Disentangling the Effects of Inter- and Intra-octahedral Distortions on the Electronic Structure in Binary Metal Trioxides

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Supporting Information

ABSTRACT: Recently, a subclass of binary perovskite-structured metal trioxides, such as WO$_3$ and MoO$_3$, have been propounded for many key optoelectronic applications due to their proper band edge positions and appropriate band gap sizes. Unlike their superclass perovskites, the structure–property relationship for these binary metal trioxides is less apparent, given that they suffer from much larger structural deformities within the octahedra. In this work, by using first-principles density-functional theory calculations and atomistic scale models, we examine the internal and external distortions of WO$_3$ and MoO$_3$ polymorphs. We then compare our results with conventional polyhedral distortion descriptors and finally use a refined data set of different perovskite-structured oxides to establish and demonstrate how these binary metal trioxides operate with a different structure–property relationship from the conventional oxide perovskites.

1. INTRODUCTION

Perovskite-structured materials (ABX$_3$) are long known for their outstanding physicochemical properties and have been exploited for a wide range of key application areas such as heterogeneous catalysis, optoelectronics, fuel cells, and multiferroics. The versatility of these functional materials originates from the complex association of their crystal and electronic structures. In particular, the so-called intra- and inter-octahedral distortions have been suggested as key structural factors that may be used to design and determine the electronic structure of these ABX$_3$ functional materials.

Adopting the same ABX$_3$ archetype crystal structure, the halide-based (hybrid) perovskite materials have rose to fame recently for their impressive track records of ever-increasing solar cell efficiencies (of more than 20%) and being cheap and simple to produce. In fact, it was recently reported that steric engineering can be an effective means to tune the optical band gaps in metal-halide perovskites, and a nontrivial role of octahedral tilting in organohalide perovskites on its optoelectronic structure exists.

This leads one to believe that the structure–property relationship for these proper conventional ABX$_3$ perovskites may well be rationalized by examining the inter-octahedral distortions within the rigid framework of close-to-ideal octahedra (i.e., no strong structural distortions within the octahedra). It is then clear that a more straightforward, tilting-only design rule can be applied to exploit their optoelectronic properties (especially the band gap energy, $E_g$) for future key energy applications.

As a subclass of ABX$_3$ perovskites, binary metal trioxides (i.e., BO$_3$ where the A cation site in perovskite is vacant, as in MoO$_3$ and WO$_3$) are gaining the limelight for their roles in important energy technologies such as in photocatalysis and carrier transport layer in organic devices. Similar to their ternary oxide counterparts, these binary metal trioxides are also highly tunable, in the sense that their electronic structure also shows a strong dependence on their explicit atomic arrangements and specific crystal structures.

Unlike their superclass ABX$_3$ perovskites, the structure–property relationship for these binary metal trioxides is less apparent, given that they suffer from much larger structural deformities within the octahedra, resulting in strongly coupled intra- and inter-octahedral distortions. Thus, recent structure–property rules outlined in refs 14 and 15 can no longer work nor be applied for these binary trioxides with tilted nonideal BO$_3$ octahedral networks. It is also not clear how strongly the intra- and inter-octahedral distortions are coupled and which will actually have a dominant effect on their desired material property (e.g., the $E_g$).

It is therefore our aim in this work to use first-principles calculations and a simple, straightforward atomistic scale model to examine and study the disentanglement of the coupled intra- and inter-octahedral distortions in perovskite-related binary oxides (exemplified by all known polymorphs of WO$_3$ and MoO$_3$). We then compare our results with conventional polyhedral distortion descriptors (e.g., quadratic elongation index) and finally use a refined data set of 35 different perovskite-structured oxides (as obtained from the Materials Project database) to establish and demonstrate how these binary metal trioxides operate with a different (but coherent) structure–property relationship from the conventional proper oxide perovskites.

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2. METHODS

2.1. Computational Details. All density-functional theory (DFT) calculations are performed using the Vienna Ab initio Simulation Package (VASP).\textsuperscript{27-29} The van der Waals (vdW) corrected semilocal generalized gradient approximations (GGA) to the exchange-correlation (xc) functional, optB88,\textsuperscript{30} is used for all geometry relaxations to obtain the optimized structural parameters. The projector-augmented wave (PAW) method\textsuperscript{31} is adopted to describe the ion–electron interactions, and a planewave basis set with a kinetic energy cutoff of 500 eV is used to expand the Kohn–Sham orbitals for all DFT calculations. The valence electron configurations for Mo, W, and O atoms are taken as 4s\textsuperscript{2}4p\textsuperscript{6}5s\textsuperscript{2}5p\textsuperscript{6}5d\textsuperscript{10}, 5s\textsuperscript{2}5p\textsuperscript{6}6s\textsuperscript{1}, and 2s\textsuperscript{2}2p\textsuperscript{4}, respectively. Furthermore, a Γ-centered k-point mesh with a grid spacing of at least 0.3 Å\textsuperscript{-1} is used to sample the Brillouin zone.

