Bandgap Optimization of Perovskite Semiconductors for Photovoltaic Applications

Abstract: The bandgap is the most important physical property that determines the potential of semiconductors for photovoltaic (PV) applications. This Minireview discusses the parameters affecting the bandgap of perovskite semiconductors that are being widely studied for PV applications, and the recent progress in the optimization of the bandgaps of these materials. Perspectives are also provided for guiding future research in this area.

1. Introduction

In recent years, perovskite solar cells (PSCs) have emerged as a "game-changer" photovoltaic (PV) technology that is not only highly efficient in the solar power conversion, but also potentially low cost.1–5 PSCs employ a family of semiconductors with a perovskite-type crystal structure (Figure 1a) as the light-absorber materials.6–8 The perovskite semiconductors possess superior electronic, optical, and defect properties,6 which has led to the swift rise in the power conversion efficiency (PCE) of PSCs to a certified 22.7%6 within only a few years since the first PSC study by Kojima et al. in 2009.6–9 Such unprecedented progress is primarily attributed to the efforts devoted towards optimizing the solution-processing and device architecture of PSCs.6,7 Perovskite-type crystals have the general chemical formula of \( ABX_3 \), in which the A ion is a relatively large cation at the center of the unit cell, the B ion is a smaller cation at the corners, and the three X anions at the centers of the edges of the unit cell (Figure 1a). While some oxide and chalcogenide perovskites are being explored, the perovskites that are used in PSCs are mainly metal halide perovskites, where A = methylammonium (MA\(^+\)), formamidinium (FA\(^+\)), Cs\(^+\) or Rb\(^+\); B = Pb\(^{2+}\) or Sn\(^{2+}\); X = I\(^-\), Br\(^-\) or Cl\(^-\). The halide perovskites that have been most widely studied are MAPbI\(_3\) and FAPbI\(_3\), which exhibit optical bandgaps of \( \approx 1.55 \) and \( \approx 1.48 \) eV, respectively.7 It is well-known that the PCE limit of solar cells is fundamentally determined by the intrinsic bandgap \( E_g \) of the semiconductor light-absorbers that are used, and, thus, substantial research effort is being devoted to exploring new perovskite semiconductors with optimal \( E_g \) for PV applications.9–11 Two prominent forms for PSCs are expected to emerge in the future PV market:12–15 (i) PSC as a single-junction solar cell (shown in Figure 1b) and (ii) PSC as the top solar cell in tandem PVs in conjunction with the conventional inorganic solar cells based on crystalline-silicon (c-Si) or copper-indium-gallium-selenide (CIGS) (shown in Figure 1d). In the case of the single-junction PSC, Figure 1c illustrates the maximum attainable PCE under sunlight as a function of the \( E_g \) of the perovskite semiconductor, which is estimated based on the Shockley–Queisser (SQ) limit.10,11 In general, a perovskite material with an ideal bandgap of \( \approx 1.3 \) eV is expected to deliver the highest PCE. This is because a larger \( E_g \) results in non-absorption of a large portion of photons in the solar spectrum. Whereas if the perovskite absorber has an \( E_g \) that is too small, most photons have much more energy than necessary to excite electrons across the bandgap, resulting in inefficient absorption of the sunlight. For achieving the highest PCE in tandem PVS, the ideal bandgap of the PSC top cell is \( \approx 1.75 \) eV in conjunction with c-Si or CIGS bottom cells.12–14 as illustrated in Figure 1e.15 PSCs can also be used in multijunction PVS, where perovskites with wider range of bandgaps (e.g. 2.1 eV for a triple-junction PV16) are needed for optimal cell design. In the search for perovskites with optimal \( E_g \) for the single-junction,
tandem, and multijunction PV applications, herein we first analyze the factors that govern the bandgap of perovskite semiconductors. We then review the recent effort towards rational bandgap tailoring of perovskite semiconductors, including halides, oxides, and chalcogenides. Finally, we provide some perspectives for this research direction in the future.

