

Crystallization, Properties, and Challenges of Low-Bandgap Sn–Pb Binary Perovskites

Hugh Lu Zhu and Wallace C. H. Choy*

Solution-process and low-temperature perovskites have motivated a broad range of interests and intensive studies for applications in solar cells (SCs) and photodetectors (PDs). Perovskite SCs with the bandgap of ≈ 1.5 eV currently exhibit the certified efficiency over 22% comparable with those of established thin film technologies. Meanwhile, perovskite PDs achieve superb performances in the visible region compared with commercial Si PDs. Partial substitution of Sn into Pb-based perovskites can tune the absorption to near-infrared (NIR) region, which would achieve an ideal-bandgap perovskite approaching the Shockley–Queisser-efficiency limit, low-bandgap perovskite-based bottom subcells in tandem devices (≈ 1.2 eV), and NIR photodetection. Here, various crystallization methods for growing low-bandgap Sn–Pb binary perovskites are presented. Their impacts on morphology, crystallinity, preferred orientation, carrier lifetimes, Urbach energy, and stability of the resultant Sn–Pb binary perovskites are highlighted. Then, a description is given of single-junction, 2-terminal, and 4-terminal SCs using these perovskites as absorbers, which achieve up-to-date efficiencies of 17.8%, 18.4%, and 21.2%, respectively. The current development of ultraviolet–visible–NIR PDs using these perovskites is also discussed. Furthermore, the challenges in controlling inter-grain Sn/Pb element distributions and perovskite stability, which will influence performance and stability of Sn–Pb perovskite-based devices, are presented. Finally, potential prospects are discussed for advancing low-bandgap Sn–Pb binary perovskite-based optoelectronic devices.

1. Introduction

Low-temperature and solution-process perovskites have evolved a broad range of interests and intensive studies toward promising applications in photovoltaics, PDs, and light-emitting diodes due to their excellent optical and electrical properties.^[1–4] In general, lead based-perovskites adopt the structure of MPbX_3 , where M generally is methylammonium (MA), formamidinium (FA), cesium (Cs), rubidium (Rb), or their mixtures, X normally is iodine (I), bromine (Br), chlorine (Cl), or their mixtures. While

compositional-engineering Pb-based perovskites present strong absorption mainly in the visible range governed by their optical bandgap of ≈ 1.55 eV,^[1,5] broadening perovskite absorption to the near-infrared (NIR) region will 1) benefit ideal-bandgap single-junction SCs approaching the Shockley–Queisser efficiency limit of $\approx 33.5\%$;^[6] 2) implement low-bandgap perovskite-based bottom subcells in tandem photovoltaics; as well as; 3) realize NIR photodetection with potential applications in biometric identification and medical fluorescent imaging.^[7]

To employ the excellent optical and electric features of perovskites and simultaneously widen absorption to the NIR range, various NIR sensitizers, including poly(diketopyrrolopyrrole-terthiophene) (PDPP3T), PbS quantum dots, poly{2,5-bis(2-hexyldecyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione-3,6-di(5-thiophen-2-yl)yl-alt-N-(2-ethylhexyl)-dithieno[3,2-b:2,3-d]pyrrole-2,6-diyl} (PDPPTDTP), CyPF₆ and Cy1BF₄ dyes, and β -NaYF₄:Yb,Er upconversion nanocrystals, have been introduced to the Pb-based perovskite system and form bulk/planar heterojunctions for carrier extraction.^[8,9] These devices achieved relative low performance in the NIR range due to the weak absorption and/or inefficient carrier extraction. Mean-

while, NIR sensitizers may influence the crystallization of perovskites, and increase the production complexity and costs.

Substituting Pb with smaller-size halogen Sn to form MSnI_3 perovskite thin films (M = MA, FA, Cs, or arbitrary mixtures of these) could lower the bandgap (1.3 eV for CsSnI_3 , 1.3 eV for MASnI_3 , 1.41 eV for FASnI_3 , 1.33 eV for $\text{FA}_{0.75}\text{MA}_{0.25}\text{SnI}_3$).^[10–13] Facile oxidation of Sn^{2+} to Sn^{4+} states in MSnI_3 perovskites could induce p-type self-doping, which could turn semiconducting perovskites into metal-like ones, causing reduced diffusion length and thus poor stability of these pure Sn-based perovskites and associated optoelectronic devices.^[14] Interestingly, Sn–Pb binary perovskites $\text{MSn}_x\text{Pb}_{1-x}\text{I}_3$ ($1 > x > 0$), partial incorporation of Sn into Pb-based perovskites, could achieve improved material stability.^[15] Meanwhile, the bandgap tuning of Sn–Pb binary perovskites can be broadly extended from the upper value of 1.55 eV to the lower value of 1.17 eV ($0.8 > x > 0.5$), as shown in Figure 1.^[15–18] It should be noted that the bandgap tuning does not obey the Vegard's law between 1.55 eV of MAPbI_3 and 1.30 eV of MASnI_3 , possibly originating from the competition between the

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DOI: 10.1002/solr.201800146

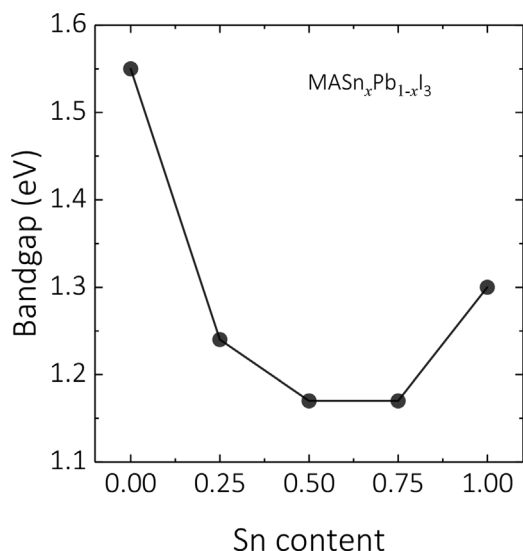


Figure 1. Bandgap evolution of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films. Bandgap tuning does not follow a linear relationship between 1.55-eV bandgap of MAPbI_3 and 1.30-eV bandgap of MASnI_3 . The lowest bandgap of Sn-Pb binary perovskites is 1.17 eV, suggesting promising applications in SCs and PDs.^[16]

spin-orbit coupling and the lattice distortion.^[19,20] Generally, low Sn-concentration perovskites ($x < 0.5$) form tetragonal $I4cm$ structure of β - MAPbI_3 , while high Sn-concentration perovskites ($x > 0.5$) show the pseudocubic tetragonal $P4mm$ structure of α - MASnI_3 .^[16,21] The structural transition would involve symmetry changes and thus influence the electronic properties of Sn-Pb binary perovskites. Summarily, Sn-Pb binary perovskites with the tunable optical absorption in the NIR region and structure-transition-influenced electronic properties exhibit their promising applications as ideal-bandgap SCs approaching the efficiency limit, bottom subcells in tandem SCs and NIR photodetection.

There has been a review on the current development of Sn and Sn-Pb binary perovskite-based SCs.^[22] Differently, in this review, we focus on the crystallization of low-bandgap Sn-Pb binary perovskite films (bandgap < 1.55 eV), which would significantly influence the morphology, crystallinity, preferred orientation, trap density, as well as carrier lifetimes, and thus determine device performances of SCs and PDs. Firstly, various crystallization methods of low-bandgap Sn-Pb binary perovskites consisted of one-step solution-process methods, two-step solution-process methods, and vacuum-process methods will be studied in detail. Meanwhile, the morphology, crystallinity, orientation, optical, and electrical properties of resultant low-bandgap Sn-Pb binary perovskite films will be discussed. Secondly, the current advances of low-bandgap Sn-Pb binary perovskite-based SCs (single-junction, 2-terminal, and 4-terminal tandem SCs) and PDs will be reviewed. Thirdly, the challenges, including controlling inter-grain Sn/Pb element distributions and stability of Sn-Pb binary perovskites, will be discussed in detail. Finally, we will summarize the discussion and offer an outlook of low-bandgap Sn-Pb binary perovskite-based optoelectronic devices in the future.

Notably, partial Sn substitution (25 mol%) in the wide-bandgap MAPb(I/Br)_3 perovskite system could improve the



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phase stability of I/Br-based perovskites.^[23] Similarly, wide-bandgap $\text{CsPb}_{0.9}\text{Sn}_{0.1}\text{IBr}_2$ perovskite films could stabilize the perovskite phase and enhance endurance against heat and moisture.^[24] Tiny Sn incorporation (5 mol%) into $\text{MAPb}_{0.95}\text{Cu}_{0.05}\text{I}_{2.9}\text{Br}_{0.1}$ perovskite films could achieve large grain sizes, low trap density, resulting into a higher efficiency.^[25] These wide-bandgap perovskites with the Sn incorporation lie outside of the scope of this review.

2. Crystallization, Properties, and Applications of Low-Bandgap Sn-Pb Binary Perovskites

2.1. Crystallization and Properties of Low-Bandgap Sn-Pb Binary Perovskites

A typical one-step method to form Sn-Pb binary perovskite films is to spin-coat Sn-Pb binary perovskite precursors in the dimethylformamide (DMF) solvent and followed by the annealing treatment. This method generally grew relatively low-quality Sn-Pb binary perovskite films with low surface coverage and rough surfaces.^[15] Since dimethyl sulfoxide (DMSO) molecules could intercalate into PbI_2 or SnI_2 structures and form $\text{PbI}_2 \cdot 2\text{DMSO}$ or $\text{SnI}_2 \cdot 3\text{DMSO}$ adducts,^[12,26–28] Sn-Pb binary perovskite precursors from DMSO-containing solvents would employ intermediate phases of $\text{PbI}_2 \cdot 2\text{DMSO}$ and $\text{SnI}_2 \cdot 3\text{DMSO}$ to retard the crystallization, and thus produce Sn-Pb binary perovskites. Furthermore, precursor engineering that either mixed individual Sn and Pb based precursors or blended with additives (such as

chloride, Rb, and Cs) would be employed to tune the crystallization. These Sn-Pb binary perovskite precursor films generally spin-coated on poly(3,4-ethylenedioxythiophene):poly(p-styrene sulfonate) (PEDOT:PSS) substrates would be washed/immersed by anti-solvents, including toluene, anisole or diethyl ether, and annealed.^[18,19,23,29–43] Meanwhile, Sn-Pb binary perovskite films can be formed by two-step solution-process methods. $\text{PbI}_2(\text{SnI}_2) \cdot x\text{DMSO}$ intermediates were firstly fabricated. MAI was spin-coated atop and experienced ionic interactions to form Sn-Pb binary perovskites.^[17,44] Additionally, the hot-casting crystallization technique as a one-step method and a vacuum-process method will also be discussed as below.

2.1.1. One-Step Solution-Process Methods

Precursor engineering: Chloride. Jen and co-workers directly blended methylammonium iodide (MAI), lead chloride (PbCl_2), and tin chloride (SnCl_2) into anhydrous DMF solvents.^[45] Precursors were deposited on the surface of PEDOT:PSS through one-step spin-coating, followed by annealing at 90 °C for 2 h to produce $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3(\text{Cl})$ perovskite thin films. They found that chloride ions not only worked as substitutional impurities in final iodide-based Sn-Pb binary perovskites, but also altered the transformation pathway during annealing via introducing the competing chloride-based perovskite phase. Meanwhile, the presence of Sn^{2+} would regulate the nucleation rate and influence the growth behavior of Sn-Pb binary perovskites. Finally, through optimizing the Sn content ($x = 0.15$), they presented rough Sn-Pb binary perovskite thin films with 97% surface coverage on PEDOT:PSS substrates, as shown in Figure 2A. When $x > 0.5$, their fabricated $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3(\text{Cl})$ perovskite thin films showed low surface coverage and rough surface. The chloride incorporation that influenced the crystallization of Sn-Pb binary perovskites and altered the optical and electronic properties also were investigated by Diau and co-workers through mixing SnCl_2 and PbI_2 in varied stoichiometric ratios.^[46] Overall, different from the case of pure Pb-based perovskites that chloride incorporation could improve perovskite crystallinity and enhance performances of SCs,^[47] the introduction of chloride has not produced high-quality Sn-Pb binary perovskite films and efficient SCs.

