

# Understanding the Structural and Electronic Properties of Bismuth Trihalides and Related Compounds

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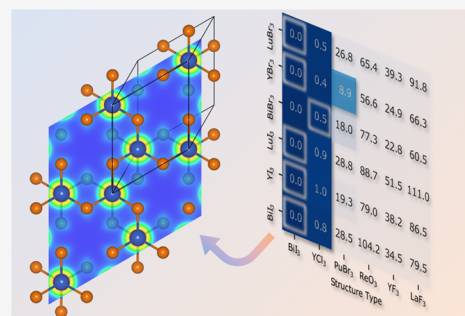
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**ABSTRACT:** Bismuth trihalides,  $\text{BiX}_3$  ( $X = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ ), have been thrust into prominence recently because of their close chemical relationship to the halide perovskites of lead, which exhibit remarkable performance as active layers in photovoltaic cells and other optoelectronic devices. In the present work, we have used calculations based on density functional theory to explore the energetics and electronic properties of  $\text{BiX}_3$  in a variety of known and hypothetical structure types. The results for  $\text{BiX}_3$  are compared with those obtained for the halides of the later rare earths, represented by  $\text{YX}_3$  and  $\text{LuX}_3$ . The relative thermodynamic stabilities of the known and hypothetical structures are calculated, along with their band gaps. For the  $\text{BiX}_3$  systems, we have explored the role of lone-pair effects associated with bismuth(III), and for  $\text{BiI}_3$ , we have compared the predicted structural behavior as a function of pressure with the available experimental data. We have also attempted to synthesize  $\text{LuF}_3$  in the perovskite-related  $\text{ReO}_3$ -type structure, which is predicted to be only  $\sim 7.7 \text{ kJ mol}^{-1}$  above the convex hull. This attempt was unsuccessful but led to the discovery of a new hydrated phase,  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\text{H}_2\text{O}$ , which is isomorphous with the known ytterbium analogue.



## INTRODUCTION

Metal halide materials possess a rich variety of interesting properties that have resulted in a number of technologically important applications, including their use as scintillator materials for X-ray detection,<sup>1</sup> ionic conductors for energy-storage applications,<sup>2,3</sup> and their adoption as photoluminescent materials for bioimaging through up-conversion.<sup>4,5</sup> Recently, hybrid perovskite halides of the general formula  $\text{A}^{\text{I}}\text{Pb}^{\text{II}}\text{X}_3$  [ $\text{A} =$  amine cation, such as  $\text{CH}_3\text{NH}_3^+$  or  $\text{CH}(\text{NH}_2)_2^+$ , and  $\text{X} = \text{Cl}, \text{Br}, \text{and I}$ ] have attracted significant interest in relation to photovoltaic (PV) and photoluminescence (PL) applications because of their excellent optoelectronic properties, facile synthesis, and low cost.<sup>6–10</sup> However, the toxicity of lead (Pb) and the sensitivity to moisture of these perovskites have stimulated efforts to find alternative materials that can provide similar or even superior optoelectronic properties without toxicity and stability issues. One strategy involves replacing the divalent metal ( $\text{Pb}^{2+}$ ) with a mixture of monovalent  $\text{M}^{\text{I}}$  and trivalent  $\text{M}^{\text{III}}$  cations to form halide double perovskites of the general formula  $\text{A}_2\text{M}^{\text{I}}\text{M}^{\text{III}}\text{X}_6$  ( $\text{A} =$  alkali metal or amine cation),<sup>11–16</sup> and thus expands the structural diversity of the family of these perovskite materials. Most of the work in this area has focused on the use of bismuth (Bi) as the  $\text{M}^{\text{III}}$  cation, although there has also been work involving antimony (Sb),<sup>17</sup> as well as rare-earth elements for possible optical and magnetic applications.<sup>18</sup> Another strategy is to use the bismuth halides themselves, especially  $\text{BiI}_3$ , which is attracting attention for PV cell applications.<sup>19,20</sup> However, the low dimensionality of the layered structure adopted by  $\text{BiI}_3$  leads to a wider band gap

( $\sim 1.8 \text{ eV}$ )<sup>21</sup> compared with the Pb-containing perovskite iodides; hence, it is not ideal for PV applications. One approach to solve this problem would be to identify accessible polymorphs of the bismuth halides that retain a 3D network architecture and should therefore have narrower band gaps. For example, the most obvious structural candidate would be the  $\text{ReO}_3$ -type structure,<sup>22,23</sup> which has a perovskite architecture with no cation in the cavity (i.e.,  $\text{MX}_3$ ).

In this paper, we address the question, can we favorably access bismuth halides in 3D structures, such as the  $\text{ReO}_3$  type? It is already known that  $\text{M}^{\text{III}}\text{F}_3$  compounds, such as  $\text{ScF}_3$  and  $\text{InF}_3$ , adopt the  $\text{ReO}_3$  structure, so this is a reasonable hypothesis. However,  $\text{BiF}_3$  and  $\text{BiCl}_3$  normally adopt 3D structures related to that of  $\text{YF}_3$  and the smaller rare-earth fluorides (Sm–Lu), while  $\text{BiBr}_3$  and  $\text{BiI}_3$  both have layered structures that are also seen for the rare-earth chlorides (Dy–Lu), bromides, and iodides (Sm–Lu).<sup>24</sup> We have therefore used a computational approach to map the thermodynamic stability of the binary trihalides,  $\text{MX}_3$ , with  $\text{M} = \text{Bi}, \text{Y}, \text{and Lu}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$ . This strategy has been applied for several structure types, specifically those of  $\text{BiI}_3$  (2D),  $\text{YCl}_3$  (2D),  $\text{PuBr}_3$  (2D),  $\text{ReO}_3$  (3D),  $\text{YF}_3$  (3D), and  $\text{LaF}_3$  (3D). We have carried out calculations using density functional theory

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(DFT) to determine the thermodynamic properties of each of the  $\text{MX}_3$  phases in the different structure types. Furthermore, we have performed simulations with hybrid functionals to assess the optoelectronic properties of a subset of relevant materials to identify novel candidates light absorbers and scintillators. We have also assessed the role of electron lone pairs on bismuth by comparing the results for the  $\text{BiX}_3$  systems with those for the rare-earth analogues,  $\text{YX}_3$  and  $\text{LuX}_3$ .

Our computational analysis suggests that although  $\text{LuF}_3$  appears to be metastable in the  $\text{ReO}_3$  prototype, it should be accessible through synthetic strategies. We explored the synthesis of this phase in the laboratory through a solution evaporation method and found a hydrated phase,  $(\text{H}_3\text{O})\text{-Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$ , crystallizing in the space group  $Fd\bar{3}m$ , which has not been reported previously.

