Lead-Free Hybrid Perovskite Absorbers for Viable Application: Can We Eat the Cake and Have It too?

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Many years since the booming of research on perovskite solar cells (PSCs), the hybrid perovskite materials developed for photovoltaic application form three main categories since 2009: (i) high-performance unstable lead-containing perovskites, (ii) low-performance lead-free perovskites, and (iii) moderate performance and stable lead-containing perovskites. The search for alternative materials to replace lead leads to the second group of perovskite materials. To date, a number of these compounds have been synthesized and applied in photovoltaic devices. Here, lead-free hybrid light absorbers used in PV devices are focused and their recent developments in related solar cell applications are reviewed comprehensively. In the first part, group 14 metals (Sn and Ge)-based perovskites are introduced with more emphasis on the optimization of Sn-based PSCs. Then concerns on halide hybrids of group 15 metals (Bi and Sb) are raised, which are mainly perovskite derivatives. At the same time, transition metal Cu-based perovskites are also referred. In the end, an outlook is given on the design strategy of lead-free halide hybrid absorbers for photovoltaic applications. It is believed that this timely review can represent our unique view of the field and shed some light on the direction of development of such promising materials.

1. Introduction

Owing to the increasing consumption of fossil energy and the deterioration of air pollution, there is an imperative need of clean and renewable energy resources for humanity. Among the new energy solutions, photovoltaic (PV) technology, which converts solar energy into electricity directly, is a promising approach to get sustainable clean energy safely. As one of the third-generation PV technologies, hybrid halide perovskite solar cells (PSCs) emerged since Miyasaka and co-workers[1] incorporated MAPbX$_3$ (X = I, Br) as sensizers into dye-sensitized solar cells (DSSCs), achieving a power conversion efficiency (PCE) of 3.8% in 2009. After numerous research endeavors in the past eight years, the PCEs of PSCs rapidly improved to 22.1%.[2] Originally, hybrid halide perovskites with the general formula of ABX$_3$ are structural analogs of the natural mineral CaTiO$_3$, while A is a monovalent, organic or alkali metal cation, M is a divalent p-block metal (typically Pb, Sn, and Ge), and X is a halide anion.[3] Depending on the demand of the researchers, hybrid halide perovskites and their derivatives for the photovoltaic application can be classified into three main categories since 2009 (Figure 1).

The first group of halide perovskites is dedicated to demonstrating the potential of PSCs in achieving PCE up to a theoretical upper limit of 31%.[4] They are the most studied hybrid halide perovskites with the formula APb$_{M_1}$X$_3$ (A = CH$_3$NH$_3$, HC(NH$_2$)$_2$, Cs, Rb, or their mixture; M = Sn (II), Ge (II), Mn (II), Co (II), In (III), Al (III), or Sb (III), etc. or their mixture; X = Cl, Br, I, or their mixture) featuring the containing of Pb as the main metal cation and 3D network of corner-sharing (Pb$_{1,3}$M)$_n$X$_{6n+4}$ octahedrons with the monovalent cation occupying the cubic-octahedral cavity. The unique electronic configuration of Pb$^{2+}$ endows 3D lead perovskites with excellent optoelectronic properties. For example, MAPbI$_3$, the archetypal hybrid halide perovskite, possesses many ideal properties as a solar absorber: a direct bandgap ($E_g$) of 1.53 eV,[16] small exciton binding energies (37 or 45 meV),[17–19] long charge carrier diffusion lengths over 3.5 µm,[20,21] and excellent charge carrier mobilities.[22–24] Inherited all the merits of tribasic MAPbI$_3$, the compositionally engineered polybasic 3D lead halide perovskite-based PSCs exhibited a skyrocketing certified PCE from initial 14.9% to state-of-the-art 22.1% within three years. Aforementioned 3D lead halide perovskites realized the highest-performing solution-processed solar cell on record, rivaling commercial crystalline silicon solar cells in efficiency.[25] However, the toxicity issue of the lead urged some researchers to seek alternatives to lead-based perovskites. We classify these alternatives as the second group of perovskites, which features less toxic lead-free hybrid halide light absorbers. Lead-free hybrid halide light absorbers mainly include group...
14 metals like tin (Sn) and germanium (Ge), group 15 posttransition metals like bismuth (Bi) and antimony (Sb), and transition metal copper (Cu) as the metal cations.[27] In this case, a variety of crystallographic polymorphs appeared: Sn- and Ge-based compounds with 3D perovskite framework; Bi- and Sb-based “pseudoperovskite” without corner-shared MX₆ octahedra structure; Cu-based typical 2D layered perovskites. As light absorbers used in solar cells, Sn-based perovskites achieved the highest efficiency so far of 8.12% among all lead-free hybrid halide compounds.[28]

In the group of high-efficiency lead halide perovskites, there is another problem of insufficient long-term stability for the application of the devices. One solution to this problem is mixing 3D perovskites with 2D perovskites,[29–32] which can be categorized as the third group of perovskites with the mission of realizing high efficiency and stability simultaneously. The mixed dimensional (MD) perovskites have a general chemical formula[30] of (A)ₓ[(CH₃)₂NH]ₙ₋₁-MX₃₋₁ (n is an integer), where A is a primary aliphatic or aromatic alkylammonium cation, M is a divalent metal, and X is a halide anion. In the MD perovskites, the large organic cations (A) defragment the 3D structure and isolate certain number (n) of inorganic perovskite layers of corner-sharing [MX₆]ₙ⁻ octahedrons.[31] This configuration was found to prevent moisture from attacks on the perovskite and therefore improve the stability of perovskite film. Additionally, the wide variety of “A and n” brings MD perovskites abundant tunability and flexibility to control the physical properties, as well as balanced stability versus optoelectronic performance of corresponding devices. So far, the quasi-2D PEAₓ[(CH₃)₂NH]ₙ₋₁-PbI₃₋₁[32] and 2D perovskite (BA)ₓ[(MA)ₓP bI₃₋₁][34] displayed good efficiency over 12% through optimizing stoichiometry of materials and showed much improved stability than intrinsic 3D perovskites.

The three groups of hybrid perovskites attracted attention to different extents. In this series review, we focus on the second group of perovskites or lead-free hybrid light absorbers used in photovoltaic devices. Recent development in structures, optoelectronic properties, and the related solar cell applications of these types of hybrid light absorbers are summarized. In the first part, group 14 metals (Sn and Ge)-based perovskites are introduced with more emphasis on the optimization of Sn-based PSCs. Then we put concerns on halide hybrids of group 15 metals (Bi and Sb), which are mainly perovskite derivatives. At the same time, transition metal Cu-based perovskites are also referred. In the end, we give an outlook on the design strategy of lead-free halide hybrid absorbers for photovoltaic applications (Figure 2). An almost complete summary of the state-of-the-art development of the lead-free halide hybrid absorbers in PV devices is listed in Table 1.

2. Lead-Free Halide Hybrid Perovskite and Related Absorbers

Although we have achieved high efficiency beyond 22% based on lead halide perovskites, which is comparable to commercial crystalline silicon solar cells, the existence of Pb is an urgent problem against the final application of PSCs. The toxicity of lead is documented to disturb the functioning of the blood, kidneys, liver, testes, brain, and nervous system.[124–126] The toxicity of lead is due, in general, to its binding affinity to thiol and cellular phosphate groups of numerous enzymes, proteins, and cell membranes.[127] Lead is toxic to the central nervous system, especially in children.[128] Thus, there come the questions that: can we eat the cake and have it too? Meaning can we have high-efficiency PSCs without being poisoned? The urge to explore authentic high-efficiency lead-free metal halide absorbers led to an abundance of works which will be shown in the following sections.

2.1. The Group 14 Metals (Sn and Ge) Based Absorbers

2.1.1. Tin-Based Absorbers

Tin (Sn) as a member of group 14 congeners and less-toxic metal (than Pb) is expected to have comparable properties with its Pb analogs. Owing to their direct and narrow bandgaps (1.2–1.4 eV), low exciton binding energies (18 meV), and super charge-carrier mobilities,[129–132] Sn-based perovskites ASnX₃ (A=MA, FA or Cs, X= halide) were the most investigated
non-lead hybrid perovskite absorbers. Depending on the types of A cations and the solid structure, we classified them into following groups and made discussions accordingly.

**MA\textsubscript{Sn}I\textsubscript{3}**

The crystal structure of MA\textsubscript{Sn}I\textsubscript{3} belongs to the cubic $Pm\bar{3}m$ (no. 221) space group at room temperature (Figure 3a). MA\textsubscript{Sn}I\textsubscript{3} possesses an optical bandgap of 1.20–1.35 eV (Figure 3b), displaying remarkably high carrier mobility ($\text{electron mobility} \approx 2320 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, $\text{hole carrier mobility} \approx 322 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$),[132,133] and long carrier diffusion lengths exceeding 500 nm.[134] In 2014, MA\textsubscript{Sn}I\textsubscript{3} and MA\textsubscript{Sn}(I\textsubscript{1−x}Br\textsubscript{x})\textsubscript{3}[51] were reported as the first completely lead-free solar absorbers in PSCs based on a traditional mesoscopic device structure of FTO/c-TiO\textsubscript{2}/mp-TiO\textsubscript{2}/absorber/spiro-OMeTAD/Au. PCEs of 6.4% and 5.73% were reported, respectively, and after three years they are still the record efficiencies among MA\textsubscript{Sn}X\textsubscript{3}-based PSCs (Figure 3c). This dramatic different situation from the lead-based perovskite can be understood by the fact that Sn-based perovskites are prone to self-doping in ambient air resulting in instability and poor reproducibility.[46–48,51–53,135]

**FASnI\textsubscript{3}**

Similar to the case of lead halide perovskite, FA is another candidate that can be employed as A site cation for Sn halide perovskites. FASnI\textsubscript{3} takes the cubic $Pm\bar{3}m$ (no. 221) space group structure at room temperature and has only one single stable phase up to 200 °C (Figure 3a). This is different from its lead analogue-FAPbI\textsubscript{3}, which has two competing $\delta$-phase and $\alpha$-phase structure.[132,136,137] Another unique point is that due to the symmetry reduction of the 3D $[\text{SnI}_3]^-$ framework with larger cations group like FA,[132] FASnI\textsubscript{3} has a larger band gap (1.41 eV) value than that of MA\textsubscript{Sn}I\textsubscript{3}.[50] In 2015, Koh et al. first took FASnI\textsubscript{3} as a light absorber in solar cell applications and realized a high short-circuit current density ($J_{SC}$) of 24.45 mA cm$^{-2}$ and PCE of merely 2.1%.[59] It was reported that FASnI\textsubscript{3} is more stable than MA\textsubscript{Sn}I\textsubscript{3} due to the reduced extent of Sn oxidation.[133,138] Accordingly, FASnI\textsubscript{3}-based PSCs exhibited much better reproducibility as compared to MA\textsubscript{Sn}I\textsubscript{3}-based devices.[138] In 2016, Liao et al.[56] reported a PCE of 6.22% based on FASnI\textsubscript{3} PSCs with high reproducibility, which is one of the best efficiencies among Sn-based PSCs (Figure 3d,e). Very recently, Shi et al.[139] studied the phenomenon theoretically and found that the antibonding coupling between Sn-s and I-p is weaker in FASnI\textsubscript{3} than in MA\textsubscript{Sn}I\textsubscript{3} due to the larger ionic size of FA, leading to higher formation energies of Sn vacancies in FASnI\textsubscript{3}. Subsequently, the conductivity of FASnI\textsubscript{3} can be tuned from p-type to intrinsic by varying the growth conditions of the perovskite semiconductor. In contrast, MA\textsubscript{Sn}I\textsubscript{3} shows unipolar high p-type conductivity independent of the growth conditions. Ion mixing is also one important approach for Sn perovskites. Ferrara et al.[61] reported the first mixed A-cation compositions of tin perovskites FA$_{1−x}$MA$_x$SnBr$_3$, with cubic structures and the band gaps ranging from 2.4 eV ($x = 0$) to $\approx$1.92 eV ($x = 0.82$). However, no device performance was reported. Very recently, Zhao et al.[28] reported another mixed-organic-cation perovskite absorber (FA)$_{0.75}$(MA)$_{0.25}$SnI\textsubscript{3}. The optimized ratio of FA and MA cations is 0.75 versus 0.25 and the resulted (FA)$_{0.75}$(MA)$_{0.25}$SnI\textsubscript{3} has an ideal bandgap of 1.33 eV. PSCs with an inverted structure based on (FA)$_{0.75}$(MA)$_{0.25}$SnI\textsubscript{3} showed an improved $V_{OC}$ of 0.61 V and the best ever PCE of 8.12%, which is the highest efficiency among the Sn-based PSCs (Figure 4).
Compared to the organic–inorganic hybrid perovskite materials, the all-inorganic halide perovskites exhibited much higher thermal stability.\[16,70,140\] Replacing the organic cations (MA\(^+\) or FA\(^+\)) with the inorganic Cs\(^+\), CsSnI\(_3\) perovskite shows a melting point of 435 °C,\[72,141\] suggesting superior intrinsic thermal stability. In contrast, hybrid perovskites MASnI\(_3\) and FASnI\(_3\) start to decompose at \(\approx 200\) °C. CsSnI\(_3\) adopts a black orthorhombic perovskite phase structure, possesses a direct band gap of \(1.3\) eV, and has a high hole mobility of \(\approx 585\) cm\(^2\) V\(^{-1}\) s\(^{-1}\) at room temperature (Figure 5a). In 2012, due to its high hole mobility, it was first taken as a hole transport material (HTM) in DSSCs.\[72\] Very recently, the further potential of CsSnI\(_3\) for solar cell applications was uncovered by Wu et al.\[142\] They reported that the melt-synthesized CsSnI\(_3\) ingots contain high-quality large single crystal (SC) grains, which bear superior properties like high bulk carrier lifetimes (\(>6.6\) ns), low doping concentrations of \(\approx 4.5 \times 10^{17}\) cm\(^{-3}\), and long minority-carrier diffusion lengths approaching 1 \(\mu\)m. In this regard, they predicted a PCE of \(\approx 23\)% for optimized CsSnI\(_3\) SC solar cells. As a light absorber, CsSnI\(_3\) was firstly used in a Schottky contact type PSC with a simple layer structure of ITO/CsSnI\(_3\)/Au/Ti in 2012, showing a PCE of 0.9%.\[71\] Four years later, Marshall et al.\[66\] designed an HTM-free CsSnI\(_3\) PSC with exceptionally high fill factor up to 0.69, and a PCE up to 3.56%. In 2017, Song et al.\[65\] assembled CsSnI\(_3\)-based PSCs with reducing atmosphere-assisted dispersible additive. The new technique produced a PCE of up to 4.81%, which is the highest efficiency among all CsSnI\(_3\) PSCs so far (Figure 5a). Meanwhile, benefiting from the superior thermal stability of CsSnX\(_3\) perovskites, Li et al.\[73\] fabricated an all-inorganic CsSnIBr\(_2\) mesoscopic PSC with thermal stability up to 200 °C, achieving an average PCE of 3.0% and long-term stability without efficiency-loss over 77 d (Figure 5c).

