Progress towards High-Efficiency and Stable Tin-Based Perovskite Solar Cells

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Abstract: Since its invention in 2009, Perovskite solar cells (PSCs) has attracted great attention because of its low cost, numerous options of efficiency enhancement, ease of manufacturing and high-performance. Within a short span of time, the PSC has already outperformed thin-film and multicrystalline silicon solar cells. A current certified efficiency of 25.2% demonstrates that it has the potential to replace its forerunner generations. However, to commercialize PSCs, some problems need to be addressed. The toxic nature of lead which is the major component of light absorbing layer, and inherited stability issues of fabricated devices are the major hurdles in the industrialization of this technology. Therefore, new researching areas focus on the lead-free metal halide perovskites with analogous optical and photovoltaic performances. Tin being nontoxic and as one of group IV(A) elements, is considered as the most suitable alternate for lead because of their similarities in chemical properties. Efficiencies exceeding 13% have been recorded using Tin halide perovskite based devices. This review summarizes progress made so far in this field, mainly focusing on the stability and photovoltaic performances. Role of different cations and their composition on device performances and stability have been involved and discussed. With a considerable room for enhancement of both efficiency and device stability, different optimized strategies reported so far have also been presented. Finally, the future developing trends and prospects of the PSCs are analyzed and forecasted.

Keywords: Perovskite Solar Cells (PSCs); Lead free; Nanomaterial; Photovoltaic, Renewable Energy

1. Introduction

For the ever-growing global energy consumption and rapidly depleting fossil fuels reserves, production of energy from clean, sustainable, and renewable energy sources is necessary. Solar radiation is an unlimited form of clean and renewable energy. Its low cost and efficient harvesting can endlessly fuel our civilization. To date, the conventional silicon based solar cells have dominated the photovoltaic (PV) market because of its superior stability and high power conversion efficiency (PCE). Its highest efficiency surpassing 26% recorded at standard test conditions [1]. However, the initial production cost associated with silicon wafers used in this technology was very high. Finding alternative technologies to Si solar cells, which can compete in providing high PCE, excellent stability, high reproducibility and low cost, are still challenges for scientific community.
In a short span of less than 10 years, organo-metal halide perovskites (OMHPs) have emerged as a champion photovoltaic technology. Its solution processed fabrication, lower manufacturing cost and high PCE, made perovskite solar cell a promising future photovoltaic technology [2,3]. The OMHPs are group of materials with a formula of ABX3, where A and B represent cations of different sizes and X represent an anion. For perovskite solar cell (PSC), the most commonly used small organic-inorganic cations (A), are methyl-ammonium CH3NH3+ [4,5], formamidinium NH2CH3NH2+ [6,7], and cesium Cs [8,9]. Pb2+, Ge2+ and Sn2+ all belonging to the group-IV(A) family, are widely reported as a divalent metal cation (B) [10,11]. Whereas F-, Cl-, Br- and I- are the most used monovalent halogen anions (X) in PSCs [12].

Known for their exceptional optoelectronic properties, perovskite materials were subject of investigation in the late 19th century for their potential applications in light emitting diodes (LEDs) and field effect transistors (FETs) [13,14]. In 2009, Miyasaka and coworkers for the first time employed these materials in solar cells [15]. By successfully using of CH3NH3PbBr3 and CH3NH3PbI3 as a sensitizer in Dye-sensitized solar cells (DSSCs), efficiencies of 3.13% and 3.81% were obtained respectively [15]. These efficiencies were further elevated to 6.54% in 2011, when Lee et al., sensitized 3.6 μm-thick TiO2 films with quantum dots of CH3NH3PbI3 employing quantum-dot sensitized solar cell (QDSSC) architecture [16]. However, the fabricated devices degraded within minutes because the corrosive redox electrolyte dissolved the QDs. This forced the researchers to focus on all solid state perovskite devices. The very first all solid state perovskite based solar cell was reported in 2012 [17], where the liquid electrolyte was replaced by organic hole transport material, spiro-OMeTAD. This significantly improved the stability of perovskite devices with elevating efficiency to exceed 9% [17]. From then on many notable groups and researchers around the globe joined the perovskite fever [18] by reporting different device architectures such as mesoscopic n-i-p [19], planar n-i-p [20], inverted mesoscopic p-i-n [21] and inverted planar p-i-n [22]. One major factor deciding the performance of the PSC was the quality of perovskite films. To achieve high quality perovskite films many different depositing techniques were reported such as one-step solution deposition [23], two-steps solution deposition [24], vapor assisted deposition [25], thermal vapor deposition [26], blade coating [27], ink jet printing [28], spray coating [29], slot die coating, screen printing and other emerging techniques [30]. To enhance the stability and overall PCE of the devices, many different approaches had been investigated, such as solvent engineering, process engineering, band gap engineering and contact engineering [31].

Within a decade the overall PCE of perovskite solar cell has dramatically improved from 3.81% in 2009 to 25.2% in 2019 [32]. Lead (Pb) was used as a divalent metal cation in almost all high-performance devices [33]. The toxicity of lead is an established fact, and risk of lead being inevitably accumulating in the food chain increases many folds with lead halide making water soluble lead compounds overtime [34]. It is therefore necessary, and compelling to common sense that perovskite solar cells must go lead free. With a smaller ionic radius of 73 (pm), a lower electronegativity and more covalent nature than Pb2+, Ge2+ was thoroughly investigated by Stoumpos et al., as a potential candidate for replacing lead in PSCs [35]. The germanium perovskites crystallize in trigonal crystal structure having a bandgap of 1.9 eV for MAGeI3 [36]. Although the theoretical calculated efficiency for CsGeI3 is 27.9% [37], practically the efficiency remained under 1% for all germanium based PSCs because of the poor film quality and instability of the Ge2+ ion towards oxidation to Ge4+ [1,35]. Gratzel and group replaced Pb with Cu only to achieve a meager efficiency of 0.017% [38]. High effective mass of holes, low absorption coefficients and the low intrinsic conductivity of the employed perovskite layer proved to be the main causes of poor performance.

Tin (Sn) has emerged as the most promising alternative to lead because of the same isoelectronic configuration of s2p2, and has considerably high mobilities [10^-10^8 cm2(V⋅s^-1)] when used in perovskites as compared to conventional lead based perovskites [10^-10^8 cm2(V⋅s^-1)] [39]. However, the facile formation of Sn vacancies along with stability of Sn in 2+ oxidation state is in question. In the presence of oxygen Sn2+ is known to be oxidized to Sn4+ oxidation state [40]. The
oxidized Sn\textsuperscript{4+} behave as a p-type dopant, and with a concentration of even less than 0.1% it has drastic effects on PCE of the device \cite{41}.

Eyeing large scale modules and commercialization of Sn based PSCs, device stability and performance must be addressed simultaneously. This review will focus on important breakthroughs reported for Sn based perovskite from 2014 to 2020 for aforementioned parameters. Factors playing key role in device performance enhancement will be discussed. Role of different cations and their composition as reported since 2014 will be summarized. Furthermore possibilities and challenges for large scale application of Sn based PSCs are profoundly summarized.

2. Methylammonium tin halides (CH\textsubscript{3}NH\textsubscript{3}SnX\textsubscript{3}, X = I, Br, Cl)

In 2014 Snaith and coworkers reported the very first methylammonium tin iodide (CH\textsubscript{3}NH\textsubscript{3}SnI\textsubscript{3}) based completely lead free PSC \cite{42}. An efficiency of 6.4\% was recorded for the best performing device. The perovskite layer was deposited by spin coating a solution having equimolar quantities of CH\textsubscript{3}NH\textsubscript{3}I and SnI\textsubscript{2} prepared in degassed N-dimethylformamide (DMF). Having a small band gap of 1.23 eV, the open circuit voltage (V\textsubscript{OC}) for the best performing device showed a remarkable value of 0.88 V, with estimated loss of only 0.35 eV. A mobility of 1.6 cm\textsuperscript{2}V\textsuperscript{-1}s\textsuperscript{-1} with diffusion length of 30 nm was calculated for CH\textsubscript{3}NH\textsubscript{3}SnI\textsubscript{3} perovskite films. While a diffusion length of almost 1 \( \mu \)m was reported for the lead based counterparts of MASnI\textsubscript{3} \cite{43}. It was observed that for Sn based perovskites the diffusion lengths can be increased up to 1 \( \mu \)m by suppressing background concentration of holes. All devices were fabricated in inert environment and properly encapsulated to minimize the exposure of perovskite layers to oxygen and humidity. While stability of Sn based perovskites remained an issue, high PCE (6.4\%) paved the way for further research.

In the same year Stoumpos et al., reported an overall PCE of 5.73\% for band gap engineered MASnI\textsubscript{x}Br\textsubscript{3-x} based perovskite devices \cite{44}. It was observed that the conduction band edge of MAPbI\textsubscript{3} is 0.23 eV higher than that of MASnI\textsubscript{3}, which was why devices fabricated with the later has lower open circuit voltage compared to MAPbI\textsubscript{3}. In order to increase the V\textsubscript{OC} of Sn based perovskite devices, band gap was tuned by substituting bromide atoms for iodide atoms. These band gap tuned perovskites were synthesized in nitrogen glove box by mixing stoichiometric amounts of MAX and SnX\textsubscript{2} (X = Br, I), finely homogenized in a mortar. Followed by sealing in silica ampules under 1\times 10\textsuperscript{-4} mbar vacuum and heated to 200 \textdegree C.