2. Factors Governing Bandgaps of Perovskite Semiconductors

Many perovskite materials have been reported so far, with electrical properties ranging from metallic to insulating. For example, Figure 2 shows a collection of iodide perovskites and related compounds, which show a wide range of bandgaps from $\approx 1.2$ to $\approx 4.0$ eV. To understand the bandgap of a perovskite semiconductor, and be able to further optimize the bandgap for desired properties, it is important to understand the factors that govern the bandgap. In a crystalline semiconductor, its chemical composition and structure primarily determine its bandgap. Thus, in this section, we discuss the chemical and structural factors that determine the bandgaps of perovskite semiconductors.

2.1. Chemical factors

For a given ABX$_3$ perovskite structure, the bandgap depends on the chemical composition, because different elements have different orbital energies and characters. Generally, the A cation is highly ionic and makes little contribution to the band edges. Therefore, the bandgap is mainly determined by the B cation and the X anion, which form the [BX$_6$] octahedra framework. In most oxide and chalcogenide perovskites, the valence band maximum (VBM) is derived from s or d states of the B cation, as shown in Figure 3a. Because of the large energy difference of the occupied X p orbitals and the unoccupied B s or B d states, these perovskites exhibit relatively large bandgaps. X anions with higher p orbitals and B cations with lower s or d states favor narrower bandgaps, provided the perovskite structure is stable. On the other hand, there are some perovskites in which the B cations exhibit high-energy occupied s$^2$ or d$^9$ orbitals that can couple with X p orbitals to push the VBM up, thereby narrowing the bandgap. Such B cations include those with ns$^2$ pseudo-closed-shell electronic configuration: Pb$^2+$, Sn$^2+$, Ge$^2+$, Bi$^3+$, Sb$^3+$, Tl$^+$, and In$^3+$, and noble cations with nd$^{10}$ configuration: Ag$^+$ and Cu$^+$. The most typical example is the Pb$^2+$ halide family of perovskites. Theoretical studies have shown that the superior PV properties of this family of perovskites are partially attributed to the unique fea-
Experimental bandgaps of some iodide perovskites (diamond symbols) and nonperovskites (triangle symbols) as a function of crystal dimensionality. For the dot-center symbols, optical bandgaps were determined by excluding the exciton band at low temperature. The structural dimensionality of an n-layered perovskite is defined as (3−n)/n. Similarly, the structural dimensionality of the compounds that comprise double-[[PbI₆]₂⁻]₂⁻ chains is qualitatively defined as 1.5, and that for biocathedra-based compounds as 0.5. C₆ indicates C(H₂)₆⁻, NH indicates C(H₂)₆⁻, C₄ indicates C(H₂)₄⁻, C₃I indicates NH₂[I]=NH, FA indicates HC(NH₂), and HA indicates C₃H₆⁻. Reproduced with permission. Copyright 2017, The Royal Society of Chemistry.

Figure 2. Schematic energy diagrams for semiconductors with VBM being a) anion p-states and b) antibonding states of cation s/d and anion p orbitals. c) Partial density of states (left) of a hypothetical sextuple perovskite Cs₆Bi₅Pb₅Sn₃TlCl₁₃ (right), showing that the energy levels of both the occupied ns² states and the unoccupied np⁵ states increase in the order Bi→Sn→Tl→In. Adapted with permission. Copyright 2017, American Chemical Society.

2.2. Structural factors

For a given perovskite system, the bandgap also depends on the structural factors such as anion size, connectivity (3D, 2D, 1D or 0D), and distortion (tilting or rotation) of the [BX₆] octahedra. Xiao et al. have studied the effect of these structural factors on the PV properties of perovskite-based absorber materials, and proposed the concept of electronic dimensionality, that is, the connectivity of atomic orbitals that comprise the CBM and the VBM, to account for the bandgap. To study the effect of the structural dimensionality, they used CsPbI₃, Cs₅PbI₉, Cs₅PbI₇, and Cs₅PbI₆ as representatives of 3D, 2D, 1D and 0D perovskites, respectively (Figure 4a). The calculated bandgaps for these 3D, 2D, 1D and 0D perovskites are 1.48, 1.90, 2.80, and 3.44 eV, respectively (Figure 4b). The bandgap increases as the structural dimensionality decreases, explaining the trend seen in Figure 2a. As the structural dimensionality reduces to 2, the connectivity of octahedra along the direction perpendicular to the octahedra layers break down. As a result, the connectivity of the atomic orbitals that contribute to the band edges breaks down, leading to reduced band dispersion along the direction perpendicular to the layers. This in turn gives rise to narrower band widths, and, thus, an enlarged bandgap (Figure 4b). As the structural dimensionality further reduces to 1 and 0, the band widths at VBM and CBM become even narrower, leading to a further enlarged bandgap that is no longer suitable for PV applications. These materials exhibit the same structural and electronic dimensionality.
making it facile for adjusting the PV properties of layered perovskites.

