Tin and Mixed Lead–Tin Halide Perovskite Solar Cells: Progress and their Application in Tandem Solar Cells

Shuai Gu, Renxing Lin, Qiaolei Han, Yuan Gao, Hairen Tan,* and Jia Zhu*

Metal halide perovskites have recently attracted enormous attention for photovoltaic applications due to their superior optical and electrical properties. Lead (Pb) halide perovskites stand out among this material series, with a power conversion efficiency (PCE) over 25%. According to the Shockley–Queisser (SQ) limit, lead halide perovskites typically exhibit bandgaps that are not within the optimal range for single-junction solar cells. Partial or complete replacement of lead with tin (Sn) is gaining increasing research interest, due to the promise of further narrowing the bandgaps. This enables ideal solar utilization for single-junction solar cells as well as the construction of all-perovskite tandem solar cells. In addition, the usage of Sn provides a path to the fabrication of lead-free or Pb-reduced perovskite solar cells (PSCs). Recent progress in addressing the challenges of fabricating efficient Sn halide and mixed lead–tin (Pb–Sn) halide PSCs is summarized herein. Mixed Pb–Sn halide perovskites hold promise not only for higher efficiency and more stable single-junction solar cells but also for efficient all-perovskite monolithic tandem solar cells.

1. Introduction

Organic–inorganic lead halide perovskites have drawn significant attention for photovoltaic applications since Miyasaka et al. first employed perovskites as the photovoltaic absorber in 2009.[1] The success of lead halide perovskites is attributed to their excellent optical and electrical properties, including tunable bandgap, low exciton binding energy, high light absorption coefficient, long carrier lifetime, and long carrier diffusion length.[2–5] After 10 years’ development,[6–14] the record efficiency for lead halide PSCs has recently reached 25.2%.[15] In spite of the inspiring PCEs, lead halide perovskites typically exhibit bandgaps over 1.5 eV, which are higher than the optimal range of the SQ limit. Further narrowing the bandgaps is desirable to approach the SQ limit and to construct all-perovskite tandem solar cells.

Tin, which has an outer electronic structure similar to lead, can be used to partially or completely replace Pb in perovskites without noticeable lattice distortion since Sn has a comparable ionic radius (1.18 Å) to Pb (1.19 Å). The binding energies of tin halide perovskites are similar to those of lead halide perovskites (nearly 2–50 meV). Tin halide perovskites show bandgaps (1.3–1.4 eV depending on A-site cations) suitable for single-junction solar cells. By mixing Pb and Sn, the bandgaps can be tuned between 1.6 and 1.2 eV.[16–21]

In the mid-1990s, Mitzi and co-workers began to work on tin halide perovskites for field-effect transistor applications.[22,23] The first tin halide solar cell with a Schottky structure was reported by Chen et al. in 2011 and achieved a PCE of 0.9%.[24] Noel et al. and Hao et al. reported performing Sn halide PSCs in 2014 at approximately the same time.[25,26] Noel et al. fabricated devices using a one-step method and a regular structure that deployed compact titanium dioxide (c-TiO2) and spiro-OMeTAD as the electron transport layer (ETL) and hole transport layer (HTL), respectively. The device gave a record performance (nearly 6.4%), though with a poor reproducibility. In 2016, Yan et al. reported formamidinium lead iodide (FASnI3) solar cells with an inverted structure, achieving a PCE of 6.22%.[27] Recently, the most efficient FASnI3 solar cells have reached a PCE over 10%.[28] FASnI3 PSCs have undergone rapid development in the recent 3 years, since FASnI3 has better air stability and exhibits suitable bandgap and matchable energy levels with charge transport materials.

Benefiting from the progress of tin halide perovskites, mixed Pb–Sn halide perovskites have also recently received significant advances. Compared with tin halide ones, the mixed Pb–Sn perovskites exhibit unique advantages: on the one hand, their bandgaps can be tuned over a wider range, which makes them suitable for fabricating all-perovskite tandem solar cells; on the other hand, device performance and stability can be simultaneously improved by Pb incorporation.

Here, we report recent progress in improving the performance of Sn-based PSCs (especially for tin halide and mixed Pb–Sn halide perovskites). In Section 2, we summarize the recent improvements in fabricating high-performance and more stable tin halide PSCs. Figure 1a and Table 1 present the progress of tin halide perovskites in the past few years. In Section 3, we discuss the recent development of mixed Pb–Sn halide PSCs. The mixed Pb–Sn halide perovskites give a way to improve both performance and stability compared to pure tin halide perovskites, while they use much less amount of Pb...
element in solar cells (Table 2). In Section 4, we also highlight the recent development of all-perovskite monolithic tandem solar cells enabled by the low-bandgap mixed Pb–Sn halide perovskites. The PCE progress of low-bandgap mixed Pb–Sn single-junction PSCs and monolithic all-perovskite tandem cells is given in Figure 1b. Finally, we provide an outlook and perspective for future development of tin-based PSCs, especially in enhancing the performance and stability.

2. Tin Halide Perovskite Solar Cells

Although tin halide PSCs have seen rapid advances,[28–38] two crucial challenges remain for the development of efficient and stable devices. The first one is the poor morphology of tin halide perovskites, which is mainly caused by the over-fast crystallization process. This usually results in rough films and flower-like grains, consequently leading to direct contact between charge transport layers. The second challenge is the easy oxidation of Sn$^{2+}$ into Sn$^{4+}$ (if without protection) in tin halide perovskites. Without encapsulation or reducing additives, tin halide perovskites would gradually degrade to tin oxide under ambient conditions. It is, therefore, crucial to develop strategies that can ultimately address the challenges mentioned above for tin halide perovskites. Here, we will summarize the recent progress and discuss feasible strategies to improve the performance and stability of tin halide PSCs.