The absorption onset of these hybrid halide perovskites can be tuned by proper substitution of bromide atoms, using MASnI\textsubscript{3} having smallest optical band gap of 1.3 eV, and MASnBr\textsubscript{3} with the largest optical band gap of 2.15 eV. An increase in V\textsubscript{OC} was observed with increasing Br content. A V\textsubscript{OC} of 0.68 V was recorded for MASnI\textsubscript{3} which increased up to 0.88 V for MASnBr\textsubscript{3} based device. However, the short circuit current density (J\textsubscript{SC}) showed an opposite trend and decreased from 16.30 mA.cm\textsuperscript{-2} for MASnI\textsubscript{3} to 8.26 mA.cm\textsuperscript{-2} for MASnBr\textsubscript{3} \cite{44}. The best PCE of 5.73\% was recorded for device with MASnBr\textsubscript{3}, having a V\textsubscript{OC} of 0.82 V, J\textsubscript{SC} of 12.30 mA.cm\textsuperscript{-2} and Fill Factor (FF) of 0.57. A considerable high photovoltaic performance and atmospheric stability still remained a major concern for these devices. However, when sealed with surlyn films and stored in nitrogen glove box, the fabricated cells retained 80\% of their initial photovoltaic performance in the first 12 h, which was very encouraging. By applying advanced sealing techniques the stability can further be significantly improved.

In an attempt to enhance the perovskite film quality and morphology, in 2015 Kanatzidis group reported a solvent mediated crystallization for MASnI\textsubscript{3} based PSCs \cite{45}. By doing so, they achieved a highly uniform and pin hole free perovskite films, with a J\textsubscript{SC} reaching to 21 mA.cm\textsuperscript{-2} and overall PCE of 3.15\%. Two major factors governing photovoltaic performance of Sn based PCSs are self-doping and film quality. The Sn perovskites were prone to easily decomposed in isopropanol along a fast reaction rate between methylammonium iodide and SnI\textsubscript{2} films. This lead to an uncontrolled crystallization process of Sn perovskite films resulting in a poor film quality with presence of micron sized pinholes \cite{45,46}.

Sn\textsuperscript{2+} has greater Lewis Acidity than Pb\textsuperscript{2+} \cite{47} resulting in a fast reaction dynamics between SnI\textsubscript{2} and MAI. When using DMF as a solvent, for the same concentrations MASnI\textsubscript{3} will crystallize more rapidly than MAPbI\textsubscript{3} while making perovskite films. This rapid crystallization gives rise to defects in
perovskite films. To address this issue Kanatzidis and coworkers employed solvent engineering, where they used dimethyl sulfoxide (DMSO) because of its strongly coordinated nature, relatively high boiling point (189 °C) than DMF and a low saturated vapor pressure (0.42 Torr at 20 °C) [47]. Two different perovskite films were prepared by using DMF and DMSO as solvents. The films prepared with DMF crystallized rapidly during spin coating resulting in a dark brown color. However, uniform and light yellow films were obtained during spin coating when DMSO was used as a solvent, which were then annealed at 100 °C for 15 min to obtain a black perovskite film.

These results were further confirmed by comparing the XRD patterns of both films before and after thermal annealing as shown in Figure 1. Annealing has no effect on the prepared films by using DMF as a solvent, as all the peaks corresponding to tetragonal MASnI₃ phase in space group P4mm, were observed before and after annealing. This confirms the films were crystallized before annealing and showed no change afterwards. While in films made with DMSO a totally different reflection pattern was observed before annealing, which corresponded to neither the starting materials nor expected perovskite films. The DMSO was known to form MAPbI₃.DMSO complex when used for lead based perovskite films [48]. Hence it was assumed that this pattern correspond to a similar intermediate solvated phase. Careful investigations of XRD pattern of this solvated phase revealed the presence of SnI₂:3DMSO, acting as a cation instead of CH₃NH₃⁺ cation. Figure 1c shows the Fourier transform infrared spectroscopy (FTIR) spectra of C=S and S=O stretching vibrations from the Sn²⁺-coordinated DMSO solvent at 960 and 1012 cm⁻¹, respectively. After annealing this phase disappeared and was converted to MASnI₃. Compared to DMF, the DMSO as a solvent in perovskite films yielded much smoother, homogeneous and pin hole free perovskite films due to its controlled crystallization. Perovskite devices based on these films showed an overall PCE of 3.15%, with extraordinary JSC of 21 mA.cm⁻² and a moderate VOC of 320 mV.

Figure 1. (a) Perovskite films prepared using DMSO as a solvent before and after annealing employing single step spin coating technique; (b) XRD patterns of the perovskite films using different solvents before (left) annealing and after (right) thermal treatment at 100 °C for 15 min; (c) FTIR spectra of the perovskite films deposited from a solution of DMSO before (Bottom) and after annealing (Top). At 960 cm⁻¹ the characteristic C=S and at 1012 cm⁻¹, C=O stretching vibrations
arising from Sn\textsuperscript{2+}-coordinated DMSO solvent can be seen before annealing. Adapted with permission from [45]. Copyright © 2020, American Chemical Society.

In a similar attempt, Bein and coworkers proved the usefulness of 1,4-dioxane mixed with methanol as a solvent for preparing high quality, pin hole free MASnI\textsubscript{3} perovskite films [49]. They choose a one-step spin coating route to prepare the perovskite films with precursors already dissolved in a mixture of MeOH:Dioxane. The perovskite was formed instantly after dropping the solution on spin coater because of the high vapor pressures of both MeOH and Dioxane. When compared with devices fabricated from DMF and DMSO as a solvent, device fabricated with MeOH:Dioxane mixture as a solvent yielded better photovoltaic results because of enhanced quality films and suppressed p-doping. An overall PCE of 1.05% was recorded for device fabricated with MeOH:Dioxane mixture which was considerably higher than that of devices fabricated with DMF and DMSO as solvents. While this method addressed issues of defects in thin films high background carrier density was still a major factor limiting PCE.

To reduce high background carrier density Kanatzidis and group proposed a process of reducing vapor atmosphere while preparing Sn based perovskite devices [50]. An overall PCE of 3.89% was achieved for MASnI\textsubscript{3}-based devices employing this technique. Perovskite layer was prepared by spin coating a solution of MASnI\textsubscript{3} in the presence of hydrazine vapors. Hydrazine is a well-known reagent, which will reduce metal oxides and metal salts to pure metals. It is also used to reduce surrounding oxygen levels. The Sn perovskite films, when grown in the hydrazine atmosphere showed a reduction in Sn\textsuperscript{4+} impurities along with suppressing unfavorable reduction of Sn\textsuperscript{2+}.

By reducing Sn\textsuperscript{4+} to Sn\textsuperscript{2+}, Sn\textsuperscript{2+} vacancies are reduced, resulting in lowering p-type conductivity in perovskite films. Also the lower amount of Sn\textsuperscript{2+} vacancies resulted a decrease in anion antisite and cation antisite formation, further contributing to lowering of p-type self-doping [50]. Using this technique the Sn\textsuperscript{4+}/Sn\textsuperscript{2+} ratio was reduced by 45.8% compared to the ratios without using hydrazine atmosphere. This work was a significant step towards high performing MASnI\textsubscript{3} based devices, but stability remained a challenge.

Kanatzidis and coworkers also suggested a low temperature vapor assisted solution process (LT-VASP) for minimizing p-type doping, reducing short circuiting and enhancing film quality for Sn based perovskites [51,52]. An overall PCE of 1.86% was reported for the best performing device. This method yielded better surface morphologies of perovskite films with great reproducibility and enhanced air stability. However, the first considerably stable MASnI\textsubscript{3} based perovskite films were reported by Horn et al., [53], where they used a two-step fabricating technique. These films showed remarkable stability as compared to all the earlier reported MASnI\textsubscript{3} films both in air and in nitrogen glove box. These stable perovskite films were obtained by depositing SnI\textsubscript{2} on FTO substrates using thermal evaporation of SnI\textsubscript{2} at a slow rate (2nm min\textsuperscript{-1}) in a vacuum. Followed by spin coating a solution of MAI in 2-propanol. Morphological studies as shown in Figure 2 revealed a higher coverage of substrate with perovskite crystals as compared to films synthesized using solution based processes.

**Figure 2.** Images of different films as seen under SEM (a) Vapor-deposited 100 nm thick SnI\textsubscript{2} film; (b) MASnI\textsubscript{3} films prepared from a solution of 6 mg mL\textsuperscript{-1} using spin-coating technique ( before
annealing); (c) 10 mg mL\textsuperscript{-1}; (d) 20 mg mL\textsuperscript{-1}; (e) 40 mg mL\textsuperscript{-1} MAI solutions; (f) and a MASnI\textsubscript{3} perovskite film prepared using 20 mg mL\textsuperscript{-1} MAI followed by thermal treatment at 80 °C for 10 min. Adapted with permission from [53]. Copyright © 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Significant variations were observed in the sizes of perovskite crystals as the concentration of MAI solution changed. Few large crystals of 3-4 μm size were present, while rest of the substrate was covered by small 100-200 nm sized crystals when a 6 mg mL\textsuperscript{-1} solution of MAI was used. An increasing trend of crystal size was observed as concentration of MAI was increased however the crystal size again decreased for MAI solution with concentration of 40 mg mL\textsuperscript{-1} [53]. When exposed to air for an hour no visible change was observed in the color confirming the superior stability of these films with respect to films reported earlier. A 20 days old sample stored in nitrogen glove box showed no signs of degradation as no MAI or SnI\textsubscript{2} were present in it. Furthermore, when illuminated for 40 min along with exposure to air for 2 h these perovskite films retained 80% of their absorbance at 550 nm and no noticeable change in color was observed.

