Tuning the near-gap electronic structure of tin-halide and lead-halide perovskites via changes in atomic layering

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Using density functional theory (DFT)-based calculations, we explore the extent to which achievable modes of atomic layering can tune the near-gap electronic structure of tin- and lead-halide perovskites with applications in dye-sensitized solar cells. We show that regardless of how atomic layering is achieved—whether by the growth of layered inorganic phases such as the Ruddlesden-Popper series, hybrid perovskites connected by organic linker molecules, or layered perovskite heterostructures—their band gaps can similarly be widened by several tenths of an eV or more. Because these classes of compounds are known to have band gaps spanning much of the visible region of the solar spectrum, the ability to controllably tune their near-gap electronic structure could further optimize their performance in solar energy conversion applications. Throughout this work, trends in band gap are explained based on the effects of atomic layering and quantum confinement on the character and energy of band-edge crystal orbitals.

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I. INTRODUCTION

Compounds crystallizing in the perovskite structure [ABX₃, Fig. 1(a)] exhibit remarkable variety in composition, physical phenomena, and potential applications. Tin- and lead-halide perovskites have generated particular interest as visible light absorbers for dye-sensitized solar cells [1,2]. Since the initial use of CH₃NH₃PbBr₃ and CH₃NH₃PbI₃ on TiO₂ photoanode in 2009 [3], a series of refinements (including improvements in materials processing [4], the use of different hole transporters [5,6], and the replacement of TiO₂ with mesoporous Al₂O₃ [7]) have improved the energy conversion efficiencies of architectures using similar perovskite materials to 18% [8]. These classes of compounds are such efficient light absorbers largely because their optical band gaps lie in the visible region of the solar spectrum. Shockley and Queisser’s analysis places the ideal optical gap of a solar cell absorber at approximately 1.4 eV [9]. For comparison, several iodide perovskites (A = Cs⁺, CH₃NH₃⁺, B = Sn²⁺, Pb²⁺; X = I⁻) have been measured to have optical gaps between 1.2 and 1.7 eV [10].

Because the light-absorption behavior of these perovskite materials depends strongly on band gap, it is desirable to develop a variety of routes to modify their atomic structure in order to controllably tune their near-gap electronic structure. Experimental work has shown that elemental substitution and doping at the A, B, and X sites bring about changes in band gap. Though the A site is not strongly involved in the band-edge electronic states, its identity has a modest effect on measured band gaps (X = Cl⁻ > Br⁻ > I⁻) [3]. Band gaps can often be controllably oriented in a variety of directions [23].

In this work we use density functional theory (DFT)-based calculations to understand and predict routes to controllably tune the near-gap electronic structure and band gaps of tin- and lead-halide perovskites using various modes of atomic layering. We rationalize trends in band gap and develop intuition regarding the character and energy of band-edge electronic states from the perspective of linear combinations of atomic orbitals. This allows us to draw conclusions that extend beyond the particular architectures and combinations of elements considered.

II. COMPUTATIONAL METHODS

All crystal structures are optimized and electronic properties obtained using density functional theory (DFT) within the Perdew-Burke-Ernzerhof (PBE) functional [24], using the VASP package [25] and PAW potentials [26]. Electrons taken to be valence are 5s²5p⁶6s² of Cs, 2s²2p⁶ of C, 2s²2p⁶ of N, 1s¹ of H, 4d¹⁰5s²5p² of Sn, 5d¹⁰6s²6p² of Pb, 3s³3p³ of Cl, 4s²4p³ of Br, and 5s²5p³ of I. A plane-wave cutoff of 500 eV is used throughout. Unit cells containing a...
FIG. 1. (Color online) (a) Cubic unit cell of a perovskite ABX$_3$, with A, B, and X atoms shown as black, orange, and gray spheres, respectively, highlighting an octahedron of X atoms surrounding B. (b) Isosurfaces of the electron densities of the DFT-PBE band-edge orbitals of CsPbI$_3$ are shown in blue. (c) The DFT-PBE near-gap electronic band structure of CsPbI$_3$ is also shown, with the highest-energy filled state defined as zero energy and red circles indicating the band edges. Density of states (DOS) and projected density of states (PDOS) curves indicate that the valence band consists primarily of X-site $p$ orbitals, while the conduction band consists primarily of B-site $p$ orbitals.

single perovskite formula unit are treated with a $\Gamma$-centered $6 \times 6 \times 6$ k-point mesh. For structures requiring larger unit cells, proportionally fewer k points are used. Zone-center phonon modes and frequencies are computed using density functional perturbation theory. Geometric constraints on the unit cells and atomic structures, as well as our rationale for them, are discussed on a case-by-case basis throughout the paper.