The structural distortion of perovskite structure, for example, distortion, tilting, and rotation of the [BX₆] octahedra, also has significant influence on the bandgap. The bandgap of a distorted perovskite structure is larger than that of its ideal high-symmetry cubic counterpart. As shown in Figures 4f and 4g, as the in-plane Pb-I-Pb bond angle \( \theta \) decreases from 180° (for the ideal cubic perovskite) to 136.4° (for a highly-distorted structure), the bandgap of 3D CsPbI₃ increases slightly from 1.48 to 1.66 eV, while that of 2D CsPbI₂ increases significantly from 1.90 to 2.51 eV. The structural distortion reduces the connectivity (overlap) of the atomic orbitals that comprise the band edges, leading to narrower band widths and thus a larger bandgap. Therefore, structural distortion also reduces the electronic dimensionality, although the structural dimensionality is not affected. This correlation explains the typical bandgap increase associated with the phase transition: cubic—tetragonal—orthorhombic. Overall, the bandgap of perovskites can be tuned by controlling the structural distortion, for example, by employing mixed A-cations. (This is also referred to as the Goldschmidt “tolerance factor” of the perovskite structure.)

3. Pb\(^{II}\), Sn\(^{II}\) and Ge\(^{II}\) Halide Perovskites

3.1. 3D Pb, Sn, and mixed Pb–Sn halide perovskites

Bandgap tuning of 3D Pb or Sn halide perovskites via organic cation or anion alloying have been studied extensively and reviewed in the literature. Although pure Pb-halide perovskites exhibit bandgaps that are invariably larger than FAPbI₃, pure Sn-halide perovskites, in spite of their more desirable bandgaps, suffer from extreme sensitivity to ambient conditions. In this context, there is significant ongoing effort to study mixed Pb–Sn perovskites which may circumvent this issue. In particular, mixed A-cation mixed Pb–Sn halide perovskites are found to not only exhibit ideal bandgaps, but also show improved environmental stability. For example, as shown in Figure 5, Zong et al. synthesized (FAPbI₃)ₓ(CsSnI₃)₁₋ₓ mixed perovskites, which show bandgap bowing effect with an bandgap of 1.3 eV (ideal for single-junction PVs) at \( x = 0.2 \). Similar findings are also reported by Im et al., Prasanna et al., and Liao et al. in their recent studies.

3.2. Layered (2D) Pb and Sn perovskites

Layered (2D) Pb and Sn iodide perovskites have attracted much attention because of their superior environmental stabi-
The most common structures are (100)-oriented with cations, for a given value of n, showing the evolution of dimensionality from 2D to 3D. Adapted with permission. Copyright 2017, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

Figure 5. a) Direct transition-type plots of (FAPbI\textsubscript{2-n}(CsSn\textsubscript{n})\textsubscript{n} (x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0) thin films showing the optical bandgap values; b) change in the lattice parameter, a, of the (pseudo)cubic perovskite structures, and the bandgap of the (FAPbI\textsubscript{2-n}(CsSn\textsubscript{n})\textsubscript{n} as a function of x (gray and black solid lines are fits). Reproduced with permission. Copyright 2018 American Chemical Society.

3.3. Ge halide perovskites

Ge halide perovskites have been examined as PV absorber materials. However, AGeI\textsubscript{3} (A = MA, FA, etc.) have bandgaps ranging from 1.63 to 2.8 eV, depending on the A cation. These bandgaps are much larger than those for Sn analogues, and are even larger than some Pb analogues, which is counterintuitive because the bandgaps are expected to decrease from Pb, Sn, to Ge analogues according to their positions in the periodic table. There are two origins for the anomalously large bandgap of Ge halide perovskites. One is deeper orbital energy for Ge 4s states than that for Sn 5s states, which leads to weaker hybridization with halogen 2p states and thus lower VBM for Ge analogues than those for Sn analogues. The other is the structural distortion of the [GeI\textsubscript{3}] octahedra caused by the small ionic radius (0.73 Å) of Ge\textsuperscript{4+}, which cannot be stabilized at the regular [GeI\textsubscript{3}] octahedral center, but depart from the center to form three short Ge–I bonds (2.73–2.77 Å) and three long Ge–I bonds (3.26–3.58 Å). But so far, Ge halide perovskites have not produced efficient PSCs, partially due to the metallic p-type conduction as well as undesirable defect properties.