**Cs\(_2\)SnI\(_6\)**

The Sn\(^{11}\) in CsSnI\(_3\) and M(F)ASnI\(_3\) has the tendency to be oxidized to Sn\(^{IV}\) leading to the spontaneous change to Cs\(_2\)SnI\(_6\) and M(F)A\(_2\)SnI\(_6\) respectively in ambient atmosphere. Cs\(_2\)SnI\(_6\) with a molecular salt structure is not bona fide perovskite but crystallizes into a face-centered cubic \(\text{Pm}\bar{3}\text{m}\) space group and the lattice parameter of which is 11.63 Å\[132,144\] (Figure 5d). The direct bandgap (\(E_g\)) of Cs\(_2\)SnI\(_6\) is \(\approx 1.3–1.6\) eV\[76,79,132\] depending on the preparation methods at room temperature with absorption coefficient over \(10^5\) cm\(^{-1}\) from 1.7 eV. Computational work based on Cs\(_2\)SnI\(_6\)\[145\] shows that the iodine vacancies and interstitial Sn are the dominant defects that give intrinsic n-type behavior, unlike the p-type behavior in CsSnI\(_3\). The carrier concentration (electrons) of Cs\(_2\)SnI\(_6\) is \(\approx 1 \times 10^{14}\) cm\(^{-3}\), and the carrier mobility is \(310\) cm\(^2\) V\(^{-1}\) s\(^{-1}\). Moreover, due to the full oxidation state of Sn\(^{IV}\), Cs\(_2\)SnI\(_6\) exhibits better stability in the air with moisture than CsSnI\(_3\). In 2014, Lee et al. used Cs\(_2\)SnI\(_6\) as a hole transporter in solid-state DSSCs and fabricated devices in the air with an efficiency close to 8%\[78\]. The study of Cs\(_2\)SnI\(_6\) as
Table 1. Lead-free hybrid absorbers comparing to the lead-containing counterparts.

| Metal Cations | Absorber | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) | $E_g$ (eV) | Architecture | Fabrication method | Additive | Ref. |
|---------------|----------|---------|-------------|-----------------|-------|----------|-------------|-------------------|----------|-----|
| Pb            | MAPbI$_3$ | 20.4    | 1.11        | 23.7            | 77.3  | 1.55     | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating+ solvent-engineering | No | [42] |
| Pb            | FAPbI$_3$ | 18.1    | 1.04        | 23.2            | 74.9  | 1.45     | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating-solvent-bathing | No | [43] |
| Pb            | FA$_{1-x}$MA$_x$PbI$_{1-y}$Br$_y$ | 22.1    | 1.1        | 25.0            | 80.3  | 1.50     | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | I$_2$ | [44] |
| Sn(II)        | Sn$_x$I$_{3-x}$ | 6.4     | 0.88       | 16.8            | 42    | 1.2      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | No | [46] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 21.4    | 0.45       | 11.8          | 40    | –        | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Ag | Spin coating-solvent-bathing | SnF$_2$ | [48] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 1.7     | 0.38       | 12.1         | 36.6  | 1.3      | ITO/PEDOT:PSS/Poly-TPD/absorber/C$_{60}$/BCP/Ag | Spin coating | VASP | [49] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.89    | 0.38       | 19.9         | 51.7  | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [50] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.15    | 0.32       | 21.4         | 46    | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [51] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 2.14    | 0.45       | 11.8         | 40    | –        | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Ag | Spin coating-solvent-bathing | SnF$_2$ | [52] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 1.86    | 0.27       | 17.4         | 39.1  | 1.26     | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | VASP | [53] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 1.7     | 0.38       | 12.1         | 36.6  | 1.3      | ITO/PEDOT:PSS/Poly-TPD/absorber/C$_{60}$/BCP/Ag | Spin coating | thermal co-evaporation | No | [54] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.89    | 0.38       | 19.9         | 51.7  | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [55] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.15    | 0.32       | 21.4         | 46    | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [56] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 2.14    | 0.45       | 11.8         | 40    | –        | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Ag | Spin coating-solvent-bathing | SnF$_2$ | [57] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 1.86    | 0.27       | 17.4         | 39.1  | 1.26     | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | VASP | [58] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 1.7     | 0.38       | 12.1         | 36.6  | 1.3      | ITO/PEDOT:PSS/Poly-TPD/absorber/C$_{60}$/BCP/Ag | Spin coating | thermal co-evaporation | No | [59] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.89    | 0.38       | 19.9         | 51.7  | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [60] |
| Rb$_{0.05}$Cs$_{0.05}$(MA$_{0.17}$FA$_{0.83}$)$_{0.95}$Pb$_x$(I$_{0.83}$Br$_{0.17}$)$_3$ | 3.15    | 0.32       | 21.4         | 46    | 1.3      | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Au | Spin coating | SnF$_2$ | [61] |
| Metal Cations | Absorber | PCE (%) | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF (%) | $E_g$ (eV) | Architecture | Fabrication method | Additive | Ref. |
|--------------|----------|---------|-------------|-----------------|--------|-----------|-------------|------------------|----------|------|
| FA$_{0.5}$MA$_{0.5}$SnI$_3$ | 5.92 | 0.53 | 21.3 | 52.4 | 1.3 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Ag | Spin coating solvent-engineering (CB) | SnF$_2$ | [28] |
| FA$_{0.75}$MA$_{0.25}$SnI$_3$ | 8.12 | 0.61 | 21.2 | 62. | 1.33 | ITO/PEDOT:PSS/absorber/C$_{60}$/BCP/Ag | Spin coating solvent-engineering (CB) | SnF$_2$ | [28] |
| (en)FASnI$_3$ | 7.14 | 0.48 | 22.5 | 66.0 | 1.5 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/PTTA/Au | Spin coating | SnF$_2$ | [62] |
| (BA)$_2$(MA)$_3$Sn$_4$I$_3$ | 2.53 | 0.229 | 24.1 | 45.7 | 1.42 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/PTTA/Au | Spin coating | SnF$_2$ | [63] |
| (PEA)$_2$(FA)$_8$Sn$_9$I$_{28}$ | 5.94 | 0.59 | 14.4 | 69 | 1.789 | ITO/NO$_x$/absorber/PCBM/Al | Spin coating solvent-engineering (Tol) | SnF$_2$ | [64] |
| CsSnI$_3$ | 4.81 | 0.38 | 25.71 | 49.1 | 1.3 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/PTTA/Au (TPE) | Spin coating SnI$_4$ | SnF$_2$ | [65] |
| CsSnI$_3$ | 3.56 | 0.50 | 9.89 | 68 | 1.3 | ITO/absorber/PC$_61$BM/BCP/Al | Spin coating SnCl$_2$ | - | [66] |
| CsSnI$_3$ | 3.11 | 0.52 | 10.2 | 62.5 | 1.3 | ITO/NO$_x$/absorber/PCBM/Al | Spin coating | SnF$_2$ | [67] |
| CsSnI$_3$ | 2.76 | 0.43 | 12.3 | 39.5 | 1.3 | ITO/Cul/absorber/ICBA/BPC/Al | Spin coating | SnF$_2$ | [68] |
| CsSnI$_3$ | 2.0 | 0.24 | 22.7 | 37 | 1.3 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/m-MTDATA/Au | Spin coating | SnF$_2$ | [69] |
| CsSnI$_3$ | 1.83 | 0.17 | 30.8 | 34.9 | 1.25 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/PTTA/Au (TPFB) | Spin coating (hydrazine vapor) | SnF$_2$ | [41] |
| CsSnI$_3$ | 1.66 | 0.20 | 27.7 | 29 | 1.27 | FTO/TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Al | Spin coating | SnF$_2$ | [70] |
| CsSnI$_3$ | 0.88 | 0.42 | 4.8 | 22 | 1.3 | ITO/absorber/Au/Ti | sequential thermal evaporation | No | [71] |
| CsSnI$_3$ | 8.51 | – | – | – | – | HTM in DSSCs | - | SnF$_2$ | [72] |
| CsSnI$_3$ | 1.67 | 0.29 | 15.1 | 38 | 1.37 | FTO/TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Al | Spin coating | SnF$_2$ | [70] |
| CsSnI$_3$ | 3.2 | 0.31 | 17.4 | 57 | 1.63 | FTO/c-TiO$_2$/Al$_2$O$_3$/absorber/C | Spin coating | SnF$_2$ | [73] |
| CsSnI$_3$ | 1.56 | 0.31 | 11.6 | 43 | 1.65 | FTO/TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Al | Spin coating | SnF$_2$ | [70] |
| CsSnI$_3$ | 3.04 | 0.37 | 14.0 | 59.4 | 1.79 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/PTTA/Au (TPFB) | Spin coating (hydrazine vapor) | SnF$_2$ | [41] |
| CsSnI$_3$ | 2.17 | 0.42 | 9.1 | 57 | 1.75 | FTO/c-TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Al | Spin coating | SnF$_2$ | [74] |
| CsSnI$_3$ | 0.95 | 0.41 | 3.99 | 58 | 1.75 | FTO/TiO$_2$/mp-TiO$_2$/absorber/spiro-OMeTAD/Al | Spin coating | SnF$_2$ | [70] |
| CsSnI$_3$ | 0.55 | 0.45 | 2.4 | 55 | 1.8 | ITO/Mo$_2$O$_5$/absorber/C$_{60}$/BCP/Ag | All vapor-deposited | SnF$_2$ | [75] |

**Table 1. Continued.**
Table 1. Continued.

| Metal Cations | Absorber | PCE (%) | V<sub>OC</sub> (V) | J<sub>SC</sub> (mA cm<sup>-2</sup>) | FF (%) | E<sub>g</sub> (eV) | Architecture | Fabrication method | Additive | Ref. |
|---------------|----------|---------|-----------------|------------------|--------|-------------|--------------|------------------|----------|-----|
| Ge            | MAGeI<sub>3</sub> | 0.2    | 0.15            | 4.0              | 30     | 2.0         | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | Spin coating | –      |     |
|               | FAGeI<sub>3</sub> | –      | –               | –               | –      | 2.35        | –            | –                | –        |     |
|               | CsGeI<sub>3</sub> | 0.01   | 0.07            | 5.7              | 27     | 1.63        | –            | –                | –        |     |
| Bi 0D         | MA<sub>2</sub>Bi<sub>2</sub>I<sub>5</sub> | 0.42   | 0.67            | 1.00             | 62.5   | 2.1         | ITO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/MoO<sub>3</sub>/Ag | Spin coating | –      | [82]|
|               | MA<sub>2</sub>Bi<sub>1</sub>I<sub>9</sub> | 0.39   | 0.83            | 1.39             | 34     | 2.22        | ITO/PEDOT: PSS/absorber/C<sub>60</sub>/BCP/Ag | Two-step evaporation–spin-coating | –      | [83]|
|               | MA<sub>2</sub>Bi<sub>2</sub>I<sub>9</sub> | 0.36   | 0.65            | 1.10             | 0.50   | 2.1         | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | Spin coating | –      | [84]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.31   | 0.31            | 0.94             | 0.61   | –           | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | –          | NMP   | [85]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.26   | 0.56            | 0.83             | 49     | –           | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | –          | –      | [86]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.19   | 0.35            | 1.16             | 46.4   | 2.11        | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/P3HT/Au | Spin coating | –      | [87]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.12   | 0.68            | 0.52             | 33     | 2.1         | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | Spin coating | –      | [88]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.11   | 0.72            | 0.49             | 31.8   | 2.26        | FTO/TiO<sub>2</sub>/absorber/spiro-MeOTAD/Au | solvent-engineering (chlorobenzene) | –      | [89]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.08   | 0.69            | 0.37             | 32     | 2.1         | FTO/TiO<sub>2</sub>/absorber/spiro-MeOTAD/Ag | Spin coating, gas-assisted | –      | [90]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | 0.07   | 0.66            | 0.22             | 49     | 2.9         | ITO/PEDOT: PSS/absorber/PCBM/Ca/Al | Spin coating | –      | [91]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>9</sub> | –      | –               | –               | –      | 2.04        | –            | –                | –        | vapor-assisted conversion | [92]|
|               | MA<sub>2</sub>Bi<sub>3</sub>I<sub>5</sub>Cl<sub>x</sub> | 0.003  | 0.04            | 0.18             | 38     | 2.4         | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Ag | Spin coating | –      | [88]|
|               | MA<sub>2</sub>Bi<sub>2</sub>I<sub>2</sub>S<sub>x</sub> | –      | –               | –               | –      | 1.45        | –            | –                | –        | In situ, thermal | [93]|
|               | (MA<sub>2</sub>Bi<sub>2</sub>I<sub>2</sub>)(BiI<sub>3</sub>)<sub>x</sub> | 0.08   | 0.57            | 0.27             | 50     | –           | FTO/TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/spiro-OMeTAD/Au | Spin coating | –      | [94]|
| 1D            | FA<sub>3</sub>Bi<sub>1</sub> | –      | –               | –               | –      | 2.0         | –            | –                | –        | –      | [95]|
|               | (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> | –      | –               | –               | –      | –           | –            | –                | –        | –      | [96]|
|               | (C<sub>6</sub>H<sub>14</sub>N)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> | –      | –               | –               | –      | –           | –            | –                | –        | –      | [97]|
|               | MA<sub>2</sub>Bi<sub>2</sub>Cl<sub>x</sub> | –      | –               | –               | –      | –           | –            | –                | –        | –      | [98]|
|               | C<sub>7</sub>H<sub>4</sub>NBi<sub>1</sub> | 0.9    | 0.62            | 2.71             | 0.54   | 1.98        | FTO/c-TiO<sub>2</sub>/mp-TiO<sub>2</sub>/absorber/ZrO<sub>2</sub>/C | Spin coating | –      | [99]|
|               | C<sub>6</sub>H<sub>8</sub>NBi<sub>1</sub> | –      | –               | –               | –      | 2.17        | –            | –                | –        | –      | [100]|