Though DFT-PBE typically underestimates band gaps relative to experimental optical gaps, we find the method satisfactory for this work for three reasons. First, DFT-PBE has been shown to accurately capture qualitative band gap trends with changes in elemental identity [27] and quantum confinement [28,29]. Second, less approximate levels of theory have struggled to improve the quantitative match between computed and measured band gaps of these classes of compounds. The inclusion of spin-orbit coupling in DFT calculations causes band gaps to be underestimated even more severely [30], while $GW$ quasiparticle corrections to DFT lead to overestimates of the gaps (unless spin-orbit coupling is included as well) [31]. Finally, for tin- and lead-halide perovskites, past work suggests that these less approximate levels of theory (spin-orbit coupling and $GW$ corrections) change neither the orbital character of the band-edge states nor the k points at which the band gaps occur [30,31].

III. RESULTS AND DISCUSSION

A. Cubic perovskites ABX$_3$

As a baseline for further exploration of atomic layering, we first consider perovskite compounds ABX$_3$ [Fig. 1(a)] with a variety of elements (A = Cs$^+$, CH$_3$NH$_3$$^+$; B = Sn$^{2+}$, Pb$^{2+}$; X = Cl$^-$, Br$^-$, I$^-$). All 12 of these compounds have been synthesized in the past, and like many perovskites, they exhibit a variety of structural distortions and phase transitions with changing temperature. At sufficiently high temperatures—often at or near room temperature (Table I)—all of these compounds are known to adopt the undistorted cubic (Fm$\overline{3}$m) perovskite structure [32–40]. For this reason, and for simplicity, we constrain the geometries of these perovskites to cubic throughout this section.

Before limiting our focus to cubic perovskites, however, two points should be noted. First, we have computed zone-center phonon modes and frequencies for the $\sqrt{2} \times \sqrt{2} \times 2$ unit cell of the six Cs-containing perovskites (summarized in the Supplemental Material [41]), and found that the largest imaginary DFT-PBE phonon frequencies in any of the compounds are 42 $i$ cm$^{-1}$ (these correspond to BX$_6$ octahedral rotations). Comparing this value to the prototypical perovskite SrTiO$_3$, whose analogous TiO$_6$ octahedral rotations appear below approximately 100 K [42,43] and have DFT-PBE phonon frequencies of 78 $i$ cm$^{-1}$, suggests that the tin- and lead-halide perovskites we study possess similar stability against distortions. Furthermore, past work suggests that even when these structures are optimized with octahedral rotations, their band gaps change by no more than a few tenths of an eV [11].

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cubic transition temp. (K)</th>
<th>DFT-PBE cubic cell edge (Å)</th>
<th>DFT-PBE cubic band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsSnCl$_3$</td>
<td>379 [32]</td>
<td>5.63</td>
<td>1.01</td>
</tr>
<tr>
<td>CH$_3$NH$_3$SnCl$_3$</td>
<td>463 [32]</td>
<td>5.72</td>
<td>1.25</td>
</tr>
<tr>
<td>CsSnBr$_3$</td>
<td>292 [33]</td>
<td>5.90</td>
<td>0.65</td>
</tr>
<tr>
<td>CH$_3$NH$_3$SnBr$_3$</td>
<td>230 [34]</td>
<td>5.97</td>
<td>0.83</td>
</tr>
<tr>
<td>CsSnI$_3$</td>
<td>425 [35]</td>
<td>6.29</td>
<td>0.48</td>
</tr>
<tr>
<td>CH$_3$NH$_3$SnI$_3$</td>
<td>275 [36]</td>
<td>6.36</td>
<td>0.59</td>
</tr>
<tr>
<td>CsPbCl$_3$</td>
<td>320 [37]</td>
<td>5.73</td>
<td>2.21</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbCl$_3$</td>
<td>179 [38]</td>
<td>5.81</td>
<td>2.36</td>
</tr>
<tr>
<td>CsPbBr$_3$</td>
<td>403 [39]</td>
<td>6.00</td>
<td>1.79</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbBr$_3$</td>
<td>237 [38]</td>
<td>6.07</td>
<td>1.89</td>
</tr>
<tr>
<td>CsPbI$_3$</td>
<td>602 [40]</td>
<td>6.40</td>
<td>1.49</td>
</tr>
<tr>
<td>CH$_3$NH$_3$PbI$_3$</td>
<td>327 [38]</td>
<td>6.46</td>
<td>1.53</td>
</tr>
</tbody>
</table>
Second, while the A-site methylammonium ions in these perovskites tend toward orientational disorder at room temperature, single-point DFT calculations can only consider one orientation at a time. We find that the orientation of methylammonium has almost no effect on near-gap electronic structure. When the C-N bond is initialized pointing along the cubic unit cell axis, face diagonal, and body diagonal, computed band gaps of CH$_3$NH$_3$PbI$_3$ are 1.53, 1.51, and 1.52 eV, respectively, and the character of band-edge orbitals (see below) is nearly identical. From this point on, we therefore discuss only calculations in which the methylammonium C-N bond is initialized pointing along the cubic unit cell axis.