## METHODOLOGY

To assess the thermodynamics of binary trihalides  $\text{MX}_3$  with  $\text{M} = \text{Lu}, \text{Y}, \text{and Bi}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{and I}$  using first-principles calculations, we computed the total energies of each compound and calculated the formation energies from their elemental constituents. The formation energies ( $E_f$ ) were calculated as  $E_f = E(\text{M}_y\text{X}_{4-y}) - yE(\text{M}) - (4 - y)E(\text{X})$  ( $y = 1$ ), where  $E(\text{M}_y\text{X}_{4-y})$ ,  $E(\text{M})$ , and  $E(\text{X})$  are the DFT total energies for the  $\text{MX}_3$  compound, M metal, and X halides, respectively.  $E(\text{X})$  is the DFT total energy of element X in its most stable form. For  $\text{X} = \text{F}$  and  $\text{Cl}$ ,  $E(\text{F}) = E[\text{F}_2(\text{g})]/2$  or  $E[\text{Cl}_2(\text{g})]/2$ , where  $E[\text{F}_2(\text{g})]$  and  $E[\text{Cl}_2(\text{g})]$  were calculated on the solid phases of  $\text{F}_2$ ,  $\text{Cl}_2$ ,  $\text{Br}_2$ , and  $\text{I}_2$ , respectively. We only focus on total energies neglecting entropy contributions,  $pV$ , and zero-point energies because these are expected to be almost identical when dense solids are compared with similar structure types.<sup>25</sup> Additional details concerning the effects of entropy and the  $pV$  term are discussed in the Supporting Information (SI), with particular reference to  $\text{LuF}_3$  in the  $\text{YF}_3$  and  $\text{ReO}_3$  structure types.

From the formation energy plots (see an example of the convex hull plot in the SI), the energies above the convex hull,  $E^{\text{hull}}$ , were then evaluated as  $E^{\text{hull}}(\text{MX}_3) = E_f(\text{MX}_3) - \min[E_f(\text{MX}_3)]$ , where  $\min[E_f(\text{MX}_3)]$  belongs to the  $\text{MX}_3$  compound with the lowest formation energy among all different polymorphs. Figure S1 shows an example of how we determine the convex hull of a  $\text{Bi}_m\text{X}_n$  system and related  $E^{\text{hull}}$  at specific compositions, e.g.,  $\text{BiX}_3$ .

DFT calculations were performed using the projected-augmented-wave potentials,<sup>26,27</sup> as implemented in VASP,<sup>28,29</sup> with the following electrons treated explicitly: Bi [ $6s^2 6p^3$ ], Y [ $4s^2 4p^6 4d^1 5s^2$ ], Lu [ $5s^2 5p^6 5d^1 6s^2$ ], F [ $2s^2 2p^5$ ], Cl [ $3s^2 3p^5$ ], Br [ $4p^2 4p^5$ ], and I [ $5s^2 5p^5$ ]. A kinetic-energy cutoff of 520 eV and a  $\Gamma$ -centered Monkhorst–Pack  $k$ -point mesh<sup>30</sup> were automatically generated along each reciprocal vector  $\vec{b}_i$  with a number of  $k$ -points  $N_i = \max(1, l \times |\vec{b}_i| + 0.5)$  where  $l$  is the  $k$ -point line density with  $l = 25$ . The exchange and correlation energy was evaluated by the generalized gradient approximation, within the Perdew–Burke–Ernzerhof (PBE) functional.<sup>31</sup> Van der Waals forces were captured by Grimme's method (i.e., DFT-D3 employing zero damping).<sup>32</sup> The total energy was considered converged within  $1 \times 10^{-5}$  eV. In all cases, both the volume and internal coordinates were optimized until the forces were less than  $0.01 \text{ eV } \text{\AA}^{-1}$ . Whenever possible, the symmetry of each prototype structure was preserved in these calculations (see the section on the structure description). For high-pressure calculations,  $H = E + pV$  was used instead of  $E$ ,

and all structures were relaxed using the same parameters as those stated above.

The band gaps of the halides were computed from the fully optimized structures (i.e., volume, shape, and internal coordinates) using the HSE06 hybrid functional<sup>33</sup> with van der Waals corrections. Because of the cost of the hybrid functional calculations, the total energies and geometries were converged within the prescribed tolerances set by the pymatgen library.<sup>34</sup> Spin–orbit coupling (SOC) effects were included by performing a single-point energy calculation on the fully relaxed HSE06+D3 structures. The inclusion of SOC has been found necessary<sup>35</sup> to describe accurately the electronic structures of compounds containing heavy elements, such as Bi and Pb. The band gaps were estimated from the total densities of states (DOSs) computed on  $k$ -point grids, including the special inequivalent symmetry points of the Brillouin zone of each polymorph. The electron localization function (ELF)<sup>36</sup> was computed with the PBE functional (on the fully relaxed PBE+D3 geometries) to establish the role of lone pairs in specific structures.

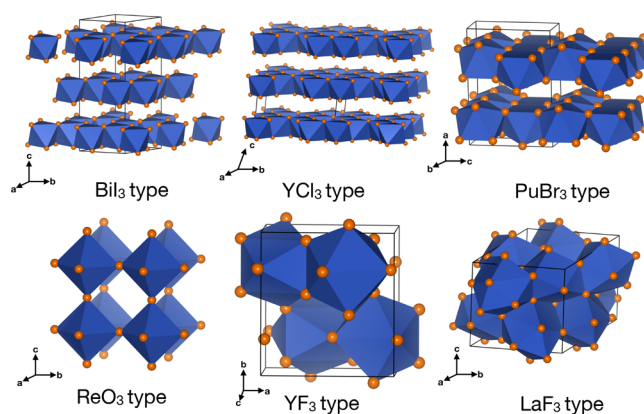
## RESULTS AND DISCUSSION

**Selection of Prototype Structures.** We have considered the six structure types shown in Table 1 and Figure 1, for a

**Table 1.** Space Group, Coordination Number (CN) of the Metal Site, and Structural Dimensionality of the Different Structure Types Considered in This Study

type	space group	CN	dimensionality	comment	ref
$\text{BiI}_3$	$R\bar{3}m$	6	2D-layered	ABCABC stacking	37
$\text{YCl}_3$	$C2/m$	6	2D-layered	ABAB stacking	38
$\text{PuBr}_3$	$Cmmm$	8	2D-layered	ABAB stacking	39
$\text{ReO}_3$	$Pm\bar{3}m$	6	3D	perovskite-type framework	40
$\text{YF}_3$	$Pnma$	9	3D	3D complex structure	41
$\text{LaF}_3$	$P\bar{3}c1$	9	3D	tysonite	42

total of 72 trihalides, known and hypothetical, spanning all combinations of the three metals (Bi, Lu, and Y) and four halogens (i.e., F, Cl, Br, and I). In addition, we have examined three other structure types,  $\text{ZrI}_3$ ,  $\text{UCl}_3$ , and  $\text{BiF}_3$  (gananite), whose results are shown in Figure S2 and Table S1. The initial



**Figure 1.** Six structure types explored for each system: the  $\text{BiI}_3$ ,  $\text{YCl}_3$ ,  $\text{PuBr}_3$ ,  $\text{ReO}_3$ ,  $\text{YF}_3$ , and  $\text{LaF}_3$  structures. The polyhedra show the metal coordination in each structure type.

structures for energy minimization and geometry optimization were taken from the Inorganic Crystal Structure Database unless stated otherwise.