All DFT calculations have been tested for convergence with respect to the kinetic energy cutoff and k-point grid where the total energies, forces, and external pressure vary by less than 20 meV, 0.02 eVÅ, and 0.5 kbar, respectively. For all self-consistent field calculations, the total energy convergence threshold is kept at 10\textsuperscript{-5} eV. After obtaining the optimized geometries, to afford a more accurate description of the electronic band structure of these oxides, the hybrid DFT xc functional due to Heyd, Scuseria, and Ernzerhof (HSE06) is employed.\textsuperscript{32,33}

Using the GULP code,\textsuperscript{34} the Madelung potentials are obtained under the point charge model using an Ewald summation technique.\textsuperscript{35} Here, the electrostatic Madelung potential only depends on the charges of the ions and their separations following the equation

\[
V_0 = \sum_{i=1}^{N} \frac{q_i}{r_{0-i}} \tag{1}
\]

where \(V_0\), \(q_i\), and \(r_{0-i}\) denote the Madelung potential, ion charges, and ion separations, respectively.

2.2. Scale Model: An Approximate Model for Binary Metal Oxides. To decouple the effects from the inter- and intra-octahedral distortions observed in the binary metal oxides, WO\textsubscript{3} and MoO\textsubscript{3}, we have adopted a simple (but tractable) atomistic scale model for both oxides. We first start from a cubic unit cell containing one MoO\textsubscript{3} octahedron (where its octahedral volume is set to that of the optimized \(\beta\)-MoO\textsubscript{3} and \(\gamma\)-WO\textsubscript{3} structures). This is taken as the ideal nondistorted scale model where the MoO\textsubscript{3} octahedra are connected at all vertices. We note that this first approximation is not completely unfounded as the optimized \(\beta\)-MoO\textsubscript{3} and \(\gamma\)-WO\textsubscript{3} structures can, in fact, be understood as distorted cubic structures. We emphasize that this starting ideal cubic nondistorted structure is free from either inter- or intra-octahedral distortions, which makes this scale model a good starting point to study the individual contributions of the inter- and intra-octahedral distortions to the electronic band gap energy of the WO\textsubscript{3} and MoO\textsubscript{3} polymorphic structures.

Next, we consider three possible contributions to general intra-octahedral distortions, \(i\): (1) distortions due to having metal cations displaced far from the center of the octahedron, \(i_{\text{lat}}\); (2) distortions due to the shape of the octahedron, \(i_{\text{shape}}\); and finally (3) distortions due to the volume (i.e., size) of the octahedron, \(i_{\text{vol}}\). To study \(i_{\text{lat}}\) while keeping the O atoms at the vertices fixed, we displace the metal cation (M) away from the central position toward the edge of the octahedron. This is in line with previous reports where the most commonly observed off-centered positions for Mo and W cations are near the edges of the octahedron.\textsuperscript{36}

To model \(i_{\text{shape}}\), we apply both compressive and tensile strain to the atomistic scale model on the z-direction while keeping the octahedral volume as a constant. This naturally determines the lattice parameters in both the x- and y-directions, while we vary that in the z-direction, distorting the overall shape of the octahedron in this scale model. Likewise, to account for \(i_{\text{vol}}\), we isotropically expand and compress the lattice constant of our cubic scale model to reflect the changes to the volume or size of the octahedra. In this way, it will allow us to independently survey and study the individual contributions—\(i_{\text{lat}}\), \(i_{\text{shape}}\), and \(i_{\text{vol}}\)—to the intra-octahedral distortions in our binary trioxides of interest.

After isolating the intra-octahedral distortions, we now turn to the inter-octahedral distortions. Here, we can also decouple individual contributions and identify two key factors: (1) distortions due to the angle tilting of the octahedra, \(I_{\text{tilt}}\), and (2) distortions due to the way the individual MO\textsubscript{3} are connected (i.e., via the vertex, edge, or face of the octahedron), \(I_{\text{connect}}\). Given that the latter \(I_{\text{connect}}\) is not straightforward to discuss (e.g., may involve changes to the stoichiometry of the system in question), at the first instance, we temporarily neglect its contribution to the inter-octahedral distortions. Thus, in this work, we focus on \(I_{\text{tilt}}\) and design our tilt angle system based on the Glazer notation.\textsuperscript{37} In particular, we choose the simplest \(a'\)b'c' tilt system.

Adapting to ref 14, we first consider the ideal cubic MO\textsubscript{3} octahedron with the center metal atom placed at the origin, and six vertex O atoms located at (±1, 0, 0)d, (0, ±1, 0)d, and (0, 0, ±1)d, respectively, where the \(d\) denotes the ideal M–O distance. To model \(I_{\text{tilt}}\) we follow the general concept of Euler angles (i.e., \(\theta, \phi,\) and \(\psi\)), as done for the previous work on halide perovskites in ref 14. Here, \(\theta\) is the tilt angle from the c-axis; \(\phi\) denotes the precession angle to the apical c-axis; while \(\psi\) is the spinning angle with the spinning axis of octahedral apical direction (c-axis). Following ref 38, the rotation matrix can be defined as

\[
\begin{pmatrix}
\cos \psi \cos \phi - \cos \theta \sin \phi \sin \psi & -\sin \psi \cos \phi - \cos \theta \sin \phi \cos \psi & \sin \theta \sin \phi \\
\cos \psi \sin \phi + \cos \theta \cos \phi \sin \psi & -\sin \psi \sin \phi + \cos \theta \cos \phi \cos \psi & -\sin \theta \cos \phi \\
\sin \theta \cos \psi & \sin \theta \sin \psi & \cos \theta
\end{pmatrix}
\]