Figure 6. a) Structure of (Cs\textsubscript{3-x}MA\textsubscript{x})(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11-x}, perovskites with different n values, showing the evolution of dimensionality from 2D (n = 1) to 3D (n = ∞). b) Absorption spectra of the (Cs\textsubscript{3-x}MA\textsubscript{x})(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11-x} perovskite films with different n values. Adapted with permission. Copyright 2016, American Chemical Society.

Ty. Layered perovskites can be structurally derived from their 3D analogues by slicing along specific crystallographic planes. The most common structures are (100)-oriented with the general chemical formula (RNH\textsubscript{2})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}B\textsubscript{X\textsubscript{n+}}\textsubscript{m}, (R = alkyl or aryl group, B = Pb, Sn, and n is the number of stacking [BX\textsubscript{n+}] octahedra layers), which are obtained by stacking n perovskite layers along the [100] direction of the 3D parent structure, separated by the long “spacer” ammonium cations RNH\textsubscript{3}+ (Figure 6a). The bandgap of (RNH\textsubscript{2})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}B\textsubscript{X\textsubscript{n+}}\textsubscript{m} for a given n value can be tuned, for example, by controlling the interlayer spacing with the spacing cation RNH\textsubscript{3}+, which leads to an increase in the interlayer spacing leading to an increase in the bandgap because of the stronger electronic confinement. For example, the bandgap of single-layered (i.e., n = 1) (RNH\textsubscript{2})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11} is 2.57 eV\textsuperscript{13} (2.70 eV\textsuperscript{14} when the spacing cation is Cs\textsubscript{3}+), and 2.1 eV\textsuperscript{15}, respectively. Such n-dependence of bandgap is also observed for other layered perovskite families including (C\textsubscript{6}H\textsubscript{4}NH\textsubscript{3})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11} \textsuperscript{16}, (C\textsubscript{6}H\textsubscript{4}NH\textsubscript{3})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11} \textsuperscript{17} and (C\textsubscript{6}H\textsubscript{4}NH\textsubscript{3})\textsubscript{x}(MA\textsubscript{3-x}FA\textsubscript{x})\textsubscript{n}Pb\textsubscript{3}I\textsubscript{11} \textsuperscript{18}. The above bandgap behavior for Pb-based layered perovskites is also observed for the Sn-based layered perovskites.

4. BiIII and SbIII Halide Perovskites

4.1. A2Bi3X9: Lower-dimensional perovskites and nonperovskites

Trivalent BiIII and SbIII have been widely used for replacing PbII to form nontoxic, or lower toxicity, halide perovskites, because they also exhibit lone-pair ns2 states.[53-72] However, the chemical formula must be modified to A+6Bi+3X−9 to maintain charge neutrality. These A2Bi3X9 compounds have two typical lower-dimensional modifications. One is a <111>-oriented vacancy-ordered layered perovskite structure and the other is a nonperovskite structure with isolated [Bi3X9] biocahedra (also referred as the “dimer” structure). The A2Bi3I9 and A2Sb3I9 layered perovskites have bandgaps around 2 eV (e.g., 2.04 eV for (NH4)2Bi3I9[64]), 2.1 eV for Rb2Bi3I9[67] and 2.05 eV for Cs2Sb3I9[68], which are suitable for tandem PVs. Huang et al. have shown the bandgaps of these layered perovskites are insensitive to the A-site cations,[70] making it difficult to achieve lower bandgaps that are suitable for single-junction PVs. On the other hand, the “dimer”-structure nonperovskites have too large a bandgap for PV applications (e.g., 2.86 eV for Cs2Bi3I9[71] and 2.9 eV for (MA)2Bi3I9[69]), because they have lower electronic/structural dimensionality than layered perovskites. So far, Bi and Sb halide perovskites have not produced efficient PSCs. Based on the electronic dimensionality concept, to achieve efficient Bi and Sb halide perovskite absorber materials, the [Bi3X9] octahedra should connect in 3D for a 3D electronic dimensionality.

