

Lead-Free Halide Double Perovskites: Fundamentals, Challenges, and Photovoltaics Applications

Naveen Kumar Tailor¹, Andrea Listorti², Silvia Colella³, Soumitra Satapathi^{1*}

¹Department of Physics, Indian Institute of Technology Roorkee, Roorkee, Haridwar, Uttarakhand 247667, India

²Department of Chemistry, University of Bari “Aldo Moro”, Via Orabona 4, Bari 70126, Italy

³CNR-NANOTEC, c/o Department of Chemistry, University of Bari, Via Orabona 4, Bari 70126, Italy

Abstract

Metal halide perovskites (MHPs) have gained tremendous interest in photovoltaics applications reaching the power conversion efficiency (PCE) of 25.8%. Despite the rapid development of MHP-based solar cells, the existence of toxic lead (Pb) and their operational instability are seen as key roadblocks for commercialization. A viable strategy for developing lead-free optoelectronic devices nests in addressing the toxicity issues in these compounds by carefully and strategically replacing lead while maintaining comparable stability and PCE. In this regard, halide double perovskite with structural flexibility, as well as lower toxicity and higher stability have caught the attention of the scientific community, surging the research of lead-free halide double perovskites with $A_2B(I)B(III)X_6$ composition. A critical analysis of such compounds is presented from a fundamental point of view considering their orbital characteristics, bonding interaction, and optical transitions and relate these properties with their solar cell performance. This review focuses on the efficiency limiting factors and critically discusses recent advancements and strategies which have been demonstrated to boost their photovoltaic performances. Finally, starting from existing double perovskite materials, prospective research directions are identified toward enhanced optoelectronic properties and device performances.

Corresponding author: Soumitra Satapathi (ssphf.fph@iitr.ac.in)

1. Introduction

In the last decade, metal halide perovskite materials presenting an ABX_3 structure have acquired a remarkable interest in the emerging photovoltaic field. These materials possess exceptional characteristics such as structure flexibility, bandgap tunability, and remarkable charge transport parameters, which translate in superior device performances.^[1] Perovskite-based solar cells (PSCs) reached power conversion efficiencies (PCE) of up to 25.8% in 2021, which is comparable to commercialized solar cells, and this value is constantly increasing every year.^[2] In addition, perovskite materials are cost-effective and easy to prepare, and this strongly motivates the effort toward commercial applications of the technology. However, despite these incredible characteristics, PSCs still face a long way to real-world acceptance due to important concerns related to the toxicity of one of its constitutive elements (lead) and their poor stability in the presence of heat, oxygen, moisture, electric field, and light.^[3] The poisonousness of Pb is a major obstruction to future commercialization. Pb is an especially tricky bioaccumulative peril that can cause irreversible health issues.^[4] Even if the perovskite devices are going to be encapsulated and provided by Pb-absorbing materials for recycling, the anticipation of Pb spillage into the environment can't be ensured.

To address these difficulties, significant resources have been invested in the replacement of lead for the development of lead-free perovskites, aiming at retrieving the outstanding optoelectronic capabilities of lead-halide perovskites, combined with nontoxicity and high stability.^[5] In the lead perovskites, the unique electronic configuration of Pb $6s^2 6p^0$ leads to exceptional optoelectronic features. Therefore, divalent tin (Sn^{2+}) and germanium (Ge^{2+}) in a similar group with identical lone pairs were initially utilized to substitute the Pb.^[6] Regardless, due to the quick oxidation of Sn^{2+} and Ge^{2+} to +4 states, Sn and Ge-based perovskites show reduced stability. Besides, the lower environmental impact of Sn is still controversial, few research reports suggest that when Sn is dispersed into the environment, it may be even more hazardous to humans than Pb, despite causing less severe damage to plants.^[7] Therefore, it is of great interest to classify new applicants that can tackle the issues of harmfulness, while yet keeping up with the captivating characteristics of Pb-halide perovskite materials. Thinking in this line of Pb replacement, the bismuth (Bi^{3+}) and antimony (Sb^{3+}) cations with trivalent lone pair have been utilized, which results in the $A_3B_2X_9$ structure.^[8] However, the photovoltaic performance of the related devices is poor because of the low-dimensional structure, large bandgap, defect intolerance, and high effective mass of carriers.

While finding the alternative of the lead-halide perovskite, the electronic dimensionality should be considered as the main factor. In this direction, if two Pb^{2+} cations were replaced with heterovalent [i.e., monovalent (I) and trivalent (III)] cations, this cation transmutation approach leads to the

formation of lead-free halide double perovskites (LFHDPs) $A_2B(I)B(III)X_6$ structure keeping the 3D connectivity of lattices and it permits the adaptability for different compositional changes. This methodology is exceptionally successful as it keeps up with the 3D perovskite structure and simultaneously offers more material variety. It is advantageous to specify that the new surge in $A_2B(I)B(III)X_6$ halide double perovskites (HDPs) research is largely driven by the ease with which various metal cations with various oxidation states can be substituted and fused in the B-site, different organic and inorganic species can be fused in the A-site, and halide composition can be varied in the X-site.^[9] The structural flexibility of HDPs takes into account a variety of interesting physical properties, such as small bandgaps, strong photon absorptions, and high photoluminescence.^[10]

Particularly, recent research activities on perovskite-based photovoltaics have been shifted to HDPs for stable and environment-friendly photovoltaic application.^[9, 11] Although, many exciting research articles have been published recently in double perovskites focusing on their applications in photovoltaics and optoelectronics, structure-property relationship, and photophysics characteristics,^[10-12] the description of HDPs in the view of orbital characteristics, bonding interactions and tuning of optical properties need to be addressed in combination with the photovoltaic performance. In this review article, we address this gap and critically present these characteristics. We focus on the structural tunability, and orbital characteristics of double perovskites compared with lead halide perovskites, bandgap tuning, electronic transitions, and their performance and consequence in solar cell applications. First, we discuss diversity in their crystal structure and orbital characteristics of band formations. Then we emphasize their bandgap tuning and transitions between bands. We discuss the solar cell application and how the device performance relies on several fundamental factors such as film quality, interface matching, and light-harvesting capability. Finally, we provide a roadmap to enhance the optoelectronic properties and solar cell performance of LFHDPs.

2. Crystal Structure

In all types of semiconductor materials, the crystal structure plays a vital role to determine their photophysical characteristics and device performance. Therefore, crystal structure should be the first focus before considering the other properties. In the case of halide perovskites, these materials exhibit structural flexibility which gives remarkable optoelectronic characteristics. The crystalline structure of HDP material is responsible for a lot of its fascinating photophysical features. As illustrated in Figure 1a, two Pb cations are substituted with nontoxic heterovalent cations having I and III oxidation states, resulting in a double perovskite $A_2B(I)B(III)X_6$ structure.^[9] In the crystal lattice, the octahedra $B(I)X_6$ and $B(III)X_6$ are aligned along with each other with shared corners. This crystal

structure opens up the possibility of replacing inorganic and organic elements at the A-site, metal cations with various oxidation states at the B-site, and halogen elements at the X-site as illustrated in Figure 1b.

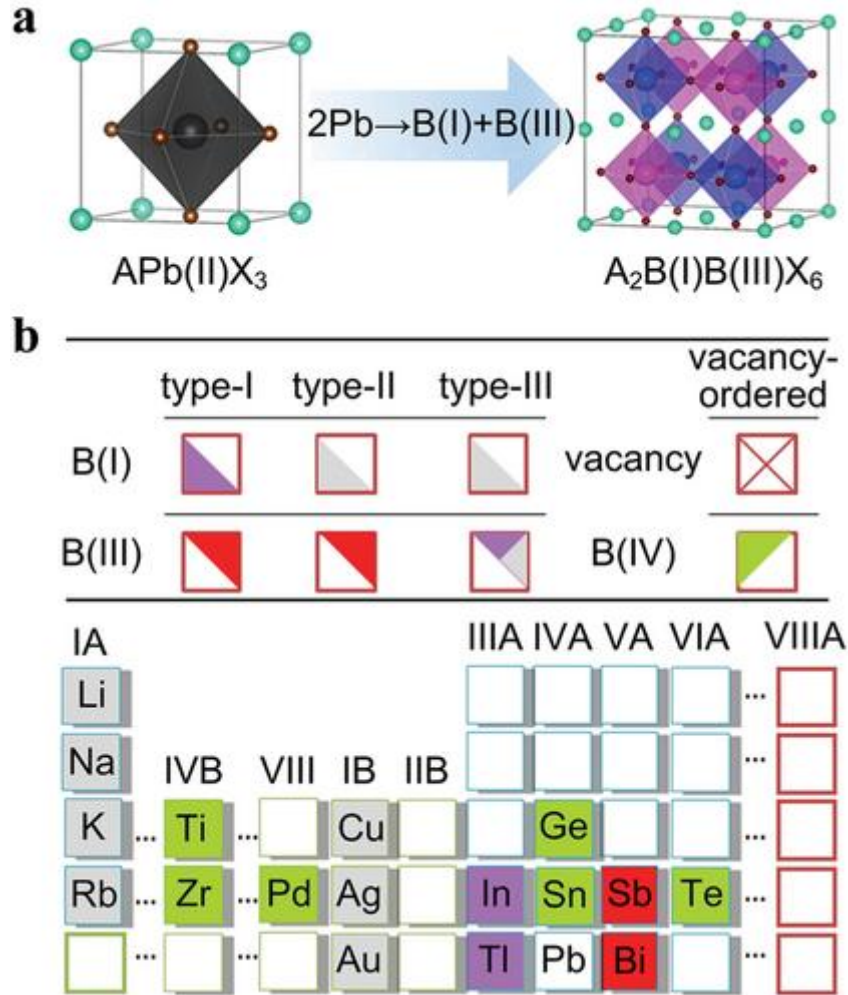


Figure 1. a) The structural description of double perovskites via cation transmutation. The B-site ions were filled with B^+/B^{3+} , as the place of B^{2+} . b) The possible elements for B-site and combination of double perovskites. Reproduced with permission.^[9] Copyright 2018, Elsevier.

It is worth noting that the perovskite's crystal structure is crucial to the electronic characteristics, and the high O_h (octahedral) symmetry of conventional lead-halide perovskites assumes a significant part in deciding their superb electronic properties.^[13] The HDPs are formed from single perovskites via cation transmutation as shown in Figure 1a, which affects the structure and symmetry properties significantly. To determine the structural stability, two metrics, the tolerance factor τ , and the octahedral factor μ are used based on Goldschmidt's observational models^[14]

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (1)$$

$$t = \frac{r_B}{r_X} \quad (2)$$

where r_A , r_B , and r_X are radii of corresponding ions. Nonetheless, a more all-encompassing tolerance factor has recently been proposed.^[14] This is given by Equation (3) and empirically relates stability to the oxidation states of the ions, notwithstanding their radii

$$\tau = \frac{r_X}{r_B} - n_A \left(n_A - \frac{\frac{r_B}{r_A}}{\ln \frac{r_A}{r_B}} \right) \quad (3)$$

r_i is the ionic radii and n_A is the oxidation state of A. As indicated by past investigations, the scopes of the octahedral factor μ are $0.44 < \mu < 0.90$ and the tolerance factor τ is $0.81 < \tau < 1.11$.^[14] In addition to the precision and probabilistic nature of τ , its pertinence across a wide scope of compounds yields a different insight into stability. Additionally, perovskite stability has a monotonic dependency on τ (e.g., as τ lowers, the likelihood of being perovskite increments). When $\tau < 4.18$, stable perovskites are expected empirically. Figure 2 presents the tolerance factor values for various double perovskites.^[15] One such example of double perovskites is $\text{Cs}_2\text{NaBiI}_6$ (CNBI), which has the τ as 0.849 and μ as 0.466.^[16] The tunable crystal structure of the HDPs has a broad range of tolerance factors, which allows the compositional engineering to customize the original structure and its properties.