FA<sub>3</sub>Bi<sub>1</sub> and (C<sub>3</sub>H<sub>5</sub>N<sub>2</sub>)<sub>3</sub>Bi<sub>2</sub>I<sub>9</sub> were prepared by spin coating. Spin coating and gas-assisted vapor-assisted conversion were used.
| Metal Cations | Absorber | PCE (%) | Voc (V) | Jsc (mA cm⁻²) | FF (%) | Eg (eV) | Architecture | Fabrication method | Additive | Ref. |
|---------------|----------|---------|---------|---------------|--------|---------|-------------|-------------------|----------|------|
| (TMP)BiX₅ (X = Cl, Br, I) | – – – – – | 2.02-3.21 | – – – – – | – – – – – | – – – – | – – – – | – – – – | – – – – | – – | [101] |
| 2D | MA₂Bi₂Br₆ | – – – – – | 2.5 | – – – – – | – – – – | – – – – | – – – – | – – – – | – – | [102] |
| (NH₄)₂Bi₂I₉ | – – – – – | 2.04 | – – – – – | – – – – | – – – – | – – | – – – – | – – – | – | [103] |
| (TMP)₁₁Bi₂I₅Cl₂ | – – – – – | 2.1 | – – – – – | – – | – – | – | – – – | – | – | [101] |
| 3D | MAₓKBrClₓ | – – – – – | 3.04 | – – – – | – | – | – | – | – | [104] |
| MAₓTlBiBr₆ | – – – – – | 2.16(direct) | – – – – | – | – | – | – | – | – | [105] |
| MAₓAgBiBr₆ | – – – – – | 2.02 | – | – | – | – | – | – | – | [106] |
| 0D | Cs₂Bi₂I₉ | 0.02 0.02 0.18 37 | 2.03 | | FTO/TiO₂/mp-TiO₂/absorber/P3HT/Ag | Spin coating | – | [100] |
| Cs₂Bi₂I₉ | 1.09 0.85 2.15 60 | 2.2 | | FTO/TiO₂/mp-TiO₂/absorber/spiro-OMeTAD/Ag | Spin coating | – | [88] |
| Cs₂Bi₂I₉ | – – – – – | 1.9 | – | – | – | – | – | – | – | [36] |
| CsBi₁₀ | 0.40 0.31 3.4 38 | 1.77 | | FTO/TiO₂/mp-TiO₂/absorber/spiro-OMeTAD/Ag | Spin coating | – | [100] |
| 2D | KₓBi₂I₆ | – – – – | 2.1 | – | – | – | – | – | – | [36] |
| RbₓBi₂I₉ | – – – – | – | – | – | – | – | – | – | – | [107] |
| CsₓBi₂Br₉ | – – – – | 2.71 | – | – | – | – | – | – | – | [107] |
| 3D | Cs₂AgBiBr₆ | – – – | 1.9 | – | – | – | – | – | – | [108] |
| Cs₂AgBiBr₆ | – – – | 1.95 | – | – | – | – | – | – | – | [38] |
| Cs₂AgBiBr₆ | – – – | 2.19 | – | – | – | – | – | – | – | [109] |
| Cs₂AgBiBr₆ | 2.43 0.98 3.93 63 | 2.21 | | FTO/c-TiO₂/mp-TiO₂/absorber/spiro-OMeTAD/Au | Spin coating | – | [110] |
| Cs₂(Ag₁ₓBi₁₋ₓ)TlₓBr₆ | – – – | 1.40 1.57(direct) | – | – | – | – | – | – | – | [111] |
| Cs₂Ag(Bi₀.₆₂Sb₀.₃₇)Br₆ | – – – | 1.86 2.15(direct) | – | – | – | – | – | – | – | [112] |
| Cs₂AgBiCl₆ | – – – | 2.2 | – | – | – | – | – | – | – | [108] |
| Cs₂AgBiCl₆ | – – – | 2.77 | – | – | – | – | – | – | – | [109] |
| Cs₂InₐNₐAgCl₆ (non-Bi) | – – – | 3.3(direct) | – | – | – | – | – | – | – | [113] |
| AgBi₂I₇ | 1.22 0.56 3.30 67.4 | 1.87 | | FTO/TiO₂/mp-TiO₂/absorber/P3HT/Ag | Spin coating | – | [114] |
| AgBi₂I₇ (R₃m AgI/BiI₃=2:1) | 2.1 0.49 6.8 63 | 1.83 | | FTO/TiO₂/mp-TiO₂/absorber/P3HT/Ag | Spin coating | – | [115] |
| AgBi₂I₇ (Fd₃m AgI/BiI₃=1:2) | 0.4 0.46 1.6 56 | 1.78 | | | | | | | | |
| Sb | (NH₄)₅Sb₂I₁₁Br₉₋ₓ | 0.51 1.03 1.15 42.9 | 2.27-2.78 | | ITO/PEDOT:PSS/absorber/PC₆₀BM/Al | Spin coating | – | [116] |
| MA₅Sb₂I₉ | 0.49 0.90 1.0 55 | 2.14 | | ITO/PEDOT:PSS/absorber/PC₆₀BM/nano-ZnO/Al | Spin coating; solvent-engineering (Tol) | – | [117] |
| MA₅Sb₂I₉ | 2.04 0.62 5.41 60.8 | 1.95 | | ITO/PEDOT:PSS/absorber/PC₆₀BM/C₆₀/BCP/Al | Spin coating | HI | [118] |
| Rb₅Sb₂I₉ | 0.66 0.55 2.11 57 | 2.1 | | FTO/TiO₂/mp-TiO₂/absorber/Poly-TPD/Au | SbI₃ in toluene treated (Tol) | SbI₃ | [35] |
| Cs₅Sb₂I₉ | <1.0 0.31 <0.1 | – | 2.05 | FTO/c-TiO₂/absorber/P3HT/Ag | Co-evaporation / vapor-assisted conversion SbI₃ vapor | [119] |
| Metal Cations | Absorber | PCE (%) | Voc (V) | Jsc (mA cm⁻²) | FF (%) | Eg (eV) | Architecture | Fabrication method | Additive | Ref. |
|---------------|---------|---------|---------|---------------|--------|---------|-------------|------------------|-----------|-----|
| Cs₃Sb₂I₉ | 0.84 0.6 2.91 48.1 2.0 | | | | Spin coating | HI | | [118] |
| [CH₃SC(NH₂)₂]SbA₅ | – – – – 2.41–3.34 | | | | | | | | | |
| Cs₂CuSbCl₁₂ | – – – – 1.0 | | | | | | | | | |
| Cu | [CH₃(CH₂)₃NH₃]₂CuBr₄ | 0.63 0.88 1.78 40 1.76 | | | | FTO/c-TiO₂/mp-TiO₂/absorber/spiro-OMeTAD/Ag | Spin coating | – | [122] |
| (p-F-C₆H₅C₂H₄-NH₃)₂-CuBr₄ | 0.51 0.87 1.46 40 1.74 | | | | | | | | | |
| MA₂CuCl₃Br₂ | 0.02 0.26 0.22 32 2.12 | | | | | | | | | |
| MA₂CuCl₂Br₃.₅ | 0.002 0.29 0.021 28 1.8 | | | | | | | | | |
| C₆H₄NH₂CuBr₂I | 0.46 0.20 6.20 46 1.64 | | | | | | | | | |

*Used as an HTM in the solid-state dye-sensitized solar cell.*

Figure 3. a) Ball-and-stick diagrams of crystal structures and the {SnI₆} octahedral structure units in the MASnI₃ and FASnI₃ single crystals. Reproduced with permission.[133] b) The spectra of MASnI₃ and FASnI₃ prepared with the solution method as compared with other perovskites. Reproduced with permission.[132] Copyright 2013, ACS. c) J–V curve of MASnI₃ on TiO₂ and bandgap of the material determined using the Tauc plot. Reproduced with permission.[46] Copyright 2014, RSC. d) Cross-sectional SEM image of the entire device with FASnI₃ and 10 mol% SnF₂ additive; e) J–V characteristics of FASnI₃-based devices under 100 mW cm⁻² AM1.5G illumination under reverse and forward voltage scans. Reproduced with permission.[56]
a light absorber in the solar cells is rare. Until 2016, Cs$_2$SnI$_6$ was first studied by Qiu et al.\cite{76,77} as a light harvester, demonstrating a PCE of ≈1%. Very recently, Lee et al.\cite{80} further improved the PCE up to 1.47%. They designed a series of compounds with the general formula of Cs$_2$SnI$_6-x$Br$_x$. With the increase of Br composition (x), the bandgaps can be tuned from ≈1.3 to ≈2.9 eV and the color of the films was changing from dark brown to brown/red, then to light yellow. The Cs$_2$SnI$_6-x$Br$_x$ films were fabricated with a two-step solution process: the crystal structure of CsI was optimized in Step-1 by postannealing at 300 °C for 30 min after electrospraying deposition and in Step-2 the CsI film was reacted with a SnI$_4$ solution at 110 °C for 20 min (Figure 5e,f). After that, a stoichiometric, smooth, uniform, and thick active layer was obtained. The freshly made films were constructed into the typical “sandwich” type device structure of FTO/bl-TiO$_2$/2wt% Sn-TiO$_2$/Cs$_2$SnI$_6-x$Br$_x$/Cs$_2$SnI$_6$ HTM/large-effective-surface-area polyaromatic hydrocarbon (LPAH)/FTO. The best-achieved efficiency was ≈2.03% when x = 2. It is worth noting that their device fabrication process was carried out in the air and did not use any additive to protect the active material. The Cs$_2$SnI$_6-x$Br$_x$ films and corresponding devices showed excellent stability in the air for 50 d (see Figure 5f). Thus, being a molecular salt (0D), Cs$_2$SnI$_6$ has the bandgap similar to that of the 3D perovskites (CsSnI$_3$ and MAPbI$_3$), high absorption coefficient, and high carrier mobility. Coupled with its intrinsic ambient stability, such Sn-perovskite variants can be explored...
with more effort in the future for achieving more efficient and stable Sn-based PSCs.

$$\text{(PEA)}_2(\text{FA})_8\text{Sn}_9\text{I}_{28}$$

In the attempt to improve the environmental stability, Cao et al.\(^{63}\) decrease the dimensionality of the perovskite materials by mixing the CH\(_3\)(CH\(_2\))\(_3\)NH\(^+\) (BA\(^+\)) and CH\(_3\)NH\(_2\) (MA\(^+\)). The obtained 2D Ruddlesden–Popper (CH\(_3\)(CH\(_2\))\(_3\)NH\(^+\))\(_2\)-(CH\(_3\)NH\(_2\))\(_n\)Sn\(_n\)I\(_{2n+1}\) perovskites possessed optimal optical bandgaps of 1.50 and 1.42 eV for solar cells when \(n = 3\) and \(n = 4\), respectively. The 2D tin perovskite outperformed its 3D analogs for higher moisture stability with an encouraging PCE of 2.5% (from \(n = 4\)). More importantly, incorporating 20% phenyl ethyl ammonium (PEA) into FA-based Sn iodide perovskites yielded low dimensional (PEA)\(_2\)(FA)\(_8\)Sn\(_9\)I\(_{28}\)\(^{64}\) which exhibited markedly enhanced air stability in comparison with their 3D counterparts FASnI\(_3\). The inverted structure-based devices with (PEA)\(_2\)(FA)\(_8\)Sn\(_9\)I\(_{28}\) perovskite exhibited the best PCE up to 5.94% and showed superior stability over 100 h without encapsulation.

### 2.1.2. Germanium-Based Absorbers

Germanium, another group IV metal, with ns\(^2\) electronic configuration, has the same valent state with the lead. Due to the 4s lone pairs of Ge is more active than the Pb 6s lone pair, Ge\(^{2+}\) is easier to be oxidized leading to metallic conductivity in the hybrid materials and short-circuit behavior in the photovoltaic devices similar to the case of Sn-based perovskites.\(^{40,135,141}\) However, germanium has demonstrated much less toxicity compared to lead\(^{146}\) and is expected to be a promising candidate in the search for Pb-free perovskite materials. To prove the concept, Sun et al.\(^{147}\) investigated the structural and electronic properties of MAGeX\(_3\) (X = Cl, Br, I) by density functional theory (DFT) methods and showed that MAGeI\(_3\) is a good absorber for applications in PSCs. Based on DFT calculation, Ming et al.\(^{148}\) also proposed that CsGeI\(_3\) might be a good HTM in solar cells. Krishnamoorthy\(^{40}\) studied the solid structure of three AGeI\(_3\) (A = Cs, MA, or FA) halide perovskites and revealed trigonal phase (with R3m space group symmetry) in contrast to Pb and Sn-based perovskites with a tetragonal phase (I4/mcm)\(^{147}\) at room temperature. All compounds are remarkably stable up to 150 °C and show no phase transition in the range of device working temperatures (r.t. to 150 °C). With increasing size of the A\(^+\) cation, the band gaps of AGeI\(_3\) are 1.63, 2.0, and 2.35 eV for CsGeI\(_3\), MAGeI\(_3\), and FAGeI\(_3\), respectively (Figure 6a). The values of the valence bands of CsGeI\(_3\), MAGeI\(_3\), and FAGeI\(_3\) perovskites measured by the PESA are −5.10, −5.2, and −5.5 eV, respectively (Figure 6b). However, unfortunately, the solar cells based on AGeI\(_3\) were fabricated with a mesoscopic structure, achieving 0.2% PCE for MAGeI\(_3\), 0.11% PCE for CsGeI\(_3\) and no photocurrent for FAGeI\(_3\) (Figure 6c). The low performance of AGeI\(_3\)-based solar cells was attributed to the low concentration of precursor solutions, poor quality of perovskite films, and the oxidation sensitivity of the materials. Recently, theorists studied mixed tin and germanium perovskites and predicted that RbSn\(_0.5\)Ge\(_0.5\)I\(_3\) possesses not only a direct bandgap within the optimal range of 0.9–1.6 eV but also a desirable optical absorption spectrum that is comparable to those of the state-of-the-art MAPbI\(_3\) perovskites. It has favorable effective masses for high carrier mobility as well as a greater resistance to water penetration than the prototypical inorganic–organic lead-containing halide perovskite.\(^{149}\)

### 2.1.3. Devices Engineering Efforts Toward High Efficiency and Stable Sn\(^{2+}\)-Based PSCs

Thanks to the great endeavor of the researchers, Sn-based PSCs have obtained relative stable PCE of ~8%.\(^{28}\) The improvement in performance of PSCs is not only due to the material itself but also the evolution in device engineering. In this small section, we will introduce various devices preparation approaches towards efficient and stable Sn\(^{2+}\)-based PSCs over the recent years.