4.2. Proposed 3D Bi− and Sb-based perovskites with mixed chalcogen and halogen anions

To achieve 3D Bi and Sb based perovskites, Sun et al. have proposed the so-called “split-anion” approach, in which mixed chalcogen and halogen anions are introduced at X sites of the perovskite structure to maintain charge neutrality.[76] Interestingly, MABI(Sel) and MABI(Sl2) have been shown to exhibit improved bandgaps, 1.29 and 1.38 eV, respectively, and stronger optical absorptions over the prototypical MAPbI3 perovskite. In a later study, Hong et al. have accessed the viability of such perovskites with mixed chalcogen and halogen anions by a combination of DFT calculation and solid-state synthesis.[79] Unfortunately, DFT calculations show that the proposed 3D Bi- and Sb-based perovskites are thermodynamically unstable against decomposition, which is confirmed by solid-state synthesis experiments.[76]

4.3. Perovskites with mixed divalent and trivalent cations

Vargas et al. recently reported the synthesis and characterization of a <111>-oriented layered double perovskite Cs4CuSb2Cl12, which incorporates Cu2+ and Sb3+ into layers that are three octahedra thick (n = 3).[76] This material can also be viewed as being derived from Cs2Sb2Cl9 by inserting a [CuCl6] octahedra layer into each of the successive [SbCl6] octahedra layers, as shown in Figure 7a. It was shown that this material behaves as a semiconductor with a direct bandgap of 1.0 eV and a conductivity that an order-of-magnitude higher than that of MAPbI3, as well as having high photo-, thermal-, and humidity-stability.[76] Note that the bandgap of Cs4CuSb2Cl12 is dramatically reduced as compared to its parent phase Cs2Sb2Cl9 (3.0 eV).[70] In a later study, Wang et al. have reported that the ground-state electronic structure of Cs4CuSb2Cl12, which exhibits a localized conduction band that is derived mainly from unpaired Cu d-Cl 3p antibonding, as shown in Figure 7b.[77] The localized conduction band leads to a large electron mass and weak optical absorption (Figure 7c), which are undesirable for an efficient PV absorber material. Nevertheless, the discovery of Cs4CuSb2Cl12 provides a new strategy for incorporating divalent and trivalent metal cations to form layered double perovskites, which may stimulate further exploration of layered perovskites with multiple B cations for PV applications.

5. Halide Double Perovskites

5.1. A2B(I)(II)III4X14 double perovskites

Halide double perovskites A2B(I)(II)III4X14, where the monovalent B(I) and trivalent B(III) cations adopt an ordered rock-salt-type arrangement (Figure 8a), have been proposed as promising candidates to overcome the toxicity and instability issues of Pb-halide perovskites.[78-81] Indeed, there have been many early reports on the experimental synthesis of A2B(I)(II)III4X14 double perovskites with B(I) = Li+, Na+, K+, Rb+; B(II) = Sc2+, Y3+, Lu3+ (Ln = lanthanide), Al3+, Ga3+, In3+, Bi3+; and X = F−, Cl−, Br−.[82] However, these halides are highly ionic, and their bandgaps

Figure 7. a) Crystal structures of Cs2Sb2Cl9 (left) and Cs4CuSb2Cl12 (right). Reproduced with permission.[76] Copyright 2017, American Chemical Society. Calculated b) band structure and c) optical absorption coefficients of Cs4CuSb2Cl12 with an antiferromagnetic configuration. Adapted with permission.[77]
are too large for PV applications. The iodide analogues should have narrower bandgaps, however, so far, there have been no reports on the successful synthesis of iodide double perovskites, which is not surprising as they are reported to be thermodynamically unstable in several DFT studies.\(^{[83, 84]}\) Alternatively, much effort has been devoted to narrowing the bandgaps of halide double perovskites by employing B(I) cations such as Ag\(^+\), Cu\(^+\), Tl\(^+\), or In\(^+\), and B(III) cations such as Bi\(^3+\) or Sb\(^3+\), because these cations are expected to be able to raise the VBM significantly due to the strong antibonding coupling between the cation d/s and anion p orbitals. Over the past year, many Ag\(^+\)-, Tl\(^+\)-, Bi\(^3+\)-, and Sb\(^3+\)-containing halide double perovskites have been synthesized, including Cs\(_2\)AgBiX\(_6\) (X = Br, Cl)\(^{[78–80]}\), (MA)\(_2\)KBI\(_6\)\(^{[81]}\), Cs\(_2\)AgInX\(_6\)\(^{[82]}\), Cs\(_2\)AgSbCl\(_6\)\(^{[83]}\), and (MA)\(_2\)TlBI\(_6\)\(^{[84]}\). However, these newly-synthesized halide perovskites exhibit bandgaps that are too large (> 1.9 eV) for single-junction PSCs.