Precursor engineering: Cesium. In the early reports, Jen and co-workers found that Sn-Pb binary perovskite films exhibited apparent pinhole and non-uniform morphology when the Sn content exceeded 25% (i.e., $x > 0.25$).^[32,45] Cs-cation incorporation into the large FA-cation based perovskite system (FAPbI_3) could tune tolerance factor and then stabilize the perovskite α -phase of FAPbI_3 , as well as potentially modulate the film formation.^[48] Differently, Cs-cation incorporation into MA-cation pure Pb-based perovskite system (MAPbI_3) has limited reports. They found that introduction of Cs cations could effectively control the film formation of Sn-Pb binary perovskite films and thus lead into high-quality perovskite films. As shown in Figure 2B–E, $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskite films with the incorporation of 10 mol% Cs exhibited a homogenous and uniform morphology, ascribing to the reduced crystallization rate induced by the addition of Cs cations. Excess Cs incorporation (≥ 20 mol%) would induce a pinhole and non-uniform morphology, possibly owing to phase separation resulting

from immiscibility.^[49] Appropriate Cs-cation incorporation (10–30 mol%) did not change the bandgap of $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskites (≈ 1.28 eV), but slightly shrink the crystal lattice due to smaller size of Cs cations.^[31] Significantly, under an ambient environment with a relative humidity of $35 \pm 5\%$, $\text{MAPb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskites presented a new peak indexing to MA_2SnI_6 (the oxidation of Sn^{2+} to Sn^{4+}), whereas no manifest peaks were observed for $\text{MA}_{0.9}\text{Cs}_{0.1}\text{Pb}_{0.5}\text{Sn}_{0.5}\text{I}_3$ perovskites (Figure 2F), suggesting the enhanced stability of Sn-Pb binary perovskites with the incorporation of Cs cations.^[31]

Precursor engineering: DMSO. Since PbI_2 and SnI_2 could coordinate with DMSO to form $\text{PbI}_2 \cdot 2\text{DMSO}$ and $\text{SnI}_2 \cdot 3\text{DMSO}$ adducts, respectively,^[12,26] Choy and co-workers successfully realized controllable crystallization of Sn-poor Sn-Pb binary perovskite films ($\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$) via tuning DMSO amount in raw precursors.^[42] Various-content DMSO with 0, 25, 50, and 75 vol % in the DMF:DMSO co-solvent were defined as DMSO-0, DMSO-25, DMSO-50, and DMSO-75, respectively. $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite precursors were spin-coated on the surface of PEDOT:PSS, sequentially washed by toluene, finally annealed at 100 °C for 10 min to produce $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films. As shown in Figure 3A–D, the introduction of DMSO could significantly increase the grain size of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites. DMSO-25 and DMSO-50-based films exhibited large grain sizes of about 250 and 200 nm, respectively, while DMSO-0-based films showed small grain sizes of about 100 nm. Excess DMSO in the raw precursor (DMSO-75) caused the small grain size.

The crystallinity and orientation of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films were characterized by the XRD measurement, as shown in Figure 3E. Remarkably, in comparison with DMSO-0-based perovskites, DMSO-25, DMSO-50, and DMSO-75-based Sn-Pb perovskites showed significantly enhanced diffraction intensities of (110) plane by over 20-, 14-, and 4-folds, respectively, indicating improved perovskite crystallinity. With the increase of DMSO amount, intensities of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites gradually decreased. It might be resulted from uncrystallized $\text{PbI}_2/\text{SnI}_2$ film induced by the excess DMSO molecules and thus lowered perovskite crystallinity.^[28] The texture coefficient was used to characterize the preferred orientation of Sn-Pb binary perovskite films. Texture coefficients of the (110) plane relative to (112) plane of DMSO-0, DMSO-25, DMSO-50, and DMSO-75-based perovskite films were estimated to be 0.34, 0.81, 0.88, and 0.74, respectively. The higher texture coefficient value for DMSO-50-based Sn-Pb binary perovskites suggested that DMSO incorporation would effectively enhance the orientation of the main plane.

Another concern is Sn and Pb element distributions in the final $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films, which was characterized by the transmission electron microscopy (TEM) integrated with energy-dispersive X-ray spectroscopy (EDS). It was found that Sn percentages (defined as the ratio of Sn atoms over the total atoms of Sn and Pb) in $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites were not a constant on 100-nm scales. Interestingly, DMSO incorporation could ameliorate inhomogeneous Sn/Pb element distributions.

Precursor engineering: FASnI_3 - FAPbI_3 and Cesium. McGehee, Snaith and co-workers firstly introduced FA-Cs cations into Sn-Pb binary perovskite films.^[18] They employed precursor-phase anti-solvent immersion to produce highly crystalline and uniform Sn-Pb perovskite films, which combined low-vapor pressure solvents

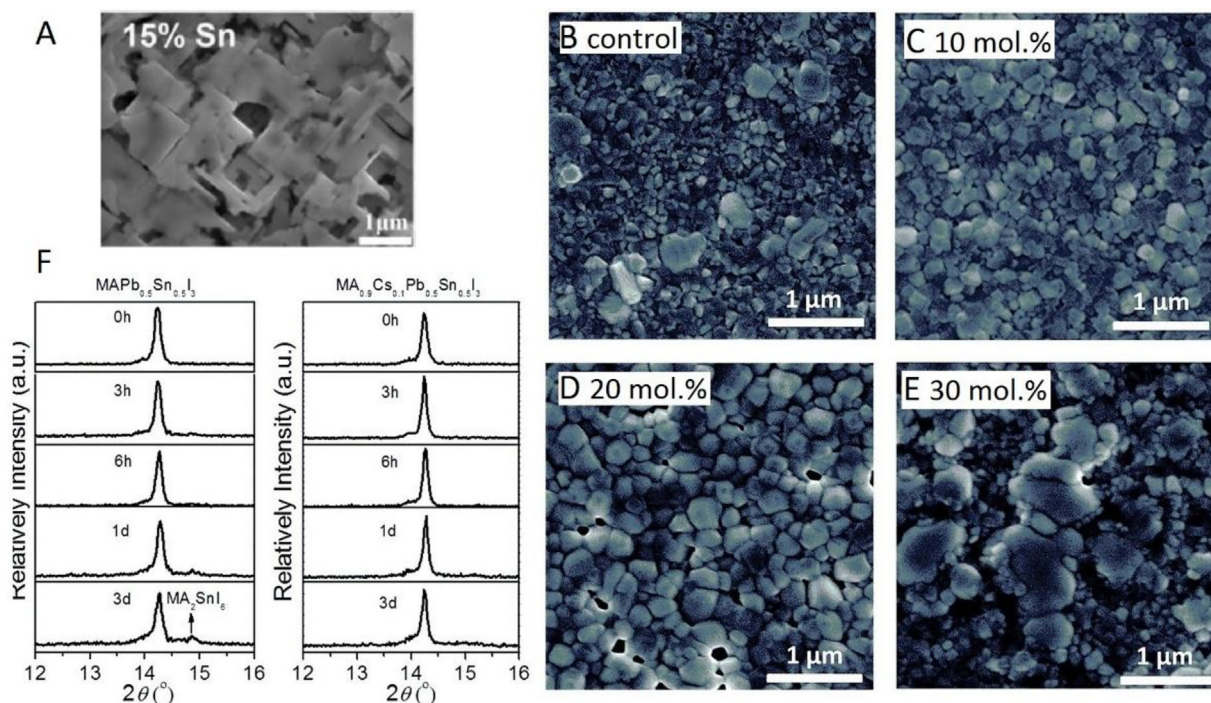


Figure 2. A) Scanning electron microscopy (SEM) image of MASn_xPb_{1-x}I₃(Cl) perovskite thin films when $x = 0.15$. B–E) SEM images of MAPb_{0.5}Sn_{0.5}I₃, MA_{0.9}Cs_{0.1}Pb_{0.5}Sn_{0.5}I₃, MA_{0.8}Cs_{0.2}Pb_{0.5}Sn_{0.5}I₃, MA_{0.7}Cs_{0.3}Pb_{0.5}Sn_{0.5}I₃, respectively. F) Time-resolved X-ray diffraction (XRD) spectra of MAPb_{0.5}Sn_{0.5}I₃ and MA_{0.9}Cs_{0.1}Pb_{0.5}Sn_{0.5}I₃ films stored in an ambient environment with a relative humidity of $35 \pm 5\%$. Figure A reproduced with permission.^[45] Copyright 2014, Wiley-VCH. Figures B–F reproduced with permission.^[31] Copyright 2016, The Royal Society of Chemistry.

to grow precursor complexes and an anti-solvent bath to crystallize perovskite films with appropriate heating. Specifically, the initial precursor solutions were prepared *via* mixing FASnI₃ and FAPbI₃ precursors both from a co-solvent of DMF:DMSO (low-vapor

pressure solvents). SnF₂ was added into the FASnI₃ precursors to retard oxidation of the Sn²⁺ to Sn⁴⁺.^[10] Spin-coated transparent precursor films were immersed in anisole (an anti-solvent bath), dried with nitrogen gas flow, and then annealed at 70 °C for 20 min

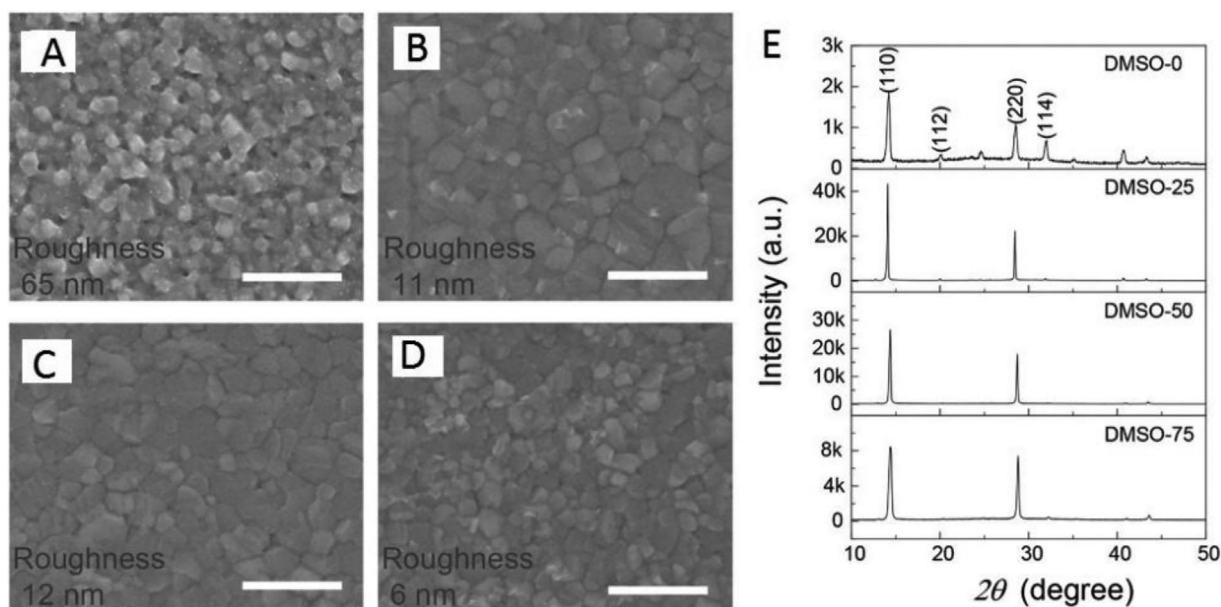


Figure 3. Top-view SEM images of Sn-Pb binary perovskite films produced from different DMSO/DMF ratios-based precursors: (A) DMSO-0, (B) DMSO-25, (C) DMSO-50, (D) DMSO-75, and (E) corresponding XRD patterns. The scale bars are 500 nm. Figures reproduced with permission.^[42] Copyright 2017, Wiley-VCH.

to fabricate smooth, highly crystalline and uniform $\text{FASn}_x\text{Pb}_{1-x}\text{I}_3$ films. The full coverage of Sn-Pb binary perovskite films on PEDOT:PSS surfaces was achieved when $x = 0.5$ and low surface coverage occurred at $x = 1.0$. Notably, $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ and $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ binary Sn-Pb perovskite films were heated at 100°C for 4 days under nitrogen. There were no changes in the absorption spectra, indicating excellent thermal stability of $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ and $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskites.