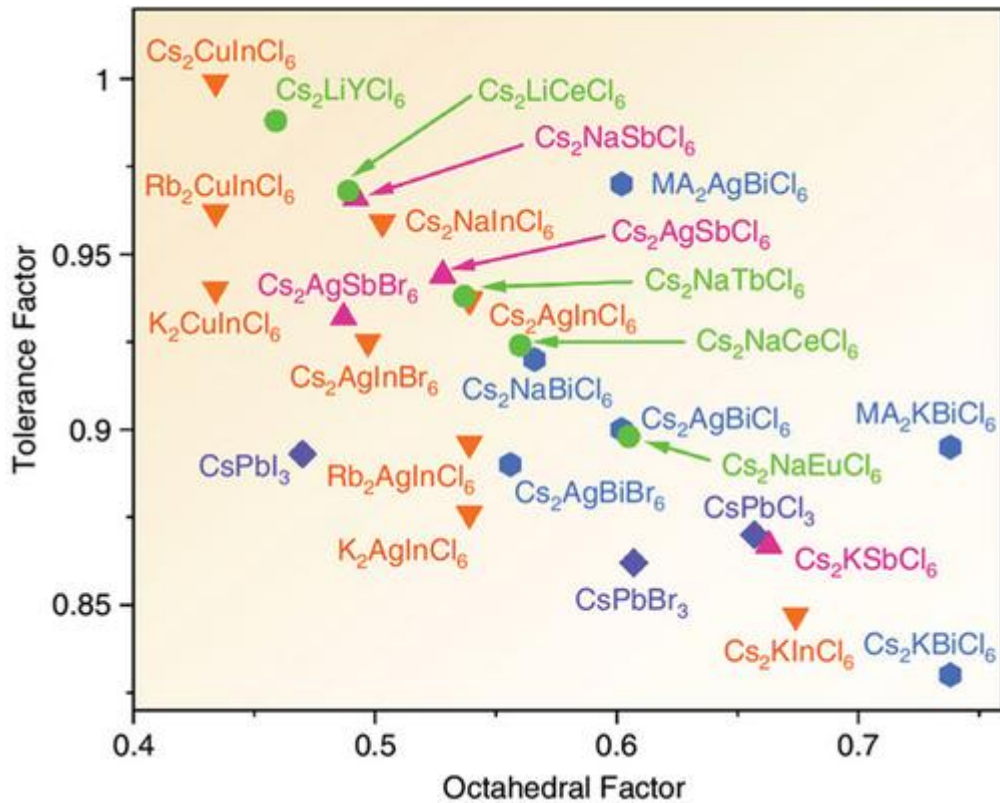


Figure 2. Schematic illustration of octahedral factor (μ) and tolerance factor (τ) of HDPs. Reproduced with permission.^[15] Copyright 2020, Wiley.

The other characteristics of the crystal structure such as lattice parameters, bond length, and distortion in the lattice unit leads are important factors to consider. The most investigated double perovskite $\text{Cs}_2\text{AgBiBr}_6$ has a unit cell axis of 11.25 Å,^[17] which is twice MAPbBr_3 (≈ 5.92 Å).^[18] The metal halide bond lengths of the B-site components (e.g., Bi and Ag) varied, as seen by the ionic radii of the Ag^+ (129 pm), Bi^{3+} (117 pm), and Br^- (183 pm).^[17] The diverse Bi-Br and Ag-Br bond lengths were relied upon to substitute the crystallization nature inside a cubic unit cell, however, no evidence can suggest that the lattice distortion may be initiated by utilizing distinctive B-site ions.^[11, 12, 19] Further examinations are needed to acquire an understanding of the relationship between the divergent bond lengths of metal halide and the disorder in the crystal structure. Up to now, the crystal structure stability of HDPs has been predicted based on computational methodology,^[20] and these predicted stabilities are consistent with the available experimental reports. Despite having the 3D connectivity and cubic crystal structure, the HDPs exhibit localized, narrow conduction band and a wide bandgap,^[12, 21] which indicates that one should be consider other parameter than the crystal lattice to achieve similar features to those observed in Pb-based perovskites. In fact, several reports demonstrate the fundamental limitation of double perovskites such as short-range interaction between successive B' or B'' cation octahedra, large deformation potential, polaron formation, and strong electron–phonon coupling.^[22] These all features are responsible for the limited transport of charge carriers which results in the poor photovoltaic performance of these double perovskites.

3. Electronic Band Structure

In an atom, electrons occupy discrete energy levels called atomic orbitals, and they are governed by the angular momentum conservation law. When two or more atoms come together to form a molecule or compound, the orbitals of these atoms overlap with each other and form bands. The overlapping of the orbitals and bands formation can be understood by the quantum mechanical band theory and crystal field theory. In the case of semiconductor materials, a bandgap exists between two bands called the valence band (VB) and conduction band (CB).^[23] The electronic band structure of semiconductor material is connected with the periodicity of the lattice and can be explained by Bloch's theorem.^[24] The halide perovskites are emerging semiconductor materials and their photophysical and electronic properties are mostly determined by their electronic band structure.^[13, 25] In the most investigated lead halide perovskites, the electronic configuration of the Pb ($6s^2 6p^0$) is the main factor behind the brilliant optical and electrical characteristics as predicted by the theoretical calculations.^[26] In the 3D APbX_3 perovskite structure, the ns^2 outer shell electronic configuration of the B-site is liable for significant direct bandgap absorption and dominating photovoltaic characteristics.^[13] Considering the fact that perovskite materials are structurally flexible, they can have their band structure easily tweaked, which directly affects their optical and electrical

characteristics. In the case of $A_2B(I)B(III)X_6$ HDPs, a wide range of B(I) and B(III) sites is acceptable, resulting in a wide range of orbital configurations in the band edges.^[12, 21] Because metal-to-metal charge transfer dominates in HDPs materials, the frontier orbitals energies of the B(I) and B(III) site cations have a strong influence on their electronic band structure.^[13] In further subsections, we will focus on the bands' formation from the orbitals, bonding interactions, tuning of band structure, and allowed and forbidden transition between bands.

3.1 Orbital Characteristics

Novel optoelectronic materials can be designed using the essential orbital characteristics at the band edges. The use of varied properties of s- and p-orbital-derived bands (Figure 3a) to alter the direct-indirect bandgap transition in semiconductors is a good example. The VB is obtained from the B(I) cation's entirely occupied d orbitals, whereas the CB relies on selecting a suitable B(III) cation which has the s- and p-states.^[27] The conduction band minimum (CBM) can be effectively modulated by changing s-orbital-derived and p-orbital-derived. In this manner, Tang et al. have suggested that by modulating the flat band character at the band edges, 2D electronic structures of bands can be designed. The hybridization of d and p orbitals leads to the formation of low-dimensional electronic structures.^[28] As presented in Figure 3b, the existence of the nondispersive band at the CB/VB edge will depend on the degree of d orbitals. As a result, by mixing two metal cations with various types of d-electron configurations, flat bands may be generated at both the CB and VB boundaries at the same time.

For example, in the all-inorganic $Cs_2AgBiBr_6$ system, the antibonding states of Br 4p and Ag 5s orbitals, as well as the antibonding states of Br 4p and Bi 6p orbitals, form the CBM. Moreover, the antibonding states of Br 4p and Ag 4d orbitals, as well as the antibonding states of Br 4p and Bi 6s orbitals, form the VBM as presented in Figure 3c.^[29] In another case, if the organic molecule $CH_3NH_3^+$ (MA) is substituted at the place of Cs to make $(MA)_2AgBiBr_6$, the formation of CBM and VBM is attributed to similar orbitals as $Cs_2AgBiBr_6$.^[30] The substitution of Cs with MA cation tends to be considered not impacting on the composition of the $A_2AgBiBr_6$ HDP band edge. These results are consistent with those of a standard perovskite, i.e., A-site cation does not result in prominent contributions at band edges, regardless of whether the perovskite is a standard or an HDP. However, the band structure modifies due to the geometric effect of the A-site cation (size and nature) and its coulombic interaction with X-site anions. In addition, the inorganic frameworks in the HDP lattice tilt due to the MA molecules; nonetheless, the tilting of the inorganic frameworks does not affect the dominant component of the band edges.

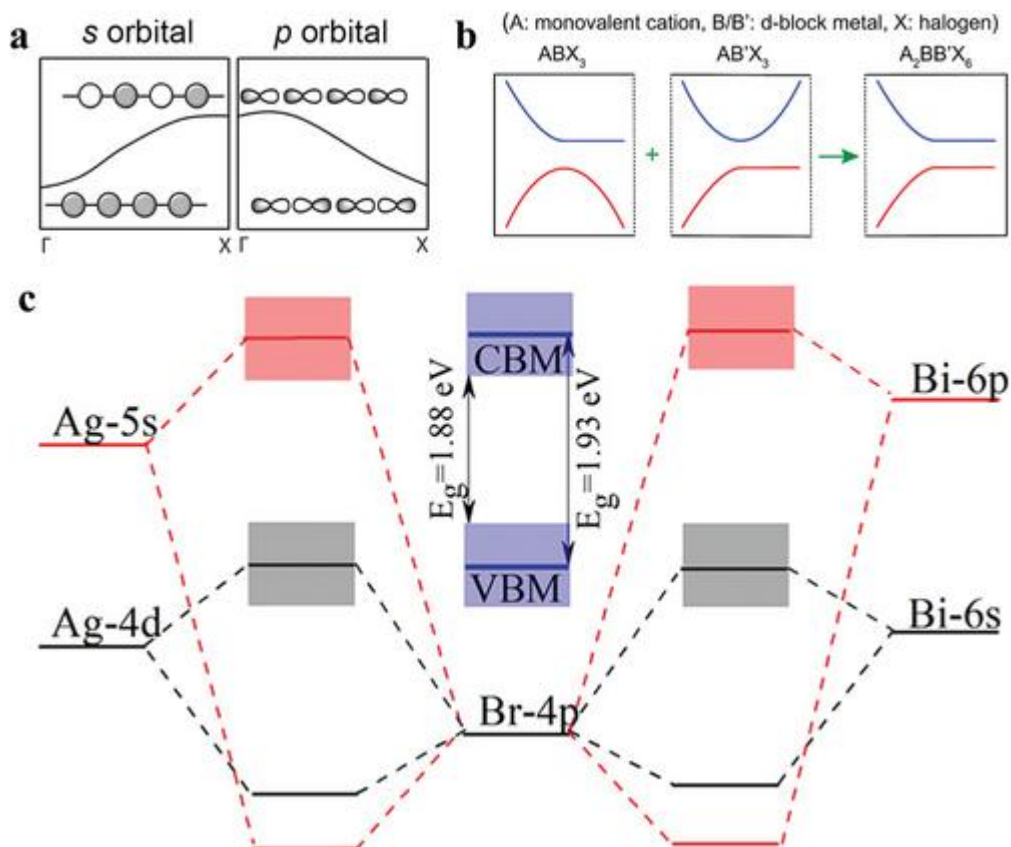


Figure 3. a) Illustration of band structures for s- and p-orbital derived bands. Reproduced with permission.^[27] Copyright 2017, Royal Society of Chemistry. b) The band structure for HDP was derived through orbital engineering for d-block metal cations. The formation of the 2D character of the CB/VB via B (e.g., empty d orbital)/B' (e.g., filled d orbital) d–X p hybridization. Reproduced with permission.^[31] Copyright 2019, American Chemical Society. c) Schematic illustration of bonding interactions in $Cs_2AgBiBr_6$ and $(MA)_2AgBiBr_6$ HDP. Reproduced with permission.^[32] Copyright 2020, American Chemical Society.