Table 1 provides the geometrical characteristics of each structure type, including the coordination number (CN) of the metal and the structural dimensionality (2D- or 3D-layered network). Of the three metals studied, Bi was chosen as a potential replacement of toxic Pb in conventional hybrid perovskite solar cells, as discussed earlier. Yttrium (Y; 0.90 Å) and lutetium (Lu; 0.86 Å) are smaller in ionic radii than Bi (1.03 Å) when occupying 6-coordinated sites and are thus potential candidates to form a  $\text{ReO}_3$  structure type. In addition, the electronic configurations of  $\text{Y}^{3+}$  and  $\text{Lu}^{3+}$  are closed-shell, unlike most of the rare-earth elements, and therefore avoid spin-polarized calculations.

$\text{BiI}_3$  and  $\text{YCl}_3$  compounds form very similar layered structures, with the major difference in the different stacking arrangements of the layers (see Figure 1 and Table 1). The  $\text{PuBr}_3$  structure type is also layered and has the same stacking arrangement as  $\text{YCl}_3$  (ABAB) but with a higher CN of the metal site (8) than  $\text{YCl}_3$  (6). The  $\text{PuBr}_3$  structure type was included because a number of rare-earth compounds are known to form with this structure type.<sup>24</sup>

Table 2 compares the performance of our computational methodology in describing the lattice constants of the known

**Table 2. Differences (%) in the Lattice Parameters and Unit Cell Volume between DFT (PBE+D3)-Calculated Values and Experiments**

structure	<i>a</i>	<i>b</i>	<i>c</i>	ref
$\text{BiF}_3$	−0.26	1.10	1.12	41
$\text{BiCl}_3$	1.08	−3.67	1.66	43
$\text{BiBr}_3$	−0.72	−0.47	0.67	44
$\text{BiI}_3$	1.22	1.22	1.26	37
$\text{YF}_3$	0.18	1.19	2.18	41
$\text{YCl}_3$	−0.15	−0.44	−0.30	38
$\text{YI}_3$	0.30	0.30	0.72	45

$\text{MX}_3$  structures for Bi and Y. More details are given in the SI. Almost all of our lattice constants from DFT agree within 2% of the experimental values. Because a number of layered structures are considered (e.g.,  $\text{BiI}_3$  and  $\text{YCl}_3$  types), van der Waals forces are treated explicitly to describe correctly the energetics and thus the structural features.<sup>32</sup> As shown in Table 3, the van der Waals corrections significantly improve the predictions of the lattice parameters and volumes of layered structures such as  $\text{BiI}_3$ . As expected, the largest improvement is observed for the *c* lattice parameters, which reflects the layer

**Table 3. Comparison with Experiments of DFT-Calculated Lattice Parameters (Å) and Unit Cell Volumes for  $\text{BiI}_3$  (Å<sup>3</sup>) for Calculations with and without van der Waals Corrections<sup>a</sup>**

	<i>a</i>	<i>c</i>	<i>a/c</i>	<i>V</i>
PBE	7.843 (4.35)	23.163 (11.79)	2.953 (7.13)	1233.91
PBE+D3	7.608 (1.22)	20.981 (1.26)	2.758 (0.04)	1051.67
Exp <sup>37</sup>	7.516	20.720	2.757	1013.66

<sup>a</sup>The ratio between *a* and the lattice constant along the stacking direction is also provided [in parentheses: the relative variation (%) to the experiment].

separation, and the *a/c* ratio reflects the quality of our simulations against experiments.

**Thermodynamic Stability of  $\text{MX}_3$  Materials.** Figure 2a shows the computed volumes (color bar) per formula unit of  $\text{MX}_3$  for each compound considered (*y* axis) across the six structure types identified (*x* axis). The volumes increase systematically from fluoride- to iodide-based structures, as well as from  $\text{Lu}^{3+}$  to  $\text{Bi}^{3+}$ , because of the increasing ionic radii of these ions. However, there are two exceptions to these trends: for  $\text{YF}_3$  in the  $\text{BiI}_3$  structure and  $\text{YI}_3$  in the  $\text{PuBr}_3$  type, the volumes are anomalously low. This appears to be caused by the significant distortions that occurred during structure relaxation; for example,  $\text{YF}_3$  (in the  $\text{BiI}_3$  type) changed dimensionality from an initial 2D to a 3D complex structure, and vice versa for  $\text{YI}_3$  (in  $\text{PuBr}_3$ ).

The thermodynamic stability for each compound is characterized by its formation energy and energy above the convex hull ( $E^{\text{hull}}$ ) for different structure types. The color bar of Figure 2b shows the energy above the convex hull (in  $\text{kJ mol}^{-1}$  per  $\text{MX}_3$ ) for each structure type (*x* axis) and compound (*y* axis). White areas indicate polymorphs that are not expected to form under any conditions, whereas blue areas show stable structures (dark blue) or potential metastable structures (in lighter shades of blue). Structures identified experimentally are boxed with white halos. We chose an upper bound of  $E^{\text{hull}}$  of  $20.0 \text{ kJ mol}^{-1}$  per  $\text{MX}_3$  ( $\sim 207 \text{ meV}$  per  $\text{MX}_3$  and  $\sim 52.0 \text{ meV}$  per atom, respectively) as the threshold between the metastable and unstable structures. Sun et al.<sup>46</sup> have recently proposed a threshold for  $E^{\text{hull}}$  of  $\sim 70 \text{ meV atom}^{-1}$  between the metastable and unstable structures, and our upper bound broadly follows this prescription.