#### 2.1.3.1. Efforts to Suppress Sn Vacancy Defects and Improve Oxidation Stability

One of the major problems of Sn-based PSCs is their poor stability originating from the facile formation of Sn vacancy associated with oxidation of Sn\(^{2+}\) to Sn\(^{4+}\) when exposed in air,\(^{150,151}\) which leads to poor reproducibility and deteriorates the devices rapidly.\(^{46,51}\) For example, Xu et al.\(^{151}\) studied the defect properties of CsSnI\(_3\) perovskite...
and depicted the influence of defects and synthesis conditions on the photovoltaic performance. They found that due to the strong Sn 4s-I 5p antibonding coupling, Sn vacancies have very low formation energies in CsSnI3, leading to a very high concentration of Sn vacancies and therefore high p-type conductivity regardless of the growth conditions. To solve the problem, reductive or sacrificial additives like Sn(II) halide salt etc., were added to cure the problem.

SnF2

Before tin halide perovskite served as a light-absorber in PSCs, Chung et al.[72] demonstrated that when CsSnI3 with SnF2 additive (though the formulation of CsSnI2.95F0.05 is not correct[152]) was used as HTM in DSSC, enhancements of 29% and 21% in JSC and η were achieved, respectively. The magic effect of SnF2 attracted researcher to investigate its working mechanism. In 2014, Kumar et al.[69] demonstrated for the first time that the introduction of SnF2 into CsSnI3 can reduce Sn vacancies and background carrier densities. Therefore, high JSC of more than 22 mA cm−2 and a PCE of 2.02% were achieved in contrast to the nonfunctioning devices without SnF2. One year later, the same group[59] further investigated the doping effects of SnF2 in FASnI3. The X-ray photoelectron spectroscopy (XPS) data show that only Sn2+ but no Sn3+ appears in the FASnI3: 20% SnF2 sample, indicating that no oxidation side reaction happened inside the doped sample (Figure 7a–d). Moreover, they claimed that the addition of SnF2 improved the environmental stability, as they found that the color of the FASnI3 films with SnF2 remained yellow when left overnight, but change into orange without SnF2 (Figure 7e). The resulting photovoltaic devices gave maximum PCE of 2.10%, with high JSC of 24.45 mA cm−2. Based on the same hypothesis, SnF2 dopant was also introduced to reduce Sn vacancies for efficient and stable CsSnBr3 based PSCs.[74,75] The author has concluded that the SnF2 cannot only improve interfacial energy alignment but also increase stability to electron beam damage. Nowadays, most Sn-based perovskites films prepared by solution deposition need additional SnF2 to get good performance.[47,48,57,58,73] including the recent (FA)0.75(MA)0.25SnI3 based PSCs with the highest PCE of 8.12%. Additionally, Ma et al.[134] claimed that SnF2 as the inhibitor of Sn2+ oxidation in the MASnI3 film could increase the fluorescence lifetime up to 10 times and give longer carrier diffusion lengths >500 nm, compared with pristine MASnI3 films.

SnX2 (X = Cl, Br, I)

Apart from the tin fluoride additives, excess tin halide salts like SnI2 were also believed to improve device stability towards air oxidation. In 2015, Marshall et al.[68] prepared the CsSnI3 films with an excess of SnI2 during CsSnI3 synthesis from CsI and SnI2. They believed that the excess of SnI2 occupies some of the space between adjacent CsSnI3 crystals, hindering the ingress of the oxygen and water so that the barrier of the transformation of CsSnI3 into Cs2CsI6 at the site of a Sn vacancy is increased. The fabricated devices have inverted planar structure of ITO/Cul/CsSnI3 (with or without the excess of SnI2)/C60/BCP/Al. The devices with the excess amount of SnI2 exhibit up to 30% increase in JSC and VOC as compared to the control devices. The devices’ stability is also enhanced in that the PCE of devices with 10 mol% excess SnI2 exhibited only 10% reduction after 10 d period of storage, contrary to the 70% loss with control devices. In 2016, they further demonstrated that excess SnI2 is beneficial to improve both efficiency and stability of CsSnI3-based PSCs.[66] Therefore, their results suggest that the excess amount of SnI2 in the precursor is also an effective

Figure 7. a,b) Top-view FESEM images of FASnI3 and FASnI3:20%SnF2 perovskite films deposited on the mesoporous TiO2 layer. c) Expanded view of the nanoplatelet-like structure found on the surface of FASnI3:30%SnF2. d) Cross-sectional FESEM image of the full device showing individual layers as follows: FTO/TiO2 + FASnI3/spiro-OMeTAD/Au. e) Color change in FASnI3 with and without SnF2 addition and XPS measurement. Reproduced with permission.[59] Copyright 2015, RSC.
strategy to improve the performance of CsSnI$_3$-based PSCs. Similarly, an excess of SnBr$_2$ was also found to reduce the density of defect states or Sn vacancies in all-thermal-vapor deposited CsSnBr$_3$ PSCs by preventing the oxidation of Sn$^{2+}$ to Sn$^{4+}$ in ambient air. The resulted devices obtained a higher $V_{OC}$ of 0.41 V than the previously reported 0.19 V.

It was not until 2016 that a systematic study was made about the effect of different Tin halide salts in resolving the problem of tin vacancies in tin halide perovskites (Figure 8a–f). Focusing on the low fill factor (FF) problem of Sn-based PSCs, Marshall et al. evaluated SnF$_2$, SnCl$_2$ and SnBr$_2$ additives in CsSnI$_3$-based PSCs. Simplified device architecture (ITO/CsSnI$_3$/PC$_{61}$BM/BCP/Al) was fabricated without HTM and the performance of SnCl$_2$ doped CsSnI$_3$ PSC devices was tested without encapsulation in ambient air at a humidity of $\approx$25% under constant 1 sun simulated solar illumination. They showed that the champion stability was exhibited only by devices with a tin halide additive: 11 h with no additive; 16 h with 10 mol% SnCl$_2$; and 22 h for SnI$_2$ (Figure 8g,h). Moreover, SnCl$_2$ as additive offers the advantage of the highest $\eta$ (3.56%), due to reduced sensitivity of device parameters to pin holes when SnBr$_2$ and SnF$_2$ gave $\eta \leq 0.4%$. For the same reason, SnCl$_2$-doped CsSnI$_3$ also showed FF up to 0.69, which is the highest FF among reported tin halide PSCs. They attributed SnCl$_2$ being the best of the tin halide additives to the interplay of three factors. First, the added SnCl$_2$ is distributed toward the surface of the crystallites to form a tin-rich top layer for the perovskites. Second, the greater covalence offers SnCl$_2$ better solubility in common solvents (including DMF) than SnF$_2$. Last, tin chloride diffusion into fullerene (ETL) is easier than other halide analogs. Therefore, SnCl$_2$ can be used as a promising additive to improve the performance of CsSnI$_3$ PSCs and probably any other Sn-based PSCs. Currently, only one report on SnCl$_2$ modified FASnI$_3$ as an inhibitor of Sn$^{4+}$, but poor PCE was achieved.

SnO and Sn(OH)$_2$

Except for the tin halide additives, the presence of SnO and Sn(OH)$_2$ in the MASnI$_3$ film was also found to be beneficial to reduce hole carrier concentration, leading to an improved air stability of the Sn-based perovskite devices. This finding suggests that not only the commonly used tin halide additives but also other divalent Sn compounds could serve as Sn vacancy suppressors assisting the realization of efficient and stable tin-based PSCs.

SnX$_2$/Organic Reduce Agents

The primary cause of the instability of tin-based PSCs is the oxidation of the Sn(II) to Sn(IV). Therefore, it is reasonable to add reductive agents besides divalent tin additives, to further suppress Sn vacancy for more stable lead-free PSCs. As an example, hypophosphorous acid (HPA) (Figure 9a) was introduced into fabricating all-inorganic CsSnIBr$_2$-based mesoscopic PSCs to reduce the concentration of Sn vacancies, achieving a higher PCE of 3.0% than 1.7% of without HPA addition. Moreover, Song et al. introduced hydrazine vapor (reducing vapor atmosphere) in the presence of SnF$_2$ additive into fabrication process of Sn-based PSCs (Figure 9b).
results showed that the additional hydrazine vapor process led to significantly suppressed carrier recombination with more than 20% reduction of Sn⁴⁺/Sn²⁺ ratios. And by tuning amounts of hydrazine vapor properly, the PCEs of MASnI₃ and CsSnI₃ devices were improved from an average of ≈0.02% to 3.40% and ≈0.16% to 1.50%, respectively. Four months later, the same group reported [65] more efficient CsSnI₃ cells with PCE up to 4.81% using the same hydrazine vapor treatment with an excess of SnI₂. In this research, they also studied the optimum ratios of monovalence cations (MA⁺, FA⁺, or Cs⁺) to SnI₂ in the MASnI₃, FASnI₃ and CsSnI₃ perovskite materials, which were 0.4–0.6, 0.6–0.8, and 0.4, respectively. Furthermore, they prepared ASnI₃ devices in a pure N₂ atmosphere for comparison. The results showed that only FASnI₃ could work with VOC > 0.15 V, while the other two devices behaved short-circuit even at the optimum AI/SnI₂ (A: MA⁺, FA⁺, or Cs⁺) ratio that worked in a weak hydrazine vapor atmosphere. This result showed the importance of using reducing agents like hydrazine to suppress SnI₂ from forming Sn⁴⁺ and ensure Sn²⁺-rich environment to compensate the Sn²⁺ vacancies for obtaining effective devices. On the other hand, the phenomenon that only FASnI₃-based devices could survive without additional hydrazine consists with aforementioned results[133,138] where FASnI₃ displayed alleviated self-doping effect possibly due to the competitive formation the hydrogen bonding between H₂O and FA⁺ (Figure 9c–e).

5-Ammonium Valeric Acid Iodide and Ascorbic Acid

In the end, beyond above-mentioned Sn(II) containing panaces, Hoshi et al.[154] claimed that the addition of 5-AVAI in the preparation process could significantly improve the oxidation stability of the MASnI₃ films in the air, due possibly to the formation of (5-AVAI)(CH₃NH₃)₁₋ PbI₃. In addition, ascorbic acid (AA)[155] as a common antioxidant, was also introduced as an effective additive to retard the oxidation of Sn-containing precursor solutions for making Pb/Sn mixed perovskites. It is of great necessity to examine these effects on the pure Sn-based perovskites.

2.1.3.2. Methods to Control the Morphology of the Sn-Based Perovskite Layers: Apart from the divalent tin additives, the film quality of the fabricated perovskite layer is another parameter that controls the final performance of the tin-based PSCs. The film quality mainly refers to the morphology of the perovskite layer, such as homogeneity and coverage, which are strongly influenced by the crystallization process of perovskite film. The conventional one-step film deposition method of tin perovskites often engenders randomly oriented film growth accompanied by forming large crystals platelets and poor surface coverage with micron-sized pinholes.[46] The flawed films further led to the poorly performing devices.[69] Moreover, due to the reaction kinetics between organic/inorganic halide and tin halide salts is faster than its lead analogs,[19,46,156] the control of tin perovskite crystallization during the deposition process is more challenging. Therefore, developing novel preparation methods to achieve high-quality tin perovskite film is of great importance to boost both efficiency and stability of Sn-based PSCs. In lead-based perovskites, the methods for morphology engineering include addition of additives,[157–159] solvent engineering,[160,161] vacuum engineering,[162,163] thermal annealing,[164] self-healing,[165] vapor deposition,[166] and so on. Herein, the reported methods used for preparing high-quality tin perovskite layers are introduced.

Additives for the Morphology Control

Additives such as methyl ammonium chloride (MACl)[157] 1,8-diiodooctane (DIO)[158] and butyl phosphonic acid
4-ammonium chloride (4-ABPACl)\(^{[159]}\) have been successfully used to obtain high-quality perovskite films for high-efficiency lead-based PSCs. In the case of tin perovskite, the popularly used SnF\(_2\) additive for the elimination of the Sn vacancy could result in poor film morphology and bad device performance due to the phase separation of SnF\(_2\) within the perovskite film.\(^{[6,135]}\) In this regard, Lee et al.\(^{[58]}\) introduced pyrazine into FASnI\(_3\) perovskite precursors in conjunction with SnF\(_2\) in the form of the SnF\(_2\)-pyrazine complex (Figure 10a,b). The complex is believed to assist a uniform distribution SnF\(_2\) in the perovskite film, thereby substantially improving the morphology of FASnI\(_3\) perovskite. Finally, the resulted FASnI\(_3\) PSCs achieved a maximum PCE of 4.8\% with high reproducibility (Figure 10c). Besides being a reducing agent, hypophosphorous acid (HPA) can also act as a morphology controller\(^{[73]}\) in the fabrication process of all-inorganic CsSnI\(_3\) mesoscopic PSCs. HPA has the P=O bond that could strongly coordinate with Sn\(^{3+}\), producing HPA-CsSnI\(_3\) clusters via Sn=O=P=O-Sn coordination bonds.\(^{[167]}\) The formed clusters in precursor solution promoted the growth of perovskite crystals and expelled the redundant SnF\(_2\) to the surface of the film. Due to the suppressed SnF\(_2\) phase separation in the CsSnI\(_3\) thin films, the highest reported PCE of \(\approx 3.2\%\) for the all-inorganic Sn-based PSCs was achieved. Likewise, hydrazine\(^{[41,65]}\) was used not only as reducing agent to reduce the oxidation of Sn\(^{2+}\) to Sn\(^{4+}\), but also as modifier asserted by Song et al.\(^{[41]}\) to achieve better film morphologies for enhanced device efficiencies. Unfortunately, there was no explanation of why hydrazine could do a good job in ameliorating perovskite film morphologies. Moreover, a hydrazine atmosphere can help the disperse of SnI\(_2\).\(^{[65]}\)

![Figure 10](image-url)
to improve the quality of perovskite film, as indicated by no observable agglomeration of SnI$_2$ from the SEM/EDS characterization (Figure 10d–i). The corresponding device displayed the best PCE (4.81%) of CsSnI$_3$-based PSCs, which is in the meantime much higher than the SnF$_2$ modified devices (1.83%). Additionally, triethyl phosphate (TEP) as a soft Lewis base can form intermediate complexes with Sn$^{2+}$ species via weak coordinating interaction, which could slow down the perovskite crystallization process and improve the film morphology as well as the device performance. The devices with TEP showed increased FF in average (from 42.0% to 53.7%), and an average PCE from 1.15% to 1.75%, with the champion device reaching ≈2% efficiency (Figure j–n).