The stability of MASnI\textsubscript{3} based devices was significantly increased by incorporating 5-ammonium valeric acid iodide (5-AVAI) in MASnI\textsubscript{3} films. Shigeeda et al., reported a very slow oxidation rate for MASnI\textsubscript{3} crystals when added with 5-AVAI [54]. When XRD patterns of films fabricated using just MASnI\textsubscript{3} and films fabricated using MASnI\textsubscript{3}: 5-AVAI was compared. It was observed that for pure MASnI\textsubscript{3} films after 64.3 h half of the cubic phase has oxidized. Moreover most of the cubic phase is oxidized just after 88.5 h. However, in the case of 5-AVAI : MASnI\textsubscript{3} films (1:20) it took 113.5 h to oxidize half of the cubic phase, which was significant improvement in the device stability.

To further enhance the stability of MASnI\textsubscript{3} based perovskite devices, Adachi and group reported a unique method of combining anti-solvents with miscibilities, which are different than that of the precursor solvent [55]. Using this technique they significantly improved the coverage of the perovskite films. An overall PCE of 2.14±0.35% was reported for planar perovskite solar cells prepared using these films. Morphology of perovskite film being a key player in deciding the overall performance of device, Adachi and coworkers controlled the crystallization of perovskite films using the SB method. In the SB method, anti-solvent bath was used to extract the good solvent in the precursor solution employing miscibility processes, where the miscibility between the solvents influences the extraction speed. By controlling the solvent extraction, growing of perovskite film is controlled. This method is also reported for Pb based perovskite solar cells and has been proved very effective in having smooth pin hole free perovskite films [56]. For MASnI\textsubscript{3} based perovskite devices the fabricated PSCs remained stable for over 200 h without degrading under standard 1 Sun illumination.

The stability of encapsulated devices based on MASnI\textsubscript{3} reached 500 h when Yamada et al., used SnF\textsubscript{2} incorporated MASnI\textsubscript{3} perovskite films [57]. Hao et al., previously used SnF\textsubscript{2} doping in MASnI\textsubscript{3} films to increase carrier diffusion length up to 500 nm [58]. Yamada and group reported a bandgap of 1.25 eV for SnF\textsubscript{2} doped MASnI\textsubscript{3} films, while films without SnF\textsubscript{2} doping showed an absorption edge that was significantly blue shifted. This blue shifted absorption edge in pure MASnI\textsubscript{3} films was assigned to unintentional p-type doping. SnF\textsubscript{2} addition increased the photocarrier lifetime by one order of magnitude. These encapsulated devices showed a PCE of 1.94% with an astonishing stability of 500 h under 1 Sun illumination.

The real breakthrough for stable methylammonium tin halide based devices was reported in 2017 by Mohanta et al., [59] where they synthesized methylammonium mixed tri-halide tin (MASnI\textsubscript{Br}_x\textsubscript{-}Cl\textsubscript{1-x}) perovskites. Mohanta and group fabricated perovskite devices based on these films on a carbon based mesoscopic structure, making it free from both lead and hole transporting layer (HTM). Equimolar solution of MAI and SnCl\textsubscript{2}/SnBr\textsubscript{2} were mixed in DMF. While keeping MAI at 100% the molar ratios of SnCl\textsubscript{2}/SnBr\textsubscript{2} were varied from 0/100, 10/90, 25/75, 50/50, 75/25 and 100/0 to vary I/Br/Cl ratios in perovskite films. The Eg = 1.81 eV along with spectral onset close to 700 nm was observed for films having 0% SnCl\textsubscript{2} (MASnI\textsubscript{Br}_x). A blue shift was observed as the ratio of SnCl\textsubscript{2} increased from 0 to 25%, confirming the presence of CI within Sn perovskite films. A significant red
shift was observed when SnCl2/SnBr2 ratio was increased to 50/50. Further increase in the ratios resulted in further red shift of absorption onset of perovskite films with the spectral edge touching 1000 nm for films made with 0% SnBr2 and 100% SnCl2 [59]. This technique resulted in having tin perovskite films with different proportions of halides such as MASnIBr2, MASnI1.8Cl0.2 and MASnIBr1.8Cl0.2 producing PCE of 2.18%, 1.87% and 3.11% respectively. The best performance parameters were obtained for devices having MASnI1.8Cl0.2 as perovskite. A Jsc of 13.99 mA.cm-2 with a Voc of 380 mV and a FF of 0.573 was recorded for this device. With a 3.11 % PCE the encapsulated device remained stable for over 2000 h which is quite remarkable.

The highest efficiency reported till date for MASnI3 based PSCs is 7.78%, achieved through ion exchange/insertion reactions approach [60]. Song and group employed a very unique strategy of using SnF2 and MAI as precursors for MASnI3 perovskite films through ion exchange/insertion reactions. This unique method resulted in the formation of a very high quality perovskite film, having large amount of SnF2 and very low concentration of Sn4+ [60]. The conversion steps are as follows:

\[
\text{SnF}_2 + 2\text{CH}_3\text{NH}_3\text{I} \rightarrow \text{SnI}_2 + 2\text{CH}_3\text{NH}_3\text{F} \quad (1)
\]
\[
\text{CH}_3\text{NH}_3\text{F} \rightarrow \text{CH}_3\text{NH}_3\text{H} + \text{HF} \uparrow \quad (2)
\]
\[
\text{SnI}_2 + \text{CH}_3\text{NH}_3\text{I} \rightarrow \text{CH}_3\text{NH}_3\text{SnI}_3 \quad (3)
\]

In the very first step of the perovskite film formation an ion exchange reaction took place between gaseous CH3NH3I and a solid state SnF2, generating the intermediate SnI2 and byproduct CH3NH3F. The byproduct is then removed via evaporation in the second step; while in the third step gaseous MAI reacted with SnI2 to form the perovskite. It was observed that as the time of ion exchange/insertion reaction was increased from 5 min to 40 min the size of MASnI3 crystals also increased forming a compact pinhole free perovskite film as shown in Figure 3. The perovskite films with excess SnF2 obtained through this method were used in planner heterojunction structure (ITO/PEDOT:PSS/MASnI3/PC61BM/BCP/Ag) PSCs. Champion device produced an overall PCE of 7.78% with a stability of over 200 h for un-encapsulated devices tested under continuous 1 Sun illumination in N2 atmosphere. Such a high efficiency with considerable stability is a very promising sign for the future of lead free perovskite devices. Table 1 summarizes the performance of best MA tin halide (s) based devices reported until 2020. Table 2 summarizes how the stability for MA tin based perovskite has shown increasing trend over the last few years.

![Figure 3](https://example.com/figure3.png)

**Figure 3.** Surface SEM images of (a) pristine SnF2/PEDOT:PSS film, and treated by the ion exchange/insertion reaction for; (b) 5 min; (c) 10 min; (d) 20 min; (e) 30 min; (f) 40 min; (g) 60 min; (h) 80 min. Adapted with permission from [60]. Copyright © 2020 The Authors. Published by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
### Table 1. Performance of best MA tin halide (s) based devices reported until 2020.

| Year | Device architecture | Perovskite Film Fabrication technique/Perovskite Film | J_{sc} (mA/cm²) | Voc (V) | FF | EFF (%) | Ref. |
|------|---------------------|-----------------------------------------------------|-----------------|--------|----|---------|------|
| 2014 | FTO/c-TiO₂/mp-TiO₂-Perovskite/HTL/Au | Spin Coating using DMF as solvent/MASnI₃ | 16.8 | 0.88 | 0.42 | 6.4 | [42] |
| 2014 | FTO/c-TiO₂/mp-TiO₂-Perovskite/HTL/Au | Spin Coating using DMF as solvent/MASnI₃–xBrₓ | 12.3 | 0.82 | 0.57 | 5.73 | [44] |
| 2015 | FTO/c-TiO₂/mp-TiO₂-Perovskite/Au | Spin Coating using DMSO as solvent/MASnI₃ | 21.4 | 0.32 | 0.46 | 3.15 | [45] |
| 2016 | FTO/c-TiO₂/mp-TiO₂-Perovskite/Au | LT-VASP/MASnI₃ | 17.8 | 0.273 | 0.39 | 1.86 | [51] |
| 2016 | ITO/PEDOT:PSS/Poly-TPD/MASnI₃/Ca/BCP/Ag | Thermal evaporation/MASnI₃ | 12.1 | 0.377 | 0.366 | 1.7 | [61] |
| 2016 | ITO/PEDOT:PSS/MASnI₃/Ca/BCP/Ag | SB Method using DMSO as solvent/MASnI₃:SnF₂ | 11.82 ± 0.45±0.0 | 0.40±0.0 | 3 | 2.14±0.3 | [55] |
| 2017 | FTO/c-TiO₂/mp-TiO₂-perovskite/perovskite capping layer/PTAA/Au | Spin Coating in Hydrazine environment using DMSO as Solvent/MASnI₃ | 19.92 | 0.377 | 0.517 | 3.89 | [50] |
| 2017 | FTO/c-TiO₂/mp-TiO₂-perovskite/PTAA/Au | Spin Coating using DMSO as solvent/MASnI₃:SnF₂ | 26.1 | 0.25 | 0.30 | 1.94 | [57] |
| 2017 | FTO/c-TiO₂/mp-TiO₂-perovskite/Al₂O₃-Perovskite/C | Spin Coating using DMF as solvent/MASnI₃Br₃-Clₓ | 13.99 | 0.38 | 0.573 | 3.11 | [59] |
| 2017 | ITO/PEDOT:PSS/MASnI₃/PC₇₀BM/BCP/Ag | Ion exchange/insertion reactions/MASnI₃ | 20.68 | 0.57 | 0.66 | 7.78 | [60] |
| 2020 | ITO/PEDOT:PSS/Perovskite/PCBM/PEI/Au | Nitrogen environment/MASnI₃ | 12.47 | 0.57 | 0.44 | 3.13 | [62] |