2.1. Fabrication Methods

The spin-coating method has been widely used in perovskite fabrication due to its low-cost and easy-fabrication process. This method can be divided into two ways, which are called the one-step solution method and the two-step sequential deposition method. The one-step method usually employs N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) as solvents. With the assistance of an antisolvent, such as chlorobenzene (Ph-Cl), toluene (TL), or diethyl ether (DE), flat and high-quality perovskite films can be fabricated. For the sequential method, DMF or DMSO is usually utilized to dissolve metal halide and the precursors are spin-coated on different structures. Then a typical solution, such as isopropyl alcohol (IPA) containing MAI or other organic salts, is dropped on the prepared film. A further reaction will occur through the direct contact between the organic salts and inorganic films. However, the high solubility of tin iodide (SnI$_2$) in IPA makes the sequential solution method difficult to process tin halide perovskites.[19,40] Apart from solution processing methods, researchers have successfully introduced other methods to fabricate tin halide perovskite films, such as thermal evaporation method[41–43] and vapor-assisted solution methods.[44–46]

In 2018, Wakamiya et al. successfully presented two techniques to fabricate high-quality tin-based perovskite film (Figure 2a).[47] Hot Ph-Cl antisolvent treatment (HAT) was utilized to increase the density of nucleation sites in order to improve the coverage of perovskite film. Then a mild DMSO atmosphere, which was released during thermal annealing, was created inside the Petri dish. This low partial pressure of DMSO vapor was employed to moderate the crystallization progress. As a result, the grain size increased while the film uniformity was improved. This method based on HAT and solvent vapor annealing (SVA) could bring out a champion device with a PCE of 7.2%.

In 2019, Jiang et al. developed a cation exchange method that can provide efficient MASnI$_3$ solar cells.[48] As shown in Figure 2b,c, they introduced hydrazinium iodide (HAI) into this new system. First, hydrazinium tin iodide (HASnI$_3$) was synthesized from a stoichiometric reaction between HAI and SnI$_2$. Then the HASnI$_3$ perovskite film was solution-deposited on substrates. In contrast to the 3D structure of MASnI$_3$,
HASnI3 usually exhibited a one-dimensional (1D) structure composed of [SnI3]n− chain. Then the MA gas was produced by the reaction between NaOH and MACl and served as the conversion atmosphere. In this process, the MA molecules diffused into the HASnI3 film. This route can be explained as the in situ organic cation exchange reaction shown below:

\[
\text{NH}_2\text{NH}_3\text{SnI}_3 (s) + \text{CH}_3\text{NH}_2 (g) = \text{CH}_3\text{NH}_3\text{SnI}_3 (s) + \text{NH}_2\text{NH}_2 (l).
\]

The favorable free energy change (\(\Delta G\)) of \(-0.93\) eV in the dynamics can be utilized to explain this transition. NH2NH2, which appeared at the beginning of this reaction, can be released by further annealing. Further disposal of NH2NH2 should be carefully performed because this liquid is rather dangerous. Based on the high-quality film, this regular structure device achieved the champion PCE of 7.13%, for MASnI3. This new method could help researchers achieve smoother and pinhole-free 3D films based on the high-quality 1D structured film.

### 2.2. Improving Photovoltaic Performance and Stability by Incorporating Large Cations

Recent works have shown that incorporating larger cations can not only enhance the performance of tin halide PSCs but can also improve their stability. Ke et al. introduced ethylenediammonium (en) into FASnI3.[49] This hollow perovskite, which has randomly distributed Schottky defects, has tunable bandgap and lower dark carrier density. The hollow devices exhibited enhanced stability and improved photoelectric properties. The best device achieved a PCE of 7.14% and retained 96% of its initial efficiency after over 1000 h exposure with encapsulation. Uncapsulated solar cells with and without 10% en exhibited better stability while the reference one degraded within 20 min in ambient air. Diau et al. added 1% ethylenediammonium diiodide (EDA12) in a trace proportion to enable the growth of pin-hole free and high-coverage film.[50] They tried various proportions of guanidinium (GA+) and FA+. In Figure 3a, X-ray diffraction (XRD) data for a single crystal confirms that GA+ cations have been inserted into the lattice structure successfully. Although GA+ is larger than FA+ and would expand the lattice unit, GA,FA,SnI3 perovskites adopt the same crystalline structure as FASnI3 when the GA proportion is below 30%. The supercell containing 1% EDA12 and 20% GAI is also shown in Figure 3a. The corresponding solar cell maintained a PCE of 9.6% after over 2000 h storage in a nitrogen (N2) glove box. As displayed in Figure 3b, the FASnI3 device containing 1% EDA12 and 20% GAI showed promising stability when exposed to 20% relative humidity (RH) and 60% RH. A certified PCE of 8.3% had been achieved.

Shao et al. introduced 2-phenylethylammonium iodide (PEAI) to form 2D/3D structured solar cells.[37,51] By mixing a small ratio (8%) of layered perovskite (PEA2SnI4) with the 3D perovskite, the device obtained a PCE of 9%, due to low trap-assisted recombination and small shunt losses. The 2D/3D device exhibited better stability and kept 60% of the initial PCE after 80 h of exposure under 20% RH atmosphere, while the device based on 3D perovskite degraded entirely. Ran et al. introduced PEAI into the bulk of perovskite via vacuum evaporation.[52] After spin-coating formamidinium iodide (FAI) on poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), they further evaporated PEAI and SnI2. After post-annealing, FAI, PEAI, and SnI2 form a (PEA, FA)SnI3 bulk heterojunction film. After 5 days in the glovebox, the bulk heterojunction device had only a slight decrement of short-circuit current (\(J_{sc}\)), while the reference device degraded at all aspects.