**Solvent Engineering**

Solvent engineering technique has been proved many times as the most effective method for preparing high-quality lead perovskite films to achieve high-performance PSCs. The work on solvent engineering of Sn-based perovskite was first reported by Hao et al., where they investigated the solvent effects on the crystallization of the MASnI$_3$ perovskite films. They found that highly uniform, pinhole-free perovskite films can be obtained by using a dimethyl sulfoxide (DMSO) as solvents in perovskite precursor. And the transitional SnI$_2$·3DMSO intermediate phase was very important in achieving a high-quality perovskite film. The heterojunction depleted hole-transporting layer-free solar cells based on mesoporous TiO$_2$ showed a high photocurrent up to 21 mA cm$^{-2}$ and a PCE of 3.15%. Furthermore, Lee et al. used mixed solvents of N,N-dimethylformamide (DMF) and DMSO in FASnI$_3$ precursor solution followed by toluene drop-casting, which led to uniform and dense FASnI$_3$ perovskite layers. The role of DMSO was to retard the crystallization of FAI and SnI$_2$ during spin-coating process (Figure 11a–d). The realized smooth and dense perovskite layer enables a maximum efficiency up to 4.8% for FASnI$_3$-based PSCs and the encapsulated devices kept stable for over 100 d. The same method was also applied in low-dimensional tin halide perovskites (PEA)$_2$(FA)$_9$Sn$_3$I$_{28}$ to obtain compact and smooth perovskite surface morphology. Chlorobenzene, as a common antisolvent applied in lead-based PSCs, was adopted by Zhang et al. as antisolvent to achieve a dense FASnI$_3$Br film giving a device PCE of 1.72%. As an antisolvent, diethyl ether seems to work better than chlorobenzene in improving the morphology of Sn-based perovskites. For example, recently, Liao et al. used diethyl ether as an antisolvent in solvent engineering process to synthesize uniform and hole-free FASnI$_3$ perovskite thin films. The fresh spin-coated films showed a reddish intermediate state after dripping with diethyl ether, which might be crucial for the good film morphology, in contrast to chlorobenzene and toluene-based antisolvents, which led to black films immediately (Figure 11i,j). However, Zhao et al. used chlorobenzene as antisolvent to obtain (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$ and FASnI$_3$ film with complete coverage and no phase separation. The exceptionally good effect of chlorobenzene may be due to the use of different solution solvent. This conjecture needs to be proved by more studies.
Solvent–solvent extraction technique is a derivative method of solvent engineering, which was first proposed by Zhou et al.\cite{168} for the fabrication of high-quality lead perovskite thin films. The same method was applied by Milot et al.\cite{171} in Sn-based perovskites with DFM and DMSO as mixed solvents for perovskite precursor solution. The wet film was immediately immersed into an antisolvent (anisole) after spin-coating, producing a smooth, and continuous FASnI₃ thin film. An appropriate crystallization speed is very important to the morphology of the perovskite films. Very recently, Fujihara et al.\cite{48} employed a mixture of toluene and hexane as the antisolvents and DMSO as the good solvent (Figure 12a). Depending on the ratio of antisolvents and temperature, they can control the crystallization speed of the MASnI₃ perovskite films to achieve high surface coverage perovskite films on a planar PEDOT: PSS electrode (Figure 12b–e). Planar junction devices with the structure of glass/ITO/PEDOT: PSS/MASnI₃/C₆₀/BCP/Ag, exhibited an efficiency of 2.14 ± 0.35% with a high open circuit voltage of 0.45 ± 0.01 V and long lifetime of over 200 h under 1 Sun illumination conditions (AM1.5, 100 mW cm⁻²).

**Vapor Deposition**

Generally, vapor deposition process is known to provide higher controllability over perovskite films fabrication in terms of higher homogeneity, smoothness, and surface coverage than solution-processed films.\cite{166,172} Moreover, the vacuum condition adopted in vapor deposition process is especially beneficial to air-sensitive tin perovskite. In 2015, Weiss et al.\cite{173} proposed a two-step process combining vapor-deposited SnI₂ precursor films and solution deposited MAI for the preparation of MASnI₃ perovskite films. The results showed homogeneous preformed SnI₂ film and complete conversion of SnI₂ to MASnI₃. The final film showed complete surface coverage even with such short contact period (Figure 13a–f). In the same year, smooth MASnBr₃ thin films were synthesized via sequential evaporation by Jung et al.\cite{52} (Figure 13g,h). The obtained planar structure device showed an efficiency of 1.12%. In addition, SnF₂-doped CsSnBr₃ film with excellent ambient air stability was also prepared by sequential vapor deposition method.\cite{75} Later, a hybrid thermal evaporation method at room temperature for the fabrication of high-quality MASnI₃ perovskite thin film was reported by Yu et al.\cite{50} The as-deposited MASnI₃ thin films have excellent morphology, with smooth surfaces, high surface coverage, and strong crystallographic preferred orientation along the <100> direction. Inverted planar architecture solar cells devices were fabricated based on these films and gave an open-circuit voltage up to 494 mV.

**Vapor-Assisted Solution Process**

The so-called vapor-assisted solution process (VASP) was first reported to construct a high-quality MAPbI₃ film by Chen et al.\cite{174} in 2013. To improve tin perovskite surface coverage, Yokoyama et al.\cite{133} developed low-temperature vapor-assisted solution process (LT-VASP), a kinetically control gas-solid

![Figure 12](image1.png)

**Figure 12.** a) Concept illustration for controlling the crystallization speed using the technique of adding a cosolvent in solvent bathing; Scanning electron microscopy (SEM) images for the b) LT-Mix, c) LT-T, and d) LT-H films. The X-ray diffraction spectra for mixed solvent (red), toluene (blue), and hexane (green) are shown in (e). Reproduced with permission.\cite{48} Copyright 2017, RSC.

![Figure 13](image2.png)

**Figure 13.** SEM images of a) 100 nm vapor-deposited SnI₂, nonannealed MASnI₃ perovskite films prepared by spin-coating of b) 6 mg mL⁻¹, c) 10 mg mL⁻¹, d) 20 mg mL⁻¹, e) 40 mg mL⁻¹ MAI solutions, and a f) MASnI₃ perovskite film prepared by use of 20 mg mL⁻¹ MAI and subsequent annealing at 80 °C for 10 min; Reproduced with permission.\cite{52} SEM image of coevaporated g) MASnBr₃ (MABr:SnBr₂ = 4:1) Reproduced with permission.\cite{52} Copyright 2015, RSC and h) MASnI₃. Reproduced with permission.\cite{50} Copyright 2016, RSC.
reaction method, to prepare lead-free \( \text{MASnI}_3 \) thin films. They pointed out that the substrate temperature (60–80 °C window) of preformed solid SnI\(_2\) is very important for achieving homogeneous and high surface-coverage perovskite films. The acquired high-quality \( \text{MASnI}_3 \) films were fabricated in solar cells with an efficiency of 1.86% with good reproducibility. It is important to point out that LT-VASP method is a pioneer work that explored alternative suitable fabrication methods for tin perovskite films (Figure 14a–c).

**Thermal Annealing**

Thermal annealing is a critical step in most of the perovskite film deposition steps. It can influence the film formation of perovskites significantly by driving solid-state coarsening of perovskite grains. An interesting work was done by Wang et al.\(^{[67]}\) involving an all-inorganic and thermally stable B-\(\gamma\)-CsSnI\(_3\) films deposited by spin-coating. The films were postannealed at different temperatures over a range between 100 and 300 °C for 2 min to coarsen the grains. The B-\(\gamma\)-CsSnI\(_3\) thin films annealed at 150 °C displayed large grain size, high film smoothness, and moderate Sn vacancy (\(V_{\text{Sn}}\)) generation, which are responsible for the best performing PSC devices. The B-\(\gamma\)-CsSnI\(_3\) film after 150 °C annealing was applied in an inverted planar device architecture with nickel oxide (NiO\(_x\)) as the photocathode. They achieved a PCE of 3.31% without the use of any additive. This work demonstrated that proper thermal annealing is another efficient method for preparing high-performance Sn-based PSCs (Figure 14d–j).

### 2.1.4. Summary

In summary, as two less toxic family members of Pb, Sn and Ge are deemed as the redeemer to the toxic Pb element and tremendous efforts have been put in optimizing the materials and devices. So far, Sn-based perovskites with lower bandgaps than lead analogs, have obtained a “stable” efficiency up to 6%. In this case, the issue of Sn\(^{2+}\) oxidization has been partly overcome by adding divalent tin halide additives and some reductive reagents. Additionally, the poor morphology of the tin halide perovskite layer has been improved by the various fabrication methods. Recently, great progress has been made in Sn-based PSCs with inverted device architecture;\(^{[28,56,64,66,67]}\) due to the omission of doped HTMs. Unlike Pb-based PSCs where the high efficiencies are usually achieved with doped HTMs, the use of dopants will accelerate the deterioration of tin perovskites. Hence, exploring high-performance and dopant-free HTMs is very important to get efficient and stable Sn-based PSCs. And it is necessary to further study tin-based perovskite material fundamentally (such as the mechanisms of self-doping) and explore novel device structures with different charge selective contact materials toward more efficient and stable Sn-PSCs. For germanium perovskites, the study of these compounds is very rare in the photovoltaic application so far. In this case, due to the relatively small ionic radius of Ge\(^{2+}\), the octahedra \([\text{GeX}_6]^{3–}\) network is heavily distorted, which leads to wide band gap (>1.6 eV). In addition, the poor solubility of these compounds in polar solvents causes terrible morphology with low efficiency of only 0.2% from solution process. It is urgent to find new preparation methods of germanium perovskites for more efficient Ge-based PSCs. Moreover, the easy oxidization of Ge\(^{2+}\) and Sn\(^{2+}\) will be definitely a challenge.

### 2.2. The Group 15 Metals Bi and Sb-Based Absorbers

Beyond group 14 elements, two of group 15 metals in the periodic table, bismuth (Bi) and antimony (Sb) have been also studied for replacing lead in the solar energy absorbing materials. In this section, a brief introduction of typical A\(_3\)Bi\(_2\)X\(_9\), A\(_3\)Sb\(_2\)X\(_9\) (A = MA\(^+\), FA\(^+\), Cs\(^+\), X = F\(^–\), Br\(^–\), Cl\(^–\)) polyhedrons and other derivatives will be given. Compared with Sn-based perovskites, they form more diverse dimensionality in terms of the connection type of Bi\(_X^0\) (Sb\(_X^0\)) octahedrons.\(^{[101]}\) Here we divided them into 0D, 1D, 2D, and 3D structures.
MA3Bi2I9 was reported to be spectroscopy in the air (PESA) [89] and 5.9–6.0 eV by ultraviolet which are all well aligned with the conduction band of TiO2. The structure of MA 3Bi2I9 features two face-sharing 0D perovskite graphs of MBI and MAPbI3 on quartz over time in the ambient air. The stability is owing to the formation of Bi2O3 or BiOI from BiI3, which could serve as a protective layer to prohibit the ingress of water and oxygen into bulk materials.[92] Therefore, on account of its good optoelectronic properties and excellent stability, MA3Bi2I9 is the prevailing candidate materials for replacing lead perovskites in the photovoltaic application.

2.2.1. Bismuth-Based Absorbers

Being adjacent to Pb2+ in the periodic table, Bi3+ has the similar 6s6p3 electronic configuration, which endows MAPbX3 with the strong light absorption and long carrier lifetimes.[176] More importantly, it is much less toxic than Pb,[177,178] and has been used in organic synthesis and medicines.[179–181] Hence, Bi-based perovskite or hybrid materials are attractive options to replace lead perovskites.

2.2.1.1. OD Hybrid Materials: MA3Bi2I9 Hybrid Bismuth Iodides:
Among all the reported bismuth-based absorbers, organic-inorganic hybrid bismuth halide MA3Bi2I9 is the most studied polymorph type. Owing to the tervalence state of Bi3+, the solid structure of MA3Bi2I9 features two face-sharing 0D perovskite structure.[88,182,183] which is constructed by the MA+ surrounded binuclear octahedral (Bi2I9)+ clusters, contrasting to the 3D MAPbI3 perovskite (Figure 15a).

The single crystal of MA3Bi2I9 normally displays color like red wine[89] and has regular hexagonal shape with a diameter ranging from 100 to 200 µm,[87] or even up to 4–5 mm,[89] adopting P63/mmc space group.[88,182,184] The optical bandgap of MA3Bi2I9 was reported to be 1.94–2.26 eV[87–89] with absorption coefficient up to σ = 1 × 105 cm−1, the same order of magnitude with MAPbI3.[185] The valence band maximum (VBM) of the MA3Bi2I9 was measured to be 5.63 eV by photoelectron spectroscopy in the air (PESA)[89] and 5.9–6.0 eV by ultraviolet photoelectron spectroscopy (UPS)[87,89] in vacuum, respectively, which are all well aligned with the conduction band of TiO2. The electron mobility of MA3Bi2I9 single crystal is 29.7 cm2 V−1 s−1 as estimated by the space charge limited conduction (SCLC),[89] which is comparable to that of MAPbI3 (38 cm2 V−1 s−1).[186] The same carrier mobility was estimated to be 1 cm2 V−1 s−1 by Hall Effect.[87] The phase-pure and compact MA3Bi2I9 film showed long PL decay over 0.76 ns, with the bulk lifetime approach to 5.6 ns. And this film exhibited robust air stability than MAPbI3 after 25 d of continuous air exposure with 61% relative humidity (Figure 15b,c). The device yielded highly reproducible PCE of 0.18%–0.2% with a JSC of 0.04 A cm−2, FF of 0.2%, and η of 0.12%. Meanwhile, it is much less toxic than Pb, [177,178] and has been used in organic synthesis and medicines. [179–181] Hence, Bi-based perovskite or hybrid materials are attractive options to replace lead perovskites.