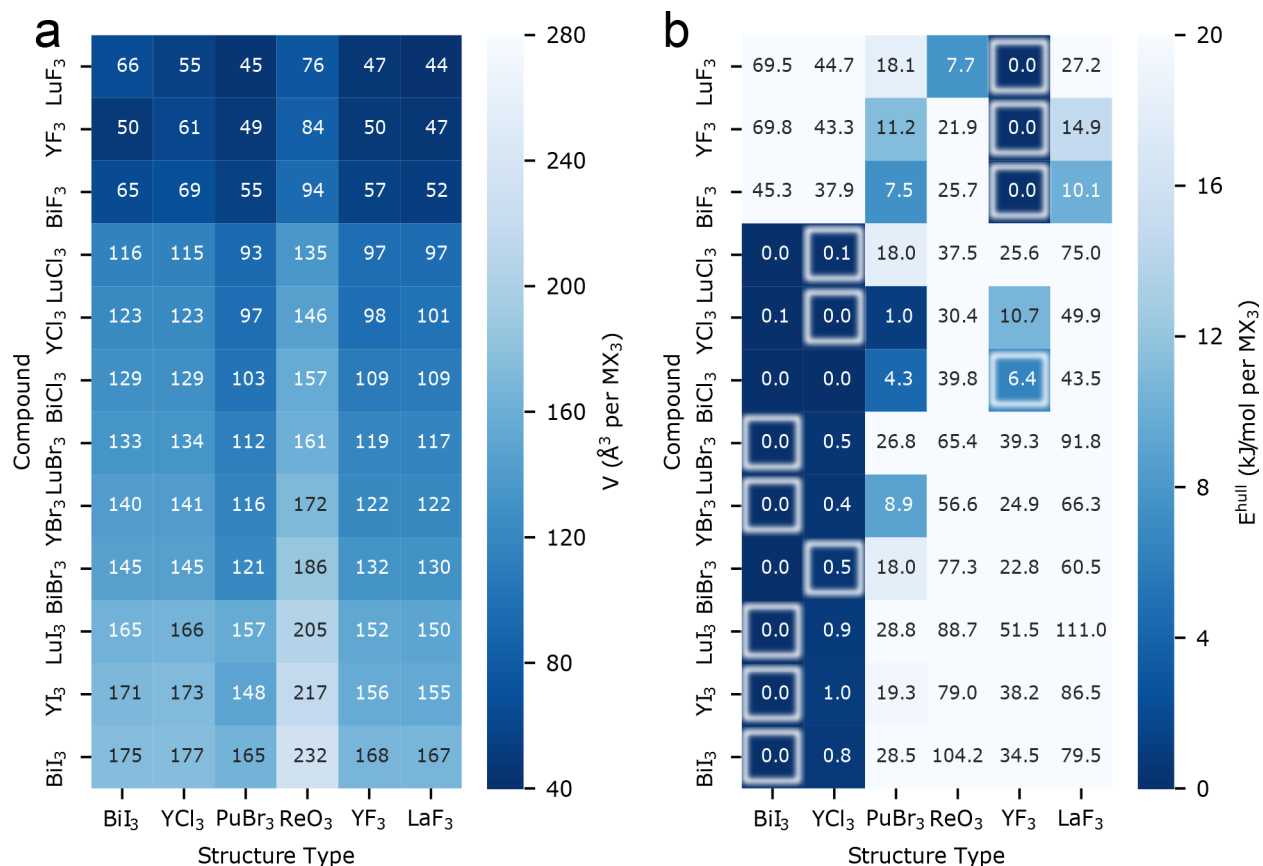
As shown in Figure 2b, the DFT calculations reproduce the correct experimental polymorphs in virtually all cases (see the white boxes), with  $E^{\text{hull}}$  close to or equal to  $0.00 \text{ kJ mol}^{-1}$ . Given the structural similarity of the  $\text{BiI}_3$  and  $\text{YCl}_3$  structure types, the values of  $E^{\text{hull}}$  for each compound with these two structure types are very similar. The only discrepancy between our DFT predictions and the experimental data is found for  $\text{BiCl}_3$ , where DFT suggests a 2D  $\text{BiI}_3$  (or  $\text{YCl}_3$ ) structure type, whereas a 3D  $\text{YF}_3$  structure type was reported experimentally.<sup>43</sup> However, the energy of the reported structure is only  $6.4 \text{ kJ mol}^{-1}$  above the convex hull, and the DFT calculation for this structure nicely reproduces the molecular nature of the bonding,<sup>43</sup> with three short Bi–Cl bonds and several much longer ones.

In general, as shown in Figures 2a,b, the stability of  $\text{ReO}_3$  structure types decreases upon expansion of the volume of either the M cation or X halide or both. We find that  $\text{LuF}_3$  has the lowest energy above the hull ( $E^{\text{hull}} \sim 7.8 \text{ kJ mol}^{-1}$  per formula unit); hence,  $\text{LuF}_3$  is the best candidate for adopting the  $\text{ReO}_3$  structure type.

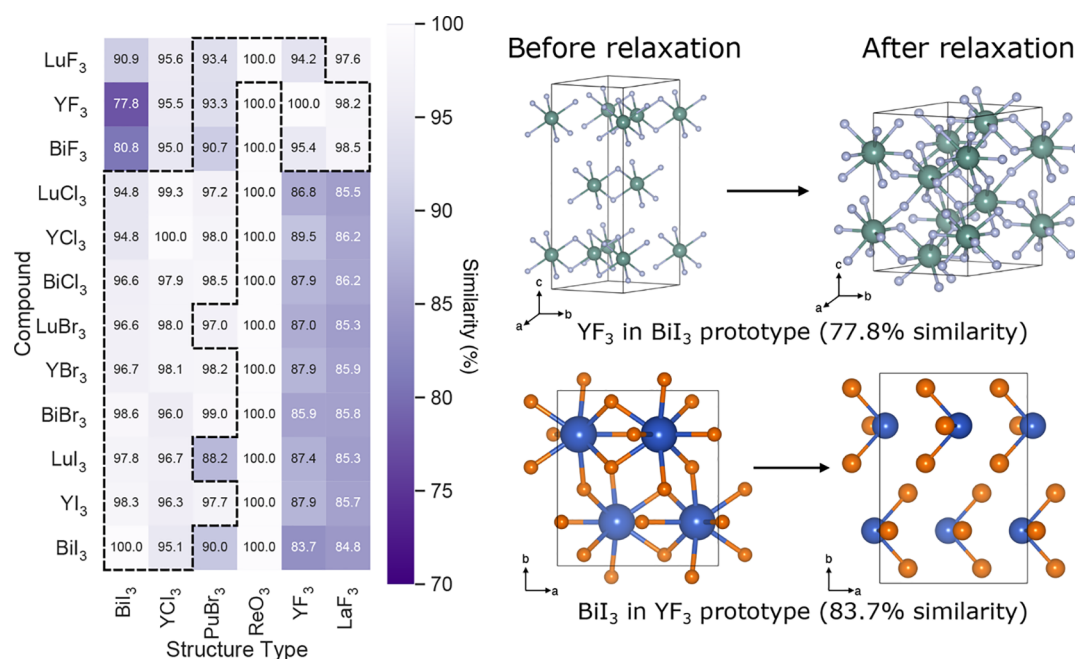
In addition to  $\text{LuF}_3$  in the  $\text{ReO}_3$  prototype, we have identified other stable or metastable structures, including  $\text{YCl}_3$ ,  $\text{BiCl}_3$ ,  $\text{BiF}_3$ ,  $\text{YBr}_3$ ,  $\text{YF}_3$ ,  $\text{BiBr}_3$ , and  $\text{LuF}_3$  in the  $\text{PuBr}_3$  structure type and  $\text{BiF}_3$  and  $\text{YF}_3$  in the  $\text{LaF}_3$  structure type. The  $\text{PuBr}_3$  structure both has a high CN (8) on the metal site and is 2D-layered, which is placed between  $\text{YCl}_3/\text{BiI}_3$  (low CN and dimensionality) and  $\text{LaF}_3/\text{YF}_3$  (high CN and dimensionality). Therefore, most of these predicted compounds in the  $\text{PuBr}_3$  structure type are close to the convex hull.