Electrical properties of $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ films, including charge-carrier diffusion length, mobility, and recombination lifetimes, were determined by the optical pump probe terahertz spectroscopy. $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite films achieved a charge-carrier mobility of $17\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ and a charge-carrier diffusion length of $\approx 210\text{ nm}$. Importantly, substituting 25% of the FA with Cs in $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ films had little impact on morphology, bandgap, photoluminescence, charge carrier diffusion lengths, but improved efficiency of SCs.^[18]

Precursor engineering: FASnI_3 - MAPbI_3 . A new precursor composed of a FASnI_3 precursor with a MAPbI_3 precursor with various ratios both in the DMSO:DMF co-solvent was employed by Yan and co-workers^[29,41] The Sn-Pb binary perovskite precursor films were produced by spin-coated the new precursor on PEDOT:PSS surfaces. After diethyl ether was dripped, formed intermediate complexes were annealed at 100°C for 5 min to fabricate dense Sn-Pb binary perovskite thin films. It was observed that this new precursor was suited for depositing Sn-rich ($x \geq 0.6$) Sn-Pb binary perovskite thin films. Sn-rich ($x \geq 0.6$) Sn-Pb binary perovskites showed relatively dense, uniform, and homogeneous thin films compared with Sn-poor ($x \leq 0.4$) Sn-Pb binary perovskites, as evidenced by SEM images. When $x = 0.6$, $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films showed the lowest bandgap of $\approx 1.2\text{ eV}$ and carrier lifetime of 6.7 ns. Distinctively, all Sn-Pb binary perovskites adopted the orthorhombic crystal structure, same to the crystal structure of FASnI_3 , which was different from previous results that Sn-Pb binary perovskites adopted the crystal structure of pure-Sn based perovskites when $x > 0.5$.^[14,16,29]

It should be noted that the short carrier lifetime (6.7 ns) of $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskites indicated low film crystallinity, which would impede efficiency advances of $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ SCs.^[41] Interestingly, through optimizing precursor concentrations, various-thickness $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films (400, 510, 620, 1010 nm) were successfully fabricated. It was found that the average grain size increased as the thickness increased, as shown in Figure 4A–D. Specially, 620-nm-thick perovskite film exhibited the smallest full-width at half-maximum values at the (110) peak, indicating the highest crystallinity. Meanwhile, 620-nm-thick film achieved the longest carrier lifetime of $\approx 255\text{ ns}$ (Figure 4F) and lowest Urbach energy of 18.8 meV, suggesting high crystallinity and low density of trap states.

Precursor engineering: FAPbI_3 - CsSnI_3 . Padture and co-workers demonstrated a new precursor composed of homogeneously mixing stoichiometric FAPbI_3 and CsSnI_3 precursors both dissolved in DMSO solvents.^[19] In order to obtain an ideal-bandgap perovskite of $\approx 1.3\text{ eV}$ for single-junction SCs, the bandgap tuning was realized in $(\text{FAPbI}_3)_{1-x}(\text{CsSnI}_3)_x$ perovskites. Similar to early reports, the anomalous bandgap tuning was observed, where smallest bandgap of 1.24 eV occurred at $x = 0.4$.^[16,18] Authors ascribed the nonmonotonic bandgap tuning to transitions of the lattice symmetry from cubic

$Pm\bar{3}m$ (FAPbI_3) to orthorhombic $Pnma$ (CsSnI_3). Finally, as shown in Figure 5A and B, an ideal bandgap perovskite at $x = 0.3$, $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$, was produced and exhibited a low Urbach energy of 30 meV. Meanwhile, enhanced material stability of $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskites was experimentally observed, originating from the entropy of mixing and reduced oxidation of Sn^{2+} due to the protection of the surrounding Pb^{2+} in the crystal structure at the atomic scale.^[19,50] They also investigated the band structure using density function theory calculations (DFT). Figure 5C presented the calculated total density of states (DOS) and projected density of states (PDOS) and the inset was the constructed $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskites model. For the PDOS, the valence band maximum was mainly contributed by I 5p, Sn 5s, and Pb 6s orbitals, while the conduction band minimum was resulted from I 5p, Sn 5p, and Pb 6p orbitals. The calculated bandgap of $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskites was 1.35 eV, which agreed with the measured optical value.

Precursor engineering: Rubidium. Choy and co-workers introduced tiny Rb cations into Sn-rich $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite precursors in the DMSO:DMF co-solvent.^[43] Conventionally, adding small-size Rb into large-size FA cation perovskites could tune tolerance factor, and stabilize the perovskite phase.^[2] Distinctively, in the Sn-rich $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite system, Rb incorporation could effectively modify surface-energy-induced kinetic process during the perovskite growth. According to the ab initio simulation, they found that Rb incorporation in Sn-rich Sn-Pb perovskite systems can facilitate the perovskite growth in (110) plane and suppress growth in (112) and (113) planes, indicating controllable crystallization. Experimentally, compared with $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskites with pinholes and roughness of 16.1 nm, $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films exhibited large grain size, pinhole-free, and smooth films with roughness of 11.2 nm, as shown in Figure 6A and B. As shown in Figure 6C, MA-Rb perovskite films achieved significantly enhanced diffraction intensities of (110) plane by over two times compared with MA-based perovskites, suggesting improved perovskite crystallinity. Meanwhile, it was found that intensities of (112), (113), and (224) planes of MA-Rb perovskite films were even reduced, which indicates the strengthened preferred orientation. These findings were consistent with the simulated results.

The influence of controllable crystallization of MA-Rb Sn-Pb perovskites on local surface potentials and charge carrier lifetimes were investigated by Kelvin probe force microscopy and time-resolved photoluminescence spectroscopy, respectively. In comparison with $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskites, $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films showed a smaller potential difference at the grain boundaries/grain interiors interface and a longer carrier lifetime, which would beneficially contribute to efficient optoelectronic devices.

Hot-casting crystallization: The hot-casting technique has been successfully applied in crystallizing high-quality $\text{MAPbI}_3(\text{Cl})$ and $(\text{BA})_2(\text{MA})_3\text{Pb}_4\text{I}_{13}$ ($\text{BA} = n\text{-butylammonium}$) perovskite films.^[51] Since the solution-process hot-casting technique could influence the perovskite crystallization, Sadhanala and co-workers employed this method to fabricate Sn-Pb binary perovskite films.^[21] $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite precursors were prepared by mixing MAPbI_3 precursors (PbI_2 : MACl with 1:1 molar stoichiometric ratio in DMF) and MASnI_3 precursors (SnI_2 : MAI with 1:1 molar

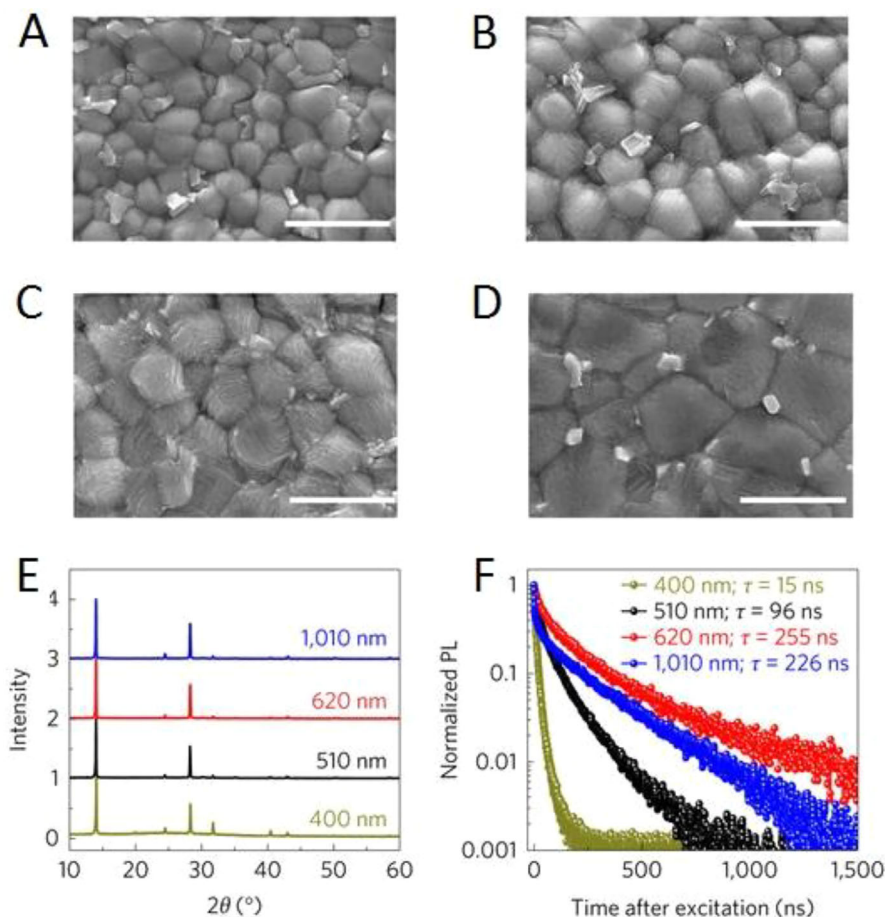


Figure 4. Top-view SEM images of various-thickness $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films: (A) 400 nm, (B) 510 nm, (C) 620 nm, and (D) 1010 nm, deposited on PEDOT:PSS substrates. E) XRD patterns of different-thickness $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films. F) Normalized time-resolved photoluminescence decay of different-thickness $(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$ perovskite films. Figures reproduced with permission.^[41] Copyright 2017, Nature Publishing Group.

stoichiometric ratio in DMF), then heated at 80 °C. After that, the hot $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite precursors were spin-coated on hot PEDOT:PSS surfaces (180 °C), followed by annealing at 100 °C for 10 min. The resultant $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films exhibited nonmonotonic bandgap tuning and the lowest bandgap of 1.19 eV at $x=0.8$. Such anomalous bandgap tuning was consistent with results by Hao et al.^[16] The material quality and disorder of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites were analyzed by the photothermal deflection spectroscopy. As shown in **Figure 7**, $\text{MASn}_{0.2}\text{Pb}_{0.8}\text{I}_3$ and $\text{MASn}_{0.4}\text{Pb}_{0.6}\text{I}_3$ perovskites showed the highest Urbach energy of ≈ 41 and 48 meV, respectively, possibly originating from lattice distortions and high defect densities. Interestingly, Sn-rich $\text{MASn}_{0.6}\text{Pb}_{0.4}\text{I}_3$ perovskites showed the lowest Urbach energy of ≈ 33 meV. Lowest bandgap $\text{MASn}_{0.8}\text{Pb}_{0.2}\text{I}_3$ perovskites showed the Urbach energy of ≈ 37 meV. Previous analysis of perovskite distortions has shown that both cation displacement and octahedral tilting are allowed in the lower-symmetry $I4cm$ space group (Sn-poor, $x < 0.5$), whereas there are no allowed octahedral tilts in the higher-symmetry pseudocubic $P4mm$ space group (Sn-rich, $x > 0.5$). This potentially contributed into different Urbach energy values of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films. Intrinsic charge carrier mobilities of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films were

characterized by terahertz pump-probe measurements. $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films exhibited high charge carrier mobilities of $240 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x=0.4$, $190 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x=0.6$, $120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $x=0.8$, which were compared with that of $260 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for MAPbI_3 films. However, $\text{MASn}_{0.2}\text{Pb}_{0.8}\text{I}_3$ perovskite films showed a relative low mobility of $11 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Overall, the hot-casting technique could fabricate high-quality Sn-rich perovskites with excellent electrical properties ($x > 0.6$), but inferior Sn-poor perovskites ($x < 0.4$).