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**Figure 1.** Efficiency progress of tin-based perovskite solar cells. a) Progress of methylammonium lead iodide (MASnI3), CsSnI3 and FASnI3 PSCs over recent years. b) Progress of low-bandgap mixed Pb–Sn single-junction PSCs and monolithic all-perovskite tandem solar cells.
Recently, PEAI has been utilized by Ning et al. to form 2D–quasi-2D–3D tin halide perovskite film with the help of ammonium thiocyanate (NH$_4$SCN). They employed grazing-incidence wide-angle X-ray scattering (GIWAXS) to characterize the hierarchy structured perovskite (HSP) and the control sample.[53] In Figure 3c,e, the Bragg spots indicate strongly preferential orientation for low-dimensional polycrystalline films in the shallow surface at the incident angle of 0.2°. While the incident angle was increased to 2°, 3D perovskite grains, which existed in the depths of the film, were indicated by three Debye–Scherrer rings (Figure 3d,f). Figure 3g shows the schematic of HSP, which includes highly parallel-orientation 2D PEA$_2$SnI$_4$ and 3D FASnI$_3$. The unencapsulated device based on HSP achieved the best PCE of 9.41% and retained 90% of its initial performance after 600 h in N$_2$ glovebox (Figure 3h). This work provides an inspiring strategy to employ the structure of low-dimensional perovskite in order to improve the performance and stability of PSCs.

Chen et al. introduced a semiconducting molecule called poly[tetraphenylethene 3,3′-(((2,2-diphenylethene-1,1-diyl)bis(4,1-phenylene))bis(oxy))bis(N,N-dimethylpropan-1-amine) tetraphenylethene] (PTN-Br) to the bulk of perovskite. [54] The bulk heterojunction formed by this molecule not only provided a more suitable highest occupied molecular orbital (HOMO) (–5.41 eV) for enhancing the hole extraction but also passivated the grain boundaries to improve the stability, especially for ultraviolet (UV) soaking. The authors attributed the improvement to the formation of Lewis adducts between the uncoordinated Sn atoms and the dimethylamino of PTN-Br. After 5 h of continuous UV irradiation, the champion device with a PCE of 7.94% maintained 66% of its initial PCE, while the reference sample only presented $\approx$10% of its initial PCE.

<table>
<thead>
<tr>
<th>Perovskite</th>
<th>Structure type</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$V_{oc}$ [V]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>Publication year</th>
<th>Reference</th>
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<td>10.18</td>
<td>2019</td>
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Table 2. Performance summary of low-bandgap mixed Pb–Sn halide PSCs.

<table>
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<tr>
<th>Perovskite</th>
<th>Structure type</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>Publication Year</th>
<th>Reference</th>
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<td>2014</td>
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<td>14.0</td>
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<td>[72]</td>
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<td>67.0</td>
<td>10.1</td>
<td>2014</td>
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<td>FA$<em>{0.71}$Cs$</em>{0.29}$Sn$<em>{0.5}$Pb$</em>{0.5}$I$_3$</td>
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<td>0.740</td>
<td>26.7</td>
<td>71.0</td>
<td>14.1</td>
<td>2016</td>
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<td>FA$<em>{0.5}$MA$</em>{0.5}$Sn$<em>{0.5}$Pb$</em>{0.5}$I$_3$</td>
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<td>0.853</td>
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<td>2019</td>
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initial performance. Similarly, Kamarudin et al. enhanced the stability of FA$_0.98$EDA$_{0.01}$SnI$_3$ by Lewis base post-treatment. Ethane-1,2-diamine (edamine) was diluted in Ph-Cl at various concentrations and the solution was spin-coated on perovskite film. The increment of open-circuit voltage ($V_{oc}$) was contributed by the suppression of tin oxidation and stabilization of under-coordinated Sn. The PCE of the device with posttreatment even increased to 10.18% after 7 days of storage in the glovebox.

2.3. Additives to Enhance Device Performance and Stability

As mentioned above, tin halide perovskites suffer from the easy oxidation of Sn$^{2+}$ to Sn$^{4+}$ in the presence of oxygen, while leads to the formation of Sn vacancies and thus self-p-type doping. Extra Sn$^{2+}$ compensation such as SnX$_2$ (X = Cl and F) can help reduce the loss of Sn$^{2+}$. These tin halides not only postpone the oxidation process but also improve the film quality. In addition to SnX$_2$, other additives can be added as well to regulate the film morphology.

In 2019, Yan et al. demonstrated that they could fabricate air-stable devices by employing hydroxybenzene sulfonic acid or its salt as an antioxidant to combine with excess SnCl$_2$. Figure 4a shows the molecular structures of the three representative additives used in this work, including phenol sulfonic acid (PSA), 2-aminophenol-4-sulfonic acid (APSA), and the potassium salt of hydroquinone sulfonic acid (KHQSA). The interaction between Sn$^{2+}$ and the sulfonate group guaranteed the long-term stability of tin halide perovskites. In Figure 4b, it exhibits the difference between the process with or without additives. The SnCl$_2$-additive complex layer, which formed in the presence of the sulfonate group, helped the devices maintain 80% of the PCE over 500 h in the air without any encapsulation. In Figure 4c, the KHQSA-PSC showed a stabilized PCE of 6.6% within 1200 s maximum power point tracking, while the pristine PSC degraded gradually from the initial PCE of 3.3% to 2.8%. Without encapsulation in 20% RH air, the average PCE of the KHQSA-PSCs was maintained over 80% of its initial PCE for more than 500 h (Figure 4d).