In Figure 2b, other general trends can be identified and serve to rationalize the relative stabilities of these  $\text{MX}_3$  polymorphs. For example, we observe that Lu-based





**Figure 2.** (a) DFT-computed unit cell volumes ( $V$  in  $\text{\AA}^3$  per  $\text{MX}_3$ ) per unit formula of  $\text{MX}_3$ . (b) DFT-calculated formation energy above the convex hull ( $E_{\text{hull}}$  in  $\text{kJ mol}^{-1}$  per  $\text{MX}_3$ ). The experimentally identified phases are boxed with white halos.



**Figure 3.** Structural similarity (%) between relaxed compounds and their prototypes based on the minimized  $d_{\text{RMS}}$  computed for each compound and a reference prototype. The dashed black lines are guides for the eye and map the stable or metastable structures identified in Figure 2b. Two examples,  $\text{YF}_3$  in the  $\text{BiI}_3$  structure type and  $\text{BiI}_3$  in the  $\text{YF}_3$  structure type, are shown here.

compounds in the  $\text{BiI}_3$  structure type strongly prefer the larger anions,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ , as demonstrated by their low energies above the hull.

It is also important to verify the relative distortions of compounds investigated in this study in comparison to their prototypical structures, e.g.,  $\text{ReO}_3$ ,  $\text{BiI}_3$ , and  $\text{LaF}_3$ . To this end,

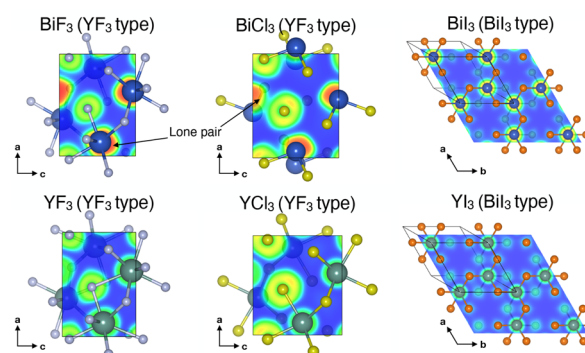
we utilize a structure matching algorithm,<sup>47</sup> which computes the minimized root-mean-square distances. This is defined as  $d_{\text{RMS}} = \sqrt[3]{n/V_{\text{avg}} \sqrt{(\sum_{i=1}^n d_i^2)/n}}$  between each compound and a reference structure, where  $d_i$  is the Cartesian distances between the  $i$ th site between two structures,  $n$  is the total number of sites, and  $V_{\text{avg}}$  is the volume of the average lattice of the two structures compared. Our reference structures are the prototypical experimental structures; for example, if we consider  $\text{LuF}_3$  in the  $\text{ReO}_3$  structure type, its reference structure would be set by the atomic arrangement in  $\text{ReO}_3$  ( $\text{Pm}\bar{3}m$ ). Thus, a value of  $d_{\text{RMS}} = 0$  means that the compound the structure of its prototype and, hence, without any distortion. In contrast, large values of  $d_{\text{RMS}}$  suggest large distortions after relaxation.

Figure 3 shows the relative changes in percent (of  $d_{\text{RMS}}$ ), here termed similarity, between different compounds and their structure prototypes of origin, where dark purple represents large distortion from the prototype structure of reference. Note that 100% similarity matches with  $d_{\text{RMS}} = 0$  and 0% stands for  $d_{\text{RMS}} = 1$ . All compounds with the  $\text{ReO}_3$  structure type have 100% similarity due to the symmetry constraint imposed during the relaxation process.

By relating trends of similarity (or  $d_{\text{RMS}}$ ) and thermodynamic stability (Figure 2b), a number of observations can be made. (i) At first glance, one can draw a unidirectional link between structures with high thermodynamic stability (i.e.,  $E^{\text{hull}} \sim 0$  kJ per formula unit) and structures with high similarity near 100% (or close to  $d_{\text{RMS}} = 0$ ). For example, most chloride, bromide, and iodide compounds in the  $\text{BiI}_3/\text{YCl}_3$  types are thermodynamically stable (Figure 2b) and, hence, show appreciable similarity with their prototypes, i.e., small distortions after relaxation. Exceptions to this trend are  $\text{YCl}_3$  and  $\text{BiCl}_3$  in the  $\text{YF}_3$  structure type. In particular,  $\text{YCl}_3$  forms a layered-type structure, whereas  $\text{BiCl}_3$  forms an almost isolated molecular structure, most likely because of the lone pair of  $\text{Bi}^{3+}$  (as discussed in the next section). (ii) Interestingly, one observes that when fluorine compounds, such as  $\text{LaF}_3$  and  $\text{YF}_3$ , are anion-exchanged with the larger halides  $\text{Cl}^-$ ,  $\text{Br}^-$ , or  $\text{I}^-$ , low values of similarity (i.e., large  $d_{\text{RMS}}$  values) and low thermodynamic stabilities (Figure 2b) are found. From a closer inspection of the structures of these compounds, we observed their transformation from 3D compact structures to layered-type structures. Similarly, a transformation implying a change of the dimensionality from 2D to 3D can be observed when iodine is exchanged with fluorine, as in the compounds in the top-left side of Figure 3. (iii) Another observation is that high values of similarity, equivalent to low values of  $d_{\text{RMS}}$ , cannot guarantee low or zero  $E^{\text{hull}}$ . While most compounds in the  $\text{ReO}_3$  structure type are thermodynamically unstable (except for  $\text{LuF}_3$ ), they appear less distorted after relaxation, which we link to the constraint of symmetry and the size of the unit cell adopted.

**Role of the Lone Pair in  $\text{BiX}_3$  Structures.** We move now to analysis of the electronic structure of the known experimental structure types (see Table 1), beginning with consideration of the lone-pair effects in the bismuth(III) compounds. It is well established that a wide range of lead(II) and bismuth(III) compounds exhibit stereochemically active  $s^2$  lone pairs in systems ranging from inorganic<sup>48</sup> and hybrid perovskites<sup>49</sup> to metal–organic frameworks,<sup>50,51</sup> so it is expected that these effects might be seen in the bismuth halides. We explore this behavior in the  $\text{BiX}_3$  phases by