2.3. Generic Measurement Indices for Polyhedral Distortions. To quantitatively determine the extent of intra-octahedral distortion \((i)\) within a single polyhedron in a given crystal structure, one can define a bond-length-based index (i.e., the quadratic elongation, \(\langle \lambda \rangle\)) and a bond-angle-based index
(i.e., the bond angle variance, $\sigma^2$, in $^\circ$). Mathematically, they can be expressed as

$$\langle \lambda \rangle = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{l_i}{l'_i} \right)^2$$

(2)

$$\sigma^2 = \frac{1}{m-1} \sum_{i=1}^{m} (\phi_i - \phi_0)^2$$

(3)

where $n$ is the coordination number of the central M atom (i.e., $n = 6$ refers to an octahedral environment); $l_i$ is the distance from the central M atom to the $i$th coordinating atom; $l'_i$ is the center-to-vertex distance of an ideal polyhedron of the same volume in eq 2; and $m$, $\phi_i$, and $\phi_0$ in eq 3 denote the number of bond angles, $i$th bond angle, and the ideal bond angle of the regular polyhedron.

2.4. Continuous Shape Measurement Method. Another means to capture the structural deviations of various binary and ternary oxide structures is to employ the continuous shape measurement methodology (CSHM). Within the CSM formalism, a vector, $\vec{q}_i$, from given a distorted structure which has $N$ vertices is first defined and then another vector, $\vec{p}_0$ which originates from a structure within a constrained symmetry and the given shape.

By using these two vectors, CSM allows one to derive the S value which then indicates the degree of distortion for a closed system with the following equation

$$S = \min \left[ \frac{\sum_{i=1}^{N} (\vec{q}_i - \vec{p}_0)^2}{\sum_{i=1}^{N} (\vec{q}_i - \vec{q}_0)^2} \right] \times 100$$

(4)

where $\vec{p}_1$ and $\vec{q}_i$ are the vectors of atomic coordinates of distorted and symmetric constrained structure in the system which has $N$ vertices, and $\vec{q}_0$ is the vector derived from the atomic position of the geometric center.

The obtained $S$ expresses the degree of agreement for a structure $Q$ in shape with respect to perfect symmetric structure, $P$. In short, when $S$ is close to 0, no polyhedral distortion is present in the structure (when compared to the target symmetry). Vice versa, if calculated $S$ is a large value, severe structural distortions are present, deviating from the ideal symmetry and shape.

2.5. Tilt Angle Measurements in Strongly Distorted Octahedra. For cases where the crystal structure suffers from a large structural distortion within the interconnected polyhedrons, strongly coupled intra- and inter-octahedral distortions may prevail (as in the cases of MoO$_3$ and WO$_3$). Geometrically, referring to Figure 1, we measure three different tilt angles: the $\theta_{\text{M}3\text{V}3\text{b}}$, $\theta_{\text{V}3\text{C}2\text{t}}$, and $\theta_{\text{V}2\text{V}3\text{C}2\text{t}}$. Specifically, we survey all pairs of adjacent octahedra (within periodic boundary conditions) and calculate every possible tilt angle between these two octahedra. We find that the measured values do not deviate significantly for each tilt angle type, thus supporting the use of a statistically averaged value for each tilt angle per crystal structure.

3. RESULTS AND DISCUSSION

3.1. Polymorphic Expressions in WO$_3$ and MoO$_3$. The basic building block in perovskites (ABX$_3$) and perovskite-related materials are BX$_6$ octahedra, with the A cation in the cuboctahedral site. In the case of the binary metal trioxides (where the A cation is missing), how the MO$_6$ octahedra are packed and connected dominates, and the origin behind the relation between MO$_6$ octahedral distortions and their physicochemical properties is nontrivial and complex. The polymorphic expressions in these binary metal trioxides are determined by the spatial network of connecting MO$_6$ octahedra (as a basic building block) and are notably energetically competitive.$^{25,41,42}$

In particular, up to eight different polymorphic phases of WO$_3$ (see Figure S1 of the Supporting Information) have been reported—namely, the cubic (cube), tetragonal (tet), orthorhombic (ort), triclinic (tri), low-temperature monoclinic ($\epsilon$), room-temperature monoclinic ($\gamma$), and two hexagonal (H1 and H2) phases, with the $\gamma$ phase most widely studied.$^{43−45}$ Less well studied, MoO$_3$ may crystallize in four different polymorphs (see Figure S2 of the Supporting Information), i.e., the orthorhombic ($\alpha$),$^{44,45}$ hexagonal ($h$),$^{36−48}$ and two monoclinic (II)$^{49−51}$ and $\beta$)$^{52−54}$ phases.