In another study, Islam et al. employed hydrazinium chloride (N$_2$H$_5$Cl) as a co-additive to hinder the oxidation process of Sn$^{2+}$ to Sn$^{4+}$. This phenomenon can be explained by the following reductive reaction: $2$N$_2$H$_4$ → $2$NH$_3$ + N$_2$ + H$_2$ + e$^-$. Due to the strong reducing property, N$_2$H$_4$ can easily release electrons to suppress the appearance of Sn$^{4+}$. To evaluate the influence of N$_2$H$_5$Cl, the authors prepared FASnI$_3$ solutions with only SnF$_2$ and with SnF$_2$+N$_2$H$_5$Cl to observe the changes in ambient air. After 2 h of aging, the oxidation signal began to appear. As shown in Figure 4e, the solution containing both additives remained light yellow, while the solution with only SnF$_2$ turned dark red, indicating the different rates of oxidation. Without encapsulation, the best device retained 65% of its initial PCE after 1000 h of storage in nitrogen (N$_2$) (Figure 4f). Besides, Li et al. utilized trihydrazine dihydriodide (THDH) as an additive for solution deposition of FASnI$_3$. This additive could not only provide full surface coverage and smooth morphology but also inhibit the rapid oxidation of Sn$^{2+}$. With 3 mol% THDH, the PCE increased to 8.51%. By observing the color change of different precursor solutions, oxidation can be inhibited by the presence of THDH.

3. Mixed Pb–Sn Halide Perovskite Solar Cells

3.1. Bowing Effect of Mixed Pb–Sn Halide Perovskites

With the decreased x value in MAPb$_{1-x}$Sn$_x$I$_3$, the valence band (VB) and conduction band (CB) both undergo a energy shift, from $-5.45$ and $-3.90$ eV ($x = 1.0$) to $-5.47$ and $-4.17$ eV ($x = 0$), respectively (Figure 5a). The relatively larger shift of CB brings about the narrower bandgap of tin-riched perovskites. Here, an abnormal phenomenon called bowing effect is observed for bandgap tuning, where the trend of the bandgaps appears like a bowing and the narrowest bandgap is achieved with Sn ratio around 60% (Figure 5b,c). Figure 5b shows the bandgaps from the Tauc plot and the photoluminescence (PL) as a function of the Sn ratio. The electronic structure, which is calculated by the first principle, indicates that the Pb and Sn atoms are ordered...
The calculated bandgaps are shown in the bottom section. According to the study by McGehee et al.,\textsuperscript{[65]} the energy band of Pb–Sn halide perovskite (ABX$_3$) is determined by the $p$ and $s$ orbitals of B site and X site. As the Sn content increases, the compression and distortion of the perovskite crystal lattice further lead to changes in the bandgap (Figure 5d). However, the exact origin of this bowing effect is still under debate.

A recent density functional theory (DFT) calculation study by Goyal et al.\textsuperscript{[66]} indicates that the nonlinear bandgap changing tendency results from the energy mismatch between $s/p$ atomic orbitals of Sn and Pb that form the band edges of the alloy (Figure 5e).\textsuperscript{[66]} Due to the less bound atomic orbitals of Sn that form the bands, both the edges of CB and VB are less bound in Sn-based perovskite relative to Pb-based analogs. This indicates that the Sn-derived valence band maximum (VBM) and Pb-derived conduction band minimum (CBM) delimit the range of the bandgap of the alloy. As a result, the bandgap becomes lower than that of either pure compounds (Figure 5f).

### 3.2. Morphology of Mixed Pb–Sn Halide Perovskites

The mixed Pb–Sn halide perovskite films usually showed better surface coverage than the tin halide perovskite films. The morphology and film quality play a crucial role in determining the performance of solar cells. Perovskite films with inadequate surface coverage and a high density of pinholes suffer from severe charge recombination loss and a high risk of shunting. The morphology of low-bandgap perovskites film is mainly adjusted by changing A- and B-site cations.

**Figure 6a** shows MASn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite film deposited on mesoporous TiO$_2$.\textsuperscript{[30]} MA is beneficial for regulating the...
crystallization process of mixed Pb–Sn halide perovskite films.[67]

To obtain better stability, Tomas et al. replaced MA with FA and Cs to form FA0.75Cs0.25Sn0.5Pb0.5I3 perovskite film (Figure 6b).[68]

Recently, mixed FA-MA low-bandgap perovskites achieved PCEs over 20%. The SEM image shows an FA0.6MA0.4Sn0.6 Pb0.4I3 perovskite film (Figure 6c).[69]

The morphologies of mixed Pb–Sn halide perovskite films for 25%, 50%, and 75% Pb are shown in Figure 6d–f, respectively.[19] As the proportion of Sn increases, the regulation of the morphology for low-bandgap perovskites is more complicated. Zhao et al. reported that the grain size is closely related to the film thickness (precursor concentration).

Increasing the film thickness from 400 to 510 and 620 nm enlarges the crystal sizes, as shown in Figure 6g–i.[70]

3.3. Device Structure and Performance

Up to 2014, most research groups fabricated solar cells with the n–i–p structure of c-TiO2/mesoporous titanium dioxide (m-TiO2)/Pb–Sn halide perovskite/poly(3-hexylthiophene) (P3HT)/gold (Au) or Ag. This structure is a continuation of the structure used for lead halide PSCs.[71] However, the n–i–p structure exhibits inferior performance compared to the
inverted p–i–n counterparts.\textsuperscript{[64]} Thus far, the highest reported PCEs for the regular and inverted low-bandgap solar cells are 14.04\%\textsuperscript{[72]} and 21.1\%\textsuperscript{[73]} respectively. The PCE difference between these two device structures can be ascribed to the fact that mixed Pb–Sn perovskite films have better contact with PEDOT:PSS compared with TiO\textsubscript{2} or other oxide-based ETLs.