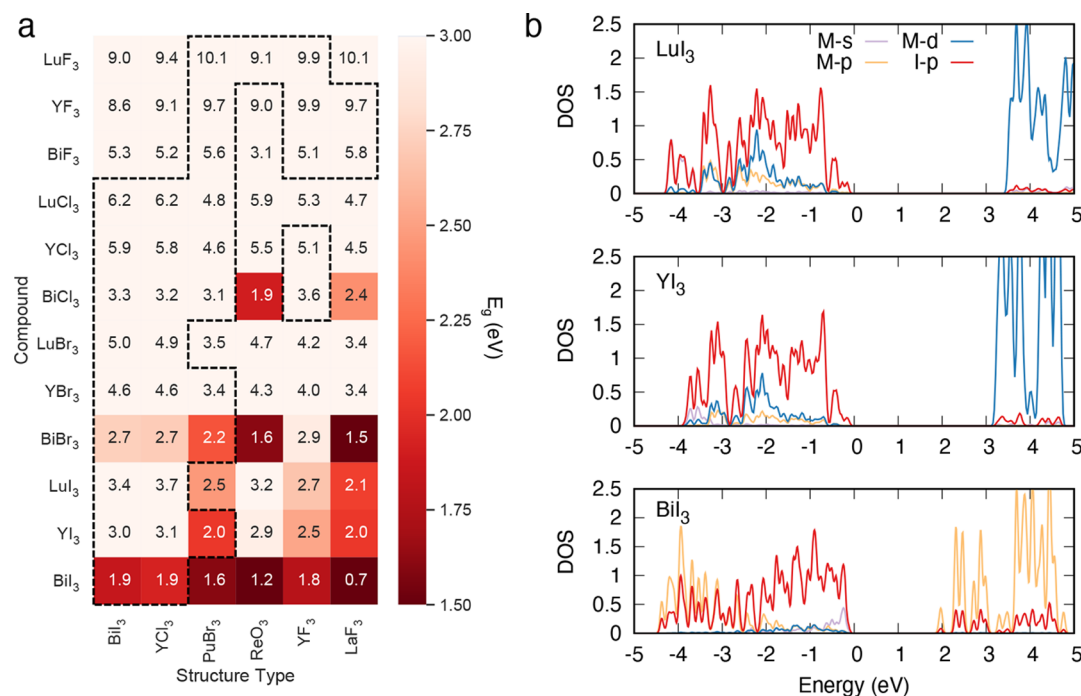
analyzing the ELF, which enables us to localize the electron lone pairs around bismuth(III) (Figure 4). For comparison, we also show the ELF functions for the corresponding yttrium(III) phases, where no lone-pair effect is expected.



**Figure 4.** Computed ELF functions for  $\text{BiF}_3$ ,  $\text{BiCl}_3$ ,  $\text{BiI}_3$ ,  $\text{YF}_3$ ,  $\text{YCl}_3$ , and  $\text{YI}_3$  in the structure type shown in parentheses. Note that  $\text{BiBr}_3$  and  $\text{YBr}_3$  are very similar to the iodide analogues. Color mapping of the ELF value is shown from 0 (blue) to 1 (red).

In ELF calculations, values near 0.5 are indicative of the delocalization of charge similar to a homogeneous electron gas, whereas  $\text{ELF} = 1$  suggests areas matching high electron localization. From Figure 4, both  $\text{BiF}_3$  and  $\text{BiCl}_3$  show large ELF values ( $\sim 0.8$ ) near the  $\text{Bi}^{3+}$  cations and the shape of the domain appears highly anisotropic, suggesting significant localization of the lone pair. The presence of lone-pair effects can directly affect the symmetry and unit cell dimensions of the crystal structures.<sup>48</sup> For example, in  $\text{BiF}_3$ , the lone pair causes an elongation of the  $c$  axis, increasing the  $c/a$  ratio to 0.75;<sup>41</sup> this can be compared with a value of 0.71 in  $\text{YF}_3$ , where the lone pair is not present. In  $\text{BiCl}_3$ , which is virtually molecular, one can observe the arrangement of pyramidal  $\text{BiCl}_3$  moieties that are held together by van der Waals forces, much as one would find in the structure of ammonia. Because of the distortion imparted by the highly localized lone pair, the overall dimensionality and CN of  $\text{Bi}^{3+}$  are reduced. This may lead to the confinement of electrons, which is partly responsible for the large band gaps in  $\text{BiCl}_3$  and  $\text{BiF}_3$  (see Figure 5). However, in the case of  $\text{BiBr}_3$  and  $\text{BiI}_3$  (Figure 4), the lone pairs are not active and the ELF functions are very similar to those of the Y structures. The tendency of lone-pair effects to be stronger with more electronegative ions has been seen in other systems, such as the  $\text{PbO}$ -layered structure (driven by the lone pair on Pb) compared with the cubic rock-salt structure in  $\text{PbS}$ ,  $\text{PbSe}$ , and  $\text{PbTe}$ .<sup>52</sup> To some extent, however, the lone-pair effect can be influenced by the structure itself because we note that  $\text{BiI}_3$  in a hypothetical  $\text{YF}_3$  structure type forms a pyramidal molecular species like that seen experimentally in  $\text{BiCl}_3$  (Figure S5).

**Band-Gap Characteristics of  $\text{MX}_3$ .** We now move our attention to the optoelectronic properties of the  $\text{MX}_3$ -based materials. Figure 5a shows the band-gap values ( $E_g$ ) computed with the HSE06 hybrid functional, while Table 4 compares our predictions with the existing experimental measurements of  $E_g$ . When the predicted values of the band gap are benchmarked against the experimentally reported values in Table 4, we observe that our data with the HSE06 hybrid functional are more accurate. As in hybrid perovskite materials, the quantitative description of  $E_g$  requires a higher level of theory



**Figure 5.** (a) Computed energy band gaps ( $E_g$  in eV) at the HSE06+D3+SOC level of theory. The dashed black lines are guides for mapping the stable or metastable structures identified in Figure 2b. (b) pDOS on selected atomic orbitals of  $MI_3$  ( $M = \text{Lu}, \text{Y}, \text{and Bi}$ ) in the  $\text{BiI}_3$  structure type.

**Table 4. Comparison of  $E_g$  (eV) between the Experiment and DFT-Calculated Values (Same Structure Type)**

compound	$E_{g,\text{DFT}}$	$E_{g,\text{Exp}}$
YF <sub>3</sub>	9.9	10.30 <sup>54</sup>
BiCl <sub>3</sub>	3.6	3.37 <sup>55</sup>
BiBr <sub>3</sub>	2.7	2.66 <sup>55</sup>
BiI <sub>3</sub>	1.9	1.67, <sup>56</sup> 1.8 <sup>19,21</sup>

(e.g., hybrid functionals or many-body treatments, such as GW), together with SOC corrections.<sup>53</sup>

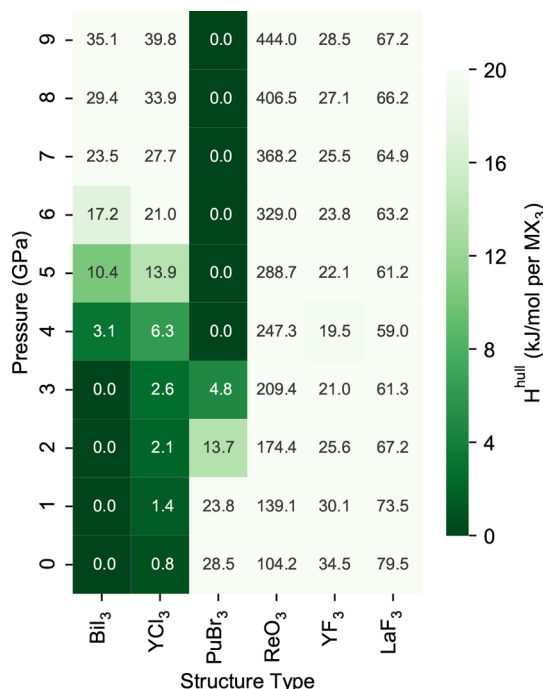
The  $E_g$  values in halides decrease upon moving down the halogen group, i.e., from F<sup>−</sup> to I<sup>−</sup>, as expected. For example, in Bi-containing compounds (experimental structure type), the band gap decreases systematically as  $\text{BiF}_3$  (5.1 eV) >  $\text{BiCl}_3$  (3.6 eV) >  $\text{BiBr}_3$  (2.7 eV) >  $\text{BiI}_3$  (1.9 eV). As for the metal site, Bi-based compounds always show the lowest band gaps compared to Y- and Lu-based compounds, with Y materials showing slightly lower band gaps than Lu compounds.