2.1.2. Two-Step Solution-Process Methods

Solvent annealing: Yu and co-workers firstly employed the two-step process to deposit Sn-Pb binary perovskite films.^[52] The Sn-Pb binary iodide polycrystalline $\text{Sn}_x\text{Pb}_{1-x}\text{I}_2$ films ($x=0.1, 0.25$) from anhydrous DMF solvents were initially spin-coated on PEDOT:PSS, followed by thermal annealing 70 °C for 20 min, then MAI was sequentially spin-coated. Thermal annealing plus following solvent annealing was used to control and manipulate film morphology, grain size, and the distribution of metal cations in Sn-Pb binary perovskites. It was observed that Sn incorporation to

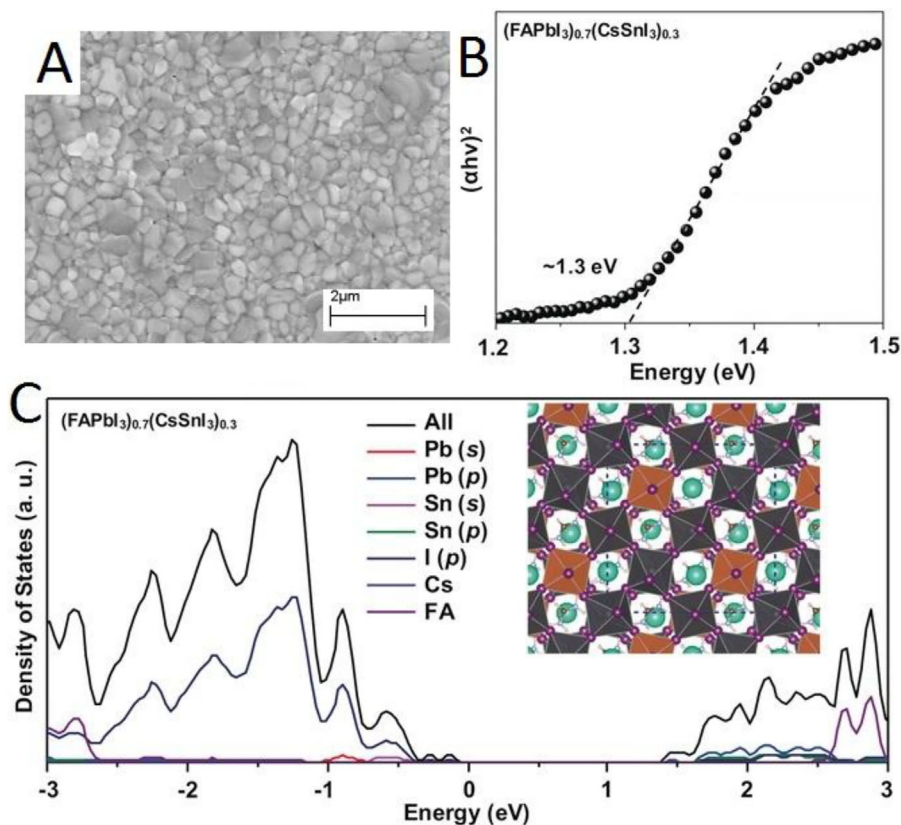


Figure 5. A) a SEM image of $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskite films. B) Tauc plot of $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskite films showing a bandgap of 1.3 eV. C) DOS of $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskites based on DFT calculations. Inset is the crystal model showing the $(\text{FAPbI}_3)_{0.7}(\text{CsSnI}_3)_{0.3}$ perovskites. Figures reproduced with permission.^[19] Copyright 2017, Wiley-VCH.

PbI_2 showed in-plane orientation of $\text{Sn}_{0.1}\text{Pb}_{0.9}\text{I}_2$ films and grain reorientation of $\text{Sn}_{0.25}\text{Pb}_{0.75}\text{I}_2$ films, indicating that the amount of Sn substitution would influence grain orientation, which would work as different templates to grow Sn-Pb binary perovskite films.

Both $\text{MASn}_{0.1}\text{Pb}_{0.9}\text{I}_3$ and $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ films treated by only thermal annealing were densely packed with small grains (124 and 158 nm, respectively) and relatively rough. When treated with the thermal plus DMSO vapor-assisted thermal annealing, both

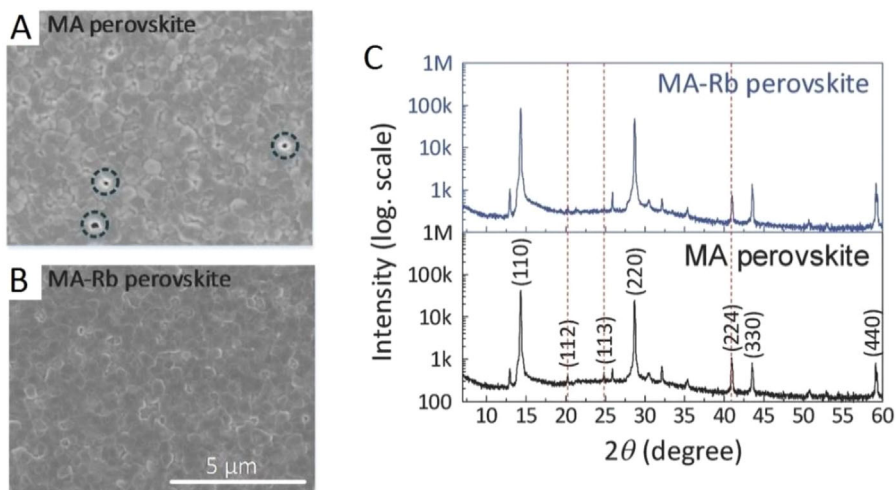


Figure 6. Top-view SEM images of (A) $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ and (B) $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ perovskite films, respectively. C) XRD patterns of $\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ (top) and $\text{MASn}_{0.65}\text{Pb}_{0.35}\text{I}_3$ (bottom) perovskite films, respectively. Figures reproduced with permission.^[43] Copyright 2018, Wiley-VCH.

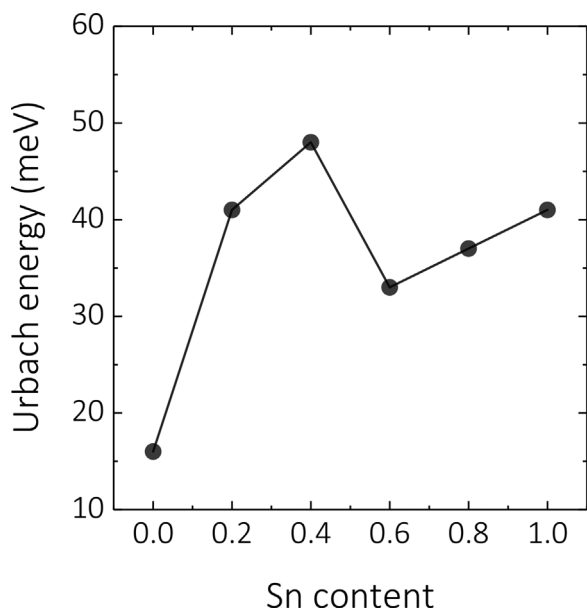


Figure 7. Urbach energies of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films ($0 < x < 1$). Data were extracted from the photothermal deflection spectroscopy.^[21]

perovskite films showed the larger grain size up to $\approx 1 \mu\text{m}$ and flat surfaces, similar with the early reports of MAPbI_3 .^[53] They proposed that the preferential bonding of DMSO to Sn broke the Sn-I bonds, created PbI_6^{4+} octahedrons with iodide dangling bonds, thus resulting into the rearrangement of Sn(Pb)-centered octahedrons and grain growth.^[52]

Precursor engineering: DMSO. As discussed above, PbI_2 and SnI_2 coordinate with DMSO to form $\text{PbI}_2 \cdot 2\text{DMSO}$ and $\text{SnI}_2 \cdot 3\text{DMSO}$ adducts, respectively.^[12,26] Mai and co-workers demonstrated the intermediate complexes of $\text{Sn}_x\text{Pb}_{1-x}\text{I}_2 \cdot x\text{DMSO}$ that could retard the crystallization of $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films.^[17] Experimentally, they simply mixed separate PbI_2 precursors and SnI_2 precursors in proper ratios both from hybrid DMSO:DMF co-solvents, and then spin-coated on the surface of PEDOT:PSS. After annealed by 60°C for 10 min, $\text{SnI}_2 \cdot x\text{DMSO}$ and/or $\text{PbI}_2 \cdot x\text{DMSO}$ were observed to form at a relatively low temperature. They found that SnI_2 governed the complexing process due to its higher activation energy. Afterward, the coated MAI would induce the intramolecular exchange with DMSO to form $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskite films. When increasing the Sn content, Sn-Pb binary perovskites showed enhanced Sn^{2+} oxidation to Sn^{4+} and enlarged grain sizes. Importantly, Sn-rich perovskite films presented a lower surface coverage. Therefore, this two-step precursor engineering using DMSO was suitable for producing the Sn-poor Sn-Pb binary perovskite films.^[17]

Precursor engineering: C_{60} . After investigated the influence of DMSO on the two-process crystallization of Sn-Pb binary perovskites,^[17] Mai and co-workers further introduced C_{60} into the precursor solution of mixed PbI_2 and SnI_2 .^[44] Since the bonding occurred between DMSO and C_{60} molecules, C_{60} molecules that mixed with $\text{Sn}_x\text{Pb}_{1-x}\text{I}_2 \cdot x\text{DMSO}$ complexes were wrapped around by the DMSO molecules and formed solvent shells.^[54] The presence of C_{60} molecules increased surface energy and thus decreased grain sizes of $\text{PbI}_2/\text{SnI}_2$

precursor thin films. Finally, C_{60} molecules could tune the crystallization of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films with decreased pinholes and uniformly disperse between grain boundaries. Importantly, $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskite films with the C_{60} molecule incorporation achieved both improved surface recombination lifetime and bulk recombination lifetime, resulting from the formation of a perovskite- C_{60} hybrid solid. In a previous report, fullerenes incorporation into perovskites has been found to passivate the key PbI_3^- anti-site defects and promote electron extraction.^[55] Moreover, C_{60} molecules as an isolating layer could effectively prevent moisture permeation and oxidation of Sn^{2+} , which could improve stability of $\text{MASn}_{0.25}\text{Pb}_{0.75}\text{I}_3$ perovskites and related devices.

Precursor engineering: Pb. A Pb-assisted two-step method was demonstrated to deposit compact and uniform $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite films by Liu, Bian and co-workers.^[56] Firstly, hot precursors ($70\text{--}80^\circ\text{C}$) consisted of $\text{SnI}_2/\text{PbI}_2$ in anhydrous DMF were spin-coated on PEDOT:PSS, followed by the natural drying for 1 h. Large-scale and uneven grains and consequently rough Sn-Pb perovskite films would be formed if any annealing was treated on spin-coated $\text{SnI}_2/\text{PbI}_2$. Secondly, MAI was spin-coated. The two-step-process films were annealed at 110°C for 45 min to complete the inter-diffusion of MAI and crystallize Sn-Pb binary perovskites. The Pb incorporation contributed to reduced crystallization rate of Sn-based perovskites, and significantly enhanced the compactness of perovskite thin films. Although the perovskite crystallinity enhanced as the annealing temperature increasing from 90 to 130°C , decomposition of perovskites would happen at the high annealing temperature of 130°C .^[56]

2.1.3. Vacuum-Process Methods

A vacuum-process method: Fan and co-workers firstly employed a chemical vapor deposition process to deposit Sn-Pb binary perovskite films.^[57] Sn-Pb binary metal precursors firstly were deposited on TiO_2 -coated indium tin oxide (ITO) glasses. Specifically, the binary metal precursors were formed via the sequential deposition of two separated layers of Pb and Sn with different thicknesses that controlled the Sn content. Afterwards, binary metal precursor-coated substrates were transferred into a chemical vapor deposition tube furnace and located near the MAI powder. The reaction was performed at 185°C for 40 min in argon atmosphere. Sn-Pb binary metal precursors transformed into $(\text{Pb}/\text{Sn})\text{I}_2$ as the intermediate phase, which further reacted with MAI molecules to produce Sn-Pb binary perovskite films. The bandgap tuning with the increase of Sn content in resultant $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites did not obey Vegard's law that was consistent with early reports^[16–18] and exhibited the lowest bandgap of 1.23 eV when $x = 0.8$. Meanwhile, the presence of Pb^{2+} stabilizing Sn^{2+} states was experimentally observed, which was consistent with early reports.^[15] The carrier lifetimes of resultant $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites were investigated by the transient photoluminescence spectroscopy. They found that $\text{MASn}_{0.62}\text{Pb}_{0.38}\text{I}_3$ perovskites achieved the longest carrier lifetime of $\approx 91 \text{ ns}$, which would benefit for efficient optoelectronic devices.

2.2. Applications in Solar Cells and Photodetectors

2.2.1. Solar Cells

Sn-Pb binary perovskites with excellent optical and electric properties have made much progress in the application of SCs. Single-junction Sn-Pb perovskite SCs have achieved a PCE of 17.8%,^[58] 2-terminal tandem perovskite-on-perovskite SCs have presented a PCE of 18.4%,^[36] 4-terminal all-perovskite SCs have achieved a PCE of 21.2%.^[41] The device parameters of Sn-Pb binary perovskite SCs are summarized in Table 1. The discussion of perovskite photovoltaics is composed of single-junction perovskite SCs, 2-terminal tandem perovskite-on-perovskite SCs, and 4-terminal all-perovskite SCs.