The DFT-PBE band gaps of these 12 cubic perovskites are shown in Table I. All gaps are direct at $k$-point $R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. Isosurfaces of the electron densities of the band-edge orbitals of CsPbI$_3$ are shown in Fig. 1(b), and the near-gap band structure in Fig. 1(c). The valence band maximum consists of an antibonding combination of Pb 6$s$ and I 5$p$ orbitals, while the conduction band minimum consists of the threefold-degenerate, essentially nonbonding Pb 6$p$ orbitals. Projected densities of states [PDOS, Fig. 1(c)] confirm that the valence band consists primarily of Pb 6$s$ and I 5$p$ orbitals, while the conducton band consists primarily of Pb 6$p$ orbitals. For all 12 combinations of elements, these band-edge orbitals remain qualitatively the same. In agreement with past measurements [3,10], band gaps are largest when the X site is most electronegative (i.e., Cl$^-$) and the B site is least electronegative (i.e., Pb$^{2+}$). These findings are not surprising, as X $p$ orbitals constitute the majority of the valence band, while B $p$ orbitals constitute the majority of the conduction band. Because the A site is not electronically involved in the band-edge orbitals, the identity of A has less impact on the band gap.

B. Layering along (100): Ruddlesden-Popper phases and their hybrid analogs

We now arrive at the main focus of this work, the effects of atomic layering and quantum confinement on the electronic structure and band gap of these perovskite compounds. In practice, perovskite regions can be electronically confined in a variety of ways, separated by (for example) organic linker molecules $A'$ [Fig. 2(a)] or additional inorganic layers AX, as in Ruddlesden-Popper phases [Fig. 2(b)]. Because the band-edge electronic states in tin- and lead-halide perovskites reside in the B-X network, it follows that either of these modes of layering would lead to similar effects on the near-gap electronic structure.

We begin by examining the Ruddlesden-Popper phases Cs$_{n+1}$B$_n$X$_{3n+1}$ ($n = 1, 2$), which avoid the $A'$-site structural complexity present in layered hybrid perovskites. Though Ruddlesden-Popper phases have not been synthesized with these elements to our knowledge, they represent a prototypical class of quantum-confined perovskite variants. We consider compounds with a variety of elements (B = Sn$^{2+}$, Pb$^{2+}$; X = Cl$^-$, Br$^-$, I$^-$) in their optimized body-centered tetragonal unit cells, free of symmetry- lowering distortions (I4/mmm). As with the inorganic perovskites, we have computed the zone-center phonon modes and frequencies for a 28-atom tetragonal unit cell of the six $n = 1$ Ruddlesden-Popper phases (summarized in the Supplemental Material [41]), and found that the largest imaginary DFT-PBE phonon frequencies in any of the compounds are 361 cm$^{-1}$ (again corresponding to octahedral rotations). Thus, if synthesized—perhaps as epitaxial thin films—we would expect these Ruddlesden-Popper phases to be more prone to structural distortions than their perovskite counterparts.

The DFT-PBE band gaps of the Cs-containing perovskite and Ruddlesden-Popper compounds (plotted versus $1/n$) are shown in Fig. 3(a). Each perovskite can be thought of as the $n = \infty$ member of the series. For all combinations of elements, confinement of perovskite regions causes monotonic widening of the band gaps by 0.41–0.65 eV. The band-edge orbitals of these Ruddlesden-Popper structures (Cs$_2$PbI$_4$ shown in Fig. 4) resemble those of the perovskites [Fig. 1(b)], except that they are electronically confined to the perovskite regions. As is typically seen in quantum-confined systems, this spatial restriction of the orbitals is responsible for the widening of the band gaps. Further evidence of this quantum confinement is provided in the Supplemental Material [41], in which the average electrostatic potential along the direction of layering is plotted for Cs$_2$PbI$_4$ ($n = 1$) and Cs$_2$PbBr$_4$ ($n = 2$).