Among the newly-synthesized halide double perovskites, Cs\(_2\)AgBiBr\(_6\) has the smallest bandgap of 1.95 eV, which could find use in tandem and multijunction PVs.\(^{[78]}\) DFT studies have revealed that the bandgap of Cs\(_2\)AgBiBr\(_6\) is indirect, with the VBM at the X point and the CBM at the L point (Figure 8b).\(^{[83]}\) Recently, there have been several reports on bandgap engineering of Cs\(_2\)AgBiX\(_6\) via cation alloying.\(^{[85, 86]}\) Slavney et al. reported that dilute Tl-alloying decreases the bandgap of Cs\(_2\)AgBiBr\(_6\) to \(\approx 1.4\) eV (Figure 8c),\(^{[87]}\) which is close to the ideal bandgap value for PV applications. The significant bandgap reduction is caused by the TI impurity-induced band edge reconstruction, which is supported by DFT results.\(^{[88]}\) Moreover, they have shown that the TI-alloyed Cs\(_2\)AgBiBr\(_6\) exhibit long-lived carriers an attractive property for PSCs. However, TI is highly toxic and, therefore, it is undesirable for PV applications. Du et al. have demonstrated bandgap engineering of Cs\(_2\)AgBiBr\(_6\) through alloying of trivalent cations such as Sb\(^3+\).\(^{[89]}\) They found that Sb alloying decreases the bandgap slightly, with the smallest value of 1.86 eV for Cs\(_2\)AgBi(Sb\(_{0.075}\)Br\(_{0.925}\)) (Figure 8d).\(^{[89]}\) The bandgap reduction is attributed to the higher energy levels of Sb 5s states than that of Bi 6s states (Figure 3c), which raises the VBM slightly.\(^{[90]}\) Recently, Li et al. reported bandgap narrowing through high pressure treatment.\(^{[90]}\) They found that the narrowed bandgap can be retained partially after releasing the pressure.\(^{[90]}\) However, the bandgaps of Sb-alloyed and high-pressure-treated Cs\(_2\)AgBiBr\(_6\) are still indirect and large, which is not suitable for single-junction PSCs. So far, there have been no reports on bandgap engineering via anion substitution, for example, I\(^-\). Further studies are needed for identifying other dopants that can afford large bandgap reductions and direct-gap transitions in environmentally-friendly halide double perovskites.

In this context, DFT methods have been used extensively to search for A\(_{n}\)B\(_{m}\)I\(_{3n}\) double perovskites with narrower bandgaps.\(^{[91–93]}\) Zhao et al. have proposed In\(^3+\)-based double perovskites such as Cs\(_2\)InBICl\(_6\) and Cs\(_2\)InBICl\(_6\) and Cu\(^+\)-based double perovskites such as Cs\(_2\)CuInBr\(_6\) as promising PV absorber candidate materials, with bandgaps suitable for single-junction PSCs, small carrier effective masses, and high optical absorption coefficients.\(^{[91, 92]}\) However, these proposed double perovskites are thermodynamically unstable because of the extremely-high-energy In \(5s^2\) and Cu \(3d^{10}\) states that raise the VBM to too high energy levels.\(^{[23, 94]}\) So far, there have been no reports on the successful synthesis of In\(^3+\) and Cu\(^+\)-based halide double perovskites.\(^{[23, 94, 95]}\) Thus, it is extremely challenging to realize stoichiometric halide double perovskites with bandgaps suitable for single-junction PSCs.