Single-junction solar cells: The first Sn-Pb binary perovskite SCs were reported by Ogomi and co-workers on 2014.^[15] The device with the structure of fluorine doped tin oxide (FTO)/compact TiO₂/porous TiO₂/MASn_xPb_{1-x}I₃/regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT)/Ag/Au achieved the maximum efficiency of 4.18% and spectral response onset to 1060 nm when the Sn content is 50% ($x=0.5$, 1.18 eV bandgap). The low efficiency was ascribed to severe charge recombination at perovskite/P3HT interfaces and reduced shunt resistance. Later, Kanatzidis and co-workers demonstrated Sn-Pb binary perovskite SCs with the structure of FTO/compact TiO₂/porous TiO₂/MASn_xPb_{1-x}I₃/(2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene) (spiro-MeOTAD)/Au, which showed a short-circuit current (J_{sc}) of 15.82 mA cm⁻², an open-circuit voltage (V_{oc}) of 728 mV, a fill factor (FF) of 64.01%, corresponding to the maximum power conversion efficiency (PCE) of 7.37% ($x=0.25$, 1.24 eV bandgap). The low efficiency resulted from p-type doping via Sn²⁺ oxidation, and back electron recombination at TiO₂/perovskite interfaces.^[16]

Later, most Sn-Pb binary perovskite films were grown on the planar surface of PEDOT:PSS and planar structures of SCs were fabricated. The first planar structure of Sn-Pb binary perovskite SCs were reported by Jen and co-workers.^[45] They introduced chlorine-containing components to tune the crystallization of Sn-Pb binary perovskite thin films and realized 97% surface coverage on PEDOT:PSS as discussed in Section 2.1. Planar devices with the structure of ITO/PEDOT:PSS/MASn_xPb_{1-x}I₃(Cl)/phenyl-C61-butyric acid methyl ester (PC₆₁BM)/fullerene surfactant (C₆₀-bis)/Ag achieved a J_{sc} of 19.5 mA cm⁻², a V_{oc} of 770 mV, a FF of 0.67, corresponding to a maximum PCE of 10.1% when $x=0.15$ (1.38 eV bandgap). When $x>0.5$, Sn-Pb perovskite SCs did not show photovoltaic properties, possibly originating from low surface coverage and Sn²⁺ oxidation. Afterwards, low Sn-content ($x=0.1$ and 0.25) Sn-Pb binary perovskites were fabricated by the two-step process and then manipulated by the thermal plus vapor-assisted thermal annealing to tune film morphology and grain size. Planar devices with the structure of ITO/PEDOT:PSS/MASn_xPb_{1-x}I₃ ($x=0.1$, 0.25)/PC₆₁BM:C₆₀/bathocuproine (BCP)/Al achieved maximum PCEs of 10.25% for MASn_{0.1}Pb_{0.9}I₃ SCs, and 7.76% for MASn_{0.25}Pb_{0.75}I₃ SCs.^[52] The intermediate complexes of Sn_xPb_{1-x}I₂·x DMSO were demonstrated by Fan, Mai and co-workers, using two-step process to control the crystallization of MASn_xPb_{1-x}I₃ perovskite films. Optimized planar devices with the structure of ITO/PEDOT:PSS/MASn_{0.25}Pb_{0.75}I₃/PC₆₁BM/

BCP/Ag achieved an average PCE up to 12.25% under the forward scan and up to 12.63% under the reverse scan, and champion SCs showed the PCE of 14.12%. In comparison to pure-Pb based cells, Sn-Pb binary perovskite SCs showed inferior stability, possibly originating from the oxidation of Sn²⁺.^[17]

The highest PCE of MASn_{0.25}Pb_{0.75}I₃ perovskite ($x=0.25$, 1.29 eV bandgap) based SCs has been achieved by Choy and co-workers.^[42] They tuned the DMSO content in the MASn_{0.25}Pb_{0.75}I₃ perovskite precursors to achieve controllable crystallization of MASn_{0.25}Pb_{0.75}I₃ perovskite films. The resultant MASn_{0.25}Pb_{0.75}I₃ perovskite films exhibited enhanced crystallinity, the preferred (110) orientation, and reduced inhomogeneous Sn/Pb distributions. After that, planar devices with the structure of ITO/PEDOT:PSS/MASn_{0.25}Pb_{0.75}I₃/C₆₀/zirconium(IV) acetylacetonate (ZrAcac)/Ag were fabricated. Using C₆₀ as the electron-transport layer, MASn_{0.25}Pb_{0.75}I₃ perovskite based SCs exhibited an average PCE of 10.70%. Interface engineering was employed to improve the device efficiency. A nanocomposite electron-transport layer consisting of PC₆₁BM and C₆₀ was proposed and found that this nanocomposite layer could efficiently passivate Sn-Pb binary perovskites, reduce the series resistance and increase the carrier lifetime. Finally, under the forward scan, MASn_{0.25}Pb_{0.75}I₃ perovskite devices achieved a J_{sc} of 26.2 mA cm⁻², a V_{oc} of 800 mV, a FF of 0.725, yielding a PCE of 15.2%; while under the reverse scan, the devices presented a J_{sc} of 26.4 mA cm⁻², a V_{oc} of 810 mV, a FF of 0.714, yielding a PCE of 15.2%, as shown in Figure 8A. Therefore, high-efficiency of 15.2% and negligible hysteresis were achieved for MASn_{0.25}Pb_{0.75}I₃ perovskite SCs. As shown in Figure 8B, the integrated J_{sc} from the incident photon-to-current efficiency (IPCE) spectrum was 25.5 mA cm⁻², which matched well with the value derived from the corresponding current density–voltage (J – V) measurement.

When $x=0.5$, a Pb-assisted two-step process was studied to deposit compact and uniform MASn_{0.5}Pb_{0.5}I₃ perovskite films. Planar devices with the structure of ITO/PEDOT:PSS/MASn_{0.5}Pb_{0.5}I₃/electron transport layer/BCP/Ag were fabricated. Three common fullerenes, including C₆₀, PC₆₁BM, and indene-C60 bisadduct (IC₆₀BA), were used to optimize the device performance. The C₆₀-based perovskite SCs achieved the highest efficiency with a J_{sc} of 26.3 mA cm⁻², a V_{oc} of 750 mV, a FF of 0.688, and a PCE of 13.6%, originating from the highest electron mobility and thermal-evaporation-induced better coverage of C₆₀.^[59] Meanwhile, a slight hysteresis was observed.^[56]

When MA was completely substituted by FA, highly crystalline and uniform FASn_xPb_{1-x}I₃ films were produced by the precursor-phase anti-solvent immersion. Planar devices with the structure of ITO/PEDOT:PSS/FASn_{0.5}Pb_{0.5}I₃/C₆₀/BCP/Ag were fabricated. FASn_{0.5}Pb_{0.5}I₃ based SCs yielded the champion PCE of 10.9%, whereas the best FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ based SCs exhibited a J_{sc} of 26.7 mA cm⁻², a V_{oc} of 740 mV, a FF of 0.71, corresponding to a PCE of 14.1% and the stabilized power output is 14.8%. Compared with reported pure lead-based perovskite cells, FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ based SCs exhibited a smaller voltage deficit (0.41 V) between bandgap and V_{oc} , which is comparable with that of crystalline silicon SCs (0.38 V).^[60] Furthermore, FASn_{0.5}Pb_{0.5}I₃ and FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ based devices achieved a better stability than the pure Pb-based devices

Table 1. Summary of Sn-Pb binary perovskite SCs.

Sn-Pb binary perovskites	E_g [eV]	J_{sc} [mA cm ⁻²]	V_{oc} [mV]	FF	PCE [%]	Ref.
Single-junction SCs						
MASn _{0.1} Pb _{0.9} I ₃	1.31	19.0	780	0.67	9.95	[52]
MASn _{0.15} Pb _{0.85} I ₃ (Cl)		19.1	760	0.66	9.77	[45]
MASn _{0.25} Pb _{0.75} I ₃	1.24	15.82	728	0.64	7.37	[16]
MASn _{0.25} Pb _{0.75} I ₃	1.24	17.7	700	0.56	6.98	[52]
MASn _{0.25} Pb _{0.75} I ₃	1.26	24.00	760	0.68	12.08	[34]
MASn _{0.25} Pb _{0.75} I ₃	1.31	23.8	745	0.79	13.9	[17]
MA _{0.9} Cs _{0.1} Sn _{0.25} Pb _{0.75} I ₃	1.39	22.80	840	0.76	14.6	[31]
MASn _{0.25} Pb _{0.75} I ₃	1.35	22.44	820	0.78	14.35	[32]
MASn _{0.25} Pb _{0.75} I ₃	1.30	23.5	736	0.79	13.7	[44]
MASn _{0.25} Pb _{0.75} I ₃	1.29	26.2	800	0.73	15.2	[42]
(FAPbI ₃) _{0.7} (CsSnI ₃) _{0.3}	1.30	26.40	770	0.72	14.6	[19]
MASn _{0.5} Pb _{0.5} (I _{0.8} Br _{0.2}) ₃	1.35	25.9	900	0.76	17.63	[40]
MASn _{0.5} Pb _{0.5} I ₃	1.17	20.64	584	0.60	7.27	[16]
MASn _{0.5} Pb _{0.5} I ₃	1.18	20.0	420	0.50	4.2	[15]
MASn _{0.5} Pb _{0.5} I ₃	1.23	17.9	638	0.61	7.0	[72]
MASn _{0.5} Pb _{0.5} I ₃	1.28	22.8	690	0.65	10.2	[30]
MASn _{0.5} Pb _{0.5} I ₃	1.18	26.3	750	0.69	13.6	[56]
FA _{0.75} Cs _{0.25} Sn _{0.5} Pb _{0.5} I ₃	1.20	26.7	740	0.71	14.8	[18]
MASn _{0.5} Pb _{0.5} I ₃	1.22	25.5	840	0.67	14.4	[36]
MASn _{0.5} Pb _{0.5} I ₃	1.20	26.1	870	0.69	15.6	[35]
FASn _{0.5} Pb _{0.5} I ₃	1.28	28.37	695	0.55	10.8	[73]
MA _{0.9} Cs _{0.1} Sn _{0.5} Pb _{0.5} I ₃	1.28	23.32	700	0.62	10.1	[31]
MA _{0.5} FA _{0.5} Sn _{0.5} Pb _{0.5} I ₃		25.69	780	0.70	14.0	[39]
MA _{0.5} FA _{0.5} Sn _{0.5} Pb _{0.5} I ₃	1.25	30.56	750	0.76	17.6	[74]
CsSn _{0.6} Pb _{0.4} I ₃	1.63	0.26	900	0.42	0.1	[75]
(FASnI ₃) _{0.6} (MAPbI ₃) _{0.4}	1.20	26.82	799	0.70	15.0	[29]
MASn _{0.6} Pb _{0.4} I ₃	1.27	20.5	767	0.63	10.0	[21]
(FASnI ₃) _{0.6} (MAPbI ₃) _{0.4}	1.25	28.5	853	0.72	17.6	[41]
(FASnI ₃) _{0.6} (MAPbI ₃) _{0.4}	1.24	27.3	830	0.80	17.8	[58]
MASn _{0.6} Pb _{0.4} I _{2.2} Br _{0.8}	1.32	19.51	720	0.67	9.3	[33]
MASn _{0.6} Pb _{0.4} I _{2.6} Br _{0.4}	1.26	20.65	780	0.75	12.1	[33]
MASn _{0.6} Pb _{0.4} I ₃	1.16	22.41	660	0.62	9.2	[33]
MASn _{0.62} Pb _{0.38} I ₃	1.30	25.5	796	0.69	14.04	[57]
MASn _{0.75} Pb _{0.25} (ICl) ₃	1.25	19.63	457	0.57	5.13	[46]
MASn _{0.8} Pb _{0.2} I ₃	1.19	20.2	658	0.57	7.6	[21]
2-terminal tandem SCs						
FA _{0.83} Cs _{0.17} Pb(I _{0.5} Br _{0.5}) ₃ /FA _{0.75} Cs _{0.25} Sn _{0.5} Pb _{0.5} I ₃	1.8/1.2	14.5	1660	0.70	16.9	[18]
MA _{0.9} Cs _{0.1} Pb(I _{0.6} Br _{0.4}) ₃ /MASn _{0.5} Pb _{0.5} I ₃	1.8/1.22	12.7	1980	0.73	18.4	[36]
4-terminal tandem SCs						
FA _{0.83} Cs _{0.17} Pb(I _{0.83} Br _{0.17}) ₃ /FA _{0.75} Cs _{0.25} Sn _{0.5} Pb _{0.5} I ₃	1.6/1.2	20.3	970	0.79	15.7	[18]
		7.9	740	0.73	4.4	
PCE of 4-terminal SCs is 20.1%						
MAPbI ₃ /MA _{0.5} FA _{0.5} Pb _{0.75} Sn _{0.25} I ₃	1.55/1.33	16.69	1080	0.75	13.52	[32]
		9.14	760	0.80	5.56	
PCE of 4-terminal SCs is 19.08%						
FA _{0.3} MA _{0.7} PbI ₃ /(FASnI ₃) _{0.6} (MAPbI ₃) _{0.4}	1.58/1.25	20.1	1141	0.80	18.3	[41]
		4.8	808	0.74	2.9	
PCE of 4-terminal SCs is 21.2%						

E_g is perovskite bandgap. J_{sc} is the short-circuit current, V_{oc} is open-circuit voltage, FF is fill factor, PCE is power conversion efficiency.