We complement this analysis with the projected density of states (pDOS) on specific atomic orbitals of selected structures to identify the orbital character of both valence and conduction bands. As an example, the pDOS of  $\text{LuI}_3$ ,  $\text{YI}_3$ , and  $\text{BiI}_3$  in the  $\text{BiI}_3$  structure type are shown in Figure 5b. For valence bands,  $\text{LuI}_3$  and  $\text{YI}_3$  are dominated by the I 5p states, whereas in  $\text{BiI}_3$ , Bi 6s also contributes significantly to the DOS. The conduction bands of  $\text{LuI}_3$  and  $\text{YI}_3$  are mostly dominated by Y 3d and Lu 4d with small contributions from the I 5p levels, whereas the  $\text{BiI}_3$  conduction band is dominated mostly by the Bi 6p and I 5p states. Therefore, the Bi 6s and Bi 6p states in the band edges result in a much smaller band gap for  $\text{BiI}_3$  compared with those for  $\text{YI}_3$  and  $\text{LuI}_3$ . As aforementioned for the halide species, the larger the ionic radius of the metal, the lower the band gap.<sup>57</sup>

It is often observed that band gaps in materials decrease under external pressure; for example, in hybrid halide

perovskites, high-pressure compression can induce a redshift of the PL energy.<sup>58</sup> Having explored a number of  $\text{BiX}_3$  phases in different structures (e.g.,  $\text{BiI}_3$  in the  $\text{PuBr}_3$  structure), we can now explain some of the observations that have been made in various high-pressure studies of  $\text{BiI}_3$ . Experimentally, Darnell et al.<sup>59</sup> suggested that there is a phase transition of  $\text{BiI}_3$  at  $\sim 2.5$  GPa, while Hsueh et al.<sup>60</sup> showed a phase transition from a rhombohedral ( $R\bar{3}$ ) structure to a monoclinic ( $P2_1/c$ ) distorted  $\text{PuBr}_3$ -type structure beyond  $\sim 7$  GPa. In addition, Devidas et al.<sup>61</sup> reported that  $\text{BiI}_3$  becomes metallic at  $\sim 1.5$  GPa and observed another phase transition to a monoclinic ( $P2_1/c$ ) structure at  $\sim 8.8$  GPa. To elucidate the relative stabilities of different forms of  $\text{BiI}_3$  at different pressures, we present in Figure 6 the computed formation enthalpies above the convex hull  $H^{\text{hull}}$  from ambient pressure up to 9 GPa. Figure 6 shows that, below 3 GPa, the 6-coordinated layered  $\text{BiI}_3$ -type structure is the most stable for  $\text{BiI}_3$ , as observed experimentally. At a pressure of  $\sim 3$ –4 GPa, we predict a phase transition from the  $\text{BiI}_3$  structure type to monoclinic distorted phase from the higher coordinated  $\text{PuBr}_3$  structure type, and it remains stable for pressures of up to 9 GPa, which is also in agreement with experiments.<sup>60,62</sup> Note that the 3D  $\text{YF}_3$  and  $\text{LaF}_3$  structure types are not expected to be stable at any pressure. We have also performed DFT calculations on the experimentally distorted  $\text{PuBr}_3$  structure type that Hsueh et al.<sup>60</sup> reported at different pressures, and the results are similar to our  $\text{PuBr}_3$ -type results (Figure S6) in the high-pressure ( $>2$  GPa) region, although it transformed back to the layered 6-coordinated  $\text{YCl}_3$  structure type in the low-pressure (0–2 GPa) region. Our lattice constants for the  $\text{PuBr}_3$  form of  $\text{BiI}_3$  at 8 GPa are in agreement with synchrotron X-ray data collected at  $\sim 7.31$  GPa by Hsueh et al.<sup>60</sup> (Table S2). The band gap of this high-pressure phase at 8 GPa was calculated (HSE06+D3+SOC) and found to be significantly lower ( $\sim 1.0$  eV) than that of the layered  $\text{BiI}_3$  structure type ( $\sim 1.6$  eV) at ambient pressure.





**Figure 6.** DFT-calculated formation enthalpy above the convex hull ( $H^{\text{hull}}$  in  $\text{kJ mol}^{-1}$  per  $\text{MX}_3$ ) of the  $\text{BiI}_3$  composition in different structure types under pressure.

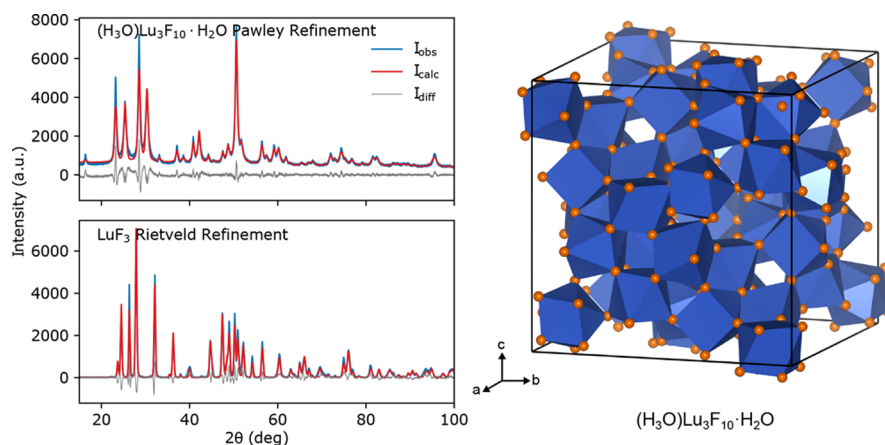
**Experimental Attempts to Make the  $\text{ReO}_3$  Form of  $\text{LuF}_3$ .** On the basis of our DFT calculations (Figure 2b),  $\text{LuF}_3$  has the lowest  $E^{\text{hull}}$  with the  $\text{ReO}_3$  structure type, so it is expected to be the best candidate for adopting that structure. Zalkin and Templeton<sup>62</sup> reported a mixture of unresolved phases in their solution preparation of  $\text{LuF}_3$ , which further encouraged us to explore this idea. They also observed that heating their initial reaction product led to formation of the orthorhombic  $\text{YF}_3$  structure type. Experimental attempts to synthesize  $\text{LuF}_3$  have therefore been carried out. Following their recipe, 15 mg of  $\text{Lu}_2\text{O}_3$  was fully dissolved in 5 mL of concentrated hydrochloric acid at 50 °C, and the solution was then neutralized by a  $\text{NH}_4\text{OH}$  solution. A few drops of concentrated hydrofluoric acid (47 wt %  $\text{H}_2\text{O}$ ) was added to the solution to obtain a white precipitate. The mixture was