For WO$_3$, depending on the polymorphic phase, the HSE06-calculated $E_g$ values can range from 1.60 to almost 3.00 eV, while for that of MoO$_3$, the corresponding range is from 2.80 to 4.12 eV (largest for $h$-MoO$_3$ with the $E_g$ variation plotted in Figure 1(a) and tabulated in Table S1 of the Supporting Information). In these structures with polyhedral networks, it is known that the local electrostatic potential each atom experiences (i.e., Madelung potential) may influence the absolute band edge positions.$^{35,55}$ In Figure S3, following the argument in ref 35, the variation in the Madelung potentials of the metal cation and oxygen anion for WO$_3$ and MoO$_3$ polymorphs are plotted. In general, the variation trend of the band edge positions (with the exception of H1- and H2-WO$_3$) is established. For the H1- and H2-WO$_3$ phases, the slight deviation may be attributed to the different coordination environment of the oxygen anion and thus the metal—oxygen orbital hybridization. However, as depicted in Figure 1(b), the octahedral network in these binary metal trioxides undergoes large intra- and inter-octahedral distortions. The extent of how
these distortions in their octahedral networks may dictate the physiochemical properties of each polymorph is still largely unexplored.

To simply disentangle the complex contributions to octahedral distortions in these pseudo-perovskite-related materials (including binary trioxides of W and Mo, where both intra- and inter-octahedral distortions can be strongly coupled), we propose that their physiochemical properties, $X$ (e.g., the band gap energy, $E_g$), can be expressed as $X = f(I, i)$, where $I$ and $i$ denote the contributions to the inter- and intra-octahedral distortions, respectively.

Here, $I_{il} \triangleq I_{il} (i_{iln})$ are inter-octahedral distortion factors due to the geometrical tilt about the connection vertex of two octahedra and that due to how the individual octahedra are interconnected (i.e., either via the vertex/corner, edge, or face of the octahedron), respectively. Likewise, $i_{dop}$, $i_{dshape}$, and $i_{dvol}$ are intra-octahedral distortion factors due specifically to metal off-center displacement, shape, and volume (or size) changes upon distortion, respectively.

To understand the contributions of these individual components for the various polymorphs of both WO$_3$ and MoO$_3$, we now turn to our simple binary metal trioxide atomistic scale model which allows us to start with the ideal nondistorted cubic for both oxides. Here, the word scale model (or scale similitude) indicates an artificial model which is designed to explain certain phenomena or properties observed in the complex system. The concept of scale model is commonly used in many fields of engineering, since it allows one to provide a physical representation of the system of interest while maintaining accurate relationships between all important aspects of the model. Here, the advantage of this approximate model allows one to break down the complexity of the real system to demonstrate some behavior or property of the original without directly involving the complex system.

3.2. Examining Inter-octahedral Distortions with Scale Models. We separate the contributions from inter-octahedral distortions into mainly two effects, $I_{il}$ and $I_{ilnn}$, where in this work we will focus predominantly on the former while neglecting the latter effect at the first instance.

As shown in Figure 2(a), to study $I_{il}$, we modulate the tilt angle of the octahedra, $\theta_{VV}$ (which is simply the oxygen vertex-to-vertex-to-angle), in our atomistic scale models from 180 to $\sim 130^\circ$ while keeping the minimum $d_{O\cdots O}$ not shorter than that observed in the optimized WO$_3$ and MoO$_3$ structures. For each $I_{il}$ model, using the hybrid HSE06 functional, we calculated the electronic $E_g$ for each tilted structure. Here, we can see that, based on our scale model, the change in the $E_g$ is found to be quite small ($\Delta E_g \leq 0.15$ eV), reflecting that distortions from geometrical tilts about the connection vertex of two octahedra are rather small and may be negligible. This weak dependence on the inter-octahedral tilt distortions is rather interesting as it is in contrast to what has been reported for organohalide perovskites$^{15,16}$ where the inter-octahedral distortions greatly modify their optical band gap energies.

To understand the possible origin of this weak dependence, we turn to the electronic density-of-states (DOS, calculated using the hybrid HSE06 xc functional) for the MoO$_3$ scale model (as plotted in Figure 2(a)) for $\theta_{VV} = 180$, 157, and 145$^\circ$. Given that the center metal atom is bound to 6 neighboring O atoms within an octahedral ligand field, we can also plot the orbital contributions to the DOS by grouping the $d_{z^2}$ and $d_{x^2-y^2}$ states as the Mo 4d $e_g$ states and the $d_{xy}$, $d_{yz}$, and $d_{xz}$ as Mo 4d $t_{2g}$ states. For $\theta_{VV} = 180^\circ$, our ideal nondistorted cubic structure clearly shows that valence band and conduction band edges are mainly composed of the O 2p and Mo 4d $t_{2g}$ states, respectively.

Upon tilting, in the valence band region, there is still a major contribution from the O 2p states, while deeper in the conduction band region, a clear further splitting of the Mo 4d $e_g$ states. For $\theta_{VV}$ between 180 and $145^\circ$, we observe a clear further splitting of the Mo 4d $t_{2g}$ states. However, this splitting is much smaller than that observed in the $\theta_{VV} = 180^\circ$ case.