(FAPbI₃) at maximum power point under 100 mW cm⁻² illumination for 50 min in ambient air with a relative humidity of ≈50%. Importantly, low bandgap FA_{0.75}Cs_{0.25}Sn_{0.5}Pb_{0.5}I₃ (1.2 eV bandgap) SCs with the high efficiency were suited for bottom subcells in solution-process tandem SCs, which will be discussed in the part of 2-terminal and 4-terminal tandem SCs below.

A graded heterojunction structure was introduced via the incorporation of fluoroalkyl-substituted fullerene (DF-C₆₀) into MASn_{0.5}Pb_{0.5}I₃ perovskites, which contributed to beneficial surface passivation and a reduced Urbach energy of MASn_{0.5}Pb_{0.5}I₃ perovskites films. Optimized devices with the structure of ITO/PEDOT:PSS/MASn_{0.5}Pb_{0.5}I₃(added 20 mol% SnF₂)/DF-C₆₀/IC₆₀BA/C₆₀-bis/Ag were fabricated. SCs exhibited an average J_{sc} of 26.23 mA cm⁻², an average V_{oc} of 870 mV, an average FF of 0.69, yielding an average PCE of 15.18%. The champion device achieved a PCE up to 15.61% and a remarkably high V_{oc} of 0.89 V, indicating a small voltage deficit (0.33 V) between bandgap and V_{oc} that is better than that of crystalline silicon SCs (0.38 V). Moreover, hydrophobic nature of DF-C₆₀ in the graded heterojunction structure improved the device stability.^[33]

Sn-rich (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskites were fabricated by spin-coating the new precursor consisted of a FASnI₃ precursor and a MAPbI₃ precursor. Dense and uniform (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskites with a thickness of about 400 nm were applied in SCs with the structure of ITO/PEDOT:PSS/(FASnI₃)_{0.6}(MAPbI₃)_{0.4}/C₆₀/BCP/Ag. The champion Sn-Pb perovskite SC exhibited a forward-scan PCE of 15.00%, a

reverse-scan PCE of 15.08%, and a stabilized PCE of ≈14.8%.^[29] (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskites with the relatively thin thickness reduced the long-wavelength absorption (700–950 nm) and then achieved low external quantum efficiency (EQE) of corresponding SCs in the spectral range. However, simply increasing the thickness of Sn-Pb binary perovskite films would induce severe photocarrier recombination owing to the short carrier lifetime of 6.7 ns as discussed in Section 2.1.1 one-step solution-process methods. Through optimizing precursor concentrations, researchers further fabricated high-quality 620-nm-thick (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite films with a long carrier lifetime of 255 ns, lower Urbach energy and higher crystallinity. Based on the same device structure, under the forward scan, (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite devices achieved a J_{sc} of 28.5 mA cm⁻², a V_{oc} of 853 mV, a FF of 0.725, yielding a PCE of 17.6%; while under the reverse scan, the devices presented a J_{sc} of 28.7 mA cm⁻², a V_{oc} of 854 mV, a FF of 0.714, yielding a PCE of 17.5%, as shown in Figure 8C. As shown in Figure 8D, the integrated J_{sc} from the EQE spectrum was 28.6 mA cm⁻², which further confirmed the value derived from the corresponding J - V measurement. Overall, 620-nm-thick (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite SCs produced a maximum PCE of 17.6% and a certified efficiency of 17.01% with a negligible current-voltage hysteresis, which is among the highest PCE among Sn-Pb binary perovskite single-junction SCs.^[41]

As discussed previously, through Sn-content engineering, we could achieve Sn-Pb binary perovskites with an ideal bandgap for approaching Shockley–Queisser-efficiency limit. Jen and co-

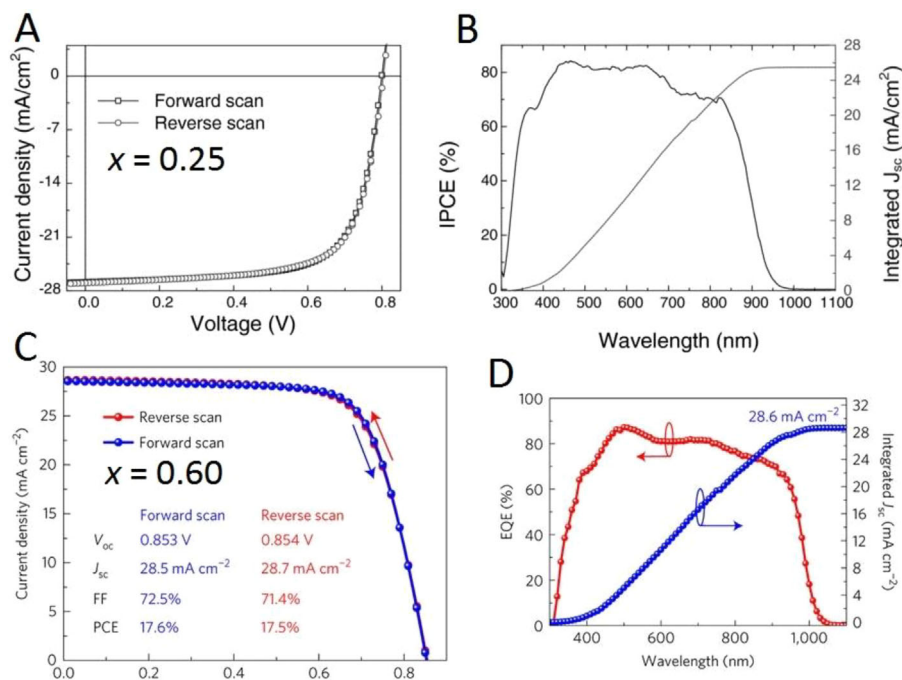


Figure 8. A) J - V curves of MASn_{0.25}Pb_{0.75}I₃ perovskite based SCs under AM1.5G illumination. Forward scan was measured from short circuit to open circuit and reverse scan was recorded from open circuit to short circuit. B) IPCE spectrum and integrated J_{sc} of MASn_{0.25}Pb_{0.75}I₃ perovskite based SCs. Integrated J_{sc} is 25.5 mA cm⁻². C) J - V curves of (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite based SCs under AM1.5G illumination. D) EQE spectrum and integrated J_{sc} of (FASnI₃)_{0.6}(MAPbI₃)_{0.4} perovskite based SCs. Integrated J_{sc} is 28.6 mA cm⁻². Figures A and B reproduced with permission.^[42] Copyright 2017, Wiley-VCH. Figures C and D reproduced with permission.^[41] Copyright 2017, Nature Publishing Group.

workers conducted Sn-content engineering with $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites and found that $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskites had the highest photoluminescence intensity, indicating high material quality among $\text{MASn}_x\text{Pb}_{1-x}\text{I}_3$ perovskites.^[40] Further, after incorporation of Br, $\text{MASn}_{0.5}\text{Pb}_{0.5}(\text{I}_{0.8}\text{Br}_{0.2})_3$ with an ideal 1.35-eV-bandgap was fabricated. Br incorporation was beneficial for reduced nonradiative defect states and band edge disorder. Typical devices with the structure of ITO/PEDOT:PSS/ $\text{MASn}_{0.5}\text{Pb}_{0.5}(\text{I}_{0.8}\text{Br}_{0.2})_3$ (240-nm-thickness)/ $\text{IC}_{60}\text{BA}/\text{C}_{60}$ -bis/Ag achieved a J_{sc} of 21.51 mA cm^{-2} , a V_{oc} of 900 mV, a FF of 0.76, yielding a PCE of 14.71%. Similar to results from Yan and co-workers,^[41] the low EQE of thin $\text{MASn}_{0.5}\text{Pb}_{0.5}(\text{I}_{0.8}\text{Br}_{0.2})_3$ -based SCs ranging from 700 to 900 nm limited the PCE improvement. Optimized $\text{MASn}_{0.5}\text{Pb}_{0.5}(\text{I}_{0.8}\text{Br}_{0.2})_3$ SCs with 560-nm-thickness exhibited a larger J_{sc} of 25.67 mA cm^{-2} and higher PCE of 17.13%, which is among highest-efficiency Sn-Pb binary perovskite SCs. Meanwhile, devices achieved minimal hysteresis and remained 92% of its initial PCE after being stored for 30 days under inert conditions ($\text{H}_2\text{O} < 0.1 \text{ ppm}$, $\text{O}_2 < 5 \text{ ppm}$).

2-terminal and 4-terminal tandem SCs: The low-bandgap Sn-Pb binary perovskites (down to 1.17 eV) enables their roles as bottom SCs in 2-terminal and 4-terminal tandem SCs that could theoretically achieve a PCE of 35%.^[61] As shown in **Figure 9**, 2-terminal tandem SCs consist of monolithically integrated subcells series-connected via a recombination layer. 4-terminal tandem SCs mechanically stack two individual subcells. Generally, wide bandgap semiconductors are employed in front cells, low bandgap semiconductors are employed in rear cells.

Using 1.2 eV bandgap $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ as the rear semiconductor, the optimized bandgaps for 2-terminal and 4-terminal architectures are ≈ 1.75 – 1.85 and 1.6 – 1.9 eV, respectively.^[18] $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ with a 1.8 eV bandgap was produced as the top material and the structure of 2-terminal tandem SCs is ITO/NiO/ $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.5}\text{Br}_{0.5})_3$ / $\text{PC}_{61}\text{BM}/\text{SnO}_2$ /zinc-tin-oxide (ZTO)/ITO/PEDOT:PSS/ $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ / C_{60} /BCP/Ag, as shown in **Figure 10A**. The recombination layer was made up of ZTO/ITO. 2-terminal tandem SCs exhibited a J_{sc} of 14.5 mA cm^{-2} , a V_{oc} of 1660 mV, a FF of 0.70, yielding an overall PCE of 16.9% and of 17.0% at its maximum power point (**Figure 10D**). The current matching between rear subcells and front subcells as

shown in **Figure 10B** positively contributed to high-efficiency 2-terminal tandem SCs. Furthermore, 2-terminal tandem cells showed no drop of PCE at its maximum power point under illumination in nitrogen for more than 18 h. Regarding 4-terminal architectures, $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ with a 1.6 eV bandgap was produced as the top monolithic material and ITO was used as a transparent top contact. Top monolithic $\text{FA}_{0.83}\text{Cs}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ cells achieved a PCE of 15.8% (**Figure 10C and D**). Rear $\text{FA}_{0.75}\text{Cs}_{0.25}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ cells filtered by top subcells presented a PCE of 4.5%. Therefore, 4-terminal yielded an overall stabilized efficiency of 20.3%.

Jen and co-workers systematically investigated the limited factors that determined the efficiency of 2-terminal tandem SCs. Regarding bottom subcells, low-bandgap (1.22 eV) $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskites with a conduction band value of 3.82 eV were fabricated. The electron-transport layer C_{60} with the highest electron-transport mobility among fullerenes would be the preferentially selected. However, C_{60} with the lowest unoccupied molecular orbital (LUMO) value of 4.0 eV would cause the energy-level mismatch at $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3/\text{C}_{60}$ interfaces that non-radiatively quenches charge carriers and hinders interfacial repopulation process, reducing the value of V_{oc} in low bandgap $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite SCs. Selected electron-transport layer IC_{60}BA would provide an intimate contact, alleviating nonradiative recombination losses from intrinsic, and photoinduced subgap defect states during charge transfer process across IC_{60}BA . Therefore, using IC_{60}BA as the electron-transport layer, low-bandgap $\text{MASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskite SCs could achieve a remarkably high V_{oc} of 0.84 V, which indicates a smaller voltage deficit (0.38 V) that is among the lowest value in reported low-bandgap Sn-Pb binary perovskite SCs and comparable with that of crystalline silicon SCs (0.38 V).^[60]

Regarding top subcells, the low bandgap Sn-Pb binary perovskites (1.22 eV) required complementary wide bandgap perovskites of 1.80–1.85 eV for photocurrent matching in 2-terminal tandem SCs. The incorporation of 10 mol% Cs in $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskites could exhibit the wide bandgap of 1.82 eV and achieve improved crystallinity. More importantly, $\text{MA}_{0.9}\text{Cs}_{0.1}\text{Pb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite SCs presented the excellent photostability, which could remain photocurrent density at the maximum power point under continuous illumination for 1 h. Moreover, wide-bandgap devices achieved a remarkably high V_{oc} of 1.20 V, indicating a voltage deficit of 0.42 V. The large voltage deficit originated from nonradiative recombination of $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskites (photoluminescence quantum yield $< 0.01\%$) and inappropriate energy-level alignment at the interface of $\text{NiO}_x/\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ (≈ 0.35 eV barrier).