3.2 Bonding Interactions

As discussed, the bandgap of the HDP is significantly different than that of the ABX_3 perovskite. **Figure 4a** shows the difference between ABX_3 and $A_2B(I)B(III)X_6$ structure properties. To better understand these differences, we analyze the bonding interactions for perovskite materials in the vicinity of their band edges. The antibonding states of Pb 6p form the CBM, whereas the VBM is made up of antibonding states of Pb 6s and I 5p orbitals in the $MAPbI_3$ perovskite.^[28] The Pb-I-Pb angle in the ideal cubic lattice equals 180° . **Figure 4b** shows that the I 5p orbitals and Pb 6p orbitals are in nonbonding states for the directionality of the wave function of the p orbitals.^[32] The introduction of MA molecules into orthogonal PbI networks leads to their imbalanced charge distribution and nonequivalent chemical activity, resulting in evident lattice distortion. The lattice distortion lowers the Pb-I-Pb bond angle and the transverse displacement between the Pb and I atoms.

The original nonbonding Pb 6p and I 5p orbitals would now be able to bind with one another when the Pb and I atoms undergo a transverse shift, as seen in Figure 4c. The band edge is changed because of the additional bonding interaction. The spherical symmetry of the s orbital permits it to bind equally with neighboring atoms in all directions, as displayed in Figure 4d. The d orbitals are fivefold degenerated orbitals with an angular momentum quantum number of $l = 2$. The electrical configuration of the Ag^+ ion is closed-shell, which means that each Ag 4d is filled with electrons. Figure 4f depicts the wave functions of d orbitals. As a result, the d orbital's bonding interactions with various atoms are similar to the spherical s orbitals.^[32]

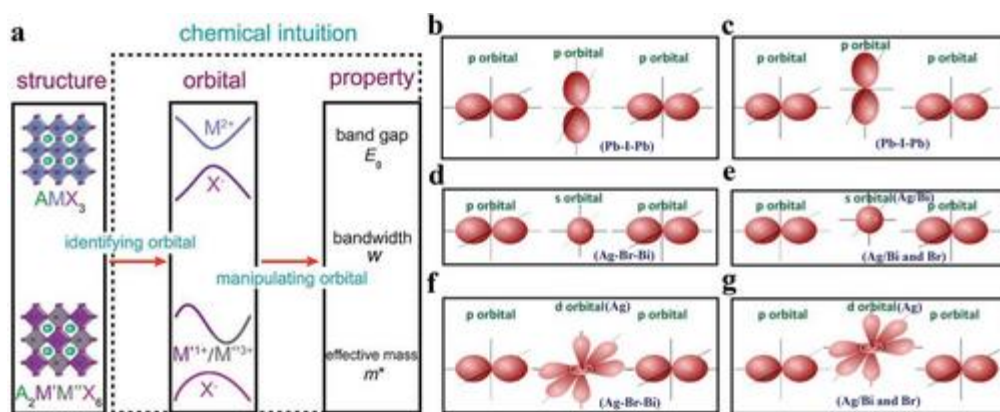


Figure 4. a) Schematic illustration of the structure, orbitals derived bands, and properties of single cation and double cation perovskite. Reproduced with permission.^[28] Copyright 2021, American Chemical Society. b–g) Illustrations of bonding interactions and transverse displacement in ABX_3 and $\text{A}_2\text{B}(\text{I})\text{B}(\text{III})\text{X}_6$ perovskites. Bonding interactions between b) p and p orbitals in ideal orthogonal Pb-I-Pb networks, d) between p and s orbitals under ideal orthogonal Ag-Br-Bi networks, and f) between p and d orbitals in ideal orthogonal Ag-Br-Bi networks. Transverse displacement (c) between Pb and I atoms, e) between Ag/Bi and Br atoms (p and s orbitals), and g) between Ag/Bi and Br atoms (p and d orbitals). Reproduced with permission.^[32] Copyright 2020, American Chemical Society.

The $\text{A}_2\text{AgBiBr}_6$ lattice tilts with the changing of A-cations and metal octahedral distortion occurs, causing transverse displacement between Ag/Bi cations and Br anions. On a broad scale, however, this transverse shift has little effect on the bonding strength of the Ag-(d/s)/Bi-s orbitals and the Br-p orbitals, as illustrated in Figure 4e,g. As a result, neither the transverse shift nor the lattice distortion affects the bandgap of $\text{A}_2\text{AgBiBr}_6$. This differs from the conventional APbX_3 perovskites. In the $\text{Cs}_2\text{AgBiBr}_6$ perovskite, each type of bond has the same bond length, and the antibonding states are at the same energy level, resulting in a distinct band edge (CBM and VBM). Nonetheless, in the $(\text{MA})_2\text{AgBiBr}_6$ perovskite, the varied bond lengths of the same sort of bond result in varying bond strengths and, consequently, in variable antibonding state energy levels. The shadow patches in Figure 3c exhibit energy level dispersion. The VB and CB are both extended by the dispersion of antibonding states, which determines the band edges. Additionally, the smaller volume of

(MA)₂AgBiBr₆ leads to shortening the average bond length and stronger interaction between atoms, resulting in the expansion of bands. Accordingly, the bandgap of the (MA)₂AgBiBr₆ decreases.

3.3 Bandgap Tuning

It is well known that materials suitable for solar cells should show a bandgap situated within 1.0–1.6 eV, excellent charge transport properties, and strong chemical stability.^[33] Several HDPs have acceptable bandgaps that satisfy the Shockley–Queisser limit requirement. In addition, in double perovskites, the substitution of various components significantly changes the electronic band structure, bandgap range, and the transition nature (direct or indirect). Similar to the lead perovskites, the bandgap can be tuned in double perovskites by altering its cations and anions. Zhang et al. demonstrated the novel HDP named Cs₂NaBiI₆ (CNBI) with the 1.66 eV bandgap, used several testing methodologies to evaluate its crystal structure and optical characteristics, and found that it is very stable in the presence of moisture and oxygen.^[16] The MA₂AgBiI₆ crystal with a 2D hexagonal structure has a bandgap of 1.96 eV.^[34] Aside from Ag/Bi HDPs, a Cs₂InAgCl₆ double perovskite with a bandgap of 3 eV was discovered.^[35] Its analogous Cs₂InAgBr₆ ought to have a smaller bandgap and it appears to be stable based on DFT calculations, however, it has yet to be synthesized. The bandgap narrows to 2 eV when Bi or Sb is replaced for In, but it also becomes indirect.^[35, 36] Although the bandgap of these materials is still too large for solar cell applications, however, these might be suitable for tandem devices as wide gap layer. Cs₂InCuCl₆ was identified as a possible solar cell semiconductor with an acceptable bandgap.^[36] Furthermore, Cs₂InCuCl₆ is expected to exhibit inherent charge carrier mobility along the L–Γ path similar to that of MAPbI₃.

Because of the existence of an unpaired electron in Cu²⁺ (3d⁹ configuration), Vargas et al. discovered Cs₄Sb₂CuCl₁₂ with a layered 2D structure, having a direct and small bandgap of 1 eV.^[37] In the extended crystalline structure, the [CuCl₆]^{4–} octahedra are placed between [SbCl₆]^{3–} layers, corner-sharing with each [SbCl₆]^{3–} neighbor. It was proposed that dilute insertion of 3d⁹ orbitals near the VBM of Cs₂SbAgCl₆ might lower the bandgap while considering the 3D double perovskite structural network remain unchanged.^[38] Additionally, metal doping can be used to change the bandgap of HDP. For instance, Slavney et al. demonstrated successful TI³⁺ doping to minimize the bandgap of Cs₂BiAgBr₆,^[39] and Nandha and Nag used Mn²⁺ doping to enhance the emission of visible light in Cs₂InAgCl₆.^[40] Heterovalent doping in lead halide perovskites has already been proven to cause conductivity enhancement and the formation of an n-type semiconductor.^[41]

3.4 Allowed and Forbidden Transitions

Regardless of the reasonable bandgap values, hypothetical forecasts show that the vast majority of the Bi-based HDPs have the indirect nature of bandgaps. The indirect band edge involves the phonons that are detrimental to the optical and carrier transport parameters. Even though In-based HDPs have direct bandgaps, these compounds are plagued with parity-induced prohibited transitions that inhibit optical transition. In the design of new HDPs for optoelectronic and photovoltaic applications, the role of inversion symmetry-induced parity-forbidden transitions should be considered. Perovskite compounds have inversion symmetry in their crystal structure, which causes parity-forbidden transitions between the CB and VB edges.^[42] This can have a big impact on the materials' optical and absorption qualities. **Figure 5a,b** shows a schematic depiction of the permitted and prohibited transitions. It was observed that direct bandgap $\text{Cs}_2\text{AgInCl}_6$ single-crystal exhibit parity-forbidden and parity-allowed transitions.^[43] This crystal's time-resolved PL spectra at room temperature demonstrate that the parity-allowable transitions have a short PL lifetime, while a longer PL lifetime is observed in the parity-forbidden transitions.^[33, 44] Figure 5c shows the nine types of HDPs designed, six of which had a direct bandgap. Five types from this six-compound showed inversion-symmetry-induced parity prohibited transitions, which prevent these materials from being used in PV applications. PSCs possessed suitable optical absorption and electronic characteristics only when B(I) = In, Tl and B(III) = Sb, Bi were combined. Due to the significant toxicity of Tl, In was chosen as the primary nontoxic choice for high-efficiency PSCs. When compared to $\text{Cs}_2\text{AgInCl}_6$, $\text{Cs}_2\text{InBiCl}_6$ displayed a variety of behaviors in which both the CBM and the VBM were located at the Γ point. In lead halide perovskite, the CsPbI_3 shows no parity-forbidden transitions. Its CBM, which is made up of Pb 6p orbitals, has odd parity, but its VBM, which is made up of Pb 6s and I 5p orbitals, has even parity. Pb-halide perovskites, as a result, have extraordinarily high optical absorption coefficients, which makes them suitable for photovoltaic applications. Despite having inversion symmetry, certain perovskites do not exhibit parity-forbidden transitions between the band edges. The CBM and VBM exhibit comparable parity when Pb is substituted with a group XII or group II element. It was estimated that transitions between the band edges are not parity-forbidden when the CBM and VBM are at different k points. A deliberate oxygen/vacuum treatment may also be used to change or optimize parity-dependent optical characteristics. Following oxygen/vacuum treatment, an enhancement in surface recombination velocity was also seen in single crystals.^[45]