### Table 2. Stability of MA tin halide(s) based perovskites.

| Year | Device architecture | Testing environment | Stability | Ref. |
|------|---------------------|---------------------|-----------|------|
| 2014 | FTO/c-TiO₂/mp-TiO₂-MASnI₃-Brₓ /HTL/Au | Devices were stored in nitrogen glove box and were sealed with Surlyn films | Retained almost 80% of initial performance for 12 h | [44] |
| 2016 | Two step process of vapor deposition + solution based technique to obtain CH₃NH₃SnI₃ films | Exposed to air and continuous illumination | Films retained almost 80% of their initial absorbance for 2 h | [53] |
| 2016 | 5-AVAI: MASnI₃ films (1:20) | Exposed to air | 113.5 h | [54] |
| 2017 | ITO/PEDOT:PSS/MASnI₃ | Under 1 Sun illumination | Devices retained 50% | [55] |
Although, the MA based lead free perovskite devices produced some excellent efficiencies with considerable stability, the lack of control over p-doping has made it very difficult to have high level of reproducibility. Theoretical calculations performed on MA tin based perovskites confirmed that perovskite with MA are more likely to be oxidized than that of perovskites having NH2CH3NH2+ (FA) as cation [63]. The MA has smaller ionic sizes compared to FA, resulting in a strong antibonding coupling between Sn-s I-p, which consequently results in very high hole densities [64]. In order to have high efficiencies with excellent stability and reproducibility it is therefore necessary to explore other options instead of MA as a cation in lead free perovskite solar cells [62].

3. Formamidinium tin halides (FASnX3, X = I, Br, Cl)

The MAPbI3 was known to undergo a phase transition at 56 °C, changing its shape from tetragonal to cubic [65]. However, when MA was replaced by NH2CH3NH2+ (FA), the resulting perovskite FAPbI3, does not show any phase transition until 150 °C. This enhancement of stability can be attributed to a comparatively rigid perovskite structure resulted from enhanced H bonding between organic cation and inorganic matrix [66]. Expecting the same for Sn perovskites, the very first work on formamidinium based tin perovskite was reported by Krishnamoorthy et al., [67] in 2015. An energy band gap of 1.41 eV, with a red shifted absorption onset (880 nm) compared to FAPbI3 was observed for FASnI3 perovskites. When left overnight, the color of pure FASnI3 solution changed from yellow to orange. To solve this issue SnF2 was added to the pure FASnI3 solution in different molar ratios. Addition of SnF2 not only increased the stability but also short circuit current of perovskite devices. The best FASnI3 perovskite films were realized with films having 20 mol% SnF2.

Perovskite devices fabricated with these films produced Jsc of 12.4 mA.cm\(^{-2}\), Voc of 262 mV, FF of 0.44 and overall PCE of 1.41%. To increase the Jsc of FASnI3 based PSCs Koh and group increased the thickness of mesoporous TiO2 from 350 nm to 500 nm [67]. This significantly reduced charge carrier recombinations inside the active material by providing more charge transfer sites. For the best performing device with 500 nm thick mesoporous TiO2 layer, a short circuit current density of 24.45 mA.cm\(^{-2}\) was reported with a Voc of 238 mV, fill factor of 0.36 and PCE of 2.10% respectively [67]. This pioneering work on FASnI3 based perovskite provided a solid reason to explore and further optimize the performance of these devices for environment friendly and stable tin based PSCs. The real push towards a stable and highly efficient FA based tin halide perovskite came from Shin et al., [68] in 2016, when they fabricated a 100 day stable encapsulated perovskite device with a PCE of 4.8% using SnF2-Pyrazine complex. To achieve this outstanding performance Shin and group deposited the perovskite film using both non solvent dripping process and solvent engineering technique [68].

They demonstrated that SnF2 incorporated perovskite films made with only DMF as a solvent showed a very poor surface coverage and morphology (Figure 4a). The results were the same even for non-solvent dripping process (Figure 4b). But when solvent engineering was applied and films were grown from a mixture of DMF and DMSO in 4:1 volume respectively, a very smooth and uniform film was obtained (Figure 4c). However excess SnF2 in the FASnI3 films caused aggregation on top of film and few plate like aggregates were found on surface. These aggregates disappeared when pyrazine was also introduced along with DMF and DMSO in the solvent mixture (Figure 4d).
This proved that pyrazine significantly improved the surface morphology by separation of phases induced by excess SnF₃. The surface of films prepared with SnF₃ addition oxidized 100% in air during fabrication process. However, Sn⁴⁺ content decreased in underneath layers. When pyrazine was added to films the oxidation decreased by 4-15% in each layer. When PSCs were fabricated using these optimized perovskite films a J_SC of 23.7 mA.cm⁻², V_OC of 320 mV, FF of 0.63 and PCE of 4.8% was recorded for the best performing device. These devices showed exceptional reproducibility and long term stability of 100 days in ambient conditions when encapsulated [68].

In addition to the same concept of solvent engineering and SnF₃ addition Zhao and group [69] modified perovskite formation by addition of diethyl ether dripping. This modification allowed them to achieve uniform perovskite films with full surface coverage. The conventional n-i-p structure was also replaced by p-i-n inverted architecture (ITO/PEDOT:PSS/FASnI₃/C₆₀/BCP/Ag) to avoid using salt-doped hole selective layers (HSLs), known to damage FASnI₃ perovskite [51,70]. Anti-solvent dripping is reported to enhance the quality of perovskite films [48] with toluene and chlorobenzene being the most popular choices. However, Zhao and group [69] observed that while using chlorobenzene or toluene to prepare FASnI₃ layers pin holes emerged in the surface of films because of rapid crystallization, reducing the quality of perovskites. When diethyl ether was used instead of chlorobenzene and toluene a comparatively slow crystallization rate was observed resulting in a pin hole free and smooth surface.

A cross sectional view of inverted p-i-n PSC fabricated using these pin hole free, high quality FASnI₃ perovskites as seen under SEM is shown in Figure 5a. Where C₆₀ and PEDOT:PSS acts as ESL and HSL respectively. The conduction band (CB) minima of FASnI₃ is well matched with the lowest unoccupied molecular orbital (LUMO) of C₆₀ facilitating effective transfer of generated electrons from perovskite to Ag. The holes were blocked as the FASnI₃ has a valence band (VB) maxima above the highest occupied molecular orbital (HOMO) of C₆₀ resulting in suppressing charge carrier recombination’s at the interface. The best device provided a PCE of 6.22% with J_SC of 22.07 mA.cm⁻², V_OC of 465 mV and FF of 60.67% under forward scan. A very small J-V hysteresis was observed due to invert device architecture. These fabricated devices showed good stability as a cell with PCE of 5.80% had only 5.86% decrease in performance even after 45 min. When kept in dark and inert environment devices were stable for 30 days. Zeng et al., [71] also used a similar approach with additional mixing of poly(α-methylstyrene) (PAMS) in diethyl ether dripping.
In an attempt to improve the PCE of FASnI₃ based devices, Kanatzidis and group suggested a thin layer of ZnS to be coated on top of mesoporous TiO₂ [72]. This cascade structure significantly reduced the interfacial recombination and enhanced the electron transfer capability. The best cell provided a PCE of 5.27% with Voc of 380 mV, a short circuit current density of 23.09 mA.cm⁻² and a FF of 60.01%. Kanatzidis and coworkers also fabricated a flexible FASnI₃ based perovskite with a PCE of 3.12% employing multichannel inter diffusion technique [73]. Perovskite films were prepared by spin coating mixture of FAI and PEDOT:PSS followed by annealing. SnI₂ film was then evaporated to have high quality, homogeneous FASnI₃ films. This fabrication technique allowed them to have a flexible PSC paving the way for commercializing of Sn based PSCs.