Finally, combining low-bandgap bottom subcells, wide-bandgap top subcells with the interconnecting layer of PEDOT:PSS/sputtered ITO/ C_{60} -bis/ C_{60} , 2-terminal perovskite-on-perovskite tandem SCs were fabricated, as shown in **Figure 11A**. Realization of current matching between two subcells was of importance and theoretically investigated that current-matched conditions could be achieved by precisely thickness engineering of low-bandgap and wide-bandgap perovskites. **Figure 11B** showed the EQE spectra of two subcells. Manifestly, these two subcells achieved excellent current

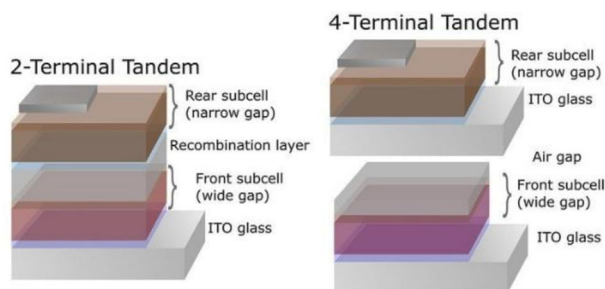


Figure 9. Schematics showing 2-terminal and 4-terminal tandem SCs. 2-terminal tandem SCs are monolithically series-integrating multicells connected via a recombination layer. 4-terminal tandem SCs are mechanically stacking two independent subcells. Figures reproduced with permission.^[18] Copyright 2016, American Association for the Advancement of Science.

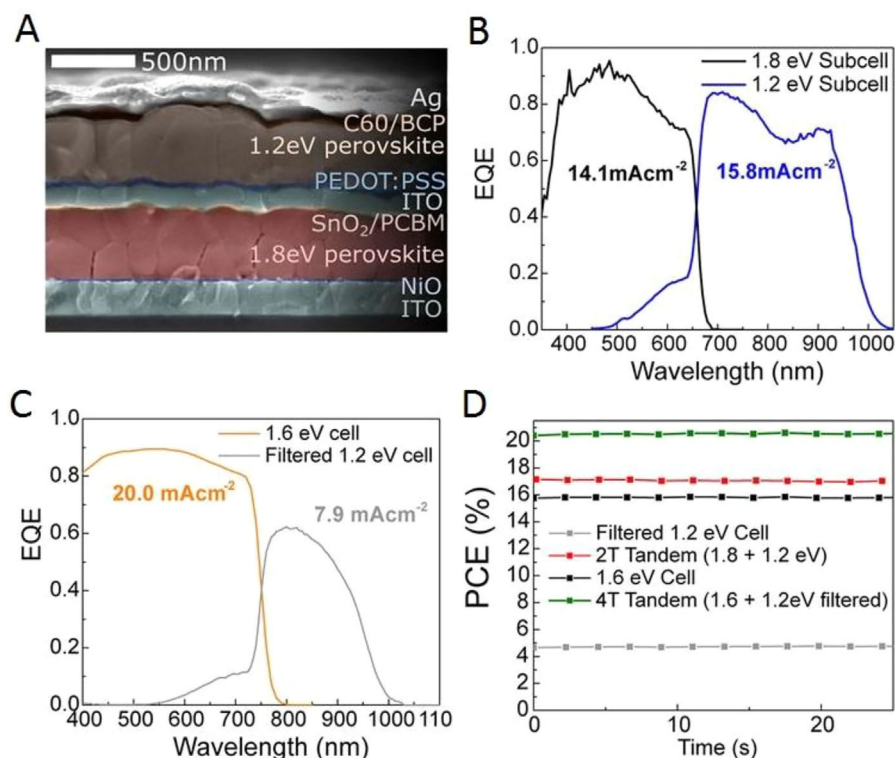


Figure 10. A) A cross-sectional SEM image of 2-terminal tandem cells. B) EQE spectra of the subcells in 2-terminal tandem cells. C) EQE spectra of the subcells in 4-terminal tandem cells. D) The time-resolved stabilized power output at the maximum power point for the 2-terminal tandem cells, the 1.2-bandgap-eV perovskite solar subcell filtered by an ITO-capped 1.6-bandgap-eV perovskite SC, the ITO-capped 1.6-bandgap-eV perovskite SC, and the mechanically stacked 4-terminal tandem cells under AM 1.5G illumination. Figures reproduced with permission.^[18] Copyright 2016, American Association for the Advancement of Science.

matching. The champion 2-terminal devices exhibited a J_{sc} of 12.7 mA cm^{-2} , a V_{oc} of 1980 mV, a FF of 0.73, yielding a PCE of 18.4% (Figure 11C), which is the highest efficiency among monolithic 2-terminal perovskite SCs reported till date.^[18,62] The steady-state power output as shown in Figure 11D tested at the maximum power point (1.55 V) was 18.5%, which was consistent with the results in Figure 11C and further confirmed the reliability of the 2-terminal tandem SCs. They also suggested some pathways to improve the efficiency of 2-terminal tandem SCs, including increased quality of perovskites, appropriate energy-level-alignment interfacial layers, minimization of parasitic losses, and molecular strategies to dope IC_{60}BA .^[36]

Yan and co-workers employed efficient low-bandgap (FASnI_3)_{0.6}(MAPbI_3)_{0.4} perovskite SCs ($\approx 1.25 \text{ eV}$) with a 17.6% PCE and semitransparent wide-bandgap $\text{FA}_{0.3}\text{MA}_{0.7}\text{PbI}_3$ ($\approx 1.58 \text{ eV}$) SCs to fabricate 4-terminal all-perovskite SCs. The top cell with a configuration of $\text{FTO}/\text{SnO}_2/\text{C}_{60}\text{-SAM}/\text{FA}_{0.3}\text{MA}_{0.7}\text{PbI}_3/\text{spiro-MeOTAD}/\text{MoO}_x$ (10 nm)/Au (8.5 nm)/ MoO_x (10 nm) achieved a steady-state efficiency of 17.9%. The bottom low-bandgap cell filtered by the top semitransparent cell achieved a PCE of 2.9%. Therefore, 4-terminal all-perovskite SCs provided a steady-state efficiency of 21.0%. It was found that the transparent Au layer had the significant absorption in the IR wavelength range and reduced the FF of the top cell. Therefore, higher efficiency of the 4-terminal all-perovskite SCs would be expected if top wide-

bandgap perovskite cells optimally matching with bottom low-bandgap cells and a semitransparent metal electrode.^[41]

2.2.2. Photodetectors

Compared with widely investigated Pb perovskite-based PDs with the spectral range from 300 to 800 nm,^[4,63] Sn-Pb binary perovskite PDs extending to NIR detection have been few reported. To widen spectral response to NIR range, polymers and quantum dots were introduced to Pb perovskite-based PDs. Nonetheless, these PDs suffered from low EQE at the NIR range that sometimes was lower than that of commercial silicon PDs, originating from tradeoff between NIR absorption and photocurrent extraction of these polymers and quantum dots.^[9] Promisingly, Sn-Pb binary perovskite PDs with excellent optical and electrical properties will address these issues and their current development with important figures of merit including responsivity (R), EQE, detectivity, rise/fall time, linear dynamic range (LDR), 3-dB bandwidth and device stability will be discussed below and summarized in Table 2.

Jen and co-workers firstly introduced ascorbic acid functionalizing as an antioxidant additive to (FASnI_3)_{0.5}(MAPbI_3)_{0.5} perovskites (1.24 eV bandgap), which strengthened the material stability and thus suppressed the leakage current of perovskite

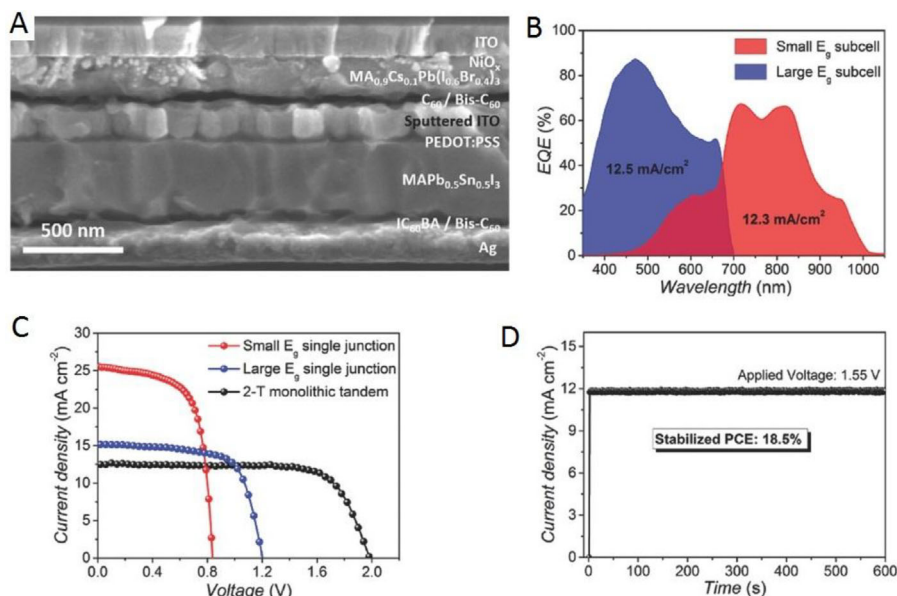


Figure 11. A) Cross-sectional SEM image of a characteristic device. B) EQE spectra of individual subcells in 2-terminal monolithic tandem cells. C) Typical J-V characteristics of 2-terminal tandem SC along with that of the small- and large-bandgap single-junction SCs. D) Steady-state current under AM1.5 illumination at the maximum power point of tandem SCs. Figures reproduced with permission.^[36] Copyright 2017, Wiley-VCH.

PDs.^[38] (FASnI₃)_{0.5}(MAPbI₃)_{0.5} perovskite PDs achieved a responsivity of over 0.2 A W⁻¹ between 800 and 950 nm, 3-dB bandwidth of 100 kHz (transit-time-limited), LDR of 40 dB, high detectivity of >10¹² Jones. Soon later, Yan, Zhang, Zhao and co-workers employed (FASnI₃)_{0.6}(MAPbI₃)_{0.4} (1.25 eV bandgap) perovskites obtained from mixed FASnI₃ and MAPbI₃ precursors to fabricate UV-vis-NIR PDs. By optimizing the thickness of perovskite layer and electron-transport layer C₆₀, they reduced noise current and simultaneously increased the value of EQE in the >650 nm wavelength range. Finally, PDs with EQE over 65% ranging from 350 to 900 nm, high detectivity of over 10¹² Jones, rise/fall time of 6.9/9.1 μs and large linear dynamic range of 83.5 dB under the negative bias of 0.2 V have been achieved.^[37]

Very recently, Choy and co-workers incorporated rubidium cations into the MA Sn-Pb perovskite system to realize controllable crystallization, as discussed in Section 2.1.1 One-step solution-process methods.^[43] Compared with MASn_{0.65}Pb_{0.35}I₃ perovskites, MA_{0.975}Rb_{0.025}Sn_{0.65}Pb_{0.35}I₃ perovskite films exhibited improved crystallinity, strengthened preferred orientation, which resulted into a smaller potential difference at the grain boundaries/grain interiors interface and a longer carrier lifetime. Consequently, as shown in **Figure 12A–E**, self-powered MA_{0.975}Rb_{0.025}Sn_{0.65}Pb_{0.35}I₃ perovskite-based PDs achieved improved responsivity of over 0.3 A W⁻¹ covering 800–950 nm, lower noise current, lower detectable signal intensity, larger LDR of 110 dB, increased detectivity of >10¹² Jones. Meanwhile, the PD presented the rise/fall time of 0.04/0.47 μs and 3-dB bandwidth of ≈1 MHz (Figure 12F). Notably, large LDR and 3-dB bandwidth were highest values among Sn-Pb binary perovskite-based PDs. The EQE value of MA_{0.975}Rb_{0.025}Sn_{0.65}Pb_{0.35}I₃ perovskite-based PDs is better than that of most commercial silicon PDs at the near-infrared region.