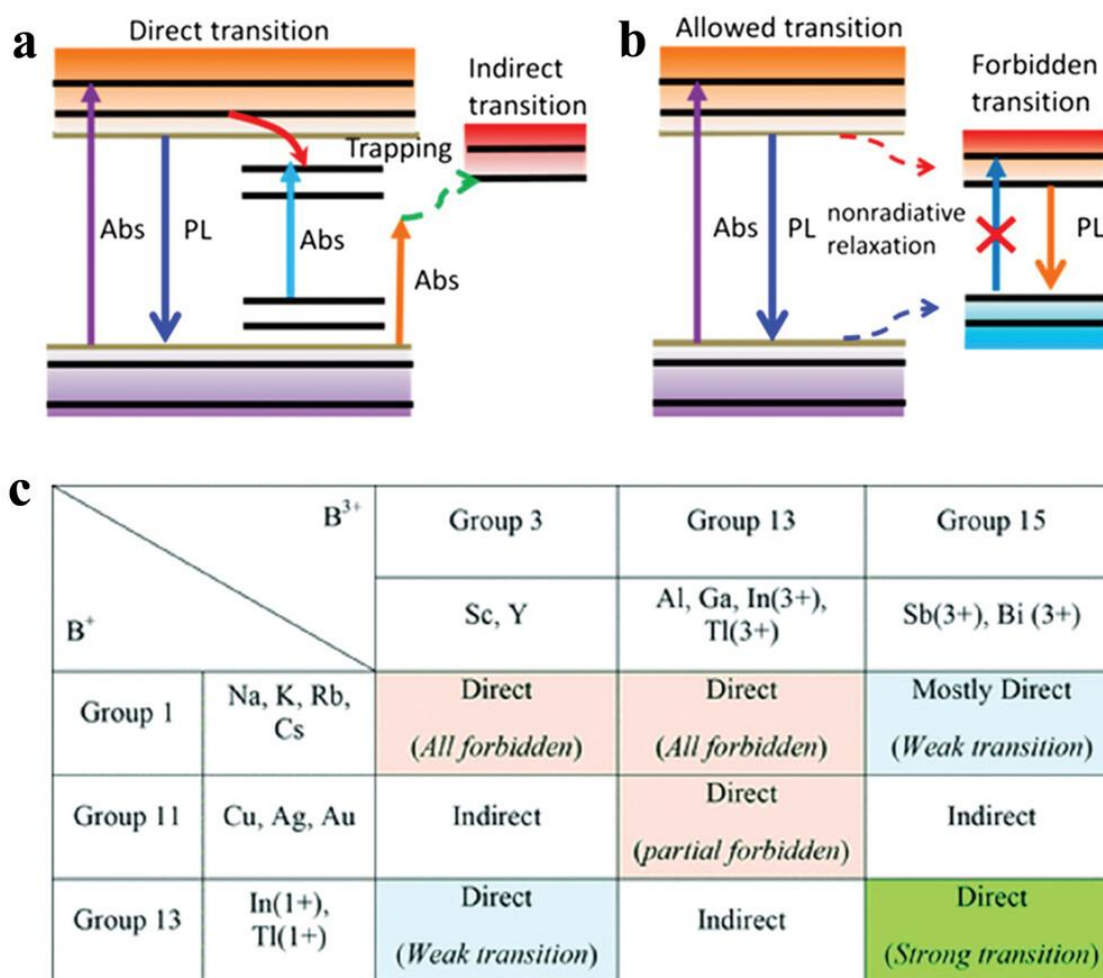


Figure 5. a,b) Schematic illustration of the direct, indirect, allowed, and forbidden transitions. Reproduced with permission.^[46] Copyright 2018, American Chemical Society. c) The table shows the probable combinations for $A_2M^+M^{3+}X_6$ double perovskites, which shows the parity-dependent transitions. Reproduced with permission.^[11] Copyright 2019, Wiley.

4. Application in Solar Cells

HDPs double perovskites are a prospective candidate as an alternative to Pb-halide perovskites in PSCs due to their outstanding structural, photoelectrical, and physical properties, as well as their nontoxicity and great stability.^[47] The problem with the possible use of HDPs as a promising light absorber, predicted by hypothetical calculations, is that they present a high enthalpy formation, low dissolvability of their precursors, and rough quality of the film. In general, HDPs solar cells perform poorly compared to their Pb-based equivalents, implying numerous major constraints that must be properly addressed.^[12, 21, 48] In the next subsections, we discussed intrinsic factors which affect the device performance along with the advancements that have been done in this line.

4.1 Film Optimization

In the fabrication of the perovskite-based devices, the quality of the prepared film is an important factor to determine all the characteristics. Therefore, the film quality should be emphasized and considered the most important part of the device fabrication. Lead-halide perovskites exhibit generally good solubility and low formation temperature.^[1] The HDPs are more delicate to the fabrication procedure than the lead-halide perovskites because these HDPs have high formation temperature and low solubility.^[9, 12] The diverse dissolvability of precursors prevents the fabrication of HDPs films with the normally utilized solution-processed techniques. It has been reported that the $\text{Cs}_2\text{AgBiBr}_6$ have very little solubility in dimethylsulfoxide ($<0.4 \text{ m}$),^[52] and the highest dissolvability of $\text{Cs}_2\text{NaBiI}_6$ in dimethylformamide (DMF) is only 1 mg mL^{-1} .^[53] Moreover, the HDPs materials show a quick crystallization rate at the time of spin coating. The fast crystallization results in poor morphology of fabricated film with a lot of pinholes and a very rough surface. Subsequently, the lessened dissolvability and quick crystallization of HDPs materials reduce the quality of the film, prompting their weak performance in optoelectronic devices. The podgy morphology can lead to insufficient charge collection due to the large hysteresis effect, which can adversely affect the performance of photovoltaic devices. Albeit uniform films of HDPs can be obtained using single crystals of these materials as precursor sources or by employing a low-pressure-assisted solution technique, still is difficult to prepare the HDPs thin films with high quality and good morphology using the solution-processed technique. In this regard, researchers have developed a few strategies to fabricate uniform double perovskite films.

One of the effective strategies for making uniform perovskite films is the antisolvent engineering technique which is widely used in lead halide perovskite films.^[54] The dripping of an antisolvent leads to the supersaturation state of the solution which is the driving force for good crystallization. In the case of double perovskites, Gao et al. demonstrated the high-quality film of $\text{Cs}_2\text{AgBiBr}_6$ perovskite with super smooth morphology, micro-sized grains, and good crystallinity is acknowledged through dropping of antisolvent and high-temperature post-annealing process (**Figure 6b**).^[50] Following the improvement, the fabricated planar heterojunction $\text{Cs}_2\text{AgBiBr}_6$ device in inverted structure displays 2.23% efficiency with no hysteresis and stability of 10 d in 50% humidity environment. It is observed that to obtain the large crystallinity in HDPs thin films, high-temperature post-annealing is important. The solvent engineering technique is valuable for the accomplishment of excellent HDPs thin films. Nonetheless, the improvement of appropriate solvents, dissolvable frameworks, and productive antisolvents is basic in future exploration.

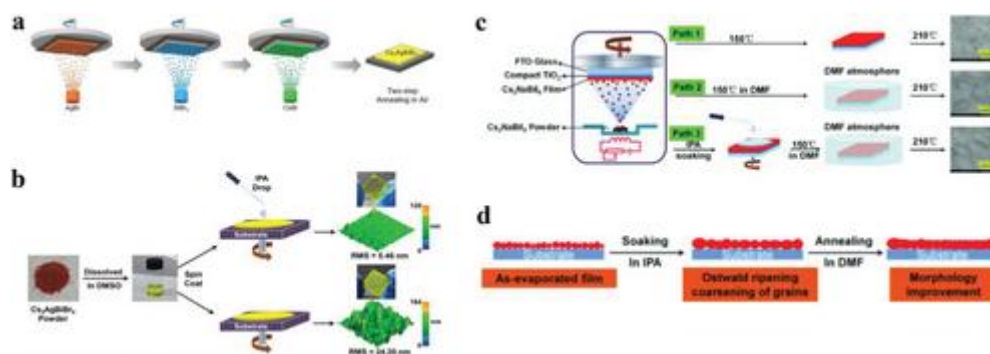


Figure 6. a) Schematic illustration of the sequential vapor deposition technique. Reproduced with permission.^[49] Copyright 2018, Wiley. b) Schematics of enhanced morphology of as-fabricated $\text{Cs}_2\text{AgBiBr}_6$ thin films followed by IPA dropping. Reproduced with permission.^[50] Copyright 2018, Wiley. c) Representation of the $\text{Cs}_2\text{NaBiI}_6$ film deposition and post-treatment routes. d) Schematic depicting the influence of post-treatment on the $\text{Cs}_2\text{NaBiI}_6$ film morphology. Reproduced with permission.^[51] Copyright 2019, Wiley.

To overcome the solubility limitation, vacuum deposition technology has also been developed to fabricate the double perovskite films. Wang et al. effectively fabricated thin films of $\text{Cs}_2\text{AgBiBr}_6$ by sequential-vapor-deposition method (Figure 6a).^[49] In this process, thermal annealing drives the diffusion reaction resulting in the formation of a double perovskite phase. Note that the succession of keeping the materials decides the development of perovskite crystals. The prepared films exhibit phase purity with enormous grain sizes, uniformity, and smooth surface properties. The fabricated planar device with this $\text{Cs}_2\text{AgBiBr}_6$ film demonstrates 1.37% efficiency, with 240 h stability in ambient conditions retaining its 90% efficiency. Peizhou Li et al. demonstrated the post-treatment strategy on the vacuum-evaporated film can significantly enhance the morphology and device performance.^[53] In this work, firstly the $\text{Cs}_2\text{NaBiI}_6$ film is vacuum evaporated, and then post-treatment is performed (Figure 6c,d). It was observed that post-treatment processes of the as-evaporated $\text{Cs}_2\text{NaBiI}_6$ film, remove the side products, extend the grain size, and reduce the density of traps and defects. The fabricated devices of evaporated $\text{Cs}_2\text{NaBiI}_6$ exhibit 0.21% efficiency, which is ten times larger in comparison to the device having no post-treatment (PCE = 0.02%). Additionally, the device demonstrates 100 d stability with no efficiency loss. These studies demonstrate the feasibility of using the vapor deposition method to prepare high-quality films of HDPs, which enables future improvements in different photovoltaic devices based on these fascinating HDPs semiconductors.

In addition to the previously mentioned techniques, the addition of external ions into perovskite lattices or GBs can increase grain size and reduce defects. For example, $\text{Cs}_2\text{AgBiBr}_6$ has four different lattice sites and the ionic replacement gives diverse potential outcomes to definitively control their

optoelectronic characteristics. Notwithstanding, the connection between the dopant and optoelectronic characteristics is at this point unclear. Thusly, Li et al. demonstrated that adding the alkali metal ions including Na^+ , Li^+ , K^+ , and Rb^+ can regulate the lattice of perovskite crystal and enhance the morphology of the $\text{Cs}_2\text{AgBiBr}_6$ perovskites film.^[55] With the control of doping percentage, good morphology is acquired of $\text{Cs}_2\text{AgBiBr}_6$ film with very less pin-holes, altogether lessening the defects. The fabricated device with the carbon-electrode yields 2.57% efficiency which is significantly enhanced in comparison to the undoped device (1.77% efficiency). Furthermore, the fabricated device with dopants shows prevalent tolerance at high temperature and ambient conditions without any encapsulation, giving new directions to advance the future improvement of $\text{Cs}_2\text{AgBiBr}_6$ HDP in the photoelectric field. Furthermore, this real-world verification of the idea device shows remarkable ecological tolerance even under high-temperature conditions. Albeit the efficiency is still lagging in comparison to other PSCs, the high environmental stability and nontoxicity additionally show that these HDPs solar cell devices have good potential for cutting edge photovoltaic technology.