2.2.1.2. Cl-Doped MA3Bi2I9 Films:

The first report on MA3Bi2I9 as light absorbers used in solar cells was by Park et al.[88] They studied the morphology of MA3Bi2I9 and Cl-doped (MA3Bi2I9Cl) films on TiO2 substrate by SEM. The results showed that MA3Bi2I9 based PSCs was improving due to the better morphology with perovskite particles surrounded by amorphous BiCl3. Two months later, Lyu et al.[87] employed poly(3-hexylthiophene-2,5-diyl) (P3HT) as the HTM to replace Spiro-OMeTAD in the MA3Bi2I9-based solar cells with a mesoscopic structure, which showed a PCE of 0.19% (Figure 16b).

It became a comment sense that the performance of MA3Bi2I9-based PSCs was improving due to the better morphology of the absorber layer. Singh et al.[86] deposited uniform MA3Bi2I9 layers atop mesoporous anatase TiO2 and exhibited best PCE of 0.2%, as well as 10 weeks stability of the device in ambient condition. Zhang et al.[187] used smooth indium tin oxide (ITO)/glass substrate to achieve a dense MA3Bi2I9 thin film, which gave a maximum PCE of 0.42% and high FF up to 0.64. This is one of the highest performances among MA3Bi2I9-based lead-free PSCs.

More efforts have been paid to modulate the morphology of MA3Bi2I9 perovskites. For example, 1-methyl-2-pyrrolidinone (NMP)[85] as morphology controller was added into the MA3Bi2I9–DMF precursor solution, producing a homogeneous film of MA3Bi2I9. The device yielded highly reproducible PCE of 0.31% and kept stable for 30 d in an ambient atmosphere (relative humidity of 50–60%). On the other hand, antisolvent assisted crystallization (ASAC) method also was used to improve MA3Bi2I9 thin films like the cases in the lead- and tin-based PSCs. Abukilik et al.[89] first used this method, but gave a PCE of only 0.11%. Very recently, Mali et al.[84]
achieved cuboid-shaped crystals of MA$_3$Bi$_2$I$_9$ on the surface of mesoporous TiO$_2$ by this method. The obtained thin film had excellent air stability with almost no color change even after two month exposure to air. The best solar cell devices made from this kind of films exhibited a PCE of 0.36%, with no substantial efficiency loss after 60 d. Gas-assisted deposition method was first reported by Huang et al.[188] to create uniform and dense lead perovskite thin films. Naturally, this method was used[90] to improve the quality of MA$_3$Bi$_2$I$_9$ films. Ultimately a PCE of merely 0.08% was obtained, which is 17% higher compared with the conventional one-step method. Besides the common n–i–p-type devices, the first p–i–n planar heterojunction device of MA$_3$Bi$_2$I$_9$ perovskite was reported by Öz et al. [91] with PCE of ≈0.1%. To achieve a smooth, uniform, and compact MA$_3$Bi$_2$I$_9$ film in the p–i–n device structure, Ran et al.[83] reported a two-step (evaporation and spin-coating) process of MA$_3$Bi$_2$I$_9$ and obtained a PCE of 0.39% and $V_{OC}$ as high as 0.83 V, which is the highest $V_{OC}$ among MA$_3$Bi$_2$I$_9$-based solar cells so far (Figure 16d).

Sulfur-Doped MA$_3$Bi$_2$I$_9$: Sulfur-doped MA$_3$Bi$_2$I$_9$ was developed[93] to reduce bandgap of MA$_3$Bi$_2$I$_9$ (2.1 eV), which is relatively higher for the ideal single junction solar cell.[129] Sulfur-doped bismuth perovskites were obtained by in situ sulfur doping of MA$_3$Bi$_2$I$_9$ perovskite by Öz et al.[91] with PCE of ≈0.1%. To achieve a smooth, uniform, and compact MA$_3$Bi$_2$I$_9$ film in the p–i–n device structure, Ran et al.[83] reported a two-step (evaporation and spin-coating) process of MA$_3$Bi$_2$I$_9$ and obtained a PCE of 0.39% and $V_{OC}$ as high as 0.83 V, which is the highest $V_{OC}$ among MA$_3$Bi$_2$I$_9$-based solar cells so far (Figure 16d).

$\text{(BiI}_3\text{)}_{0.8}(\text{MA}_3\text{Bi}_2\text{I}_9\text{)}_{0.2}$: One of the problems with MA$_3$Bi$_2$I$_9$ is that its bandgap is even wider than that of BiI$_3$ (1.8 eV). Therefore, to improve light absorption of MA$_3$Bi$_2$I$_9$, Lan et al.[94] designed active composite layers taking advantages of optoelectronic properties of BiI$_3$[190–193] and suitable energy level alignment of MA$_3$Bi$_2$I$_9$ with TiO$_2$ (Figure 17b). When 20% of MA$_3$Bi$_2$I$_9$ perovskite was introduced into the active layers, the $\text{(BiI}_3\text{)}_{0.8}(\text{MA}_3\text{Bi}_2\text{I}_9\text{)}_{0.2}$ solar cells displayed improved $V_{OC}$ from 0.44 to 0.57 V, with a PCE of 0.08%.

$\text{A}_3\text{Bi}_2\text{I}_9$ (A: Cesium, Formamidinium, Imidazolium, Cyclohexyl Ammonium): Replacing MA with formamidinium (FA), the FA$_3$Bi$_2$I$_9$[95] exhibits the same structure as MA$_3$Bi$_2$I$_9$, with a bandgap of 2.0 eV. Additionally, when more bulky cations like imidazolium and cyclohexyl ammonium are used as the A cation, 0D perovskite-like structure are formed. The synthesized (C$_3$H$_5$N$_2$)$_3$[Bi$_2$I$_9$][96] has two temperature induced solid–solid structural phase transition, and (C$_6$H$_{14}$N)$_3$Bi$_2$I$_9$[97] has red emissions at room temperature. All-inorganic bismuth halide compounds have also been studied to replace lead perovskites in PSCs. Cs$_3$Bi$_2$I$_9$ as a light harvester was first studied by Park et al.[88] with face-sharing octahedra dimer ((Bi$_2$I$_9$)$_3^-$, P6$_3$/mmc space group, 0D structure) similar to MA$_3$Bi$_2$I$_9$. It possesses a bandgap of 2.2 eV close to MA$_3$Bi$_2$I$_9$ (2.1 eV). A detailed study of its band gap structure was shown by Zhang et al.[194] Compared with MA$_3$Bi$_2$I$_9$ and MA$_3$Bi$_2$I$_9$Cl$_x$, Cs$_3$Bi$_2$I$_9$ displays a

Figure 16. a) Large 70 mm thick single crystal of (CH$_3$NH$_3$)$_3$Bi$_2$I$_9$ grown on the ITO substrate. Reproduced with permission.[89] Copyright 2016, RSC. J–V curve of b) the P3HT based n–i–p device. Reproduced with permission.[87] Copyright 2016, Springer. And c,d) p–i–n devices. c) Reproduced with permission.[91] Copyright 2016, Elsevier. d) Reproduced with permission.[83] Copyright 2017, ACS.
relatively high PL yield, suggesting low losses in nonradiative recombination. Consequently, the best Cs$_3$Bi$_2$I$_9$-based solar cell shows a PCE of 1.09% ($V_{OC} = 0.85$ V, $J_{SC} = 2.15$ mA cm$^{-2}$, and $FF = 0.6$) (Figure 17c).

2.2.1.2. 1D Hybrid Materials: MA$_3$Bi$_2$Cl$_9$: MA$_3$Bi$_2$Cl$_9$\cite{98} is a 1D organic–inorganic hybrid bismuth compound with zig-zag double chains of distorted BiCl$_6^{3-}$-octahedra structure. The past studies of MA$_3$Bi$_2$Cl$_9$ focused mainly on structural phase transition, which revealed two-phase transitions\cite{195} at $T_{c1} = 349$ K and $T_{c2} = 247$ K, respectively.

(H$_3$NC$_6$H$_12$NH$_3$)BiI$_5$ and (TMP)BiX$_5$: 1,6-hexane diammonium bismuth halide (H$_3$NC$_6$H$_12$NH$_3$)BiI$_5$ (HDABiI$_5$) showing 1D chains structure has early been reported by Mousdis et al.\cite{196} and Mitzi et al.,\cite{197} respectively (Figure 18a,b). Owning an optical bandgap of $\approx 2.0$ eV, Fabian and Ardo\cite{198} first applied HDABiI$_5$ as a light absorber in PSCs. HDABiI$_5$ layer had near-complete surface coverage on mesoporous TiO$_2$. The low volatility of organic 1,6-hexane diamine group endowed HDABiI$_5$ with good thermal stability up to 200°C. However, the final PCE of the device was only 0.027%. TMP (N,N,N',N'-tetramethylpiperazine) can also be used as organic cation and yielded (TMP)BiX$_5$ (X = Cl, Br, I) with 1D chains structure and optical band gaps of 2.02–3.21 eV.\cite{101}

C$_5$H$_6$NBiI$_4$ and C$_6$H$_8$NBiI$_4$: Another two 1D chained organic–inorganic iodobismuthates, C$_5$H$_6$NBiI$_4$ ([py][BiI$_4$]) (py: pyridinium) and C$_6$H$_8$NBiI$_4$ ([mepy][BiI$_4$]), (mepy: methyl pyridinium) were prepared by Li et al.\cite{102} and applied in HTM-free PSCs with mesoscopic anode and carbon counter electrode (Figure 18c,d). They pointed out that the protonated aromatic heterocycles play an active role in intermolecular interactions through the frontier orbitals, which endows them with pseudo-3D charge transfer ability. [py][BiI$_4$] and [mepy][BiI$_4$] have bandgap of 1.98 and 2.17 eV, respectively. The best device efficiency of 0.9% was obtained using [py][BiI$_4$], which is comparable with that of other reported Bi–iodide based devices\cite{83,88,187} (Figure 18e).

2.2.1.3. 2D Hybrid Materials: A$_3$Bi$_2$I$_9$ (A: K$^+$, Rb$^+$, NH$_4^+$): By replacing the Cs$^+$ in typical 0D Cs$_3$Bi$_2$I$_9$ perovskite with K$^+$ and Rb$^+$, K$_3$Bi$_2$I$_9$ and Rb$_3$Bi$_2$I$_9$\cite{36} are achieved. The decreased size of cations induces 2D layered defect-perovskite structure, with corrugated layers of Bi–I octahedra. K$_3$Bi$_2$I$_9$ and Rb$_3$Bi$_2$I$_9$ have direct bandgaps of 2.1 eV, while Cs$_3$Bi$_2$I$_9$ has an indirect bandgap of 1.9 eV (Figure 19a). Lehner et al. pointed out that direct gaps coupled with the high DOS with a strong p-character across the gap are criteria for effective light absorption. Besides, substituting MA cation for NH$_4^+$ cation in MA$_3$Bi$_2$I$_9$, Sun et al.\cite{103} achieved a 2D layered perovskite-like architecture (NH$_4$)$_3$Bi$_2$I$_9$, with a dark red color and a bandgap of 2.04 eV. But no device study was provided in these reports (Figure 19c).

A$_3$Bi$_2$Br$_9$ (A: MA, Cs): Besides the change of A cations, when the halide atom is changed to Br$^-$, one can change the typical 0D Cs$_3$Bi$_2$I$_9$ to 2D layered perovskites. For example, MA$_3$Bi$_2$Br$_9$\cite{102} crystallizes into trigonal symmetry ($P\overline{3}$m1) space group, forming corrugated layers of BX$_6$ octahedra (Figure 19b). MA$_3$Bi$_2$Br$_9$ possesses a direct bandgap of 2.5 eV\cite{100} and emits at 430 nm as quantum dots with photoluminescence quantum yield (PLQY) up to 12%. Another layered inorganic halide bismuth compound, Cs$_3$Bi$_2$Br$_9$ was reported by Bass et al.\cite{199} It occupies the 2D structure, with corrugated layers of corner-sharing BiBr$_6^{3-}$ octahedra, as illustrated in Figure 19d, different from iodine analogs with 0D structure. Cs$_3$Bi$_2$Br$_9$ has a large exciton binding energy of 940 meV, which is indicative of a strongly localized character and resulted in highly structured...
emission. However, this large exciton binding energy will extremely limit its application in photovoltaic technologies, particularly as a light harvester.

CsBi$_3$I$_{10}$ Johansson et al.\cite{100} reported another type of cesium bismuth iodine compound CsBi$_3$I$_{10}$. In contrast to previously reported Cs$_3$Bi$_2$I$_9$, CsBi$_3$I$_{10}$ has a different orientation of crystal growth, which may explain a more uniform and smoother coverage on TiO$_2$. CsBi$_3$I$_{10}$ film possesses a smaller bandgap of 1.77 eV and higher absorption coefficients up to $1.4 \times 10^5$ cm$^{-1}$, which are advantageous to PV application, compared with the bandgap of Cs$_3$Bi$_2$I$_9$ at 2.03 eV and absorption coefficients of $7 \times 10^4$ cm$^{-1}$ (Figure 19e). For the same reason, this material was also used in a red-light photodetector recently.\cite{200} The PV device with a structure of glass/FTO/compact TiO$_2$/mesoporous TiO$_2$/CsBi$_3$I$_{10}$/P3HT/Ag, showed a PCE of 0.4%, with a notable $J_{SC}$ of 3.4 mA cm$^{-2}$. This work proved the possibility to further...
increase light absorption and photocurrents in bismuth halide absorbers based solar cells.

\(\text{(TMP)}_{1.5}[\text{Bi}_2\text{I}_6\text{Cl}_2]\): It is interesting that \(\text{(TMP)}[\text{Bi}_2\text{I}_6]\) with one kind of halide species show 1D chain structure, while the addition of Cl leads to the formation of \(\text{(TMP)}_{1.5}[\text{Bi}_2\text{I}_6\text{Cl}_2]\) with a 2D structure.\(^{[101]}\) It has an optical bandgap of 2.10 eV and improved electrical conductivity of \(2.37 \times 10^{-6} \text{ S cm}^{-1}\). Moreover, it displayed efficient photocconductivity response and very high stability either in humid air or long-time irradiation in a simple device.