5.2. Vacancy-ordered double perovskites

Vacancy-ordered double perovskites with the chemical formula A\(_{n}\)BX\(_{n}\) have also been examined for PV applications.\(^{[96–99]}\) These compounds are also viewed as 0D nonperovskites since the [BX\(_x\)] octahedra are corner-sharing, but are isolated.\(^{[100]}\) The most typical representative of these compounds is Cs\(_2\)SnI\(_6\), which exhibits a direct bandgap of \(\approx 1.3\) eV\(^{[96]}\) that is almost ideal for single-junction PV application. It has been shown that the bandgap of Cs\(_2\)SnI\(_6\) can be tuned over a wide range, up to a large value of 2.9 eV by Br\(^-\) substitution of I\(^-\).\(^{[100]}\) which provides desired bandgaps for tandem and multijunction PVs. So far, thin-film solar cells based on Cs\(_2\)SnI\(_6\)-based absorbers have not achieved high PCEs.\(^{[38]}\) Theoretical studies have shown that Cs\(_2\)SnI\(_6\) exhibits some properties that are undesirable in the context of PV applications: (i) bandgap transition is dipole-forbidden;\(^{[101]}\) (ii) hole effective mass is rather large;\(^{[27]}\) and (iii) dominant defects create deep states in the bandgap.\(^{[102]}\) These findings suggest that, compared with the 3D ABX\(_3\) perovskite, 0D A\(_{n}\)BX\(_{n}\) nonperovskites show less promise for PV applications. Most recently, Ju et al., using DFT calculations and experimental measurements, have shown that the bandgaps of va.
cancency-ordered double perovskites in Cs₂TiI₅Brₓ can be tuned between 1.0–1.8 eV.[103]

6. Oxide and Chalcogenide Perovskites

6.1. Oxide perovskites

Originally the name “perovskite” was used to describe the oxide mineral CaTiO₃. In fact, there exist many oxide perovskites with the chemical formula ABO₃, where the average ion charges of A and B metal cations are +2 and +4, respectively (e.g., B⁴⁺ can be (Mg⁵⁺,1/2, Nb⁵⁺,1/2) for Pb(Mg₇/₈,Nb₁/₈)O₃), or both can have 3+ charge.[105] Perovskite-type oxides are used widely in various applications, including high-capacity capacitors (e.g., BaTiO₃-based solid solutions), high-k dielectrics, piezoelectric actuators, ferroelectric memory (Pb(Zr,Ti)O₃), positive-temperature-coefficient thermistors (BaTiO₃-based semiconductors), etc.[106] Generally, oxide perovskite dielectrics exhibit wide bandgaps (>4 eV), because the VBM consists mainly of localized 2p orbitals of O²⁻ anions with a large electronegativity, while the CBM consists mainly of localized transition-metal d orbitals. There has been significant research effort devoted to reducing the bandgaps of oxide perovskites for visible-light absorbers. In fact, several Bi-based oxide double perovskites have been reported to exhibit small bandgaps, for example, 2.05 eV for Ba₂Bi₂₃/₈Bi₂₁/₈O₆, and 1.64 eV for Ba₂Bi₂¹/₄Bi₂¹/₄₉₆Bi₁₆O₆.[104] Interestingly, theoretical studies have shown that both the valence band and conduction band of these Bi-based oxide double perovskites contain a large portion of Bi 6s orbitals, leading to narrow bandgaps, highly mobile charge carriers, and small exciton binding energies.[104–106] These oxide double perovskites have shown high performance as photocatalyst and photoanode for water oxidation.[104,105] Grinberg et al. reported a family of oxide perovskite solid solutions [K₂/₃Nb₂/₃O₃]₁ₓ[Ba₂/₃Ni₂/₃O₃]₀₁₋ₓ (KBNNO), exhibiting both ferroelectricity and a wide variation of direct bandgaps in the range 1.1–3.8 eV.[107] In particular, the x = 0.1 composition is polar at room temperature, has a direct bandgap of 1.39 eV, and a photocurrent-density approximately 50 times higher than that of the classic ferroelectric (Pb,La)(Zr,Ti)O₃ phase with corner-sharing [BX₆] octahedra. Other chalcogenide compounds form nonperovskite phases with corner-sharing or isolated [BX₆] octahedra (the so-called “needle-like” and “hexagonal” nonperovskite phases), which are expected to exhibit less promising PV properties due to the lower electronic dimensionality, as compared to the corresponding perovskite phases.[108,109] The calculated bandgaps for CaZrS₂, CaHFS₁, BaZrS₂, and BaHFS₄ perovskites are 1.96, 2.30, 1.76, and 2.02 eV, respectively (Figure 9a).[108] The experimental optical bandgaps for CaZrS₂ and BaZrS₂ perovskites are reported to be 1.90 eV[109] and 1.74–1.85 eV (Figure 9b),[109–111] respectively, which are suitable for tandem PVs. Among the sulfide perovskites, BaZrS₂ exhibits a smaller bandgap, which, however, is still larger than the optimal bandgap for single-junction PSCs. Meng et al. have demonstrated, using DFT calculations, that the bandgap of BaZrS₂ can be reduced significantly by Ti alloying.[110] With a small amount of Zr substituted by Ti (x = 0.1) in BaZr₁₋ₓTiₓS₂, they have been able to reduce the bandgap to 1.47 eV (Figure 9c), a level within the optimal bandgap range for single-junction PSCs.[110] Interestingly, the alloy BaZr₁₋ₓTiₓS₂ perovskites show reasonable small carrier-effective masses, ambipolar self-doping properties, and theoretical PCEs that are even higher than those of the emerging Pb-halide perovskites for the same thickness. However, DFT calculations and experimental synthesis have also shown that it may be difficult to synthesize alloy BaZr₁₋ₓTiₓS₂ perovskites, as they tend to transform into BaZrS₂ and BaTiS₄ phases.[111]