In addition, with the preparation of HDPs thin films, we have also considered the role of grain boundary formation and its passivation too. For the most part, the GBs are commonly blamed as the main reason for the weak performance of polycrystalline thin film-based devices. The deep trap states in grain boundaries can enhance the recombination of charge carriers and decrease the open-circuit voltage essentially.^[56] In this way, the passivating GBs to remove the harmful trap states from the fabricated films turn into a long-standing and significant concern for achieving the high efficiency of photovoltaic devices. In this manner, Xu et al. demonstrated the first-principles estimations, and methodically concentrated on the atomic and electronic structure properties of prototype GBs in two HDPs, i.e., $\text{Cs}_2\text{AgInCl}_6$ (type I) and $\text{Cs}_2\text{AgBiCl}_6$ (type II).^[57] The authors observed that the $\Sigma 5(310)[001]$ and $\Sigma 3(112)[110]$ have exceptionally low formation energies. It was found that the $\Sigma 5(310)$ GBs have deep-level defect states within the bandgap, whereas the $\Sigma 3(112)$ GBs were found to be defect-free. Furthermore, the $\Sigma 5(310)$ GBs have very low formation energy and can operate as a site of carrier recombination, causing HDPs to lose their photovoltaic features. Surprisingly, following the spontaneous segregation of $\text{InAg} + \text{Cl}_i$, the $\Sigma 5(310)$ GB framework in $\text{Cs}_2\text{AgInCl}_6$ ($\text{Cs}_2\text{AgBiCl}_6$) becomes n-type (p-type) conductive. When certain carefully predesigned growth conditions are met, these faults or defect complexes can abruptly integrate into the GB cores recognizable by the massive number of synthetic compounds in a potential screening process. Likewise, the self-passivated GBs may induce band bending, which might be advantageous for the separation of charge carriers.^[58] The idea of GB engineering via a special synthetic methodology is nonexclusive, and it might apply to an expansive scope of HDPs and other various types of

polycrystalline materials, giving another perspective to the improvement of high-performance photovoltaic devices.^[56]

4.2 Enhancement in Light-Harvesting

As a result, narrowing the bandgap or allowing for an indirect–direct transformation is an effective procedure for increasing the light absorption capabilities of HDPs and the J_{SC} of the accompanying PSCs. Using the essential techniques, such as structural transition and functional doping, bandgap design should be doable.^[59] Wang et al. demonstrated the $Cs_2AgBiBr_6$ PSCs using methyl trans-32-carboxy-pyropheophorbide-a (C-Chl)-sensitized mesoporous TiO_2 (m- TiO_2) ETL.^[60] The addition of C-Chl to $Cs_2AgBiBr_6$ -based PSCs improved and extended the absorption spectrum to 750 nm, boosting the photocurrent and accomplishing a new PCE record of 3.11%. Furthermore, these C-Chl-based PSCs demonstrated enhanced electron extraction efficiency, suppressed recombination of carriers, and decreased defects. Besides, inserting a thin layer of di-tetrabutylammonium cis-bis(isothiocyanato) bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) (N719) dye between the absorbing-layer of $Cs_2AgBiBr_6$ and the hole-transporting layer results in 2.84% efficiency with enhanced stability. The enhancement in efficiency due to this thin interlayer can be attributed to expanding the absorbance region, lowering the recombination of charge carriers, fastening the transportation of holes, and modifying the active layer's band alignment.

In their following work, this group proposed the idea of heterojunction solar cells with organic dyes, in which they demonstrate the PCE > 4% first time in $Cs_2AgBiBr_6$ double perovskite solar cells.^[61] In this work, three indoline organic dyes, D131, D102, and D149, were introduced to sensitize the mesoporous TiO_2 . Compared with the chlorophyll derivative, the absorbance was strongly enhanced beyond 500 nm (where $Cs_2AgBiBr_6$ almost does not absorb) by indoline dyes. The cross-sectional scanning electron microscope image of the hybrid device (D149- $Cs_2AgBiBr_6$ hybrid film) is presented in **Figure 7a** and the corresponding energy band diagram is displayed in Figure 7b. The device parameters are presented in Figure 7c–e. It was observed that the external quantum efficiency of the perovskite-hybridized DSSCs was enhanced in comparison to corresponding DSSCs. In the short-wavelength region, a striking increment of photoresponse was observed for the perovskite-hybridized DSSCs, because the $Cs_2AgBiBr_6$ absorbs in this region. This proposes that both indoline dyes and $Cs_2AgBiBr_6$ contribute to the photocurrent. The device efficiency was obtained as of 4.23% by D149-based perovskite-hybridized DSSCs. Therefore, it tends to be reasoned that usage of organic dyes with a perovskite layer can provide large absorption following with high efficiency.

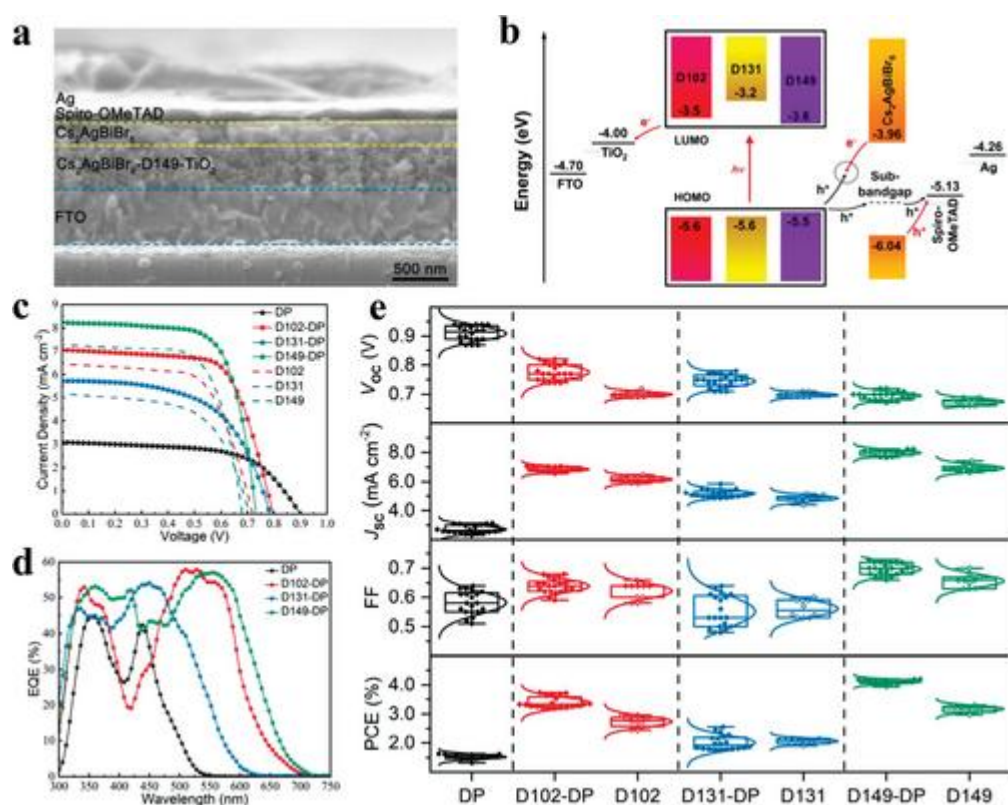


Figure 7. a) The cross-sectional scanning electron microscope image of a $\text{Cs}_2\text{AgBiBr}_6$ -hybridized D149-sensitized solar cell. b) Energy levels of $\text{Cs}_2\text{AgBiBr}_6$ -hybridized dye-sensitized solar cells (DSSCs). c) I - V curves of the DP (double perovskite $\text{Cs}_2\text{AgBiBr}_6$) solar cell, perovskite-hybridized DSSCs, and DSSCs. d) EQE of the PSC and perovskite-hybridized DSSCs. e) Distribution of the photovoltaic parameters of the PSC, perovskite-hybridized DSSCs, and DSSCs. Reproduced with permission.^[61] Copyright 2021, American Chemical Society.

4.3 Interface Engineering

In the PSCs, the interface of the perovskite layer with the transport layers is critical for charge carrier extraction and transfer.^[62] The charge carrier can recombine at the interface because of the surface imperfections of perovskite film and the mismatching of the energy levels of perovskite with the transport layer. A suitable energy level matching between perovskite and transport layer can promote the transfer of charge carriers. Consequently, the engineering of the interface is indispensable to achieving excellent results in PSCs.^[63] A few methodologies, for example, passivation of surface defects and matching the energy level of perovskite with the transport layers using new molecules/compounds have been researched to modify the interface and increase the

PCE of $\text{A}_2\text{BB}'\text{X}_6$ -based PSCs.^[65] The passivation of the perovskite layer surface is critical for effectively decreasing the recombination of carriers and enhancing carrier lifespan. In this manner, surfactants such as oleic acid may be applied to the perovskite surface to passivate the surface

defects.^[66] The organic N719 dye was also employed to reduce the surface defects of Cs₂AgBiBr₆ while concurrently developing an alignment between energy levels. The PCE of the modified device with organic N719 dye was enhanced in comparison to the pristine device, and its stability improved as well. Pantaler et al. investigated several HTLs with variable HOMO and LUMO values to enhance the PCEs of Cs₂AgBiBr₆-based devices. It was observed that the Cs₂AgBiBr₆-based device exhibited the 1.26% efficiency with poly[bis(4-phenyl)- (2,4,6-trimethylphenyl) amine] (PTAA) as the HTL and no hysteresis was observed.

The usage of zinc chlorophyll derivative (Zn-Chl) in Cs₂AgBiBr₆ device as a hole-transporting layer (HTL) demonstrate the 2.79% efficiency, which is 22%–27% greater than devices nonphotoactive HTLs, for example, 2,20,7,70-tetrakis (N, N-di-p-methoxyphenylamine)- 9,90-spirobifluorene (Spiro-OMeTAD), poly(triarylamine) (PTAA), and poly(3-hexylthiophene) (P3HT).^[67] The adequate enormous energy difference between the LUMO energy level of Cs₂AgBiBr₆ and the Soret energy level of Zn-Chl empowers the photoelectrons excited in Zn-Chl to pass into the Cs₂AgBiBr₆ film, prompting 22%–27% enhancement in J_{SC} . In addition, the Zn-Chl-based device has a much greater extinction coefficient and better charge extraction capabilities in comparison to P3HT, Spiro-OMeTAD, and PTAA-based devices. Furthermore, the efficiency was enhanced from 0.93% to 1.57% with dual interfacial engineering using C60 and PCDTFBT to change the interface of the ETL and HTL, respectively.^[65] The HDPs and single perovskite exhibit different energy band structures, which can result in an energy-level mismatch between transport layers and HDP, thereby limiting the further improvement of the solar cell performance. One way is the optimize hole transport systems for improving the device performance. As shown in **Figure 8**, three distinct HTLs are being explored to show the efficiency increment and how MoO₃ acts as a protective layer in multi-HTLs.^[64] The P3HT and PTAA are primarily responsible for constructing the energy-level gradient. P3HT was the referenced layer in the first HTL (HTL-1). P3HT/PTAA was the second HTL (HTL-2) and P3HT/MoO₃/PTAA was the third HTL (HTL-3). The J_{SC} of HTL-2 and HTL-3 have dramatically risen in comparison to HTL-1, as evidenced by the experiments. Particularly, HTL-3 had the highest average PCE at 1.82%, which was 34% higher than that of HTL-1 (1.31%). Using a multihole transport layer having a band gradient may effectively extract carriers and increase PSC performance. Additionally, the highest efficiency was accomplished at 1.94% in the champion device with a J_{SC} of 2.80 mA cm⁻². It is a stage forward in enhancing the opportunities for HDPs to be utilized in the field of photovoltaics.