In the quest of achieving high PCE and considerable stability for lead free FA based tin PSCs, Chueh et al., [74] used sequential deposition route. To form defect free homogeneous FASnI₃ films the reaction rate between FAI and SnI₂ was controlled. In the first step of deposition tri-methylamine (TMA) was incorporated in Sn solution to form SnY₂-TMA (Y=I⁻,F⁻) complexes [75] followed by intercalating with FAI to produce FASnI₃. This method allowed Jen and group to realize PCE of 4.34% and 7.09% for conventional n-i-p and inverted p-i-n PSCs, respectively [74]. When tested for stability the inverted device comparatively showed better stability than conventional device. In ambient air with 50% relative humidity the un-encapsulated devices degraded within the first 24 h. However, when stored in inert environment both devices retained more than 80% of their performance for 20 days. Figure 6 relates the PCE of devices with respect to storage time in different environments.

**Figure 5.** (a) A cross-sectional view of the fabricated device having 10 mol% SnF₂ additives as seen under SEM; (b) Energy level diagram. Adapted with permission from [69]. Copyright © 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

**Figure 6.** Room temperature stability tests of PSCs both in n-i-p and p-i-n architectures based on FASnI₃+SnF₂+TMA : (A) stored in N₂ environment and (B) stored in ambient condition (50% relative humidity). Adapted with permission from [74]. Copyright © 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
As tin based perovskite is relatively new compared to Pb based perovskites, so many techniques that have already been proved useful for Pb based perovskites were applied to its Sn counterparts. It was well established with Pb perovskite lattice that introduction of Br atom in perovskite structure changed the shape from tetragonal to cubic. It also affected band gap and significantly improved the stability of these PSCs [76,77]. To enhance the stability of FASn halide based perovskite devices Lyu et al., [78] applied band gap engineering method to fabricate a considerably stable FASnI3Br perovskite with a band gap of 1.68 eV. When devices were fabricated from these perovskite films employing p-i-n architecture and with C60 as electron transport layer (ETL), a maximum PCE of 1.72% was recorded. When PCBM was used as ETL the efficiency dropped to 1.43% mainly because of a lower Voc. However, the stability of un-encapsulated devices in nitrogen glove box increased from few hours to 30 h. This stability although is not enough, but the fact that it was recorded for un-encapsulated devices make it appealing. Applying proper encapsulation it can be significantly enhanced.

Using the same idea Shin et al., [79] incorporated Br atoms in FASnI3 perovskite structure. The doping concentration of bromine was kept from 0 to 33 mol%. To investigate the effect of bromine addition in crystal structure of FASnI3 perovskites, films with and without bromine addition were prepared and their absorption spectra was measured for about 100 h while being exposed to air. The absorption of pure FASnI3 films at 500 nm reduced to almost zero when exposed to air for 100 h while films with bromine maintained almost 40% of its initial absorption for the same time when tested under same conditions. This experiment further verified notion that addition of bromine not only shifts the band gap but also decrease Sn2+ oxidation, making films more stable in air.

The C-V measurements revealed that films produced with 25 mol% Br doped FASnI3 have 3 order of magnitude less carrier density compared to film produced without any Br doping. This significant decrease of carrier density proved the initial assumption of Br doping reducing Sn2+ oxidation. A maximum PCE of 5.5% was obtained for Br doped device with a JSC of 19.8 mA.cm\(^{-2}\), Voc of 0.414 V and FF of 66.9%. When encapsulated these devices showed outstanding stability in ambient air, by retaining almost 100% of their initial performance for 600 h under continuous 1 Sun irradiation. Even after 1000 h only 17% reduction in the initial performance was observed for these remarkably stable Br doped FASnI3 based PSCs. This considerably high efficiency along with remarkable stability was a great step towards lead free perovskite solar cells.

To further improve the PCE of FASnI3 based devices Bian and group came up with a low cost solution of tin source purification [80]. Any commercial SnX2 source contains Sn4+, even those with 99% purity contain a significant concentration of oxidized Sn4+ resulting in poor performance and reproducibility issues. To solve this, Bian and coworkers added Sn powder to SnI2. Tin powder reacts with Sn4+ and reduce it to Sn2+ state (Sn4+ + Sn >>>> 2Sn2+) [80]. A maximum PCE of 6.75% was achieved for inverted p-i-n architecture when annealing temperature and reaction time was optimized. However, the real breakthrough for record efficiency in FASnI3 based devices was achieved in 2019 when Wu et al., [81] reported a 10.1% efficient device. To obtain a pin hole free film and control the grain boundaries Wu et al., [81] introduced π-conjugated Lewis base molecules during crystallization of FASnI3 perovskite films.

The precursor solution for the films were prepared mixing 0.1% - 1% in molar ratio, 2-cyano-3-[5-[4-(diphenylamino)phenyl]-2-thienyl]-propenoicacid (CDTA) in DMSO. During film fabrication this additive formed a stable intermediate phase and optimized the crystallization process of perovskite film by significantly slowing down the crystal formation. This method resulted in pin hole free and smooth FASnI3 perovskite films with a larger carrier lifetime of 3.87 ns compared to pristine FASnI3 film with a carrier lifetime of 2.09 ns. Perovskite devices were fabricated using these films employing ITO/PEDOT:PSS/FASnI3/C60/BCP/Ag architecture. The champion device with an active area of 0.09 cm\(^2\) yielded record efficiency of 10.17% when 0.2% molar ratio of CDTA was used. The CDTA treatment of the perovskite films enhanced the Voc to 0.63 V and FF to 74.7%. When tested for stability, the encapsulated device retained 90% of its initial performance even after 1000 h under continuous light soaking.
Recently Chen et al., [82] introduced poly(ethylene-co-vinyl acetate) a unique polymer, as anti-solvent during spin coating FASnI₃ perovskite film. The C=O groups present in EVA had a very strong Lewis acid-base complexation with the uncoordinated tin atoms present in the perovskite film. This resulted in a considerably improved grain size, optimized orientation and significant decrease in surface defects of perovskite films. PSCs fabricated by this method gave a PCE of 7.72%, incorporating self-encapsulation properties. When tested for stability the un-encapsulated devices retained almost 62.4% of their initial efficiency even after 48 hr storage in ambient conditions with 60% relative humidity [82]. Such high efficiency along with self-encapsulation properties is a promising sign for future of highly efficient and stable lead free perovskite solar cells. Table 3 summarizes the performance of best FA tin halide (s) based devices reported until 2020 while, Table 4 includes the stability profiles of FA tin halide (s) reported until 2020.

Table 3. Performance of best FA tin halide (s) based devices reported until 2020.

| Year | Device architecture | Perovskite Film Fabrication technique /Perovskite Film | Jsc (mA. cm⁻²) | Voc (V) | FF | EFF (%) | Ref. |
|------|---------------------|-----------------------------------------------------|----------------|--------|----|---------|------|
| 2015 | FTO/c-TiO₂/mp-TiO₂-Perovskite/spiro-OMeTAD/Au | Spin Coating + Annealing/ FASnI₃+SnF₂ | 24.45 | 0.238 | 0.36 | 2.10 | [67] |
| 2016 | ITO/PEDOT:PSS/Perovskite/C₆₀/Ca/Al | Spin Coating using DMF as solvent +chlorobenzene dripping +Annealing/ FASnI₂Br | 6.82 | 0.467 | 0.543 | 1.72 | [78] |
| 2016 | FTO/c-TiO₂/mp-TiO₂-Perovskite/spiro-OMeTAD/Au | Spin Coating using DMF+DMSO as solvent +Annealing/ FASnI₃+SnF₂+Pyrazine | 23.7 | 0.32 | 0.63 | 4.8 | [68] |
| 2016 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | Spin Coating using DMF+DMSO as solvent +diethyl ether dripping +Annealing/ FASnI₃+SnF₂ | 22.07 | 0.465 | 0.606 | 6.22 | [69] |
| 2016 | FTO/c-TiO₂/mp-TiO₂-ZnS-Perovskite/PTAA/Au | Spin Coating using DMF+DMSO as solvent +diethyl ether dripping +Annealing/ FASnI₃+SnF₂ | 23.09 | 0.380 | 0.601 | 5.27 | [72] |
| 2017 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | FASnI₃/FAI/PEDOT:PSS using water as solvent +Annealing+Evaporation of SnI₂/ FASnI₃ | 17.78 | 0.33 | 0.679 | 3.98 | [73] |
| 2017 | FTO/c-TiO₂/mp-TiO₂-Perovskite/spiro-OMeTAD/Au | Spin Coating using DMF+DMSO as solvent/ FASnI₂Br+SnF₂+Pyrazine | 19.8 | 0.414 | 0.669 | 5.5 | [79] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C₆₀ 1 wt% TBAI/Ag | Sequential Deposition Route/ FASnI₃+SnF₂+TMA Adding Sn powder in precursor solution + Spin | 22.45 | 0.47 | 0.678 | 7.09 | [74] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | Coating using DMSO as solvent+Annealing/ FASnI₃+SnF₂ | 17.5 | 0.58 | 0.663 | 6.75 | [80] |
| 2019 | ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag | Spin Coating using DMF+DMSO as solvent +diethyl ether blended with | 17.64 | 0.314 | 0.410 | 2.28 | [71] |
Table 4. Stability of FA tin halide(s) based perovskites.