Figure 2. (a) Calculated band gap energies ($E_g$ in eV) of the scale model (triangle: MoO$_3$; circle: WO$_3$) as a function of $V$–$V$–$V$ inter-octahedral tilt angle ($\theta_{VV}$). (b) Calculated $E_g$ as a function of shape distortion. (c) Calculated $E_g$ as a function of volume changes. (d) Calculated $E_g$ as a function of how far the metal cation is displaced from the center of the ideal cubic octahedron toward the edge. Dotted vertical lines denote the ideal cubic model limit. The corresponding projected density-of-states for selected MoO$_3$ scale model structures in each case are presented in the left panel. Red, purple, and blue shaded regions denote the O 2p, Mo 4d $e_g$, and Mo 4d $t_{2g}$ states, respectively.
and Mo 4d $t_{2g}$ states is noticed. The O 2p states also overlap more locally with the Mo 4d $t_{2g}$ states. We find that overall DOS is modified by the inter-octahedral tilts (especially in the conduction band Mo 4d states); however, these changes are found much deeper in both the valence and conduction bands rather than the states near the band edges, thus unraveling the weak dependence of the $E_g$ on the inter-octahedral tilt distortions. We note that the DOS for the WO$_3$ scale model gives qualitatively the same results as the MoO$_3$ scale model for all distortion contributions and thus is not shown.

### 3.3. Examining Intra-octahedral Distortions with Scale Models

Moving on the intra-octahedral distortions, using the scale model, we explore three contributions from intra-octahedral distortions, namely, $i_{\text{shape}}$, $i_{\text{tilt}}$, and $i_{\text{rotation}}$ sequentially.

For many classes of materials composed of polyhedral units, it is common to find geometrical shape distortions that contribute to the overall stability of the material. One of the most common distortion types is that of the Jahn–Teller effect, which resolves degeneracies in electronic levels by breaking certain crystal symmetries, resulting in a lowering of the total energy of the system.\(^6,\)\(^5\) To study the $i_{\text{shape}}$ contributions, we mimic the Jahn–Teller effect by applying both compressive and tensile strain (up to ±6% of the original shape) to the atomic scale model along the z-direction while keeping the original equilibrium octahedral volume fixed (see the atomic structure inserts in Figure 2(b)).

For each shaped-distorted structure, we calculate the $E_g$ and plot this in Figure 2(b). Here, we also find that this Jahn–Teller-type shape distortion has minimal impact on the $E_g$ values ($\Delta E_g \leq 0.3$ eV). On this note, we do observe that $E_g$ decreases almost monotonically for both compressive and tensile strains. While inspecting the corresponding calculated DOS in Figure 2(b), we find almost no significant change to the overall DOS (except for some delocalization of Mo 4d $e_g$ states deep in the valence band region and minor renormalization of the O 2p states). Similar to the $i_{\text{tilt}}$ contributions, the weak dependence of $E_g$ on $i_{\text{shape}}$ is also due to the unaffected band edge states upon shape distortion.

Referring now to Figure 2(c), we find that for the next contribution, $i_{\text{tilt}}$, a slightly larger influence on the $E_g$ variation is noted. Here, we simply vary the volume of the MO$_x$ octahedron in theatomic scale model isotropically (for $\pm 1$% of the original volume) and find that the $E_g$ value monotonically decreases with increasing octahedron volume for $\Delta E_g$ of up to 0.35 eV. From the calculated DOS presented in Figure 2(c), this weak correlation is again clear from the unchanged band edge states, while the largest alteration to the DOS occurs deeper in the bands, especially so for Mo 4d $e_g$ states.

Gathering both orthogonal intra-octahedral distortion ($i_{\text{shape}}$ and $i_{\text{tilt}}$) and inter-octahedral tilting ($i_{\text{rotation}}$) effects, based on our simple atomic scale model, we can deduce that $\Delta E_g$ does seem to have a weak dependence on all these orthogonal and tilt distortion effects.

Now, we turn to the last nonorthogonal intra-octahedral distortion, $i_{\text{rotation}}$, the distortions due to having metal cations displaced far from the center of the octahedron. Based on our scale model, we examine the $i_{\text{rotation}}$ effect by moving the central metal cation in finite steps toward the edge of the octahedron and calculate the electronic $E_g$ value for each distorted structure. In Figure 2(d), as the off-center displacement of the metal cation increases, for both the scale models of WO$_3$ and MoO$_3$, the $E_g$ dramatically increases and then saturates to a constant value, (i.e., ~4.25 and 3.32 eV in WO$_3$ and MoO$_3$, respectively). The maximum $\Delta E_g$ upon cation off-center displacement is approximately 2.7 eV in both MoO$_3$ and WO$_3$.

This large increase in $\Delta E_g$ is strongly corroborated in the changes to the calculated DOS, as shown in Figure 2(d). Though not much variation to the filled valence bands is found, a direct upshifting to higher energies for the conduction band states is found. The Mo 4d $t_{2g}$ and O 2p states are now more localized upon a larger $i_{\text{rotation}}$ effect, and the splitting of Mo 4d $e_g$ states is observed (which results in a small overlapping of the Mo 4d $e_g$ and O 2p states).