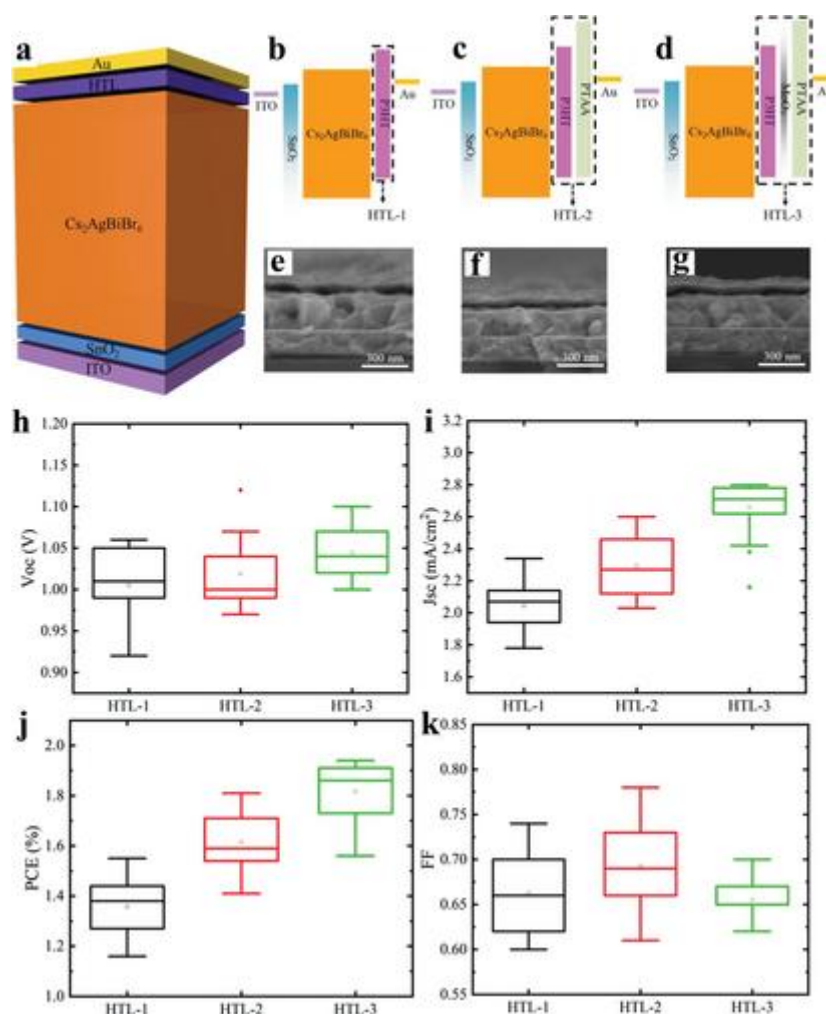


Figure 8. a) Schematic of $\text{Cs}_2\text{AgBiBr}_6$ based n-i-p PSCs device. b–d) Schematic energy-level structures of the PSCs with HTL-1, HTL-2, and HTL-3, respectively. e–g) Cross-sectional SEM images of the PSCs with three different HTLs. Statistic photovoltaic parameters: h) V_{oc} , i) J_{sc} , j) PCE, and k) FF of devices with HTL-1, HTL-2, and HTL-3. Reproduced with permission.^[64] Copyright 2020, American Chemical Society.

Besides, Xiao et al. introduced the band matching methodology in $\text{Cs}_2\text{AgBiBr}_6$ with a low-cost compound, cuprous oxide (Cu_2O) as a replacement for HTL from the device.^[65] The authors fabricated a dense $\text{Cs}_2\text{AgBiBr}_6$ thin film with enormous grains and a smooth surface using the vacuum deposition technique. The Cu_2O was also deposited using the vacuum deposition method to coordinate the perovskite film. It was observed that with the 50 nm thick Cu_2O film, the device gives the best efficiency as 1.52% with 33 d of air stability retaining 96% of the initial efficiency. Finally, we can conclude that interface matching with new and efficient transport layers can accelerate the realization of LFHDPs solar cells with high efficiency.

5. Challenges and Perspectives

A massive research effort is devoted to achieving highly efficient and stable lead-free HDPs solar cells, starting from a fundamental understanding of device engineering. These lead-free HDPs might exhibit remarkable optoelectronic features, such as the tuning of bandgap absorption in the range of ultraviolet to near-infrared and transition from indirect to direct bandgap according to computational studies. In this manner, HDPs are specially intended for solar cell devices, as they have great moisture stability, as well as are usually innocuous to the environment. Notwithstanding, the device performance of HDPs is still far behind the Pb-halide counterparts. This section discusses the existing hurdles and unsolved concerns in the performance of HDPs based devices as well as potential future research in this area. The following should be prioritized to make actual progress:

1. One of the most urgent obstructions that HDPs face is the wide-bandgap feature, which prevents absorption of a significant range of the solar spectrum. Another obstacle is the indirect bandgap, which results in the infeasible generation of charge carriers. One method for changing this natural characteristic is to fuse various kinds of metal cations which can modify the approved electronic configuration. The joining of different metal cations of Co^{2+} , Mn^{2+} , Ni^{2+} , Fe^{3+} , and Cu^{2+} might be surveyed, which empowers to search for stable specimens having suitable bandgap ranges.
2. The localization of defect and trap states in the bulk and lattice of HDPs can inconveniently interfere with their performances. Understanding carrier dynamics in depth provides insights into how defects are trapped in the structure. More knowledge of this area is fundamental for finding the pathways toward better-performing devices.
3. Several studies have examined the role of irradiation on the evolution of the defect in Pb-halide perovskites, but this research has received much less attention for HDPs. Henceforth, examining the effect of light irradiation on the properties of these materials is of great interest to fully understand their structure and optical and electrical properties. The optical methods, for example, steady-state photoluminescence (PL), TRPL, micro-PL, and ultrafast spectroscopy, can help to comprehend the charge transporter elements in HDPs. Moreover, the dynamics of excited states and the peculiarities of hot carrier cooling in HDPs should be examined in depth.
4. The carriers' recombination kinetics in the range of nanoseconds to microseconds is of relevance since those are closely linked to device performance. Those depend upon defects and surface trapping, Auger recombination, etc. These processes should be thoughtfully

evaluated for HDPs. Ideally combined with confocal microscopy and other microscopic methodologies, micro-spectroscopic approaches providing widespread spatial and temporal resolution, would allow for a significant real-world understanding of materials, interfaces, and devices.

5. The poor film quality of double perovskite is a big obstacle in the development of high-efficiency solar cells. Several techniques have been developed to improve this issue but the film quality is not as standard as lead perovskites. Therefore, new strategies such as post-treatment, solvent engineering, precursor aging, additives in perovskite solution, Lewis acid-base adduct approach, and post-device ligand treatments should be explored to enhance the quality of double perovskites films.
6. It is necessary to know the interface of double perovskite devices and energy level alignment between perovskite and transport layers for preventing interfacial recombination and to make an efficient charge transfer. Therefore, research should be devoted to preparing new molecules where energy levels can be aligned with the double perovskite materials.
7. The migration of ions in double perovskites might be causing the device's performance to deteriorate. Negligible attention has been paid to revealing the mobile ion dynamics in the double perovskites. Therefore, an investigation of ion dynamics is urgently needed to understand the effect of ions in charge transport. Several spectroscopic techniques such as impedance spectroscopy and transient capacitance can be used to investigate ion dynamics.
8. Theoretically, many halide double perovskite materials might exist, but only a few numbers have been investigated experimentally. Hence, a more experimental procedure should be developed for synthesizing the double perovskites. Especially iodine-based double perovskites should be mainly focused on. In addition, most of the focus in double perovskites is devoted to altering the B(I) and B(III) site cations, and so less attention was paid to replacing them with A-cations. More research efforts should be directed toward the compositional engineering of A-cations.
9. In HDPs, the strong electron–phonon coupling is a serious concern because it affects carrier scattering, PL linewidth broadening, charger carrier mobility, PLQY, and recombination of electron–hole. Further examinations are expected to comprehend the regulation of the electron–phonon coupling, for instance, clarifying the connection between the Jahn-Teller distortion, the structure dimensionality, the B-site octahedra disordering, and the electron–phonon coupling in HDPs. Doping/alloying in combination with heterojunction structures,

dielectric confinement, and bond length compression (by chemical/mechanical pressure) are all viable ways of reducing electron–phonon coupling. The effective decrease in an electron–phonon coupling should result in the rise of current density which should provide enhanced efficiency.

A significant effort to solve all these issues (**Figure 9**) is needed aiming to achieve accomplishments in this field.

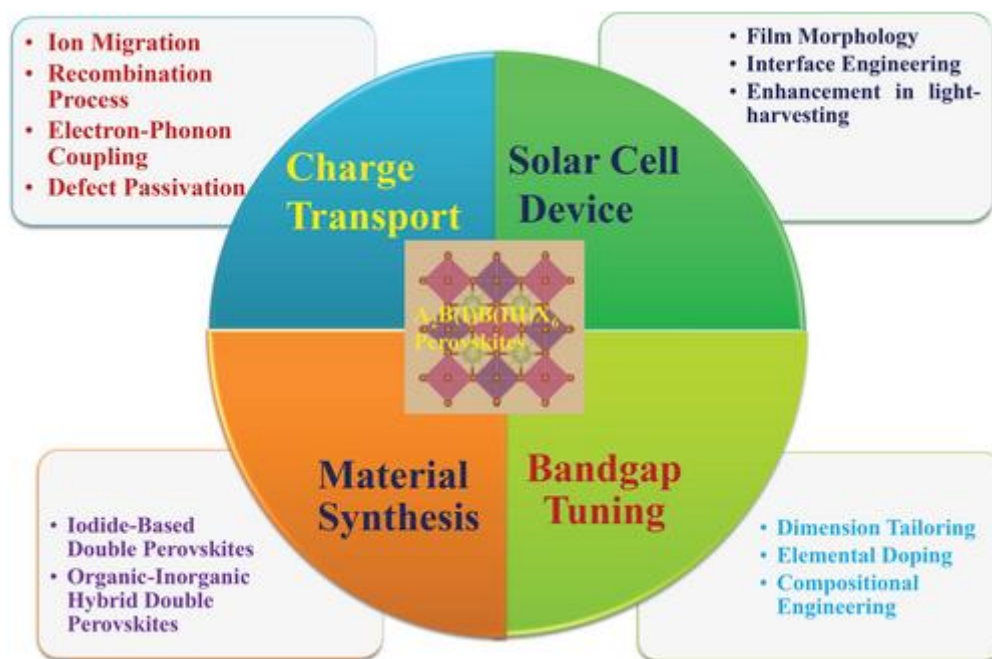


Figure 9. Future prospects for the lead-free halide double perovskites.

6. Conclusion

The halide double perovskites are potential alternative eco-sustainable materials to lead-halide perovskites. In recent years, HDPs have made significant progress, starting from the synthesis of the thin films to the device fabrication, having good light-harvesting capability with excellent stability and low poisonousness. This review frames this progress achieved thanks to a focused research effort. Additionally, we critically examined the fundamental characteristics of the HDPs for photovoltaic applications. HDPs exhibit large structure flexibility which provides tunable optical and electrical properties. Herein the orbital characteristics of the s, p, and d orbitals help to understand the bands formation process, as this depends on the degree of freedom of the orbitals. Therefore the bandgap of HDPs can be tuned easily with changing of the cations and anions. In addition, the incorporation of various elements as doping/alloying leads to drastic bandgap modification. Some of the HDP materials exhibit parity forbidden transitions due to the inversion symmetry of crystal structure which

limits the optical performance, for these materials the role of phonons in their optical transitions should be addressed in future research.