### 3.2.1.4. 3D Hybrid Materials (Double Perovskites)

The organic–inorganic hybrid bismuth perovskites mentioned above are all low dimensional structures with PSCS efficiency of only \(\approx 1\%\). To realize the 3D perovskite architecture which has demonstrated advantages for high efficiency in lead perovskites, double perovskite with 3D structure was developed. Incorporating a monovalent metal into bismuth perovskites could yield a 3D double perovskite with the chemical formula of \(\text{A}_2\text{Bi}_x\text{B}_y\text{X}_6\). Double perovskites usually exhibit a high tolerance to defects owing to the strong ionic nature of the constituents and 3D structure similar to organolead halide perovskites.\(^{[201]}\) But they usually have large bandgaps that prevent absorption of the whole solar spectrum.\(^{[38,109,202,203]}\)

\(\text{MA}_2\text{Bi}^{11/4}\text{X}_6\) \((\text{X}: \text{I}, \text{Br}, \text{Cl}; \text{B}: \text{Tl}, \text{K}, \text{Ag})\): Early in 2015, Giorgi et al.\(^{[175]}\) proposed double-perovskite structure \(\text{MA}_2\text{TiBiI}_6\) computationally, by substituting \(\text{Pb}^{2+}\) with \(\text{Tl}^{3+}\) and \(\text{Bi}^{3+}\) from parental \(\text{MAPbI}_3\), but stayed in theory because monovalent metal \(\text{Tl}\) is toxic. As a compromise, the toxic thallium can be replaced by other monovalent metals like potassium. Therefore, organic–inorganic hybrid double-perovskite \(\text{MA}_2\text{KBiCl}_6\) was first synthesized by Wei et al.,\(^{[104]}\) which is solution processed but with a bandgap of 3.04 eV similar to that of the prototypical \(\text{MAPbCl}_3\) perovskite. Because its bandgap is too large to be used for the photovoltaic application. They\(^{[105]}\) finally turned to \(\text{MA}_2\text{TiBiI}_6\), which is isostructural with \(\text{MAPbI}_3\). \(\text{MA}_2\text{TiBiBr}_6\) shows a long PL decay of 660 ns at room temperature (Figure 20g–i). The bandgaps of double perovskites were between 1.95 and 3.04 eV, which were too wide to be used as absorbers in single junction photovoltaic cells. To lower bandgap, Slavney et al.\(^{[111]}\) incorporated \(\text{Tl}^{3+}\) as a dilute impurity into \(\text{Cs}_2\text{AgBiBr}_6\), achieving an opaque black octahedral perovskite crystals \(\text{Cs}_2(\text{Ag}_{1-x}\text{Bi}_x)\text{Ti}_6\text{Br}_{16}\) \((0.003 < x = a + b < 0.075)\) with very stable structure. The \(\text{Ti}\)-doped compounds \(\text{Cs}_2(\text{Ag}_{1-x}\text{Bi}_x)\text{Ti}_6\text{Br}_{16}\) displayed low bandgap down to 1.40 eV (indirect) and 1.57 eV (direct) when \(x = 0.075\), which is competitive with that of \(\text{MAPbI}_3\).\(^{[16]}\) Moreover, time-resolved photocconductivity measurements showed that the \(\text{Ti}\)-doped materials had long-lived carriers up to microseconds, though shorter than that of \(\text{Cs}_2\text{AgBiBr}_6\) due to the extra doping of \(\text{Ti}\). This study demonstrated the first double perovskite that has comparable bandgap and carrier lifetime to those of \(\text{MAPbI}_3\), but regrettably, there was still toxic \(\text{Tl}\) in the compounds (Figure 20l). Additionally, through alloying of trivalence \(\text{In}^{11/4}\)/\(\text{Bi}^{11/4}\) into \(\text{Cs}_2\text{AgBiBr}_6\), the bandgap of double perovskite \(\text{Cs}_2\text{AgBiI}_{1-x}\text{Br}_x\) can be modulated. For example, when \(x = 0.11\) and \(x = 0.37\), \(\text{Cs}_2\text{Ag}(\text{Bi}_{0.625}\text{I}_{0.375})\text{Br}_6\) had a bandgap 1.86 eV, which is lower than the previous ternary compound.

To obtain an absorber with a direct bandgap, Volonakis et al.\(^{[113]}\) replaced \(\text{Bi}\) with \(\text{In}\) and calculated the band structure of \(\text{Cs}_2\text{InX}_6\) \((\text{X}: \text{Cl}, \text{Br})\) by first-principles calculations. The combined experiments identified that \(\text{Cs}_2\text{InAgCl}_6\) has a direct bandgap of 3.3 eV. The potential of \(\text{A}_2\text{B'}\text{X}_6\) type double perovskites for PV application was further studied by theoretical methods,\(^{[105,202,204]}\) and focus was put on \(\text{A}_2\text{In}^{11/4}\text{Bi}^{11/4}\text{X}_6\) perovskites. For example, Zhao et al. proposed \(\text{Cs}_2\text{InBiCl}_6\) and \(\text{Cs}_2\text{InBiSbCl}_6\) with low direct bandgaps \(\approx 1\) eV by HSE+SOC calculation.\(^{[204]}\) However, Xiao et al.\(^{[205]}\) used a combination of theoretical and experimental study to show that \(\text{Cs}_2\text{InBr}_6\) and \(\text{Cs}_2\text{InSbCl}_6\) were unstable due to spontaneous oxidation of In\(^{3+}\) into In\(^{4+}\). Lately, Volonakis et al.\(^{[206]}\) proposed the rule of designing a useful double perovskite material: mimicking the electronic structure of \(\text{MAPbI}_3\). To stabilize the double perovskite of \(\text{A}_2\text{In}^{11/4}\text{Bi}^{11/4}\text{X}_6\), they suggested the use of mixed-A-site-cation double perovskite \((\text{Cs}/\text{MA}/\text{FA})\text{InBr}_6\) rather than all-inorganic double perovskites. Although their attempts to synthesize \(\text{MA}_2\text{InBiBr}_6\) and \(\text{FA}_2\text{InBiBr}_6\) were failed, more efforts are needed to explore the suitable composition of the cations.

Among the reported double-perovskites, \(\text{Cs}_2\text{AgBiBr}_6\) is the only one that was applied in a working device. Very recently, Greul et al.\(^{[116]}\) prepared phase pure \(\text{Cs}_2\text{AgBiBr}_6\) films with a optimal post-annealing temperature of 285 °C. The corresponding mesoscopic devices displayed an incredible maximum PCE of 2.43%, with \(\text{J}\text{SC} = 3.93 \text{ mA cm}^{-2}\), \(\text{V}\text{OC} = 0.98 \text{ V}\) and \(\text{FF} = 0.63\). Moreover, stability of \(\text{Cs}_2\text{AgBiBr}_6\)-based devices was tested under constant illumination at ambient conditions during 100 min. This work suggested the potential of double-perovskites as lead-free alternatives to \(\text{MAPbI}_3\).
Figure 20. a) Single-crystal structure of AgBi₂I₇ cubic structure six-coordinated silver-iodide octahedron sites. b) Tauc plot of AgBi₂I₇ from the UV/Vis spectroscopy to determine $E_g$ under the assumption of a direct bandgap. c) $J$–$V$ curves in the dark and illumination under 100 mW cm$^{-2}$ AM 1.5 G. Reproduced with permission.[114] d) Single-crystal structure of Cs₂AgBiBr₆; Photograph of the single crystal; The Bi$^{3+}$ face-centered-cubic sublattice, consisting of edge-sharing tetrahedra. e) Absorbance spectrum of Cs₂AgBiBr₆ powder; f) Time-resolved room-temperature PL and fits for the PL decay time (τ) in powder and single-crystal samples. Reproduced with permission.[138] Copyright 2016, ACS. g) Refined crystal structure of Cs₂AgBiCl₆; Diffuse reflectance spectra for h) Cs₂AgBiBr₆ and CH₃NH₃PbBr₃ and i) Cs₂AgBiCl₆ and CH₃NH₃PbCl₃; Reproduced with permission.[109] Copyright 2016, Springer. Crystal structure of (j) (MA)$_2$AgBiBr₆; Reproduced with permission.[106] Copyright 2017, Springer. And k) (MA)$_2$TlBiBr₆; l) Photographs of Cs₂AgBiBr₆ and Cs$_2$(Ag$_{1-a}$Bi$_{1-b}$)Tl$_x$Br$_6$ ($x = a + b = 0.075$) single crystals and change of absorption onset. Reproduced with permission.[111] Copyright 2017, ACS.
AgBi\textsubscript{2}I\textsubscript{7} and Ag\textsubscript{2}BiI\textsubscript{5}: Besides double-perovskites, Kim et al.\cite{114} synthesized AgBi\textsubscript{2}I\textsubscript{7} with cubic phases composed of vacancy-free corner-sharing bismuth iodide hexahedra and silver iodide octahedra. (Figure 20a–c) They fabricated dense, smooth, and pinhole-free AgBi\textsubscript{2}I\textsubscript{7} thin films with 200–800 nm large grains after annealing at 150 °C. The AgBi\textsubscript{2}I\textsubscript{7} film absorbs light across the range from 350 to 750 nm, with an $E_g$ value of 1.87 eV. They applied it in solar cells and the best AgBi\textsubscript{2}I\textsubscript{7}-based device had a PCE of 1.22% and showed good stability with only 8% PCE reduction over 10 d under ambient conditions. From solutions with different ratios of AgI and BiI\textsubscript{3} (AgI/BiI\textsubscript{3} = 2:1), Zhu et al. got a new crystal structure of Ag\textsubscript{2}BiI\textsubscript{5} with a space group of R\textsuperscript{3} m.\cite{115} The Ag\textsubscript{2}BiI\textsubscript{5}-based devices showed a maximum IPCE of 45% and a promising PCE above 2%. The results show the potential of finding new lead-free absorbers and the possibility to tune the properties of bismuth halides by adding a different ratio of precursors.

2.2.2. Antimony-Based absorbers

Antimony (Sb) is on the top right-hand corner of lead in the periodic table, and its trivalent cation possesses a similar electronic configuration with divalent Pb\textsuperscript{2+}. Antimonial compounds have been studied and used as therapeutic agents for human leishmaniasis and demonstrated low toxicity with appropriate regulations.\cite{207,208} Hence, Sb is expected to be a nontoxic alternative to lead as well. Due to the high oxidation state (+3), Sb\textsuperscript{3+}-based halides have crystal structures of low dimensionality with the typical chemical structure $A_3Sb_2X_9$, forming in dimer structure or layered structures.\cite{119,209}

$Cs_3Sb_2I_9$: Depending on the synthesis conditions, $Cs_3Sb_2I_9$ forms completely different solid structure. From solution preparation, $Cs_3Sb_2I_9$ preferentially forms 0D structure with isolated dimers of face sharing octahedrons (space group $P6_3/mmc$, no. 194) similar to that of $Cs_3Bi_2I_9$. While from solid-state or gas-phase reactions, it forms 2D layered structure ($P\overline{3}m1$, no. 164) (Figure 21a,b). In 2015, Saparov et al.\cite{119} reported preparation and characterization of $Cs_3Sb_2I_9$ thin films, and the first solar cell using $Cs_3Sb_2I_9$ as light absorbers. The prepared $Cs_3Sb_2I_9$ derivative from two-step deposition approach has a layered structure and shows large grains above 1 µm. The layered $Cs_3Sb_2I_9$ film shows red color as opposed to the orange color of the 0D $Cs_3Sb_2I_9$. The film has a bandgap of 2.05 eV, high absorption coefficients up to $10^5$ cm\textsuperscript{-1}, an ionization energy of 5.6 eV, and better stability in ambient air than MAPbI\textsubscript{3} films.

![Figure 21](image-url).

Figure 21. a) Removal of every third Sb layer along the $\langle 111 \rangle$ direction of a) the perovskite structure results in b) the 2D layered modification of $Cs_3Sb_2I_9$; c) Bandgap of the layered modification of $Cs_3Sb_2I_9$ (inset shows a thin film) using the Tauc relation. Reproduced with permission.\cite{119} Copyright 2015, Springer. d) Schematic showing the influence of the cation size on the structure of $A_3Sb_2X_9$; e) $J$–$V$ curve under forward and reverse scans of the best device with the energy levels of $Rb_3Sb_2I_9$ shown in inset; Reproduced with permission.\cite{35} Copyright 2016, Springer. f) Crystal structure of $(CH_3NH_3)_3Sb_2I_9$; g) Comparison of the absorption coefficient of various Bi-based perovskites and $(CH_3NH_3)_3Sb_2I_9$ determined by PDS measurements; h) $J$–$V$ curve of $(CH_3NH_3)_3Sb_2I_9$ solar cell measured with “up” and “down” sweep with a rate of 0.1 V s\textsuperscript{-1}. Reproduced with permission.\cite{117} Copyright 2016, ACS.
structures via solution processing (Figure 21d). They compared dimer type 0D structure when obtained via a solution process. Compared to the pristine films, with an absorption coefficient $3(AgSb2I9)3$0D dimer structure, with octahedral anionic metal halide units PEDOT: PSS/absorber/PC61BM/ZnO-NP/Al, which showed a significant ($\eta$) absorption spectrum contrasting with the related Bi compounds. The Urbach tail energy of this amorphous compound is $\approx 40$ to $200 \, °C$, which is beneficial for operating in a solar cell. Additionally, they obtained a near ideal stoichiometry $RbSb2I4$ film with a single 3+ oxidation state of $Sb$ by an excess $SbI3$ treatment method. The perovskite films with the $SbI$ treatment showed better coverage compared to the pristine films, with an absorption coefficient of $>1 \times 10^3 \, cm^{-1}$ and an indirect bandgap of $2.1 \, eV$. The solar cells based on $RbSb2I4$ with poly-TPD as HTM exhibited $JSC \approx 2.11 \, mA/cm^2, VOC = 0.55 \, V$ and a PCE of 0.66% (Figure 21e).