| Year | Device architecture | Testing environment | Stability | Ref. |
|------|---------------------|---------------------|-----------|------|
| 2016 | ITO/PEDOT:PSS/FASnI₃/Br/Cao/Ca/Al | Un-encapsulated devices were stored in nitrogen environment | Retained over 60% of their initial efficiency for more than 30 h | [78] |
| 2016 | ITO/PEDOT:PSS/FASnI₃+SnF₂/Cao/BCP/Ag | Encapsulated devices stored in dark under inert environment | Retained almost 85% efficiency for 720 h | [69] |
| 2016 | FTO/c-TiO₂/mp-TiO₂/FASnI₃+SnF₂+Pyrazine/Spiro-OMeTAD/Au | Encapsulated devices stored in dark under ambient conditions | Retained almost 98% of their initial efficiencies for 2400 h | [68] |
| 2017 | FTO/c-TiO₂/mp-TiO₂/FASnI₃+SnF₂+Pyrazine/Spiro-OMeTAD/Au | Encapsulated devices under continuous 1 Sun irradiation in ambient environment | Retained almost 83% of initial performance after 1000 h | [79] |
| 2018 | ITO/PEDOT:PSS/FASnI₃+SnF₂+TMA/Cao 1 wt% TBAI/Ag | Encapsulated devices stored in ambient conditions | Retained almost 80% of initial performance for 420 h | [74] |
| 2019 | ITO/PEDOT:PSS/FASnI₃+CDTA+SnF₂/Cao/BCP/Ag | Encapsulated devices under continuous 1 Sun irradiation | Retained almost 90% of its initial efficiency for 1000 h | [81] |
| 2020 | ITO/PEDOT:PSS/FASnI₃-EVA/PC₆₁BM/BCP/Ag | Un-encapsulated devices stored in ambient conditions with RH of 60% | Retained 62.4% of their initial efficiencies for 48 h | [82] |

4. Cesium tin halides (CsSnX₃, X = I, Br, Cl)

Kanatzidis and coworkers were the very first to demonstrate effective use of CsSnI₃ in all solid state DSSC as a hole transport material [83]. The commonly used corrosive redox electrolyte was replaced with CsSnI₃ to realize efficiencies up to 10.2% in the DSSCs. The first use of CsSnI₃ as light harvesting material was reported by Wang et al., [84] in 2012, when a simple configuration of ITO/CsSnI₃/Au/Ti produced a PCE of 0.9%. To produce the perovskite film SnCl₂/CsI stack was deposited by e-beam deposition and thermal evaporation of CsI and SnCl₂, respectively. Followed by annealing at 175 °C for 1 min. This process created a single phased, dense and black colored polycrystalline perovskite film with a grain size of 300 nm. The Schottky solar cell based on these films provided a Voc of 0.42 V, with a Jsc of 4.80 mA.cm⁻², FF of 22% and PCE of 0.9%.

Kumar et al., were also among the very first researchers who reported the use of CsSnI₃ in perovskite solar cells [85]. With a band gap close to ideal (1.3 eV) [83] and higher theoretical limit of
achievable $J_{SC}$ (34.3 mA cm$^{-2}$) than its lead based counterparts (25.9 mA cm$^{-2}$) [86], this material was expected to yield extraordinary efficiencies. However, theoretical calculations revealed that although the material is a semiconductor, it exhibits metallic characteristics with a very high hole mobility arising from intrinsic defects associated with Sn-cation vacancies [87]. To control this metallic conductivity Kumar et al., added SnF$_2$ to CsSnI$_3$. Perovskite films were prepared by Stichometric mixing of SnI$_2$, SnF$_2$ and CsI in proper solvents followed by spin coating and thermal annealing (70 °C). Perovskite solar cells employing conventional n-i-p architecture (FTO/c-TiO$_2$/mp-TiO$_2$/CsSnI$_3$+SnF$_2$/HTM/Au) were fabricated using 4', 4.- 4, tris (N,N-phenyl-3-methylamino) triphenylamine (m-MTDATA) as hole transport material.

To compare performance and effect of SnF$_2$ on Sn vacancies, CsSnI$_3$ pervoskite films with 0, 5, 10, 20 and 40 mol% of SnF$_2$ were used. Devices without any SnF$_2$ doping were not functioning at all, while devices with SnF$_2$ doping were properly functioning with the best efficiency of 2.02% recorded for device with 20 mol% SnF$_2$ doping. These results were further explained by measuring the carrier densities of perovskite films. A very high carrier density of $10^{19}$ cm$^{-3}$ was recorded for pure CsSnI$_3$ with holes as majority charge carriers. This p-type conductivity was caused by Sn-vacancies. With increasing mol % of SnF$_2$ the carrier densities tend to decrease. This proves that SnF$_2$ doping can significantly suppress Sn vacancies. Surprisingly, when stored in glove box these devices were stable for more than 250 h. While these devices show some stability, a very low open circuit voltage hinders the performance of these devices. With an astonishing $J_{SC}$ of 22.70 mA cm$^{-2}$ obtained for the best performing device a very low $V_{OC}$ of 0.24 V was recorded.

In an attempt to increase the $V_{OC}$ of CsSnI$_3$ based perovskite devices the same group incorporated Br in CsSnI$_3$ perovskite structure [88]. As the bromine content was increased, the crystal structure of CsSnI$_3$ showed a phase transition from orthorhombic for CsSnI$_3$ to cubic for CsSnIBr$_2$ and CsSnBr$_3$ respectively. Also the optical bandgap of material changed from 1.27 eV for pure CsSnI$_3$ to 1.37 eV for CsSnI$_3$Br. For CsSnIBr$_2$ and CsSnBr$_3$ the optical bandgap of 1.65 eV and 1.75 eV was recorded respectively. The increasing bromine content also induced a change in the color of perovskite films from black to light brown, resulting in reduced light harvesting but simultaneously increasing the $V_{OC}$. Bromine doping also resulted for lowering charge carrier densities by one order of magnitude for CsSnI$_3$Br ($1.42 \times 10^{17}$ cm$^{-3}$) and 2 order of magnitude for CsSnIBr$_2$ ($6.32 \times 10^{15}$ cm$^{-3}$) compared to pure CsSnI$_3$ films ($5.28 \times 10^{18}$ cm$^{-3}$) [88]. Overall the reduced charge carrier densities along with increase in the bandgap made it possible to achieve a maximum $V_{OC}$ of 0.41 V for CsSnBr$_3$ based devices. However, this increase in the $V_{OC}$ came at the expense of $J_{SC}$, and a very meager $J_{SC}$ of 3.99 mA cm$^{-2}$ was recorded with a low PCE of 0.95%.

Remarkably Marshall and coworkers achieved a $V_{OC}$ of 0.55 V using inverted p-i-n architecture (ITO|CuI|CsSnI$_3$|fullerene|BCP|Al) with indene-C$_6$ bis-adduct (ICBA) as electron transport layer [89]. A 50 nm perovskite film prepared by spin coating 8 wt% CsSnI$_3$ in DMF was used as light harvester. To minimize charge carrier recombination’s and enhance device stability the CsSnI$_3$ films were prepared using 10 mol% excess SnI$_2$. A highest efficiency of 2.76% was recorded for device incorporating these perovskite films and using ICBA as ETL. The excess SnI$_2$ played a major role in deciding different performance parameters of fabricated devices. Firstly the excess SnI$_2$ provided a Sn rich source during perovskite formation which is known to suppress Sn vacancies and hence reduce background carrier density. Secondly it facilitated charge carriers transfer to CuI because of its favorable band alignment, reducing recombination losses. Most importantly the use of excess SnI$_2$ significantly improved device stability. When un-encapsulated devices fabricated without any excess SnI$_2$ lost almost 70% of their initial efficiency within 10 days while being stored in nitrogen glove box, surprisingly devices fabricated with 10 mol% excess SnI$_2$ retained 90% of their performance for the same period of time. The FF and $V_{OC}$ of these devices remained stable even when exposed to air for 14 h.

The same approach was employed by Kanatzidi and coworkers to report one of the highest efficiencies of 4.81%, among all CsSnX$_3$ perovskite films based devices [90]. Perovskite films were produced from CsI/SnI$_3$ solutions in DMF and DMSO with different molar ratios starting from 0.1 reaching up to 1. As discussed in previous sections Kanatzidis and group used reducing vapor
atmosphere as the films were produced in hydrazine environment to suppress Sn^{2+} oxidation during film formation. In conventional n-i-p architecture the best performance was recorded from devices incorporating films made with 0.4 molar ratio of CsI/SnI₂ having TiO₂ as ETL and PTAA doped with tetrakis(pentafluorophenyl)borate (TPFB) as HTL. When molar ratio was increased from 0.4, devices gave a low VOC corresponding to high conductivities, while devices with molar ratio less than 0.4 gave poor JSC due to lack of CsSnI₃ phase. A strong hydrazine environment was created in the glove box dropping 800 μL on glass substrate while spinning it to have the PCE of 4.81% with JSC of 25.71 mA.cm⁻², VOC of 381.66 mV and FF of 49.05%.

Marshall and group went on to investigate effectiveness of SnCl₂ addition, while preparing CsSnI₃ perovskites [91]. While devices prepared with 10 mol% of SnCl₂ presence during perovskite fabrication show no considerable effect on stability with respect to devices prepared with 10 mol% excess SnI₂, the efficiency jumped from 2.76% (as reported by the same group earlier) to 3.56%. Instead of incorporating Cl in the crystal lattice, the SnCl₂ formed a thin layer covering the perovskite crystallite surface. This resulted in a sacrificial oxidation of SnCl₂ layer when exposed to air, hence saving CsSnI₃ from oxidation. The elevated efficiencies using SnCl₂ can be attributed to lowering device performance parameters sensitivity to pin hole defects in the perovskite films. Because of its small size and lower mass the excess SnCl₂ present at the surface of the CsSnI₃ crystallites diffuse into fullerene layer causing its moderate n-doping. This resulted in forming a Schottky barrier limiting leakage current at ITO/Fullerene junction at the site of pinholes in the CsSnI₃ films.