3. Challenges of Sn-Pb Binary Perovskites

3.1. Controlling Inter-Grain Sn/Pb Element Distributions

Some early works exhibited homogeneous Sn/Pb element distributions for Sn-Pb binary perovskite films,^[16,19,56] while Choy and co-workers investigated individual grains and observed that the molar ratio of Sn over Pb was not a constant, indicating inhomogeneous Sn/Pb element distributions between separate grains.^[42] In kesterite SCs, spatially inhomogeneous Cu(In,Ga)Se₂ semiconductors could induce bandgap fluctuations that would influence the photoluminescence and charge carrier transport properties.^[64] In the study of Choy and co-workers, they introduced DMSO molecules to realize the crystallization of MASn_{0.25}Pb_{0.75}I₃ perovskite films and thus tune the level of inter-grain inhomogeneous Sn/Pb element distributions. They observed bandgap fluctuations and different Urbach energies that suggested different energetic disorder levels for MASn_{0.25}Pb_{0.75}I₃ perovskite films. Importantly, reducing inter-grain inhomogeneous Sn/Pb element distributions beneficially improved the efficiency of Sn-Pb binary perovskite SCs. Therefore, it is of high importance to investigate inter-grain inhomogeneous Sn/Pb element distributions and further crystallize Sn-Pb binary perovskites to ameliorate such distributions.

It has been reported that the reaction between SnI₂ films and MAI is much faster than for the Pb analogue.^[65] MASnI₃ perovskite films normally exhibited pinhole, low surface coverage, which resulted into a poor efficiency of SCs.^[66] Hence, it is possible that competing transformation pathway from Sn-Pb binary perovskite precursors into solid thin films between Sn-based and Pb-based perovskites would be existed. This potentially resulted into inter-grain inhomogeneous Sn/

Table 2. Summary of Sn-Pb binary perovskite PDs.

Sn-Pb perovskites	Spectral range [nm]	R [A W^{-1}]	D^* [Jones]	t_r/t_f [μs]	3-dB bandwidth [MHz]	LDR [dB]	Ref
$\text{FA}_{0.5}\text{MA}_{0.5}\text{Sn}_{0.5}\text{Pb}_{0.5}\text{I}_3$	300–1000	0.2 @950 nm	$>1.0 \times 10^{12}$		0.1	40	[38]
$(\text{FASnI}_3)_{0.6}(\text{MAPbI}_3)_{0.4}$	300–1100	0.47 @920 nm	1.1×10^{12}	6.9/9.1		83.5	[37]
$\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$	300–1100	0.4 @910 nm	$>1.0 \times 10^{12}$	0.04/0.47	1	110	[43]

Spectral range means the detecting range of a PD. Responsivity (R) is the ratio of the output current signal to the intensity of incident light. Detectivity D^* is defined as $D^* = (A \cdot \Delta f)^{1/2} \cdot R / i_n$, where A is the device area, Δf is the bandwidth of a PD, R is the responsivity, and i_n is the total noise current. Rise/fall time (t_r/t_f) of a PD is the time that photocurrent reaches/reduces from 10%/90% to 90%/10% of the maximum photocurrent. LDR of a PD is defined by the linear responsivity, meaning that its output photocurrent is linearly proportional to its input intensity of incident light.

Pb element distributions. Controllable crystallization would tune the competing reaction and potentially produce high-quality Sn-Pb binary perovskite films with reduced inter-grain inhomogeneous Sn/Pb element distributions. As we discussed in Section 2.1, various crystallized methods have been

demonstrated to fabricate high-quality Sn-Pb binary perovskites. Consequently, inter-grain inhomogeneous Sn/Pb element distributions should be further investigated and its influence on the optical features, Urbach energy, photoluminescence, carrier lifetimes of Sn-Pb binary perovskites

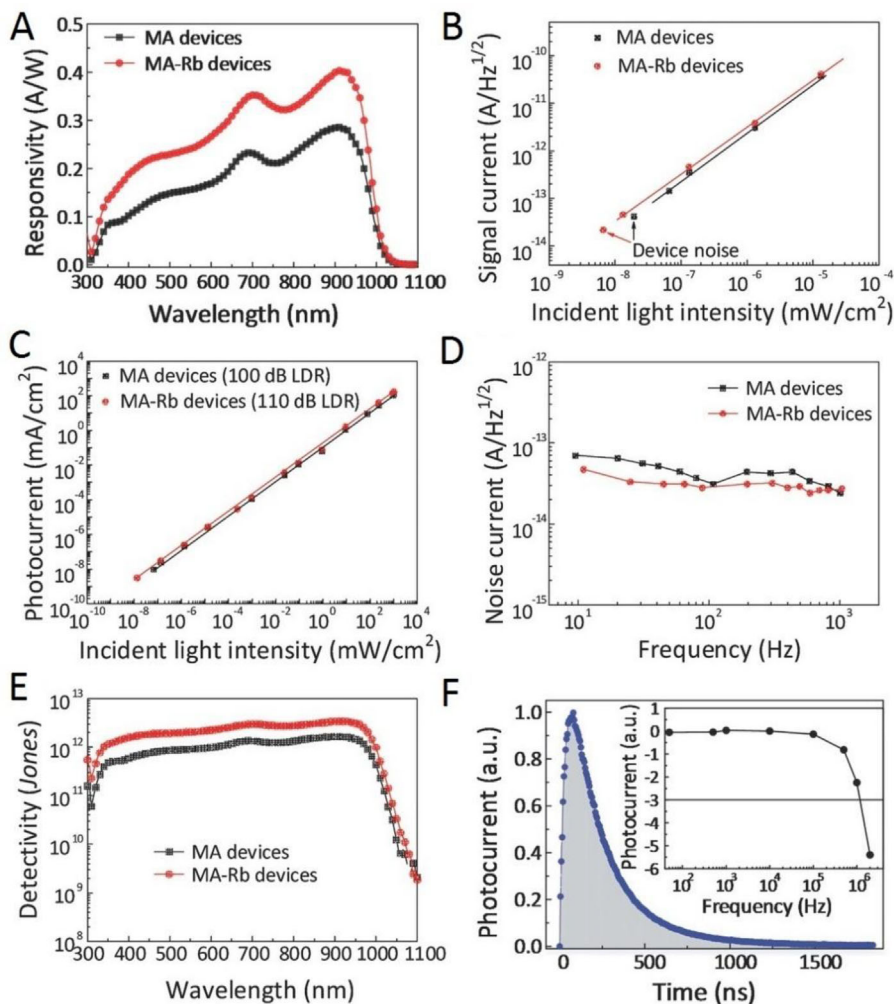


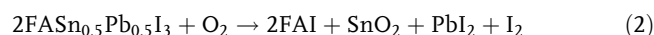
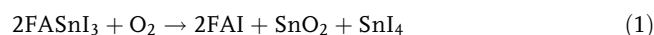
Figure 12. A) Responsivity, B) signal current against incident light intensity, C) linear dynamic range plot (i.e., photocurrent density vs. incident light intensity), D) noise current as a function of signal frequency, E) specific detectivity versus spectral response range of self-powered MA-based and MA-Rb-based PDs, respectively. F) Transient photocurrent response of self-powered MA-Rb Sn-Pb perovskite PDs. Inset shows the frequency response of self-powered MA-Rb Sn-Pb perovskite PDs. Figures reproduced with permission.^[43] Copyright 2018, Wiley-VCH.

should be studied in detail. Meanwhile, different inter-grain crystal facets induced by the crystallization of inhomogeneous Sn/Pb element distributions on optical and electric properties of Sn-Pb binary perovskites and on performances of SCs could be thoroughly investigated.^[67]

3.2. Stability of Sn-Pb Binary Perovskites

Early works suggested that the oxidation of Sn^{2+} in MASnI_3 perovskites to Sn^{4+} would cause SnI_4 gas evolution and related Sn^{2+} and I^- vacancies that worked as recombination centers.^[11,66,68] Meanwhile, the fast deterioration of absorption, crystalline structure, and associated device performances was experimentally observed. Distinctively, several research groups demonstrated that Sn-Pb binary perovskites could achieve better material stability in comparison with pure Sn-based perovskites and even pure Pb-based perovskites.^[15,18,43] Encapsulated Sn-rich perovskite PDs ($\text{MA}_{0.975}\text{Rb}_{0.025}\text{Sn}_{0.65}\text{Pb}_{0.35}\text{I}_3$) could remain the photocurrent and dark current density over 200-day storage.^[75] These results highlight that Sn-Pb binary perovskites might have superb material stability.

Recently, oxidation mechanism and related reaction products of $\text{FASn}_{0.5}\text{Pb}_{0.5}\text{I}_3$ perovskites have been experimentally studied.^[69] As shown in reaction Equations (1) and (2), the predominant degradation mechanism produced I_2 instead of SnI_4 that was generated from degraded FASnI_3 perovskites.



The degradation reaction (2) required the oxidation of both the tin and iodide species, and broke many Sn-I bonds, while the degradation reaction (1) broke fewer Sn-I bonds. Meanwhile, the activation energy for the reaction (2) was 731 meV, which is larger than that of 537 meV for the reaction (1). Therefore, SnI_4 formation was prevented, forcing the oxidation reaction to proceed through the less favorable pathway, requiring more Sn-I and Pb-I bonds to break to form I_2 , which explained the enhanced stability of Sn-Pb binary perovskites.^[69] Meanwhile, the material instability of pure Sn-based perovskite MASnI_3 was observed,^[70] which was investigated through surface- and bulk-sensitive photoelectron spectroscopy with synchrotron radiation and theoretical calculations. It was found that changes of surface chemical states, including broken chemical bonding in Sn-I and the depletion of MA^+ cation on the surface region, result into the material instability of Sn-based perovskite MASnI_3 . These suggest that enhanced stability of MA Sn-Pb binary perovskite-based devices originates from the Pb incorporation.

In addition, other factors that result into degradation, including water immersion, light-induced phase instability that are common concerns in Pb-based perovskites, have been scarcely discussed in low-bandgap Sn-Pb binary perovskites. Pb-based perovskite films will generally suffer from the fast degradation when stored in the atmosphere of O_2 and water, various surface treatments and hole/electron-transport-layer engineering have been demonstrated to improve the stability of

related SCs.^[71] Therefore, after understanding the degradation mechanism of Sn-Pb binary perovskites, effective methods, including surface treatments and interfacial engineering, could be proposed to study its influence on the stability, and finally lead into increased stability of Sn-Pb binary perovskites and related optoelectronic devices.

4. Conclusion and Outlook

In this article, we have reviewed crystallization, properties, and challenges of low-bandgap Sn-Pb binary perovskite films and associated applications in single-junction, 2-terminal, 4-terminal tandem SCs, and PDs. Different crystallization through precursor engineering, the hot-casting technique and vacuum-process method, and its impacts on the morphology, crystallinity, preferred orientation, and optical/electrical features of resultant Sn-Pb binary perovskites have been detailedly studied. Challenges, including controlling inter-grain Sn/Pb element distributions and the stability of materials and related optoelectronic devices have also been detailedly discussed.

Currently, low-bandgap Sn-Pb perovskite-based single-junction, 2-terminal, and 4-terminal SCs have achieved the PCE values of 17.8%, 18.4%, 21.2%, respectively. These values of efficiency are far lower than the efficiency limits, suggesting a large gap to advance device performances. The efficiency loss mainly originates from 1) low-surface-coverage Sn-Pb binary perovskite films; 2) traps and defects, such as Sn^{2+} vacancies, I^- vacancies and Sn^{4+} states; 3) un-passivated surfaces of Sn-Pb binary perovskites; 4) inappropriate energy-level alignment between Sn-Pb binary perovskites and hole/electron transport layers; 5) mismatched carrier mobilities between perovskites and hole/electron transport materials. Moreover, inter-grain inhomogeneous Sn/Pb element distributions would decrease the efficiency improvement. Consequently, the profound investigation of controllable crystallization, compositional engineering, surface passivation, selection of hole/electron interfacial materials of Sn-Pb binary perovskites will be beneficial for advancing the efficiency of SCs. Meanwhile, the investigation will positively contribute to suppress noise current, raise photocurrent and optimize response speed of PDs, although low bandgap Sn-Pb perovskite-based PDs have achieved better EQE than most commercial PDs at the NIR region. In the near future, device stability and appropriate encapsulation should be further investigated toward commercializing these solution-process and low-temperature Sn-Pb binary perovskite-based devices.

Acknowledgements

This work was supported by the University Grant Council of the University of Hong Kong (Grant 104003113), the General Research Fund (Grants 17211916 and 17204117), the Collaborative Research Fund (Grants C7045-14E) from the Research Grants Council of Hong Kong Special Administrative Region, China.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

inter-grain element distributions, low-bandgap Sn–Pb perovskites, perovskite crystallization, perovskite solar cells, perovskite photodetectors

Received: May 24, 2018

Revised: June 21, 2018

Published online:

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