Focusing only on the band edge states after $i_{\text{rotation}}$ distortion, the O 2p states are still the major contribution to the valence band edge states, while the contribution of the Mo 4d $e_g$ and O 2p states to the conduction band edge states increases. One may rationalize that the anisotropic overlapping between metal cation 4d orbitals and O 2p orbitals increases as the metal cation moves toward the octahedral edge position. Moreover, this nonorthogonal intradistortion will also be somewhat responsible for the breaking of the octahedral crystal field to a distorted tetrahedral field, which is then reflected in the splitting and lowering of the Mo 4d $e_g$ energy levels.

Collectively, with our simplified binary metal trioxide atomistic scale models, we can now disentangle the individual contributions of inter- and intra-octahedral distortions to the electronic band gap energies of these pseudoperovskite oxides, where the largest dominant factor comes from $i_{\text{rotation}}$, the off-center metal cation intradistortion (and not the speculated inter-octahedral tilts as seen in proper pervoskites\(^6,\)\(^5\)).

### 3.4. Generalized Angle-Based Descriptors and Polyhedral Measurement Indices

Concentrating now on the dominant influence on the metal cation off-center distortions within the octahedron ($i_{\text{rotation}}$), it will be timely to move away from the atomistic scale models and survey this effect in the various polymorphic expressions for both WO$_3$ and MoO$_3$ (cf. Figures S1 and S2). To compare and contrast our results for both WO$_3$ and MoO$_3$, we have also turned to the Materials Project database\(^5\) to extract the structural and $E_g$ information for oxide perovskites (where available). Details for this data extraction are reported in our Supporting Information. Thus, this results in a pool of 46 oxide materials with perovskite-related structures (including the binary metal trioxides examined in this work).

To take into account the importance of $i_{\text{rotation}}$ in studying the structural variations in the oxides with an octahedral network, we define three angle-based descriptors: (1) M–V–M angle ($\theta_{\text{MVM}}$), (2) C–V–C angle ($\theta_{\text{CVC}}$), and (3) V–V–V angle ($\theta_{\text{VVV}}$). The M–V–M angle measures the angle between center metal cations in two adjacent octahedra and the sharing vertex O atom ($M_1$–V$_1$–M$_2$ in Figure 1(b)), and the C–V–C angle is then the angle between two geometric centroids of neighboring octahedra (which explicitly takes the $i_{\text{rotation}}$ nonorthogonal intra-octahedral distortion effect into account) and the sharing vertex O atom ($C_1$–V$_1$–C$_2$ in Figure 1(b)). Last, the V–V–V angle is defined as the angle between sharing vertex O atoms and their diagonal vertices in adjacent octahedra ($V_1$–V$_2$–V$_3$ in Figure 1(b)). Here, the geometric centroid of the octahedron is simply calculated by numerically averaging the positions of six vertex oxygen atoms. The nontilted structures are expected to possess the inter-octahedral distortion angle descriptor of 180°.

From these definitions, our angle-based descriptors are general and flexible enough to include cases where only interoctahedral tilts are dominant (i.e., with almost no $i_{\text{rotation}}$).
effect, such as for conventional proper perovskites, in situations where intra-octahedral distortions become severe (as in the binary metal trioxides considered in this work). In passing, for conventional proper perovskites, owing to the close-to-ideal geometry of the octahedron (with negligible metal-oxygen bond elongation), $\theta_{\text{MVM}}$ and $\theta_{\text{VVV}}$ are often used as a standard descriptor for studying octahedral distortions.

Other useful structural descriptors commonly found in the literature are also used as a benchmark to test if our generalized angle-based descriptors can successfully capture the expected features of the structure (distortion)–property relations. Namely, we have calculated the quadratic elongation index, $(\lambda)^{39}$ (cf. eq 2), bond angle variance index, $\sigma^{39}$ (cf. eq 3, given in $^2$), and last using the continuous shape measurement method (CShM) $^{36,40}$ to quantify polyhedral distortions (cf. eq 4). By and large, these polyhedral measurement methods focus predominantly on intra-octahedral distortions (with explicit considerations for inter-octahedral distortions, where our generalized angle descriptors may appear superior).