Because of their well-known stability and tunable features, HDPs are predicted to play a significant role in the development of eco-friendly photovoltaics with high efficiency and stability for commercial applications. Albeit critical advancements have been accomplished in HDPs, numerous obstacles remain to overcome. The indirect electronic structures, the quality of the fabricated films, suitable transport layers, and the device design are the main limitations that hinder the high performance of these HDPs. Therefore, suggested strategies should be reinforced to solve these issues and achieve superior PV performance of HDPs-based devices.

Acknowledgements

N.K.T. would like to acknowledge UGC Fellowship. The authors acknowledge Prathul Nath for scientific discussion. S.S. would like to acknowledge SERB grant (IPA/2021/000096).

References

- [1] a) N. K. Tailor, M. Abdi-Jalebi, V. Gupta, H. L. Hu, M. I. Dar, G. Li, S. Satapathi, *J. Mater. Chem. A* 2020, 8, 21356; b) N. K. Tailor, S. P. Senanayak, M. Abdi-Jalebi, S. Satapathi, *Electrochim. Acta* 2021, 386, 138430; c) S. Arya, P. Mahajan, R. Gupta, R. Srivastava, N. K. Tailor, S. Satapathi, R. R. Sumathi, R. Datt, V. Gupta, *Prog. Solid State Chem.* 2020, 60, 100286; d) S. Kadian, N. K. Tailor, N. Chaulagain, K. Shankar, S. Satapathi, G. Manik, *J. Mater. Sci.: Mater. Electron.* 2021, 32, 17406; e) N. K. Tailor, Yukta, R. Ranjan, S. Ranjan, T. Sharma, A. Singh, A. Garg, K. S. Nalwa, R. K. Gupta, S. Satapathi, *J. Mater. Chem. A* 2021, 9, 21551.
- [2] H. Min, D. Y. Lee, J. Kim, G. Kim, K. S. Lee, J. Kim, M. J. Paik, Y. K. Kim, K. S. Kim, M. G. Kim, T. J. Shin, S. I. Seok, *Nature* 2021, 598, 444.
- [3] a) M. Ren, X. Qian, Y. Chen, T. Wang, Y. Zhao, *J. Hazard. Mater.* 2022, 426, 127848; b) G. Schileo, G. Grancini, *J. Mater. Chem. C* 2021, 9, 67.
- [4] a) A. Binek, M. L. Petrus, N. Huber, H. Bristow, Y. Hu, T. Bein, P. Docampo, *ACS Appl. Mater. Interfaces* 2016, 8, 12881; b) M. Boskabady, N. Marefati, T. Farkhondeh, F. Shakeri, A. Farshbaf, M. H. Boskabady, *Environ. Int.* 2018, 120, 404; c) R. A. Michaels, *Environ. Claims J.* 2019, 32, 6.
- [5] a) A. Abate, *Joule* 2017, 1, 659; b) R. Ali, G. P. Hou, Z. G. Zhu, Q. B. Yan, Q. R. Zheng, G. Su, *Chem. Mater.* 2018, 30, 718.
- [6] a) M. G. Ju, J. Dai, L. Ma, X. C. Zeng, *J. Am. Chem. Soc.* 2017, 139, 8038; b) H. Yao, F. Zhou, Z. Li, Z. Ci, L. Ding, Z. Jin, *Adv. Sci.* 2020, 7, 1903540; c) M. Pitaro, E. K. Tekelenburg, S. Shao, M. A. Loi, *Adv. Mater.* 2022, 34, 2105844.
- [7] J. Li, H. L. Cao, W. B. Jiao, Q. Wang, M. Wei, I. Cantone, J. Lu, A. Abate, *Nat. Commun.* 2020, 11, 310.
- [8] a) A. Singh, S. Satapathi, *Adv. Opt. Mater.* 2021, 9, 2101062; b) N. K. Tailor, P. Maity, M. I. Saidaminov, N. Pradhan, S. Satapathi, *J. Phys. Chem. Lett.* 2021, 12, 2286; c) N. K. Tailor, P. Maity, S. Satapathi, *ACS Photonics* 2021, 8, 2473; d) N. K. Tailor, S. Mishra, T. Sharma, A. K. De, S. Satapathi, *J. Phys. Chem. C* 2021, 125, 9891; e) N. K. Tailor, S. Satapathi, *ACS Appl. Energy Mater.* 2020, 3, 11732; f) N. K. Tailor, S. Satapathi, *J. Mater. Res. Technol.* 2020, 9, 7149; g) N. K. Tailor, S. Satapathi, *J. Phys. Chem. C* 2021, 125, 5243; h) J. K. Wenderott, A. Raghav, M. Shtein, P. F. Green, S. Satapathi, *Langmuir* 2018, 34, 7647; i) N. K. Tailor, A. Mahapatra, A. Kalam, M. Pandey, P. Yadav, S. Satapathi, *Phys. Rev. Mater.* 2022, 6, 045401.

- [9] a) G. Volonakis, M. R. Filip, A. A. Haghighirad, N. Sakai, B. Wenger, H. J. Snaith, F. Giustino, J. Phys. Chem. Lett. 2016, 7, 1254; b) X. G. Zhao, D. W. Yang, J. C. Ren, Y. H. Sun, Z. W. Xiao, L. J. Zhang, Joule 2018, 2, 1662; c) M. K. Chini, S. G. Srinivasan, N. K. Tailor, Yukta, D. Salahub, S. Satapathi, Chem. Phys. 2020, 529, 110547; d) M. A. Afroz, C. A. Aranda, N. K. Tailor, Yukta, P. Yadav, M. M. Tavakoli, M. Saliba, S. Satapathi, ACS Energy Lett. 2021, 6, 3275; e) N. K. Tailor, S. Kar, P. Mishra, A. These, C. Kupfer, H. L. Hu, M. Awais, M. Saidaminov, M. I. Dar, C. Brabec, S. Satapathi, ACS Mater. Lett. 2021, 3, 1025.
- [10] a) T. S. Li, X. G. Zhao, D. W. Yang, M. H. Du, L. J. Zhang, Phys. Rev. Appl. 2018, 10; b) F. Igbari, Z. K. Wang, L. S. Liao, Adv. Energy Mater. 2019, 9, 1803150; c) N. R. Wolf, B. A. Connor, A. H. Slavney, H. I. Karunadasa, Angew. Chem. 2021, 60, 16264.
- [11] a) P.-K. Kung, M.-H. Li, P.-Y. Lin, J.-Y. Jhang, M. Pantaler, D. C. Lupascu, G. Grancini, P. Chen, Sol. RRL 2019, 4, 1900306; b) M. Usman, Q. F. Yan, Crystals 2020, 10, 62.
- [12] a) C. N. Savory, A. Walsh, D. O. Scanlon, ACS Energy Lett. 2016, 1, 949; b) E. Meyer, D. Mutukwa, N. Zingwe, R. Taziwa, Metals 2018, 8, 667; c) L. Chu, W. Ahmad, W. Liu, J. Yang, R. Zhang, Y. Sun, J. Yang, X. Li, Nanomicro Lett. 2019, 11, 16; d) L. Lu, X. Pan, J. Luo, Z. Sun, Chemistry 2020, 26, 16975; e) A. Bibi, I. Lee, Y. Nah, O. Allam, H. Kim, L. N. Quan, J. Tang, A. Walsh, S. S. Jang, E. H. Sargent, D. H. Kim, Mater. Today 2021, 49, 123.
- [13] a) W. J. Yin, T. T. Shi, Y. F. Yan, J. Phys. Chem. C 2015, 119, 5253; b) J. H. Lee, N. C. Bristowe, J. H. Lee, S. H. Lee, P. D. Bristowe, A. K. Cheetham, H. M. Jang, Chem. Mater. 2016, 28, 4259; c) M. Shi, G. Li, W. Tian, S. Jin, X. Tao, Y. Jiang, E. A. Pidko, R. Li, C. Li, Adv. Mater. 2020, 32, 2002137.
- [14] a) C. J. Bartel, C. Sutton, B. R. Goldsmith, R. Ouyang, C. B. Musgrave, L. M. Ghiringhelli, M. Scheffler, Sci. Adv. 2019, 5, eaav0693; b) W. Travis, E. N. K. Glover, H. Bronstein, D. O. Scanlon, R. G. Palgrave, Chem. Sci. 2016, 7, 4548.
- [15] Y. Wu, X. Li, H. Zeng, Small Struct. 2020, 2, 2000071.
- [16] C. Zhang, L. G. Gao, S. Teo, Z. L. Guo, Z. H. Xu, S. Zhao, T. L. Ma, Sustainable Energy Fuels 2018, 2, 2419.
- [17] L. Schade, A. D. Wright, R. D. Johnson, M. Dollmann, B. Wenger, P. K. Nayak, D. Prabhakaran, L. M. Herz, R. Nicholas, H. J. Snaith, P. G. Radaelli, ACS Energy Lett. 2018, 4, 299.
- [18] A. Bernasconi, L. Malavasi, ACS Energy Lett. 2017, 2, 863.

- [19] M. S. Shadabroo, H. Abdizadeh, M. R. Golobostanfard, *Mater. Sci.Semicond. Process.* 2021, 125, 105639.
- [20] Y. Cai, W. Xie, Y. T. Teng, P. C. Harikesh, B. Ghosh, P. Huck, K. A. Persson, N. Mathews, S. G. Mhaisalkar, M. Sherburne, M. Asta, *Chem. Mater.* 2019, 31, 5392.
- [21] a) K. Dave, M. H. Fang, Z. Bao, H. T. Fu, R. S. Liu, *Chem. Asian J.* 2020, 15, 242; b) M. Ghasemi, M. M. Hao, M. Xiao, P. Chen, *Adv. Mater. Technol.* 2023, 8, 2200442. c) D. X. He, Y. R. Zhang, W. J. Chen, J. D. Fan, J. H. Yun, B. H. Jia, X. M. Wen, *Nanophotonics* 2021, 10, 2181.
- [22] a) J. Leveillee, G. Volonakis, F. Giustino, *J. Phys. Chem. Lett.* 2021, 12, 4474; b) V. A. Ha, G. Volonakis, H. Lee, M. Zacharias, F. Giustino, *J. Phys. Chem. C* 2021, 125, 21689; c) B. Wu, W. Ning, Q. Xu, M. Manjappa, M. Feng, S. Ye, J. Fu, S. Lie, T. Yin, F. Wang, T. W. Goh, P. C. Harikesh, Y. K. E. Tay, Z. X. Shen, F. Huang, R. Singh, G. Zhou, F. Gao, T. C. Sum, *Sci. Adv.* 2021, 7, eabd3160; d) L. Zhang, Y. Fang, L. Sui, J. Yan, K. Wang, K. Yuan, W. L. Mao, B. Zou, *ACS Energy Lett.* 2019, 4, 2975.
- [23] a) D. B. Dougherty, M. Feng, H. Petek, J. T. Yates, Jr., J. Zhao, *Phys. Rev. Lett.* 2012, 109, 266802; b) Y. Zhang, L. Meng, C. Yam, G. Chen, *J. Phys. Chem. Lett.* 2014, 5, 1272.
- [24] J. Maciejko, S. Rayan, *Proc. Natl. Acad. Sci. USA* 2022, 119, e2116869119.
- [25] J. M. Frost, L. D. Whalley, A. Walsh, *ACS Energy Lett.* 2017, 2, 2647.
- [26] a) B. Philippe, B. W. Park, R. Lindblad, J. Oscarsson, S. Ahmadi, E. M. J. Johansson, H. Rensmo, *Chem. Mater.* 2015, 27, 1720; b) D. Niesner, *APL Mater.* 2020, 8, 090704.
- [27] T. T. Tran, J. R. Panella, J. R. Chamorro, J. R. Morey, T. M. McQueen, *Mater. Horiz.* 2017, 4, 688.
- [28] G. Tang, P. Ghosez, J. Hong, *J. Phys. Chem. Lett.* 2021, 12, 4227.
- [29] A. Menedjhi, N. Bouarissa, S. Saib, M. Boucenna, F. Mezrag, *Acta Phys. Pol., A* 2020, 137, 486.
- [30] F. Wei, Z. Deng, S. Sun, F. Zhang, D. M. Evans, G. Kieslich, S. Tominaka, M. A. Carpenter, J. Zhang, P. D. Bristowe, A. K. Cheetham, *Chem. Mater.* 2017, 29, 1089.
- [31] G. Tang, Z. Xiao, J. Hong, *J. Phys. Chem. Lett.* 2019, 10, 6688.
- [32] R. Yin, G. Yu, W. Y. Cong, C. Guan, J. Li, Y. B. Lu, *ACS Appl. Mater. Interfaces* 2020, 12, 44798.