$MA3Sb2I9$: Unlike inorganic $RbSb2I4$ and $CsSb2I4$, which tend to form different structures (layered or dimer) depending on the crystallization conditions, when organic cation $MA^+$ is used, the hybrid antimony-based perovskites $MA3Sb2I9$ only forms 0D dimer structure, with octahedral anionic metal halide units ($Sb2I9)^-$ surrounded by ($MA^+$) cations $^{(210)}$ (Figure 20f). $MA3Sb2I9$ used in the photovoltaic application was first reported by Hebig et al.$^{(117)}$ They prepared flat and homogeneous thin films of $MA3Sb2I9$ by a two-step spin-coating process followed by toluene treatment. The $MA3Sb2I9$ thin film shows a peak absorption coefficient ($\alpha$) above $10^5 \, cm^{-1}$ and an optical bandgap of 2.14 eV. Additionally, they found that the $Sb$-perovskite showed no exciton peak and low dimensional structure with low efficiency. $Sb3$ has the poor morphology of Bi-based perovskite, which might originate from the preferred tendency to form regular hexagonal crystalline phase. Thus, two main strategies may be used by the community to construct ideal high-efficiency Bi-based PSCs: (i) compositionally engineered bismuth perovskite with 3D electronic structure and therefore low bandgap and (ii) new film fabrication methods which are suitable for Bi-based perovskite. At the same time, the development of $Sb3$-based perovskites is still in its infancy. Owing to the trivalence oxidation state similar with $Bi3$, $Sb3$-based perovskites also have wide bandgap and low dimensional structure with low efficiency. $Sb3$-based perovskite has deep level defects (versus shallow levels in MAPbI3$^{(211)}$), which is extremely detrimental to solar cells performance. Besides, $Sb3$-based perovskites ($CsSb2I4, RbSb2I4$) are prone to form in 0D dimer structure with poor charge transport when they are prepared via a solution process, which is also disadvantageous to high-efficiency solar cells. Though these research results on the photovoltaic performance are unsatisfactory, they paved the way to lead-free halide hybrid absorbers for photovoltaic applications. The dimensionality variation of bismuth and antimony-based absorbers is shown in Table 2.

2.3. Copper-Based Perovskites

Copper (Cu), one of the first-row transition metals, is essential in the human body as part of enzymes, and also could be applied in medical research and clinical practice for radiotherapy of cancer cell.$^{[215]}$ Hence Cu is relatively environmentally friendly, which is also used as a plain conductor in our...
Table 2. Dimensionality variation of bismuth and antimony-based absorbers.

| B Cation | 0D | 1D | 2D | 3D |
|----------|----|----|----|----|
| Bismuth  |    |    |    |    |
| Cs3Bi2I9 | MA3Bi2I9 | FA3Bi2I9 | (C3H5N2)3Bi2I9 | (C6H14N)3Bi2I9 |
|          | MA3Bi2Cl9 | (H3NC6H12NH3)BiI5 | C5H6NBiI4 | C6H8NBiI4 |
|          | (TMP)BiX5 (X = Cl, Br, I) | | | |
| Antimony |    |    |    |    |
| Cs3Sb2I9 | MA3Sb2I9 | [CH3SC(NH2)2]2SbA5 | Cs4CuSb2Cl12 | |
|          | Rb3Sb2I9 | (NH4)3Sb2I _9−_ xBr9 | Cs2AgBiCl6 | |
|          | MA2Sb2I9 | | Cs2AgBiBr6 | |
|          | | | Cs2(Ag1−aBi1−b)Tl_xBr6 | |
|          | | | Cs2Bi0.625Sb0.375Br6 | |
|          | | | Cs2InAgCl6 | |
|          | | | MA2TlBiBr6 | |
|          | | | MA2TlBiI6 | |
|          | | | MA2AgBiCl6 | |
|          | | | AgBi2I7 | |
|          | | | C$_2$AgBiCl6 | |
|          | | | C$_2$AgBiBr6 | |
|          | | | C$_2$AgBi(Tl0.5Bi0.5)Br6 | |
|          | | | Cs$_2$InAgCl$_6$ (non-Bi) | |
| a)Transformed. | | | | |

daily life. Unlike conventional Pb-based perovskites with 3D structure, Cu-based perovskites usually form 2D layered structure, due to its smaller ionic radii. Their general formula is (RNH$_3$)$_2$CuX$_4$, where R-NH$_3^+$ is aliphatic or aromatic ammonium cation and X is a halogen.$^{[122]}$ Cu$^{2+}$ with an electronic configuration of 3d$^9$ (t$_{2g}^6$ e$_g^3$), is more stable in the air than other two divalent Sn$^{2+}$ and Ge$^{2+}$ (Figure 22a). In 2015, Cui et al.$^{[122]}$ synthesized two cupric bromide hybrid perovskites, ($p$–F–C$_6$H$_5$C$_2$H$_4$–NH$_3$)$_2$CuBr$_4$, and (CH$_3$CH$_2$)NH$_3$CuBr$_4$, with absorption from 300 to 750 nm and studied their photovoltaic performance. This is the first report on Cu-based PSCs and showed PCEs of 0.51% and PCE of 0.63%, respectively. Both devices exhibited good air stability with less than 5% decrease of the efficiencies after 1 d in the air with humidity of 50% without encapsulation. Later, Cortecchia et al.$^{[39]}$ reported Cl-doped MA$_2$CuBr$_4$ perovskites, and found that the Cl was essential for stabilizing MA$_2$CuCl$_x$Br$_{4−x}$ perovskites against copper reduction and enhancing the perovskite crystallization. By tuning the Br/Cl ratio, the optical absorption can be adjusted and extended to the near-infrared. Further optimizing the infiltration of mesoporous TiO$_2$ by 2D copper perovskites yielded a PCE of 0.017% using MA$_2$CuCl$_2$Br$_2$ as the light harvester (Figure 22b). Moreover, Li et al.$^{[123]}$ claimed the syntheses of a highly stable C$_6$H$_4$NH$_2$CuBr$_2$I compound by equimolar reaction of hydrophobic C$_6$H$_4$NH$_2$I (2-indoaniline) with low-toxic CuBr$_2$. The XRD patterns of the C$_6$H$_4$NH$_2$CuBr$_2$I thin film showed almost no change after 4 h of immersion in water, and the printable mesoscopic solar cell based on carbon back-contact achieved the best PCE of 0.46% (Figure 22c). The low device performance is due to low absorption coefficient (<10$^5$ cm$^{-1}$),$^{[39]}$ anisotropic charge transport in low-dimensional structure and heavy mass of the holes. Moreover, the existence of Cu$^{2+}$ reduction could introduce higher trap density, which is unfavorable to photovoltaic performance.

3. Conclusion and Outlook

We have thoroughly reviewed a series of lead-free halide hybrid absorbers with various metallic cations including Sn, Ge, Bi, Sb, and Cu etc. in the context of solar cells application. It has been proved that the variation of halide elements in the X position of a typical perovskite material will change the $E_g$ significantly and the trend follows the electronic negativity of the
halide ions. Similarly, the variation of A cations also influences the $E_g$ in various ways depending on the type of central metal ion (Figure 23a). In the case of lead halide perovskite, the $E_g$ is decreasing with the increase of radii of A cations. However, in the case of Ge halide perovskite, the trend is reversed with CsGeI$_3$ has the smallest $E_g$. For Sb and Bi-based absorbers, the lowest $E_g$ appears when Cs$^+$ is used as the A cation. The $E_g$ will increase no matter the radii of A cation are larger or smaller than Cs$^+$. This phenomenon may be due to the change in the dimensionality of the material. In the case of Sn-based material, MASnI$_3$ has the lowest $E_g$. Among all the metal cations under study, Sn perovskite has the lowest $E_g$ while Ge perovskite gives the highest $E_g$. The differences in $E_g$ reflect directly in the short current density ($J_{SC}$) of the corresponding devices. As can be seen from Figure 22b, Sn-based perovskites provide the highest $J_{SC}$ while materials based on Bi and Sb yield the lowest $J_{SC}$ due to the low dimensionality and wide $E_g$. A comparison of the device performance between different lead-free absorbers is visualized in Figure 23c. It is clear that there is still a huge gap in PCEs between them and Pb-based perovskite. Hence, a wise decision should be made while efforts should be put in the most plausible direction.

As the most studied lead-free perovskites, Sn-based absorbers with the retaining 3D framework like Pb analogs hold excellent optoelectronic properties, especially the narrow bandgaps and high carrier mobilities. However, the notorious “self-doping” effect impedes their further development. To suppress “self-doping” effect, various tin halide additives and organic reducing agents were introduced into the active layers. As usual, the bad morphology of perovskite films is detrimental to the device performance. Thus, strategies containing the use of additives, solvent engineering, vacuum process, vapor-assisted solution process (VASP), and thermal annealing were adopted to improve the quality of tin perovskites film. Recently, great progress was made in an inverted device architecture. The combination of SnF$_2$ additive and antisolvent treatment with chlorobenzene gave a new record efficiency of 8.12% with good reproducibility from (FA)$_{0.75}$(MA)$_{0.25}$SnI$_3$-based PSCs. More importantly, 80% of PCE retained after 400 h. Among the various types of tin-based perovskites (different A cations), different cations showed different advantages. First, Sn-based perovskites with FA cation showed higher efficiency and stability than MA and Cs counterparts. It has been speculated that FA cation can endow the perovskite with higher formation energies of Sn vacancies and more resistance against oxidation. On the other hand, FA-based hybrid perovskites have better solubility than all-inorganic perovskites. According to the summary in Table 1, no spin coating with solvent-engineering was used in Cs-based perovskites due to their poor solubility, but in

Figure 23. a) $E_g$ versus the type of metal cation; b) $J_{SC}$ versus $E_g$ of the absorbers with different metal cation; c) Comparison of the performance of the device between different lead-free absorbers (data were analyzed based on Table 1).
the case of FA counterparts, most good results\cite{28,56,57} originated from solvent-engineering resulted in excellent morphology. Second, mixing organic cations at A position seems an effective method to improve devices performance. FA–MA mixed tin perovskite showed $V_{OC}$ up to 0.61 eV, while FA(MA)–BA(PEA) mixed Sn perovskite yielded a 2D structure with improved air stability. Thirdly, Cs-based perovskites have the best thermal stability up to 200 °C. Due to the high valence Sn$^{+}$ cation, Cs$_3$SnI$_6$, Br$_x$, showed the highest environment stability, the PSCs based on which were processed in the air without using any additives. Despite that the Sn-based absorbers attained a promising efficiency of $\approx$8%, it is still far from the best Pb-based perovskites. “Self-doping” effect will still be a challenge to all the researchers working on Sn-based perovskite. A deep insight into the mechanisms of “self-doping” effect is crucial for achieving efficiency up to 15% or higher. A more suitable procedure only employs “intermediate agent” that could be removed in the final stage or even without using any sacrificial additives. Successful compositional engineering could help to give efficient and stable compounds similar to Pb-based perovskites. Additionally, high-performance and dopant-free HTMs could also assist in achieving more efficient and stable Sn-PSCs.

For the absorbers based on metals beyond the group 14, owing to the low dimensionality and wide band gaps, the photovoltaic performance of Bi, Sb and Cu-based devices are still unsatisfactory with efficiency $\approx$2%. More efforts are needed at two possible directions to open up the avenues toward high-performance Bi-based absorbers. The first one is new double perovskites, which may involve a lot of theoretical calculation and the corresponding experimental study. So far, researchers have used Cs$_x$AgBiBr$_6$ to make device with PCE up to 2.43%. The other one is the ferroelectric perovskites represented by Bi-based compounds. As far back as 1956, photovoltaic (PV) effect has been found in oxide perovskite BaTiO$_3$ which has no lead elements.\cite{216} Afterward, more lead-free oxide perovskites were studied on PV effect, such as BiFeO$_3$,\cite{217,218} BiMnO$_{3}$,\cite{219} KNbO$_3$, BaNi$_{1/2}$Nb$_{1/2}$O$_3$,\cite{220} and Bi$_2$FeCoO$_6$.\cite{221} etc. So far, the highest PCE among all oxide perovskites was obtained as 8.1% by using double-perovskite Bi$_2$FeCoO$_6$.\cite{221} The ferroelectric perovskites often showed exceptionally high photovoltages, which are normally much larger than their bandgaps.

For the transition metal Cu-based absorbers, like 2D lead perovskites, their wide compositional tunability, and increased environmental stability are their intrinsic advantages. For example, one can introduce optoelectronically active organic cations to increase optical absorption cross-section and improve vertical charge transport. Another approach is to make multidimensional (MD) perovskites by mixing the 2D and 3D materials.

Among all the above-mentioned lead-free absorbers, Sn-based perovskites possess the most efficient PCE up to 8.12% while other absorbers showed only below 2.1%, although Bi-based absorbers showed the highest air stability. Moreover, theoretical calculation\cite{222,223} indicated that efficiencies above 15% could be obtained from MA$\text{SnI}_3$ PSCs. Thus, we argue that the Sn-based absorbers are the most promising surrogate for Pb in PSCs. However, we have bear in mind that Sn element is still harmful to the human body in their practical utilization.\cite{224,225}

while Bi, Sb, and Cu are more environmentally friendly. Finally, we should think about our initial question: can we get the clean power output from the new hybrid absorbers without the danger of environmental contamination?\cite{226,227} The answer may need to be found in the future development of new lead-free hybrid light harvesting materials.

During the revision of our manuscript, we noticed that there are two important Sn-based and one bismuth-based absorbers reported recently. Firstly, ethylenediammonium(en) cations were incorporated into FASnI$_3$,\cite{85} MASnI$_3$ and CsSnI$_3$,\cite{35} and then form so-called “hollow” (en)ASnI$_3$ perovskite. For the sake of incorporation of appropriate amount of en cations, the 3D structure of perovskite is retained while perovskite film morphology is significantly improved. Finally, the best-performing solar cells display a high efficiency of 6.63% of (en)MASnI$_3$ and 7.14% of (en)ASnI$_3$, respectively. These results are presented in table 1. Furthermore, Zhang et al. report a novel two-step vacuum deposition procedure to get homogeneous transformation of BiI$_3$ to MA$_3$Bi$_2$I$_9$ for highly compact, pinhole-free, large-grained films. The solar cells realized a record PCE of 1.64% and also a high EQE approaching 60%.\cite{227}

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

bismuth halide perovskite, lead-free absorbers, low dimensional materials, perovskite solar cell, tin halide perovskite

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