### 3.4. Additive to Improve the Device Performance

#### 3.4.1. Halogen

Halogen is widely used as an additive in lead halide perovskites to improve the crystallization of perovskite films and to improve...
the efficiency of PSCs.[11,13] The Sn\(^{2+}\) in mixed Pb–Sn halide PSCs has the tendency to be oxidized to Sn\(^{4+}\).[74] By adding SnF\(_2\) to mixed Pb–Sn halide perovskites, the oxidation of perovskite films can be retarded, resulting in reduced Sn vacancies and improved quality. However, the addition of SnF\(_2\) does not completely prevent the oxidation of Pb–Sn halide perovskites. Some residual Sn\(^{4+}\) ions remain, which will cause Sn vacancies and I vacancies in the films.

Halide doping, including chlorine (Cl) and bromine (Br), is an effective strategy to enhance the photovoltaic performance of mixed Pb–Sn halide PSCs. Li et al. added a small amount of Br to the Pb–Sn halide perovskite solution.[16] The precursor films gradually converted into a perovskite phase consisting of homogeneously intermixing of Br and I in the lattice, reducing Sn vacancies and I vacancies in the grain boundary at the high-temperature annealing due to the Br rich to the grain boundary. Although the introduction of Br led to a higher bandgap and thus a decreased \(J_{\text{sc}}\), the \(V_{\text{oc}}\) of the cell was significantly improved due to the incorporation of Br.

Incorporation of Cl can enlarge the grain size, functionalize grain boundaries, and reduce electronic disorder, consequently improving the efficiency of solar cells. Perovskite films with large grain sizes and high crystallinity were obtained through the introduction of Cl, while the grain boundaries were passivated by the excess Cl ions. SEM image of perovskite films with Cl incorporation is shown in Figure 7a. Compared with the reference film, the film with Cl is more uniform. Moreover, Cl incorporation enables higher charge mobility according to transient photocurrent characterization. The best efficiency of the 2.5% Cl-incorporated PSC is 18.4%, with a \(V_{\text{oc}}\) of 0.85 V, a fill factor (FF) of 74.4%, and a \(J_{\text{sc}}\) of 29.31 mA cm\(^{-2}\).[69]

3.4.2. SCN Series

Similar to the strategy of halide doping, the addition of SCN\(^{-}\) salts can also improve the performance, e.g., adding lead thiocyanate (Pb(SCN)\(_2\)), methylammonium thiocyanate (MASCN), and guanidinium thiocyanate (GuaSCN). The Yanfa Yan group studied the effects of Pb(SCN)\(_2\) in mixed Pb–Sn halide PSCs.[17] Using the composition of (FASnI\(_3\))\(_{0.6}\)(MAPbI\(_3\))\(_{0.4}\), the researchers obtained excellent performance by mixing FASnI\(_3\) and MAPbI\(_3\) perovskite precursor solutions (6:4) in 2016. The best efficiency was 15.08%, with a \(V_{\text{oc}}\) of 0.799 V, an FF of 70.6%, and a \(J_{\text{sc}}\) of 26.86 mA cm\(^{-2}\). By introducing Pb(SCN)\(_2\) into the precursor solution, the researchers obtained perovskite films with higher quality. The grains of the film without Pb(SCN)\(_2\) were small and chaotic, while those of the film with Pb(SCN)\(_2\) were large and uniform. Larger grains were beneficial to the performance as they reduce grain boundary scattering, extend the carrier lifetime, and improve the crystal quality. The best efficiency of Pb–Sn halide PSCs with Pb(SCN)\(_2\) was improved to 17.6%, with a \(V_{\text{oc}}\) of 0.854 V, an FF of 71.4%, and a \(J_{\text{sc}}\) of 28.7 mA cm\(^{-2}\). The device showed a certified efficiency of 17.01% with negligible current–voltage hysteresis.[70]

Similarly, a high-quality FASn\(_{0.3}\)Pb\(_{0.7}\)I\(_3\) film was deposited using a two-step solution process by introducing a MASCN additive into the precursor solution.[75] The SCN\(^{-}\) ion not only
Figure 7. Strategies to improve the performance of mixed Pb–Sn PSCs. a) SEM images of FA0.6MA0.4Sn0.6Pb0.4I3 with 2.5% Cl incorporated and the $J$–$V$ curves of FA0.6MA0.4Sn0.6Pb0.4I3 with 0% Cl-incorporated and 2.5% Cl-incorporated solar cells. Reproduced with permission.[69] Copyright 2018, Springer Nature. b) SEM images of FA0.6MA0.4Sn0.6Pb0.4I3 without and with GuaSCN and the $J$–$V$ curves of FA0.6MA0.4Sn0.6Pb0.4I3 without and with GuaSCN. Reproduced with permission.[76] Copyright 2019, The Authors, published by AAAS. c) SEM images and the $J$–$V$ curves of Cd–Pb–Sn halide perovskite. Reproduced under the terms of the CC-BY Creative Commons Attribution 4.0 International License (http://creativecommons.org/licenses/by/4.0/).[77] Copyright 2019, The Authors, published by Springer Nature. d) SEM images of MA0.3FA0.7Pb0.5Sn0.5I3 film and the $J$–$V$ curves of solar cells fabricated with tin-reduced precursor solution. Reproduced with permission.[73] Copyright 2019, Springer Nature.
prevented Sn$^{2+}$ oxidation to Sn$^{4+}$ but also regulated the crystallization through strong coordination between SCN$^{-}$ and Sn$^{2+}$, which allows FAI to penetrate into the PbI$_2$/SnI$_2$ film. XRD showed that the Pb–Sn halide perovskite film without MASCN has a PbI$_2$/SnI$_2$ peak, indicating that PbI$_2$/SnI$_2$ remained in the perovskite film. However, no PbI$_2$/SnI$_2$ occurred in the perovskite film with MASCN. The introduction of MASCN was beneficial for realizing sufficient contact and completing interaction between PbI$_2$/SnI$_2$ and FAI. The device without MASCN exhibited a PCE of 12.84%, a $J_{sc}$ of 23.50 mA cm$^{-2}$, and an FF of 73%. In the case of 0.25 m MASCN, the device exhibited the best PCE of 16.26%, with an enhanced $J_{sc}$ of 26.46 mA cm$^{-2}$ and an FF of 79%.