- [33] a) S. Maiti, S. Ferro, D. Poonia, B. Ehrler, S. Kinge, L. D. A. Siebbeles, *J. Phys. Chem. Lett.* 2020, 11, 6146; b) Z. Xiao, Z. Song, Y. Yan, *Adv. Mater.* 2019, 31, 1803792; c) Q. Zhang, L. Pei, J. Li, K. Wang, Q. Zeng, H. Yu, *J. Phys. Chem. Lett.* 2021, 12, 7207.
- [34] P. Cheng, T. Wu, Y. Li, L. Jiang, W. Deng, K. Han, *New J. Chem.* 2017, 41, 9598.
- [35] G. Volonakis, A. A. Haghighirad, R. L. Milot, W. H. Sio, M. R. Filip, B. Wenger, M. B. Johnston, L. M. Herz, H. J. Snaith, F. Giustino, *J. Phys. Chem. Lett.* 2017, 8, 772.
- [36] H. Q. Pham, R. J. Holmes, E. S. Aydil, L. Gagliardi, *Nanoscale* 2019, 11, 11173.
- [37] B. Vargas, G. Rodriguez-Lopez, D. Solis-Ibarra, *ACS Energy Lett.* 2020, 5, 3591.
- [38] T. Appadurai, S. Chaure, M. Mala, A. K. Chandiran, *Energy Fuels* 2021, 35, 11479.
- [39] A. H. Slavney, L. Leppert, D. Bartesaghi, A. Gold-Parker, M. F. Toney, T. J. Savenije, J. B. Neaton, H. I. Karunadasa, *J. Am. Chem. Soc.* 2017, 139, 5015.
- [40] N. Nandha K, A. Nag, *Chem. Commun.* 2018, 54, 5205.
- [41] a) O. A. Lozhkina, A. A. Murashkina, V. V. Shilovskikh, Y. V. Kapitonov, V. K. Ryabchuk, A. V. Emeline, T. Miyasaka, *J. Phys. Chem. Lett.* 2018, 9, 5408; b) P.-P. Sun, D. R. Kripalani, L. Bai, K. Zhou, *J. Phys. Chem. C* 2019, 123, 12684.
- [42] a) M. Kepenekian, J. Even, *J. Phys. Chem. Lett.* 2017, 8, 3362; b) S. McKechnie, J. M. Frost, D. Pashov, P. Azarhoosh, A. Walsh, M. van Schilfgaarde, *Phys. Rev. B* 2018, 98, 085108; c) T. Schmitt, S. Bourelle, N. Tye, G. Soavi, A. D. Bond, S. Feldmann, B. Traore, C. Katan, J. Even, S. E. Dutton, F. Deschler, *J. Am. Chem. Soc.* 2020, 142, 5060.
- [43] W. Meng, X. Wang, Z. Xiao, J. Wang, D. B. Mitzi, Y. Yan, *J. Phys. Chem. Lett.* 2017, 8, 2999.
- [44] R. A. DeCrescent, X. Du, R. M. Kennard, N. R. Venkatesan, C. J. Dahlman, M. L. Chabinyc, J. A. Schuller, *ACS Nano* 2020, 14, 8958.
- [45] a) H. H. Fang, S. Adjokatse, H. Wei, J. Yang, G. R. Blake, J. Huang, J. Even, M. A. Loi, *Sci. Adv.* 2016, 2, e1600534; b) Y. Yang, Y. Yan, M. Yang, S. Choi, K. Zhu, J. M. Luther, M. C. Beard, *Nat. Commun.* 2015, 6, 7961; c) L. T. Mix, D. Ghosh, J. Tisdale, M. C. Lee, K. R. O'Neal, N. Sirica, A. J. Neukirch, W. Nie, A. J. Taylor, R. P. Prasankumar, S. Tretiak, D. A. Yarotski, *J. Phys. Chem. Lett.* 2020, 11, 8430.
- [46] B. Yang, X. Mao, F. Hong, W. Meng, Y. Tang, X. Xia, S. Yang, W. Deng, K. Han, *J. Am. Chem. Soc.* 2018, 140, 17001.

- [47] a) Z. Gao, G. Mao, S. Chen, Y. Bai, P. Gao, C. Wu, I. D. Gates, W. Yang, X. Ding, J. Yao, *Phys. Chem. Chem. Phys.* 2022, 24, 3460; b) H. Tang, Y. Xu, X. Hu, Q. Hu, T. Chen, W. Jiang, L. Wang, W. Jiang, *Adv. Sci.* 2021, 8, 2004118; c) P. G. Han, K. L. Han, *Energy Fuels* 2021, 35, 18871.
- [48] Y. Wang, F. Zhang, J. Ma, Z. Ma, X. Chen, D. Wu, X. Li, Z. Shi, C. Shan, *EcoMat* 2021, 4, e12160.
- [49] M. Wang, P. Zeng, S. Bai, J. W. Gu, F. M. Li, Z. Yang, M. Z. Liu, *Sol. RRL* 2018, 2, 1800217.
- [50] W. Gao, C. Ran, J. Xi, B. Jiao, W. Zhang, M. Wu, X. Hou, Z. Wu, *Chem. Phys. Chem.* 2018, 19, 1696.
- [51] P. Z. Li, W. Y. Gao, C. X. Ran, H. Dong, X. Hou, Z. X. Wu, *Phys. Status Solidi A* 2019, 216, 1900567.
- [52] X. Q. Yang, W. Wang, R. Ran, W. Zhou, Z. P. Shao, *Energy Fuels* 2020, 34, 10513.
- [53] P. Li, W. Gao, C. Ran, H. Dong, X. Hou, Z. Wu, *Phys. Status Solidi A* 2019, 216, 1900567.
- [54] a) B. Gogoi, A. Yerramilli, K. M. Luboowa, S. M. Shin, T. L. Alford, *J. Mater. Sci.: Mater. Electron.* 2022, 33, 4415; b) J. Li, X. Hua, F. Gao, X. Ren, C. Zhang, Y. Han, Y. Li, B. Shi, S. Liu, *J. Energy Chem.* 2022, 66, 1; c) Y. Huang, T. Liu, B. Wang, J. Li, D. Li, G. Wang, Q. Lian, A. Amini, S. Chen, C. Cheng, G. Xing, *Adv. Mater.* 2021, 33, 2102816.
- [55] J. Li, J. Duan, J. Du, X. Yang, Y. Wang, P. Yang, Y. Duan, Q. Tang, *ACS Appl. Mater. Interfaces* 2020, 12, 47408.
- [56] a) W. Nie, H. Tsai, R. Asadpour, J. C. Blancon, A. J. Neukirch, G. Gupta, J. J. Crochet, M. Chhowalla, S. Tretiak, M. A. Alam, H. L. Wang, A. D. Mohite, *Science* 2015, 347, 522; b) N. De Marco, H. Zhou, Q. Chen, P. Sun, Z. Liu, L. Meng, E. P. Yao, Y. Liu, A. Schiffer, Y. Yang, *Nano Lett.* 2016, 16, 1009; c) L. Liu, S. Huang, Y. Lu, P. Liu, Y. Zhao, C. Shi, S. Zhang, J. Wu, H. Zhong, M. Sui, H. Zhou, H. Jin, Y. Li, Q. Chen, *Adv. Mater.* 2018, 30, 1800544; d) D. Luo, W. Yang, Z. Wang, A. Sadhanala, Q. Hu, R. Su, R. Shivanna, G. F. Trindade, J. F. Watts, Z. Xu, T. Liu, K. Chen, F. Ye, P. Wu, L. Zhao, J. Wu, Y. Tu, Y. Zhang, X. Yang, W. Zhang, R. H. Friend, Q. Gong, H. J. Snaith, R. Zhu, *Science* 2018, 360, 1442; e) H. Tan, A. Jain, O. Voznyy, X. Lan, F. P. Garcia de Arquer, J. Z. Fan, R. Quintero-Bermudez, M. Yuan, B. Zhang, Y. Zhao, F. Fan, P. Li, L. N. Quan, Y. Zhao, Z. H. Lu, Z. Yang, S. Hoogland, E. H. Sargent, *Science* 2017, 355, 722
- [57] J. Xu, J. B. Liu, B. X. Liu, J. F. Wang, B. Huang, *Adv. Funct. Mater.* 2019, 29, 1805870. [58] a) Z. Fang, L. Wang, X. Mu, B. Chen, Q. Xiong, W. D. Wang, J. Ding, P. Gao, Y. Wu, J. Cao, *J. Am.*

- Chem. Soc.2021, 143, 18989;b) N. Faraji, C. J. Qin, T. Matsushimia, C. Adachi, J. Seidel, J. Phys.Chem. C 2018, 122, 4817.
- [59] F. Wei, Z. Deng, S. Sun, N. T. P. Hartono, H. L. Seng, T. Buonassisi,P. D. Bristowe, A. K. Cheetham, Chem. Commun. 2019, 55, 3721.
- [60] B. Wang, N. Li, L. Yang, C. Dall’Agnese, A. K. Jena, S. I. Sasaki,T. Miyasaka, H. Tamiaki, X. F. Wang, J. Am. Chem. Soc. 2021, 143, 2207.
- [61] B. Wang, N. Li, L. Yang, C. Dall’Agnese, A. K. Jena, T. Miyasaka,X. F. Wang, J. Am. Chem. Soc. 2021, 143, 14877.
- [62] a) R. D. Chavan, M. M. Tavakoli, S. Trivedi, D. Prochowicz,A. Kalam, P. Yadav, P. H. Bhoite, C. K. Hong, ACS Appl. EnergyMater. 2021, 4, 10433; b) H. Chen, F. Zhou, Z. Jin, Nano Energy 2021,79, 105490.
- [63] H. Pan, H. Shao, X. L. Zhang, Y. Shen, M. K. Wang, J. Appl. Phys.2021, 129, 130904.
- [64] Z. H. Zhang, C. C. Wu, D. Wang, Q. H. Zhang, Y. Q. Zhang, X. Guo,Y. N. Lao, B. Qu, L. X. Xiao, Z. J. Chen, ACS Appl. Energy Mater.2020, 3, 9594.Adv. Mater. Technol. 2023, 8, 2200442