Now, we proceed to compare the structure (distortion)–property relations for this group of perovskite-related oxide materials. First, we plot the relations between various generalized angle descriptors—$\theta_{\text{MVM}}$ versus $\theta_{\text{CVC}}$ in Figure 3(a), $\theta_{\text{CVC}}$ versus $\theta_{\text{VVV}}$ in Figure 3(b), and $\theta_{\text{MVM}}$ versus $\theta_{\text{VVV}}$ in Figure 3(c). In all cases, the size of markers is weighted by the magnitude of the band gap energies, $E_g$. The diagonal trend line in the plot of $\theta_{\text{MVM}}$ versus $\theta_{\text{CVC}}$ allows us to distinguish the extent of metal cation off-center intra-octahedral distortions ($i_M$) in the presence of inter-octahedral tilts, while that in the plot of $\theta_{\text{CVC}}$ versus $\theta_{\text{VVV}}$ then expresses the severity of both $i_{\text{shape}}$ and $i_{\text{vol}}$ in the presence of $I_{\text{dir}}$. The plot of $\theta_{\text{MVM}}$ versus $\theta_{\text{VVV}}$ then truly measures the full effect of $i_M$, $i_{\text{shape}}$, and $i_{\text{size}}$ including $I_{\text{dir}}$

By virtue of our definition, oxide structures without strong intra-octahedral distortions will fall nicely on the diagonal linear line where $\theta_{\text{MVM}} \equiv \theta_{\text{CVC}} \equiv \theta_{\text{VVV}}$. This happens to be the clear case for most of the oxide perovskites where only the inter-octahedral tilts are thought to be the most important. Most of our calculated binary MoO$_3$ polymorphs fall out of the diagonal trend lines, largely suggesting that the $i_M$ effect for MoO$_3$ polymorphs can be very large and critical. In contrast, the WO$_3$ polymorphs tend to exhibit a much smaller $i_M$ effect (but not negligible).

We have also employed another sensitive polyhedral shape measurement approach using the CShM $^{36,40,40,61}$ and plotted the relation between MoO$_3$ octahedron distortions and the O$_6$ octahedron distortions in Figure 3(d), weighting the markers by the magnitude of $E_g$. Within the CShM approach, the volume of the octahedron is normalized, and the explicit influence of inter-octahedral tilts is not considered (i.e., $i_{\text{vol}}$ and $I_{\text{dir}}$ are not included explicitly). Here, it is now clear that our generalized angle-based descriptors can capture the complex interplay of both inter- and intra-octahedral distortions in both binary trioxides of W and Mo, where it is apparent that the $E_g$ of the MoO$_3$ polymorphs shows a stronger reliance of $i_M$ while that of WO$_3$ is much weaker. We have also unequivocally established and demonstrated that by using both our atomistic scale models and generalized angle descriptors the binary metal trioxides do operate with a different (but coherent) structure (distortion)–property relationship as compared to the conventional proper oxide perovskites, i.e., intra-octahedral distortions versus inter-octahedral distortions, respectively.
3.5. Establishing the Structure–Property Relationship in WO$_3$ and MoO$_3$. Lastly, to afford a clearer “structure–property” (i.e., $E_g$ versus distortion) relation map, we proceed to plot the $E_g$ versus $(\lambda)$ and $\sigma^2$ in Figures 4(a) and 4(b), respectively. Here, we can finally understand that in the absence of large intra-octahedral distortions (e.g., in many of the conventional oxide perovskites) they lie very close to the $(\lambda) = 1$ and $\sigma^2 = 0$ lines. The further they deviate from these lines the larger their intra-octahedral distortions. It is also interesting to note that these intra-octahedral distortion (only) descriptors are generally proportional to $\Delta E_g$ for the binary metal trioxides, where intradistortions are dominant, while the other oxide perovskites show no clear trend due to their lack of appreciable intra-octahedral distortions.

We find that the calculated values of $(\lambda)$ for the various MoO$_3$ polymorphs range from 1.032 to 1.070, while that for WO$_3$ polymorphs take values from 1.000 to 1.020. This implies that the octahedral networks in MoO$_3$ undergo a more severe internal distortion than those in WO$_3$, corroborating with our atomistic scale models, and generalized angle descriptor data. This is in line with previous works that have reported that the average off-center displacements of the Mo$^{VI}$ cation may be predicted to be more severe than that of the W$^{VI}$ cation, due to relatively higher effective electronegativity.

Furthermore, following ref S7, we also calculate the covalency metric ($C_{4d}$), and plot the variation in $(\lambda)$ and $E_g$ as a function of $C_{4d}$ in Figure 4 of the Supporting Information. We find that both $(\lambda)$ and $E_g$ are directly proportional to $C_{4d}$ implying that the covalency in these binary metal oxides (i.e., more overlap and hybridization between the metal d and oxygen p orbitals) increases as the octahedral distortion becomes more severe. Interestingly, this trend is somewhat opposite to what was observed in ref S7 for proper perovskites. We tentatively attribute this opposite behavior of the differences in the atomic structures as well as the distortion index used in this work, where the distortion behavior and the character of chemical bonding in proper perovskites and the binary metal trioxides can be different. Noting these differences, we argue that our distortion analysis method may be more general, highlighting the usefulness of the distortion indices in this work.

In addition, the role of the metal cation in bond covalency may be approached from the point of view of effective electronegativity, as already discussed in ref 36. From the proposed trend study in a large set of MO$_x$-containing compounds in ref 36, a clear predictive trend of the MO$_x$ octahedral distortion as a function of effective electronegativity was suggested, and this clearly is also reflected in our work (see Figure S4 in Supporting Information).