Cahen and group reported an optimization strategy for CsSnBr₃ based devices by selecting different electron transport materials (ETM) and hole transport materials (HTM) layers for conventional n-i-p architecture based PSCs [92]. Devices were fabricated using TiO₂ and Al₂O₃ as ETM while PTAA, CBP and Spiro-MeOTAD were chosen as HTMs. By using TiO₂ as ETM, spiro-MeOTAD as HTM and 20 mol% SnF₂ doping, optimized PCE of 2.1% was achieved with a JSC of 9.1 mA.cm⁻², a VOC of 0.42 V and a FF of 57%. All other combinations of HTM and ETM produced unsatisfactory results. The band alignment diagram of optimized device comparing effect of SnF₂ addition in CsSnBr₃ is given in Figure 7. When work function and ionization potential (valence band maximum, EVBM) of pristine CsSnBr₃ was compared to CsSnBr₃ doped with 20 mol% of SnF₂, the role of SnF₂ doping was revealed as it decreased work function (WF) and the ionization potential of CsSnBr₃ as shown in Figure 7. This decrease in EVBM of CsSnBr₃ resulted in reducing the voltage loss by bringing it close to HOMO of spiro-MeOTAD.

![Figure 7](image_url). VBM energies from UPS measurements and CBM energies calculated using the UPS measurements and the optical band gap, i.e., neglecting the exciton binding energy, and the Fermi level (from UPS data) of dense TiO₂, pristine CsSnBr₃, and CsSnBr₃ (with 20 mol% SnF₂). Adapted with permission from [92]. Copyright © 2020, American Chemical Society.
Moghe and group fabricated CsSnBr$_3$ based PCSs using thermal deposition [93] to achieve 50 min stable devices under continuous 1 sun irradiation and ambient conditions without any encapsulation. Planar heterojunction architecture was selected for device fabrication with CsSnBr$_3$:SnF$_2$ sandwiched between MoO$_3$ and C$_60$. Figure 8(a) gives the band alignment diagram of fabricate devices. SnF$_2$ dopant was incorporated in the devices with different concentrations of 0%, 2.5%, 5% and 7.5%. The position of SnF$_2$ vapor deposited layer was also varied as shown in Figure 8. The best efficiency of 0.50% was obtained for devices having 2.5 mol% of SnF$_2$ doping and SnF$_2$ layer sandwiched between CsBr and SnBr$_2$. While these devices are expected to have considerable stability when properly encapsulated, the low PCE limit its application on commercial scale. Kanatzidi’s group further optimized the CsSnBr$_3$ perovskite layer by using hydrazine vapor atmosphere to grow CsSnBr$_3$ films [50]. This technique along its effects on perovskite layer has already been discussed in previous sections. Using reducing vapor atmosphere during CsSnBr$_3$ film growth they were able to suppress tin vacancies and reduce Sn$^{2+}$ oxidation. A maximum PCE of 3.04% was recorded for CsSnBr$_3$ based devices.

![Figure 8. (a) Band alignment diagram of the planar CsSnBr$_3$ structure; (b) Crystal structure of CsSnBr$_3$; (c) SnF$_2$ layers splitting SnBr$_2$-CsBr layers in configuration 1(C1); (d) Single SnF$_2$ layer is inserted in configuration 2(C2), and (e) SnF$_2$ is inserted as split layer before SnBr$_2$ in configuration 3(C3). Adapted with permission from [93]. Copyright © 2020, Elsevier Limited.](image)

In a similar attempt of enhancing the performance of CsSnX$_3$ based devices, Kanatzidi’s group explored the possible effects of adding Piperazine to precursor solution of CsSnI$_3$ perovskite films [94]. Adding piperazine significantly suppressed the self-doping of the perovskite films and increased surface coverage while simultaneously reducing the crystallization of excess SnI$_2$. Perovskite films were spin coated keeping ratio of CsI/SnI$_2$ as 0.4. The molar ratio of piperazine to tin was changed from 0 to 25% by adding 2 M of piperazine solution to CsSnI$_3$ solution. Films were annealed at 90 °C for 25 min. Addition of piperazine significantly improved the film coverage by suppressing excess SnI$_2$ crystallization. Figure 9 reveals the morphologies of perovskite films prepared from 0, 10 and 20 mol% of piperazine addition as seen under scanning electron microscope (SEM).
When no piperazine was added, the excess SnI₂ crystallized resulting in poor surface coverage. However, with piperazine addition the surface coverage enhanced as can be seen in Figure 9 (b, c). Addition of piperazine significantly increased the resistance of films as can be seen in Figure 9 (d). With 20 mol% of piperazine with resistance of perovskite films increased almost 4 orders of magnitude compared to resistance of pristine CsSnI₃ films. An optimized device was fabricated using 10 mol% of SnF₂ doping and 15 mol% of piperazine addition to achieve a maximum PCE of 3.83% with a JSC of 20.63 mA.cm⁻², VOC of 0.338 V and a FF of 54.18%. Although, the efficiency increased significantly the stability of these devices still remained considerably low.

In 2016 Li et al., reported 77 day stable CsSnIBr₂ films based devices [95]. This extraordinary stability was achieved by adding hypophosphorous acid (HPA) to precursor solution of CsSnIBr₂ perovskite films. Addition of HPA in precursor solution made tiny clusters of CsSnX₃–HPAy (X = Br, I). These tiny clusters promoted growth of perovskite crystals by removing the redundant SnF₂, hence suppressing phase separation. When films were tested for conductivity, samples prepared with HPA had one order of magnitude less conductivity then those prepared without any HPA addition. Moreover, the charge carrier density reduced by one order of magnitude for films prepared with HPA addition (1.5 × 10¹⁵ cm⁻³) compared to film prepared without any HPA addition (1.6 × 10¹⁶ cm⁻³). Overall addition of HPA proved effective in reducing trap densities and Sn vacancies in CsSnBr₃ films. The best device was fabricated with 0.5 μL mL⁻¹ concentration of HPA acid, presenting efficiency of 3.02% with a JSC of 17.4 mA.cm⁻², a VOC of 0.31 V and Fill factor of 56%. When encapsulated these devices retained almost all of their initial performance for a time period of 77 days in ambient conditions. This extraordinary stability with moderate efficiency demonstrated the effective use of CsSnIBr₂ perovskite layer in lead free stable perovskite devices, paving the way for its commercial applications.

Sun and coworkers reported 3.31% efficient perovskite device based on a coarse grain B-γ-CsSnI₃ perovskite film [96]. A single step spin coating technique was employed to produce the perovskite films from the precursor solution, followed by 2 min annealing at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C. The grain size showed an increasing trend with increase in annealing temperature as can be observed in Figure 10. Grain size averaged 50 nm for films without any
temperature treatment. For films annealed at 100 °C average grain size of 100 nm was reported, which further increased to 350 nm for 150 °C annealing temperature. Figure 10 (G) represents the annealing temperature vs. average grain size.

Figure 10. Top view of the B-γ-CsSnI3 perovskite films as seen under SEM. (A) as-deposited; (B) annealed at 100 °C for 2 min; (C) annealed at 150 °C for 2 min; (D) annealed at 200 °C for 2 min; (E) annealed at 250 °C for 2 min and (F) annealed at 300 °C for 2 min; (G) Average grain size of the B-γ-CsSnI3 thin films show increasing trend as the annealing temperature is increased. Adapted with permission from [96]. Copyright © 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

It was confirmed from both theoretical and experimental calculations that as annealing temperature increased number of Sn vacancies also increased. Devices with different architectures were fabricated and tested for photovoltaic parameters. Devices having TiO2 as ETL and Spiro-OMeTAD as HTL in conventional n-i-p architecture showed almost no performance when incorporated with B-γ-CsSnI3 annealed at 100 °C as perovskite layer. When TiO2 was replaced by Al2O3 as ETL in the same architecture, a very meager efficiency of 0.32% was achieved. A low crystallinity, perovskite making non ideal interfaces with scaffold material and presence of impurities, such as Y-CsSnI3 and Cs2SnI6 were identified as causes of poor performance. To address these issues an inverted p-i-n architecture was used with a compact p-type nickel oxide (NiOx) as HTL, PCBM as ETL and the perovskite layer was annealed at 150 °C. This device gave an outstanding efficiency of 3.31% with a Jsc of 10.21 mA.cm⁻², Voc of 0.52 V and a FF of 62.5%.

During the past few years many unique attempts were also reported to elevate the efficiency and enhance the stability of inorganic Sn based perovskite solar cells. Chen and group reported CsSnX3-based quantum rods to achieve a champion cell efficiency of 12.96% [97]. Quantum rods of CsSnI3, CsSnBr3 and CsSnCl3 were synthesized respectively by solvothermal method as described in literature [97]. These high quality rods had lengths of several tens of nanometers with a diameter of 5 nm. The image of these rods as seen under transmission electron microscope (TEM) along with its elemental mapping from TEM energy-dispersive X-ray spectroscopy (EDS) is shown in Figure 11.
PSCs were fabricated in planar p-i-n heterojunction architecture using these CsSnX₃ quantum rods as perovskite layers. The best PCE of 12.96% was obtained for devices based on CsSnI₃ quantum rods, whereas devices based on CsSnBr₃ and CsSnCl₃ quantum rods yielded efficiencies of 9.66% and 10.46% respectively. When tested for stability, devices fabricated with CsSnI₃ quantum rods remained stable for more than 240 h.