Ji et al. have also theoretically predicted that Sn⁴⁺-based chalcogenide perovskites SrSnS₃ and SrSnSe₂ are promising PV absorber materials, primarily because of the predicted optimal bandgaps (1.56 and 1.0 eV, respectively), relatively small effective masses for both electrons and holes, and high optical absorption coefficients.[112] Experimentally, SrSnS₃ has been syn-

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Figure 9. a) Bandgap of 18 ABX₃ compounds in the distorted perovskite, “needle-like,” and “hexagonal” phases calculated using the HSE06 functional. Reproduced with permission.[104] Copyright 2014, American Chemical Society. b) Diffuse reflectance data measured on a powdered dark brown BaZrS₂ sample gives a bandgap of 1.85 eV. c) Calculated bandgaps of alloy BaZr₁₋ₓTiₓS₂ perovskites. Reproduced with permission.[110] Copyright 2016, American Chemical Society.
thesized, which, however, crystallizes into the “needle-like” nonperovskite structure\cite{114,115} rather than the desirable perovskite structure. So far, SrSnSe$_2$, with its simple chemical composition, has not been synthesized. It would be interesting but challenging to synthesize these proposed chalcogenide perovskites.

7. Summary and Outlook

In closing, the vast compositional space and various dimensionalities have allowed us to tailor the bandgaps of ABX$_3$ perovskites over a very wide range. Promising candidate perovskites that exhibit optimal bandgaps for single-junction and tandem PVs have been realized through a combination of compositional and structural tuning in-practice, and this success has been driven by both theoretical and experimental efforts. From the above discussion, it is obvious that while it is relatively easy to obtain various perovskite materials with suitable bandgaps for tandem and multijunction PV applications, it is much more challenging to achieve small bandgaps (<1.4 eV) in perovskite semiconductors that are optimum for single-junction PSCs. A handful of small-bandgap candidates such as (FAPbI$_3$)$_{1-x}$(CsSnI$_3$)$_x$\cite{36} and Cs$_5$Ti$_2$Br$_{12}$\cite{116} have been recently reported, but whether they can meet other key criteria such as optical absorption, favorable defect properties, stability, toxicity, and crystallization behavior for being good PV materials remains to be explored. There is no doubt that searching for more small-bandgap perovskite semiconductors is an important research direction. We envision that the discoveries will be led by further expanding the compositional space and the dimensionalities of perovskite semiconductors.\cite{114,115} Furthermore, the unprecedented combination of organic and inorganic chemistry in perovskite semiconductors may also make it possible to find new bandgap-tuning mechanisms in these material systems.

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Conflict of interest

The authors declare no conflict of interest.

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