The power of this analysis lies not in the Ruddlesden-Popper phases specifically, but in the fact that it can be generalized to any compounds or superlattices with confined perovskite regions. Because recent solar-cell technologies have typically employed hybrid perovskites rather than fully inorganic ones [1–7], we now consider layered compounds in which hybrid perovskite regions are separated by organic linker molecules. For the same six combinations of B and X, we compute the band gaps of (C$_3$H$_7$NH$_3$)$_2$BX$_4$ [Fig. 2(a)], which resemble compounds that have been synthesized in the past [17,23]. For computational simplicity we limit our calculations to a single perovskite layer (analogous to the $n = 1$ Ruddlesden-Popper phases), three carbon atoms in the linker molecules, and constrain the structures to tetragonal unit...
FIG. 3. (Color online) DFT-PBE band gaps of perovskite compounds layered in the ⟨100⟩ direction: (a) Ruddlesden-Popper phases (A = Cs⁺) as in Figs. 2(b) and 5(a), and (b) hybrid organic-inorganic perovskites (A′ = C₃H₇NH₃⁺, A = CH₃NH₃⁺) as in Fig. 2(a). Line style indicates the B-site element (solid = Pb²⁺, dashed = Sn²⁺), and marker shape and color indicate the X-site element (red circle = Cl⁻, blue square = Br⁻, green triangle = I⁻).

Electrostatic potential along the direction of layering for (C₃H₇NH₃)₂PbI₄ (n = 1) and comparing it to that of Cs₂PbI₄ (n = 1).

C. Inorganic perovskites layered in other crystallographic directions

In the previous section we showed that quantum confinement of tin- and lead-halide perovskites can tunably increase their band gaps by several tenths of an eV. While we have thus far considered only layering in the ⟨100⟩ direction, techniques have been developed with the flexibility to synthesize perovskites layered in other crystallographic directions as well [23]. In this section we explore the effect of quantum confinement in the ⟨110⟩ and ⟨111⟩ directions on the band gap of these classes of perovskite compounds. Having already established that effects on electronic structure are similar whether quantum confinement is accomplished using inorganic layers or organic linker molecules, we limit our focus in this section to the computationally simpler inorganic structures.

Examples of structures layered in the ⟨100⟩, ⟨110⟩, and ⟨111⟩ directions—each with two layers in their perovskite regions—are shown in Fig. 5. Consistent with past literature [23], we use the letters n, m, and q to indicate the number of adjacent perovskite layers in structures layered along ⟨100⟩, ⟨110⟩, and ⟨111⟩, respectively. Structures layered along ⟨100⟩ are the already discussed Ruddlesden-Popper phases. In the structures layered along ⟨111⟩, in order to accommodate the A′₂Aₙ₋₁BₚXₚ₋₃ stoichiometry with charges balanced, it is necessary to change the valency of one or more sites [23]. We accomplish this by placing Ba⁺⁺ at the A’ sites, while leaving Cs⁺ at the A sites.

FIG. 5. (Color online) Examples of perovskite compounds layered in the (a) ⟨100⟩, (b) ⟨110⟩, and (c) ⟨111⟩ crystallographic directions. Each structure has two connected layers in each perovskite region, meaning the values of n, m, and q in the structures shown are all equal to 2.

Valence band maximum Conduction band minimum

FIG. 4. (Color online) Isosurfaces of the electron densities of the (a) valence band maximum and (b) conduction band minimum of the Ruddlesden-Popper phase Cs₂PbI₄.

The DFT-PBE band gaps of the compounds layered along ⟨110⟩ and ⟨111⟩ (plotted versus 1/m and 1/q) are shown in Fig. 6. Band-edge orbitals in all of these compounds are qualitatively similar to those seen for the perovskites.
[Figs. 1(b) and 1(c)], confined to the continuous perovskite regions of these layered structures. As with the Ruddlesden-Popper phases layered along ⟨100⟩ [Fig. 3(a)], the computed gaps of the ⟨110⟩ and ⟨111⟩ compounds widen with the narrowing of the perovskite regions. Gaps of the ⟨110⟩ layered compounds widen by up to 0.78–1.37 eV for each narrowing of the perovskite regions. Gaps of the ⟨111⟩ layered structures are occupied by Ba⁴⁺.