3.5. Strategies to Increase the Diffusion Length

Mixed Pb–Sn halide perovskites have shorter carrier diffusion lengths and lower absorption coefficients compared with the lead halide perovskites, which limit the performance of Pb–Sn based PSCs. Recently, GuaSCN was used to lower the defect density, which led to a long carrier lifetime beyond 1 μs and increased the diffusion length to 2.5 μm. With 7% GuaSCN addition, the densities of small grains and pinholes were substantially reduced, and grain boundaries became more compact (Figure 7b). The PCE improved from 15.3% to 18.4% (Figure 7b). The best PCE reached 20.5% for reverse scans.[76] A trace amount of cadmium iodide (CdI$_2$) added into Pb–Sn halide based perovskite precursors was also shown to effectively reduce the free hole concentration and electron trap density, which improved the diffusion length of electron up to 2.72 μm.[77] This resulted in a champion PCE of 20.3% (Figure 7c).

High trap density caused by Sn vacancies (mainly resulting from Sn$^{2+}$ oxidizing to Sn$^{4+}$) was a common challenge for Pb–Sn halide perovskites. We recently used metallic tin powders to reduce Sn$^{2+}$ ions to Sn$^{0}$ in the precursor solution.[78] This approach can considerably reduce the trap density and thus increase the diffusion length up to 3 μm. The devices fabricated from the tin-reduced precursor solution reached a champion PCE of 21.1%, with a $V_{oc}$ of 0.831 V, an FF of 80.8%, and a $J_{sc}$ of 31.4 mA cm$^{-2}$ (Figure 7d). This represented the highest PCE among mixed Pb–Sn PSCs reported to date.

3.6. Interface Engineering

3.6.1. The Interface Between ETL and Perovskite

Interface engineering is critical to improve the performance of PSCs. Defect sites in the low-bandgap CH$_3$NH$_3$Sn$_{0.5}$Pb$_{0.5}$I$_3$ perovskite were passivated through the incorporation of fluoroalkyl-substituted fullerene (DF-C$_{60}$) via planar heterojunction (PHJ) and graded heterojunction (GHJ) structures (Figure 8a).[79] The binding between C$_{60}$ and DMSO changes the grain growth mechanism, leading to high-quality perovskite films with fewer pinholes and a homogeneous distribution of C$_{60}$ located at the crystal boundaries. C$_{60}$ at the surface and grain boundary passivates the trap sites, leading to reduced charge recombination in the perovskite films. C$_{60}$-incorporated PSCs have better performance and stability than those without C$_{60}$.

The PCE increases from 12.6% to 13.9%, with highly improved FF and decreased hysteresis due to the optimal passivation. The best GHJ device has the highest PCE of 13.46%, with a $V_{oc}$ of 0.75 V, a $J_{sc}$ of 26.3 mA cm$^{-2}$, and an FF of 70%.

Similarly, a thin phenyl-C$_{61}$-butyric acid methyl ester (PCBM) layer (~25 nm) on top of the perovskite absorber resulted in an improved $V_{oc}$ of 0.75 V, leading to the best PCE of 17.6% (Figure 8b).[79] This enhancement is attributed to the facile charge flow at the interface due to the reduction of interfacial traps and carrier recombination with the spike structure. The average PCE of the device with PCBM-C$_{60}$ is improved to 15.7% compared with PCE of 12.9% for the control device. The main parameter $V_{oc}$ was enhanced from 0.66 to 0.71 V. Besides, the FF was improved from 72% to 76%, and the $J_{sc}$ was improved from 27.15 to 29.20 mA cm$^{-2}$.

3.6.2. The Interface Between HTL and Perovskite

The $V_{oc}$ loss can be reduced by forming a graded energy band structure to match the band structure of the mixed Pb–Sn halide perovskite with the HTL. An ultrathin bulk-heterojunction (BHJ) organic semiconductor poly[[2,6-(4,8-bis(5-(2-ethylhexyl) thiophen-2-yl)benzo[1,2-b:4,5-b0]dithiophene)]-alt-[5,5-(10,30-di-2-thienyl-50,70-bis(2-ethylhexyl)benzo[10,20-c:40,50-c0] dithiophene-4,8-dione)] [PBDB-T]: 3,9-bis(2-methylene-3-[1,1 dicyanomethylene]-indanone)-5,5,11,11-tetrakis(4-hexylphenyl)-dithieno[2,3-d:20,30-d0]-indaceno[1,2-b:5,6-b0]-dithiophene (ITIC) layer was used as an intermediary between the HTL and mixed Pb–Sn halide low-bandgap perovskite films to minimize the energy loss.[80] The inserted PBDB-T:ITIC layer has a medium HOMO level, lying between those of PEDOT:PSS and the perovskite, thus forming a gradient band alignment at the hole-selective interface that facilitates charge transfer (Figure 8c). Additionally, PBDB-T:ITIC helps passivating defects at the HTL/perovskite interface. As a result, the authors obtained a PCE of 18.03%, with a $V_{oc}$ of 0.86 V, a $J_{sc}$ of 27.92 mA cm$^{-2}$, and an FF of 75.1%. In contrast, the control device (W/O PBDB-T:ITIC) has a $J_{sc}$ of 27.82 mA cm$^{-2}$, a $V_{oc}$ of 0.77 V, an FF of 72.0%, and a PCE of 15.42%.

