td>[40]</td>
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<td>CaTaN$_2$</td>
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<td>[41]</td>
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<tr>
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<td>[42]</td>
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<tr>
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<td>LiWN$_2$</td>
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<td>[43]</td>
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<td>1.33</td>
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</tr>
<tr>
<td>1.33</td>
<td>Li$<em>{0.5}$Ta$</em>{1.5}$N$_2$</td>
<td>(Li$<em>{0.5}$Ta$</em>{0.5}$)TaN$_2$</td>
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<tr>
<td>1.4</td>
<td>Nb$_2$N$_6$</td>
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Table 1 shows a list of ABX$_2$ oxides, oxinitrides, and nitrides and their BX$_2$ coordination and d electron count assuming charge transfer from the alkali/alkali-earth metals and O$^{2-}$/N$^{3-}$ ions to Nb/Mo/Ta/W. The main conclusions are as follows:

1. Compounds with electron counts of around 1–2.4 formed layered structures with trigonal prism coordinations.

2. The trends were not strongly related to the cation and anion species and vacancies.

To confirm these experimental trends, we calculated the differences in the formation energies of various ABX$_2$ compounds with various cations (A site: alkali/alkali-earth metals; B site: Nb, Mo) and anions (X site: N/O), which were isostructural with NaNbN$_2$ (octahedral) and NaNbO$_2$ (trigonal).

Figure 11 reveals that the trigonal-prism coordination is stabilized in the range of electron counts between 1 and 2.7; this is similar to what has been reported experimentally (Table 1). This trend is also similar to the computational calculations of transition-metal calcogenides, which was explained by stabilization of the trigonal structure by the formation of metal-metal bonds with suitable Fermi levels [15].
Figure 11 Formation energy differences of various ABX$_2$ oxides, oxynitrides, and nitrides that are isostructural with NaNbN$_2$ (octahedral) and NaNbO$_2$ (trigonal) calculated using the VASP code. A charge transfer from the alkali/alkali-earth metals and O$^{2-}$/N$_3^-$ ions to Nb/Mo is assumed to calculate d electron counts. Some of these compounds are hypothetical and have not been experimentally reported. The dashed line is provided to guide the eye.

It is possible to assess this relationship between electron counts and structures in compounds with 3d transition metals in the A sites, such as FeWN$_2$ [50-53], MnWN$_2$ [54], and MnMoN$_2$ [50]. These materials have layered structures consisting of octahedral layers with 3d transition metals and trigonal-prismatic layers with 4d or 5d metals. The 3d metals can be considered to be divalent cations considering their ionic radii, and, if so, the electron count of the d orbitals of Mo and W would be close to d$^2$ and these could follow the structural rule found in this work, i.e., the relationship between the d electron count of the 4d/5d metal and octahedral/trigonal coordination. Their octahedral sites might be somewhat flexible with respect to the vacancies, and substitution in the octahedral sites has
been reported in Fe$_x$WN$_2$ [55, 56], (Fe$_{0.8}$Mo$_{0.2}$)MoN$_2$ [57], (Fe$_{0.8}$W$_{0.2}$)WN$_2$ [58], and (Co$_{0.8}$Mo$_{0.4}$)MoN$_2$ [59, 60].

Additionally, some nitrides with monovalent transition metals (i.e., Cu/Ag) can be understood similarly, e.g., CuNbN$_2$ [61, 62], CuTaN$_2$ [63], and AgTaN$_2$ [64, 65]. We could treat these as d$^0$ compounds, and they have octahedral (Nb-Ta)–N planes, as expected. Nonetheless, these compounds have linear Ag/Cu–N bonds, which are commonly seen in delafossite oxides, such as AgCoO$_2$ [66].

3.4 Remarks on the properties and syntheses of ABX$_2$ compounds

In the previous section, the coordination and vacancies of these layered ABX$_2$ oxides, nitrides, and oxynitrides were found to be related to both the anion and cation species; this relationship suggests that the properties of these compounds are affected by these species, and thus their syntheses should be performed with control of the anion and cation species. Herein, we describe a short description of the properties and syntheses of ABX$_2$ oxides, oxynitrides, and nitrides to help further exploration of related materials.

The d$^0$ nitrides show semiconductive behavior, and their visible or infrared absorption properties show the potential for solar energy conversion [61, 62]. SrZrN$_2$ and SrHfN$_2$, which are isostructural with NaNbN$_2$, have been computationally predicted to be thermoelectronic materials [67]. The d$^1$ and d$^2$ nitrides, oxynitrides, and oxides show metallic or semiconductive transport properties depending on their electron counts and hybridization of the orbitals. Some of these compounds show
superconductive properties, including Li$_x$NbO$_2$ ($T_c \approx 5$ K) [68], Na$_x$NbO$_2$ ($T_c \approx 4$ K) [30], CaTaN$_2$ ($T_c \approx 9$ K) [41], and (Li$_{0.88}$□$_{0.12}$)Nb$_3$O$_{10.13}$N$_{0.87}$)$_4$ ($T_c \approx 3$ K) [37]. The electrochemical performances of Li$_x$MoN$_2$ [42], Li$_x$WN$_2$ [69], and Li$_x$MoO$_2$ [70] have been examined for potential applications as electrodes for rechargeable lithium batteries. Ferromagnetic-like properties have been found in Fe$_{0.74}$WN$_2$ with defective Fe triangles [56]. The electrocatalytic properties of Co$_{0.6}$Mo$_{1.4}$N$_2$ for hydrogen evolution reaction and oxygen reduction reaction have been examined [59, 60]. Even though there are potential applications, most of the reported properties include the effects of the surface layers, impurities, and grain connections. For the synthesis of oxynitrides and nitrides, a major approach is to heat (typically above 600–1000 °C) the oxide, sulfide, or chloride precursors under an ammonia flow; in these reactions, the temperature profile and ammonia flow rate should be kinetically controlled [12, 71-73]. Single crystals of several ABX$_2$ compounds have been grown using flux methods (LiNbO$_2$ [74, 75], CaNb$_2$O$_4$ [47], and NaNbN$_2$ [76]); however, many ABX$_2$ compounds are only available in the powder form. Therefore, further development of synthetic techniques to control the cationic and anionic species and morphologies are important for finding new compounds and examining the intrinsic properties and exploring new applications of these ABX$_2$ compounds.

4. Conclusions

The structural preferences and bonding of various ABX$_2$ oxides and nitrides consisting of octahedral and trigonal-prismatic layers were investigated. In both the oxides and nitrides, the
octahedral and trigonal coordinations were closely related to the Fermi level, which was controlled by the anions, cations, and vacancies. The trigonal layer formed metal-metal bonds, which lowered the hybridized states composed of $d_{xz} + d_{x^2-y^2}$ and $d_{x^2}$ orbitals below the Fermi level. Layered structures with prismatic-trigonal coordination formed when the d electron count was around 1–2.5 assuming charge transfer from the alkali or alkali-earth metals. The structures of the $ABX_2$ compounds together with their synthetic routes and magnetic and electronic properties were summarized. This work elucidated a systematic trend for understanding layered oxides, oxynitrides, and nitrides consisting of octahedral and trigonal-prismatic layers, which is important for further exploration of new layered compounds and their properties by mixing cations and anions and controlling vacancies.

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**Supplementary material**

Detailed results of the Rietveld refinement of LiNbO$_2$ and Ta$_{5-x}$(O,N)$_6$ are summarized in the supporting material.
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