A notable exception to the usual band gap trend is seen in the q = 1 compounds layered along ⟨111⟩, whose gaps are narrower than expected. As mentioned previously, in structures layered along ⟨111⟩, A′ sites are populated with Ba⁴⁺. This means that for q = 1, all Cs⁺ is replaced by significantly smaller Ba⁴⁺, shortening all interatomic spacings. As a result, the average B-X bond lengths in the q = 1 structures (3.10 Å for Pb-I) are significantly shorter than they are in the q = ∞ and q = 2 structures (3.20 and 3.19 Å for Pb-I, respectively). Shorter B-X bonds in the q = 1 compounds reduce their band gaps by intensifying the antibonding interactions in their valence band maxima. 

D. Layered perovskite heterostructures: Incomplete quantum confinement

In recent years, layered perovskite heterostructures [21,22] have proven an exciting parameter space for controlling structural and electronic properties. In this section we examine (CsSnI₃)$_n$(CsPbI₃)$_m$ heterostructures layered along ⟨100⟩ direction [Fig. 7(a)] and show that, although the band-edge electronic states in these heterostructures penetrate both the tin and lead layers, quantum confinement plays a role in tuning their band gaps. Because the DFT-optimized cubic lattice parameter of CsPbI₃ is 1.8% larger than that of CsSnI₃, the lattice mismatch between these compounds is not so large that it would rule out the growth of such layered heterostructures [44]. As we have throughout this paper, we constrain these superlattices to their high-symmetry tetragonal unit cells, free of symmetry-breaking distortions such as octahedral rotations. To focus on the effects of layering and quantum confinement rather than strain, the in-plane lattice parameters of all structures are constrained to the DFT-optimized cubic lattice parameter of CsPbI₃ (6.40 Å) as if they were grown as thin films on CsPbI₃ substrate [45].

Throughout this work we have seen that the band gaps of tin-halide perovskites tend to be smaller than their lead-halide counterparts. One might therefore expect that the band-edge electronic states in (CsSnI₃)$_n$(CsPbI₃)$_m$ superlattices would reside primarily in the CsSnI₃ regions, and that their band gaps would exhibit trends similar to other tin-iodide perovskites confined in the ⟨100⟩ direction. These expectations prove true to a large extent. In Fig. 7(b) we see that band gaps tend to increase as SnI₃ regions become narrower. Furthermore, the (n = 1, m = 3) and (n = 2, m = 3) superlattices in which tin-iodide regions are well separated by lead-iodide regions have gaps within 0.01 eV of the n = 1 and n = 2 tin-iodide Ruddlesden-Popper phases, respectively. Another perhaps less expected trend in Fig. 7(b) is that band gaps tend to increase with increasing thickness of CsPbI₃ regions. This is most likely due to the fact that band-edge electronic states, which reside mainly in the CsSnI₃ regions of each of these heterostructures, can penetrate the CsPbI₃ regions as well. That is, confinement of band-edge states in these heterostructures is incomplete, especially for thin regions of CsPbI₃. The band-edge orbitals become in a sense more confined with increasing thickness of CsPbI₃, which as we have seen, leads to larger band gaps. The overall message of Fig. 7 is that layering tin- and lead-halide perovskites in superlattices is yet another parameter that can be tuned.
space in which to potentially dial in desired near-gap electronic structure.

IV. CONCLUSIONS

In summary, we have shown that atomic layering can controllably tune the electronic structure of tin- and lead-halide perovskites, widening their band gaps (which are known to span significant regions of the solar spectrum) by several tenths of an eV or more. Trends have been explained broadly in terms of the confinement of band-edge orbitals, and it has been shown that the effects of various modes of layering—the growth of layered inorganic phases, hybrid perovskites, and perovskite heterostructures—can be understood and manipulated in similar ways. As the efficiencies of perovskite solar cells continue to be optimized in the coming years, it will likely be necessary to explore new ways to structurally and electronically tune these classes of materials, and also to use such materials together in multijunction architectures. The diverse range of layered structures and the accompanying intuition discussed in this work are intended to suggest how to develop and utilize a flexible toolset toward this optimization.

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[45] We have also performed the set of band gap calculations analogous to Fig. 7(b) in which tetragonal unit cell parameters are relaxed, rather than constrained. To the eye, the results of these calculations are nearly identical to Fig. 7(b).