By doping PEDOT:PSS with a perfluorinated ionomer (PFI), Tang et al. tuned the work function from 5.02 to 5.19 eV, reducing the energy level mismatch between the FA$_{0.6}$MA$_{0.4}$ Sn$_{0.6}$Pb$_{0.4}$I$_3$ absorber and HTL (Figure 8d).[81] The best device based on PEDOT:PSS showed a PCE of 14.19%, with a $V_{oc}$ of 0.730 V, a $J_{sc}$ of 27.14 mA cm$^{-2}$, and an FF of 71.60%, with slight hysteresis. By replacing the HTL with PFI-PEDOT:PSS = 1:1, the PCE was boosted to 15.85%, with an over 50 mV improvement in $V_{oc}$. The $V_{oc}$ was improved to 0.783 V, with simultaneous improvement of the FF to 74.36%, while the $J_{sc}$ values remained almost the same, with a value of 27.22 mA cm$^{-2}$. The $J$-$V$ curve exhibited negligible hysteresis behavior for PFI-PEDOT:PSS = 1:1 (Figure 8d).

4. Monolithic All-Perovskite Tandem Solar Cells

The monolithic all-perovskite tandem solar cell, which can surpass the SQ limit of single-junction cells, is a promising...
route for next-generation solar cells with high efficiency and low fabrication cost.\cite{Eperon2016, yan2020, yan2020b, yan2020c} The structure of all-perovskite tandem solar cells is usually p–i–n (inverted structure). An efficient low-bandgap PSC is a prerequisite to obtain efficient all-perovskite tandem solar cells. The progress of all-perovskite tandem solar cells is summarized in Figure 1b and Table 3.

### 4.1. Optimizing the Bandgap of Subcells

Fabricating monolithic all-perovskite tandem solar cells is non-trivial due to the requirement for current matching. On the one hand, high-efficiency narrow-bandgap PSCs are indispensable for absorbing long-wavelength sunlight. On the other hand, the bandgap of wide-bandgap perovskite should match the narrow-bandgap subcell such that the optimal current can be achieved.

In 2016, Eperon et al. developed the infrared-absorbing 1.2 eV bandgap perovskite $\text{FA}_0.75\text{Cs}_0.25\text{Sn}_0.5\text{Pb}_0.5\text{I}_3$ with a PCE of 14.8%.\cite{Eperon2016} By combining this perovskite with an 1.8 eV bandgap perovskite $\text{FA}_0.83\text{Cs}_0.17\text{Pb(I}_0.5\text{Br}_0.5)\text{I}_3$, they achieved a PCE of 17.0% in tandem solar cells (Figure 9a). In solution processing of all-perovskite tandems, a recombination layer that can protect the top cell from being dissolved when fabricating the bottom cell is essential. For the recombination layer in their tandem cells, SnO$_2$ and zinc tin oxide (ZTO) were deposited via atomic layer deposition (ALD) before the sputter-coating of indium tin oxide (ITO). The best tandem solar cell gave a PCE of 16.9%, with a $V_{oc}$ of 1.66 V, a $J_{sc}$ of 14.5 mA cm$^{-2}$, and an FF of 70% (Figure 9b). The EQE measurements indicated that the two subcells were fairly well matched (Figure 9c), with a current density of 14.1 mA cm$^{-2}$\cite{yan2020b}. To achieve a higher matched current density, $\text{FA}_0.6\text{Cs}_0.4\text{Pb(I}_0.7\text{Br}_0.3)\text{I}_3$ with a bandgap of 1.76 eV was fabricated as the top cell, and $\text{FA}_0.75\text{Cs}_0.25\text{Sn}_0.5\text{Pb}_0.5\text{I}_3$ was manufactured as the low-bandgap absorber.\cite{yan2020c} The re-optimized tandem solar cell demonstrated a stabilized PCE of 19.1%, with a $J_{sc}$ of 14.8 mA cm$^{-2}$ and a $V_{oc}$ of 1.81 V.