4. CONCLUSION

From our atomistic scale models and generalized angle descriptors, we disentangled two different types of octahedral distortions present in binary metal trioxides, namely, the intra- and inter-octahedral distortions. Different from their superclass perovskites, the inter-octahedral distortion is found to influence the electronic structure nominally, while the intra-octahedral distortion, especially the metal off-center, dictates the electronic structure dominantly. Based on these observations, we can now appreciate the physical insights and origins of these deviations (or not) for these binary metal oxide materials. We envisage that this suit of general structural analysis tools will largely benefit our understanding of the structure–property relations in other octahedrally connected functional materials. For instance, our models can be extended to investigate and explore alloys of binary oxide materials in an octahedral network (e.g., W$_2$Mo$_{1-x}$O$_{3}$ alloys for electrochromic smart window applications).

ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b11295.

Crystal structures of different WO$_3$ and MoO$_3$ polymorphs (ZIP)
Calculated ionization potential, electron affinity, electronic band gap, lattice constants, quadratic elongation, bond angle variance of WO$_3$ and MoO$_3$ polymorphs; information on perovskites from the Materials Project database; calculated Madelung potential of metal cation and oxygen anion in WO$_3$ and MoO$_3$; calculated quadratic elongation and electronic band gap as a function of covalency metric of WO$_3$ and MoO$_3$ (PDF)

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Notes
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(22) Lee, T.-C.; Lee, Y.; Jang, W.; Soon, A. Understanding the Advantage of Hexagonal WO


Supporting Information

Disentangling the Effects of Inter- and Intra-Octahedral Distortions on the Electronic Structure in Binary Metal Trioxides

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Band edge alignment

We have computed the electronic band gap ($E_g$) and determined the respective band edges – namely, the conduction ($\epsilon_{\text{CBM}}$) and valence ($\epsilon_{\text{VBM}}$) band edges. Both edges are aligned with respect to the absolute vacuum level, for all twelve oxide polymorphs of WO$_3$ and MoO$_3$ (with the HSE06 electronic structure calculations performed on the optB88-vdW optimized geometry). The full list of the calculated energy values are tabulated in Table S1.

In aligning the band edges of these metal oxides, we first perform core-level calculations for all polymorphic phases of WO$_3$ and MoO$_3$. Using the bulk O 1s energy core-levels of each polymorphic phase as an absolute reference, we align the band edge energies of the WO$_3$ polymorphs and then for that of MoO$_3$ separately. Next, to align the band edges between
both WO$_3$ and MoO$_3$, we calculate both the bulk and unrelaxed surface O 1s core-levels (in order to neglect the surface states) for h-WO$_3$(1010) and α-MoO$_3$(010) to obtain the vacuum level with respect to the corresponding bulk phases. Now, the difference between aligned $\epsilon_{\text{CBM}}$, $\epsilon_{\text{VBM}}$, and vacuum level ($V_{\text{vac}}$) can be used to define the electron affinity (EA) and ionization potential (IP), respectively.

Figure S1: The crystal structures of different WO$_3$ polymorphs: Cubic cub-WO$_3$, tetragonal tet-WO$_3$, hexagonal H1-WO$_3$, hexagonal H2-WO$_3$, orthorhombic ort-WO$_3$, triclinic tri-WO$_3$, low temperature monoclinic $\varepsilon$-WO$_3$, and room temperature monoclinic $\gamma$-WO$_3$. The W and O atoms are represented by the dark grey and red spheres, respectively (with the faces of the WO$_6$-octahedron shown in grey). The unit cell is denoted as black solid lines.
Figure S2: The crystal structures of different MoO₃ polymorphs: Orthorhombic α-MoO₃, monoclinic II-MoO₃, monoclinic β-MoO₃, and hexagonal h-MoO₃. The Mo and O atoms are represented by the light grey and red spheres, respectively (with the faces of the MoO₆-octahedron shown in grey). The unit cell is denoted as black solid lines.

Figure S3: Calculated Madelung potential of metal (upper panel) and oxygen (lower panel) in WO₃ and MoO₃ polymorphs. Scale of lower panel is intentionally inverted for discussions.
Table S1: HSE06-calculated ionization potential (IP), electron affinity (EA), and electronic band gap ($E_g$) for various WO$_3$ and MoO$_3$ polymorphs.

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Table S2: Calculated lattice parameters, quadratic elongation index ($\langle \lambda \rangle$), and bond angle variance index ($\sigma^2$) for various WO$_3$ and MoO$_3$ polymorphs, as determined with the optB88-vdW xc functional.

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Table S3: Chemical formulae and ID tags for the 35 oxide perovskites obtained from the Materials Project database.\textsuperscript{1} We have refined and chosen this set of oxide perovskites using the following selection criteria: 1) Data tagged with the keyword “perovskite”, 2) GGA $xc$ functional calculations, 3) Planewave kinetic cutoff energy of $\geq 500$ eV, 4) Negative formation energy, and 5) No additional assumptions in the band gap determination due to the sparse $k$-point grid.

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Figure S4: Calculated (a) quadratic elongation ($\langle \lambda \rangle$) and (b) electronic band gap ($E_g$) of WO$_3$ (red circles) and MoO$_3$ (blue triangles) polymorphs as a function of covalency metrics ($C_{dp}$).
References