centrifuged, washed with deionized water, and then dried in air. Zalkin and Templeton were unable to solve the complicated pattern, but we have found that it is a complex acid hydrate,  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$ , and is isomorphous with  $(\text{H}_3\text{O})\text{Yb}_3\text{F}_{10}\cdot\text{H}_2\text{O}$ <sup>63</sup> (Figure 7, right).  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$  has cubic symmetry and space group  $Fd\bar{3}m$  with  $a = 15.2967(5)$  Å. Structure solution was carried out using TOPAS Academic 6.0, and Pawley refinement is shown in Figure 7, top left (details on the structure determination and associated crystallographic information are reported in the SI). After heating of the powder at 100 °C for 1 h, an orthorhombic phase with the  $\text{YF}_3$  structure type was obtained, as described by Zalkin and Templeton<sup>62</sup> (powder X-ray diffraction results are shown in Figure 7, left bottom). Other synthetic methods, e.g., thermal evaporation until dryness at 90 °C or hydrothermal synthesis using  $\text{Lu}(\text{NO}_3)_3$  or  $\text{Lu}_2\text{O}_3$  and diluted hydrofluoric acid at 120 °C, also give the orthorhombic  $\text{YF}_3$  structure type. We have found no evidence for the formation of  $\text{ReO}_3$  modification of  $\text{LuF}_3$ .

## CONCLUSIONS

In this study, systematic first-principles calculations have been used to map the chemical space of  $\text{BiX}_3$  halides and the analogous  $\text{MX}_3$  compositions with  $M = \text{Y}$  and  $\text{Lu}$ . Calculations for 12 different  $\text{MX}_3$  compositions, each with 9 potential polymorphs, reveal the thermodynamic stabilities of  $\text{MX}_3$  in different structure types. The results for the thermodynamically stable phases are in very good agreement with experiments. The qualitative trends follow the radius ratios of the cation  $M$  and anion  $X$  ( $r_M/r_X$ ) such that the CN of the cations increases as the anion size decreases. For example, the smallest anion,  $\text{F}^-$ , strongly favors the highly coordinated environment that is found in the  $\text{YF}_3$  structure, whereas larger anions, especially  $\text{I}^-$ , prefer a 6-coordinated cation environment and form  $\text{YCl}_3$  or  $\text{BiI}_3$  structures.

It is also found that the dimensionality of the crystal structures of  $\text{MX}_3$  is strongly correlated to the size of the anion. For compositions with large anions, such as  $\text{Br}^-$  and  $\text{I}^-$ , a lower-dimensional structure is favored, e.g.,  $\text{BiI}_3$  (2D),  $\text{YCl}_3$  (2D),  $\text{PuBr}_3$  (2D),  $\text{ZrI}_3$  (1D), and  $\text{AlI}_3$  (0D, molecular dimer). The reason for this is that the cation–anion packing density plays an important role in determining its dimensionality, and a higher cation–anion packing density is favored energetically.



**Figure 7.** Left: Pawley refinement (top) for the white precipitates of  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$  with space group  $Fd\bar{3}m$  and  $a = 15.2967(5)$  Å and Rietveld refinement (bottom) of  $\text{LuF}_3$  in  $Pnma$  with  $a = 6.1149(3)$  Å,  $b = 6.7595(3)$  Å, and  $c = 4.5064(3)$  Å. Right: Crystal structure of  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$  ( $\text{H}_2\text{O}$  molecules are not shown).

From Figure 2a, it is shown that, with the same CN of 6, the unit cell volumes of the high-dimensional  $\text{ReO}_3$  structure types are much higher than those of the corresponding layered  $\text{BiI}_3/\text{YCl}_3$  structure types in the case of large anion ( $\text{Br}^-$  and  $\text{I}^-$ ). van der Waals interactions also provide additional stabilization in denser structures and not only to the layered ones. We note that, even without considering van der Waals forces explicitly in our calculations, the layered  $\text{BiI}_3/\text{YCl}_3$  structure types remain the most stable structures for large anions (Figure S4). This observation shows that layered structures are not solely stabilized by van der Waals forces. However, when van der Waals forces are not included in the calculations, the  $\text{ReO}_3$  structure type is predicted to be favored relative to the  $\text{YF}_3$  structure type for  $\text{LuF}_3$  (Figure S4). In this case, the observed structure is clearly stabilized by the van der Waals forces.

Taken together, these considerations confirm that, in order to form a 3D 6-coordinated  $\text{ReO}_3$ -type structure, small anions, e.g.,  $\text{F}^-$ , together with small cations such as  $\text{Al}^{3+}$ ,  $\text{Sc}^{3+}$ , or smaller transitional metal cations, are required.  $\text{LuF}_3$  follows this trend, although our experimental synthesis also showed that even  $\text{LuF}_3$  cannot form an  $\text{ReO}_3$ -type framework. We find that other candidates with desirable properties for PV applications, such as  $\text{BiI}_3$  in the  $\text{ReO}_3$  structure type, are not energetically accessible because of their low packing densities. Even under pressure, it is not possible to stabilize  $\text{BiI}_3$  with the  $\text{ReO}_3$  structure type because the denser  $\text{PuBr}_3$  structure type becomes more stable.

The important role of electron localization as lone pairs in the  $\text{BiX}_3$  compounds has been seen in the cases of both  $\text{BiF}_3$  and  $\text{BiCl}_3$ , in terms of both their structures and band gaps. Although it is widely believed that stereochemically active lone pairs are particularly prevalent in systems containing more electronegative anions, e.g., fluoride, chloride, and oxide, we also find that even  $\text{BiI}_3$  would be distorted if it was to adopt a  $\text{YF}_3$  structure type. It would appear that the ability of different structure types to accommodate distortions is more important than was hitherto believed in determining the sensitivity to lone-pair effects.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.9b03214>.

Convex hulls of  $\text{BiX}$  (with  $X = \text{F}, \text{Cl}, \text{Br}$ , and  $\text{I}$ ; Figure S1), details of other structure types also considered in this study (Figure S2 and Table S1), effects of pressure on a number of structure types (Table S2), computed formation energies and volumes using the PBE and PBE+D3 functionals, respectively (Figures S3 and S4), ELF plots of selected structures (Figure S5), formation enthalpies of the  $\text{BiI}_3$  composition in different structure types (Figure S6), details on the effects of entropy and  $pV$  terms on the thermodynamic stability of different structure types (Table S3), and a final section on the experimental method and determination of the newly synthesized  $(\text{H}_3\text{O})\text{Lu}_3\text{F}_{10}\cdot\text{H}_2\text{O}$  structure, including Tables S4–S6 (PDF)

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### Notes

The authors declare no competing financial interest.  
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