### 4.2. Improving the Performance of Tandems Using Efficient Low-bandgap Solar Cells

The lack of high-quality low-bandgap perovskites severely hampers the development of efficient and stable all-perovskite tandem solar cells in the beginning years.\cite{yan2020c} Yan et al. reported bulk passivation via the use of chlorine to enlarge the grains and to reduce the electronic disorder in mixed Pb–Sn halide low-bandgap ($\approx 1.25$ eV) perovskite films.\cite{yan2020c} SEM image showed large and uniform grains due to the addition of Cl (Figure 9d). Vacuum-processed multiple stacks of Ag (1 nm), MoO$_3$ (3 nm), and ITO (>120 nm) were used as the recombination layer to fabricate all-perovskite tandem solar cells. The $J$–$V$ curve (Figure 9e) exhibited a reverse-scanned PCE of 21% and a steady-state efficiency of 20.7%. The tandem solar cell showed a matched $J_{sc}$ of 14.1 mA cm$^{-2}$ and a $V_{oc}$ of 1.922 V.
Table 3. Performance summary of monolithic all-perovskite tandem solar cells.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>(V_{oc} ) (V)</th>
<th>(J_{sc} ) [mA cm(^{-2})]</th>
<th>FF [%]</th>
<th>PCE [%]</th>
<th>Publication Year</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/nickel oxide (NiOx)/FA(<em>{0.83})Cs(</em>{0.17})PbI(<em>{0.83})Br(</em>{0.17})/PCBM/SnO(<em>{2})/ZTO/ITO/PEDOT:PSS/FA(</em>{0.75})Cs(<em>{0.25})Sn(</em>{0.5})Pb(_{0.5})I(_3)/PCBM/BCP/Ag</td>
<td>1.660</td>
<td>14.5</td>
<td>70.0</td>
<td>16.9</td>
<td>2016</td>
<td>[64]</td>
</tr>
<tr>
<td>ITO/NiO(<em>3)/MA(</em>{0.9})Cs(<em>{0.1})Pb(I(</em>{0.6})Br(<em>{0.4}))(<em>3)/C(<em>60)/Bis-C(<em>60)/ITO/PEDOT:PSS/MA(</em>{0.3})FA(</em>{0.7})Sn(</em>{0.5})Pb(</em>{0.5})I(_3)/BCP/Ag</td>
<td>1.980</td>
<td>12.7</td>
<td>73.0</td>
<td>18.4</td>
<td>2017</td>
<td>[85]</td>
</tr>
<tr>
<td>ITO/poly[bis(4-phenyl)bis(2,4,6-trimethylphenyl)amine] (PTAA)/FA(<em>{0.8})Cs(</em>{0.2})PbI(<em>{0.8})Br(</em>{0.2})/C(<em>60)/C(</em>{60})/BCP/Ag</td>
<td>1.922</td>
<td>14.0</td>
<td>78.1</td>
<td>21.0</td>
<td>2018</td>
<td>[69]</td>
</tr>
<tr>
<td>ITO/poly[4-butylnaphthyl-diphenylamine] (PolyTPD)/poly(ethylene naphtalate) (PEN)/dimethylammonium (DMA)(<em>3)/FA(</em>{0.8})Cs(<em>{0.2})PbI(</em>{0.8})Br(<em>{0.2})/lithium fluoride (LiF)/C(<em>60)/poly(ethyleneimine) ethoxylated (PEIE)/aluminium-doped zinc oxide (AZO)/IZO/PEOT:PSS/FA(</em>{0.75})Cs(</em>{0.25})Sn(<em>{0.5})Pb(</em>{0.5})I(_3)/C(_60)/BCP/Ag</td>
<td>1.820</td>
<td>15.6</td>
<td>75</td>
<td>21.3</td>
<td>2019</td>
<td>[86]</td>
</tr>
<tr>
<td>ITO/PTAA/C(<em>{60})/FA(</em>{0.8})MA(<em>{0.2})PbI(</em>{2.3})Br(_{0.7})/C(_60)/Ag/MoO(_x)/ITO/PEDOT:PSS/(FASnI(<em>3))(</em>{0.6})(MAPbI(<em>3))(</em>{0.4})/C(_60)/BCP/Ag</td>
<td>1.915</td>
<td>15.0</td>
<td>79.8</td>
<td>23.1</td>
<td>2019</td>
<td>[76]</td>
</tr>
<tr>
<td>ITO/PTAA/C(<em>{60})/FA(</em>{0.8})Sn(<em>{0.2})PbI(</em>{0.8})[BCP/Au/IZO/PEDOT:PSS/FA(<em>{0.75})Cs(</em>{0.25})Sn(<em>{0.5})Pb(</em>{0.5})I(_3)/C(_60)/BCP/copper</td>
<td>1.965</td>
<td>15.6</td>
<td>81.0</td>
<td>24.8</td>
<td>2019</td>
<td>[73]</td>
</tr>
</tbody>
</table>

Figure 9. Structure and performance of monolithic all-perovskite tandem solar cells. a,d,g) Cross-section SEM images of monolithic all-perovskite tandem solar cells without various recombination layers. b,e,h) J–V curves of representative tandem solar cells. c,f,i) EQE curves of corresponding tandem solar cells. a–c) Reproduced with permission.[64] Copyright 2016, AAAS. d–f) Reproduced with permission.[66] Copyright 2018, Springer Nature. g–h) Reproduced with permission.[73] Copyright 2019, Springer Nature.
impressively high PCE of 24.8%, with a \(V_{oc}\) of 1.915 V, and an FF of 79.8% in monolithic all-perovskite tandem solar cells. Very recently, we improved the charge carrier diffusion length in mixed Pb–Sn perovskites to 3 nm via a comproportionation reaction strategy.[7] The high \(J_{sc}\) values achieved here provided the chances to further increase the matched current density in tandem solar cells. An ALD-SnO\(_2\)/ultrathin Au recombination layer structure was developed to avoid the sputtered ITO layer (Figure 9g). As a result, the champion tandem device exhibited a layer structure was developed to avoid the sputtered ITO layer (Figure 9g).

5. Conclusions

We have summarized the recent progress in the development of tin halide and mixed Pb–Sn halide PSCs. Methods that have been utilized to improve performance and to enhance stability are discussed. Two intertwined major challenges need to be addressed for the development of tin halide PSCs. To overcome the over-quick crystallization of tin halide perovskites, the cation exchange method has been developed except for the thermal evaporation and vapor-assisted methods. By incorporating large organic cations, the performance and stability of tin halide devices can be enhanced under ambient conditions. To mitigate the oxidation of Sn\(^{2+}\), Sn\(_x\)X\(_y\) (X = F, Cl) serving as Sn\(^{2+}\) compensator and other reducing additives have been introduced. With reducing additives and posttreatment passivation, FASnI\(_3\) PSCs exhibit improved performance and stability. The mixed Pb–Sn halide perovskites have demonstrated great potentials to address the three main challenges, including morphology, performance, and stability, leading to high-performance devices. The low-bandgap mixed Pb–Sn halide perovskites are promising candidates for fabricating highly efficient all-perovskite tandem solar cells. The monolithic all-perovskite tandem solar cells have achieved an impressive PCE of 24.8%, which is comparable with those of silicon cells. It is expected that the nontoxic (or less-toxic) Sn-containing perovskites will have up-and-coming prospects for both single-junction and tandem solar cells in the future.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

mixed Pb–Sn halide perovskites, perovskite solar cells, tandem solar cells, tin halide perovskites

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