Quan and coworkers reported 0D Cs₄SnX₆ nanocrystals having 21% Photoluminescence quantum yield (PLQY) [98] but with no considerable stability. In an attempt to enhance the air stability of perovskites Guo et al., [99] synthesized cubic nanocages of CsSnBr₃. When treated with perfluorooctanoic acid (PFOA), perovskite film of these CsSnBr₃ nanocages showed stability for over 24 h while being in ambient air. However in these unique approaches Kanatzidis and group were the first to report a considerably stable device based on Cs₂SnI₆ [100]. This material had a bandgap of 1.48 eV with a high absorption coefficient. While achieving a modest efficiency of 0.96% for the best device based on these perovskites, its stability remained outstanding. Un-encapsulated devices were stable for more than one week in ambient conditions which is quite remarkable. Recently Wang and group reported a 3% efficient CsSnI₃ based device by chemically doping cobaltocene (CoCp₂) into perovskite layer [101]. Doping of CoCp₂ into CsSnI₃ helped create a reducing environment which resulted in effective suppression of Sn²⁺ oxidation. This method also considerably enhanced the overall stability of these devices.

Although all the techniques discussed above for CsSnI₃ PSCs produced some excellent results, very recently Li et al., [102] reported one of state-of-the-art performance with a PCE of 3.8% and stability of 180 days. For the very first time vacuum flash-assisted solution processing (VASP) was used to fabricate the high quality CsSnI₃ perovskite films. The VASP method involved transferring the already spin coated Sn-based perovskite precursor to a vacuum (60 Pa) for 40 s. Followed by annealing at 60 °C for 10 min. The controlled solvent removal method allowed to produce high quality CsSnI₃ films with very few pin holes, reduced background charge carrier density and considerably enhanced perovskite stability. Films produced by VASP showed greatly improved stability than that of films produced using single step spin coating (controlled films). UV absorption spectrum revealed that at 450 nm VASP films retained 95% of their initial absorption even after 100 min exposure to air, while the controlled film retained only 85.5% absorption. The VASP PSCs yielded a PCE of 2% which increased to 3.8% upon storing in glove box for 3 months. The controlled PSC produced PCE of 1.1% and almost lost all of its performance within the first month of storage. As can be seen from Table 5 the performance of CsSnX₃ based devices has considerably progressed even in ambient conditions. These elevated efficiencies along with enhanced stability as
Table 5. Performance of best Cs tin halide (s) based devices reported until 2020.

| Year | Device architecture | Perovskite Film Fabrication technique | Jsc (mA. cm$^{-2}$) | Voc (V) | FF | EFF (%) | Ref. |
|------|----------------------|--------------------------------------|----------------------|--------|----|---------|------|
| 2014 | FTO/c-TiO$_2$/mp-TiO$_2$-Perovskite/m-MTDATA/Au | Spin Coating using DMSO as solvent + Annealing/CsSnI$_3$ + SnF$_2$ | 22.70 | 0.24 | 0.37 | 2.02 | [85] |
| 2015 | FTO/c-TiO$_2$/mp-TiO$_2$-Perovskite/Spiro-OMeTAD/Au | Spin Coating using DMSO as solvent + Annealing/CsSnI$_3$+SnF$_2$ | 15.06 | 0.289 | 0.38 | 1.67 | [88] |
| 2015 | ITO/Cul/Perovskite/ICBA/BCP/Al | Spin Coating using DMF as solvent + CsSnI$_3$+excess SnI$_2$ | 12.30 | 0.430 | 0.395 | 2.13 | [89] |
| 2016 | ITO/Perovskite/PC$_6$1BM/BCP/Al | Spin Coating using DMF as solvent + CsSnI$_3$+SnCl$_2$ | 9.89 | 0.50 | 0.43 | 3.35 | [91] |
| 2016 | FTO/c-TiO$_2$/mp-TiO$_2$-Perovskite/Al$_2$O$_3$-Perovskite/C-Perovskite | Spin Coating using DMSO as solvent + Annealing/CsSnIBr$_2$+SnF$_2$+Hypophosphorous Acid (HPA) | 16.7 ± 0.7 | 0.33 | 0.53 | 3 ± 0.2 | [95] |
| 2016 | FTO/c-TiO$_2$/mp-TiO$_2$-Perovskite/Spiro-MeOTAD/Au | Spin Coating using DMSO as a Solvent +Annealing/CsSnBr$_3$+SnF$_2$ | 9.1 | 0.42 | 0.57 | 2.17 | [92] |
| 2016 | ITO/MoO$_3$/Perovskite/C$_x$/BCP/Ag, | Vapor Deposition + Annealing/CsSnBr$_3$+SnF$_2$+Excess SnBr$_2$ | 2.1±0.2 | 0.45 | 0.52 | 0.50 | [93] |
| 2016 | ITO/NiO$_x$/Perovskite/PCBM/Al | Spin Coating using a mixed polar Solvent +Annealing/B-γ-CsSnI$_3$ | 10.21 | 0.52 | 0.625 | 3.31 | [96] |
| 2016 | ITO/mp-TiO$_2$–Quantum Rods of CsSnI$_3$/spiro-OMeTAD/Au | (160 mg/mL) in toluene +Annealing/QBs of CsSnI$_3$ | 23.2 | 0.86 | 0.65 | 12.96 | [97] |
| 2017 | FTO/c-TiO$_2$/mp-TiO$_2$-perovskite/perovskite capping layer /PTAA/Au | Spin Coating in Hydrazine environment using DMSO as Solvent/CsSnBr$_3$ | 13.96 | 0.366 | 0.593 | 3.04 | [50] |
| 2017 | FTO/c-TiO$_2$/mp-TiO$_2$-Perovskite/PTAA/Au | Spin Coating using DMF + DMSO as solvent+ Annealing+ Hydrazine environment/CsSnI$_3$+Excess SnI$_2$ | 25.71 | 0.381 | 0.49 | 4.81 | [90] |
Table 6. Stability of Cs tin halide(s) based perovskites.

| Year | Device architecture | Testing environment | Stability | Ref. |
|------|---------------------|---------------------|-----------|------|
| 2014 | FTO/c-TiO2/mp-TiO2-CsSnI3+SnF2/m-MTDATA/Au | Devices stored in inert environment | Showed no significant loss of performance for almost 250 h | [85] |
| 2015 | ITO/CuI/ CsSnI3+excess SnI3/ICBA/BCP/Al | Un-encapsulated devices tested under 1 Sun constant illumination in ambient conditions | Retained 70% of their initial efficiencies for 16 h | [89] |
| 2016 | ITO/MoO3/ CsSnBr3+SnF2+Excess SnBr2/C60/BCP/Ag | Un-encapsulated devices tested under 1 Sun illumination in ambient conditions | Devices remained stable for 50 min | [93] |
| 2016 | ITO/mp-TiO2-Quantum Rods of CsSnI3/spiro-OMeTAD/Au | Sealed Devices remained stable for 240 h | Retained almost all of their initial efficiencies for 1848 h | [97] |
| 2016 | FTO/c-TiO2/mp-TiO2-Perovskite/Al2O3-CsSnIBr2+SnF2+HPA/C-Perovskite | Encapsulated devices stored under ambient condition | | [95] |
| 2017 | Cubic nanocages of CsSnBr3 | Ambient conditions | | [99] |
| 2020 | ITO/ VASP-CsSnI3/C60/ BCP/Ag | Stored in inert environment | Increased its PCE from 2% to 3.8% after 2160 h | [102] |

Over the years a steady progress has been made in elevating the efficiency and enhancing air stability of this single cation (MA, FA, Cs) based Sn perovskites. However, the challenge of commercialization has pushed the scientific and research community to come up with unique ideas. A new trend of combining two or more cations in a single perovskite has emerged, as it offers numerous possibilities of enhancing device performance and stability. This idea proved very successful in lead based perovskites [103–106], simultaneously gaining the attention of groups working on Sn based perovskites. The coming section summarize all work done in this regard.
based on Sn based perovskite, keeping in view the objective that high efficiency and long term stability should go hand to hand.

5. Mix-Cations (MC) tin halides (MCSnX₃, X = I, Br, Cl)

Liu and coworkers were the first to report a mixed cation (FA)ₓ(MA)₁₋ₓSnI₃ perovskite in 2017 [107]. By employing an inverted p-i-n architecture for device fabrication and by optimizing the ratio of both cations within the perovskite layer, a maximum PCE of 8.12% was achieved. By changing the volume ratio x: (1-x) of FASnI₃ and MASnI₃ precursor solutions, different mixed cations perovskite layers were obtained with ratios of FA and MA as 0:100, 25:75, 50:50, 75:25 and 100:0 respectively. Perovskite films were realized by a one-step spin coating technique with chlorobenzene and SnF₂ addition to precursor solution made in DMSO. Bandgap of these films as calculated from photo luminescence (PL) spectra showed an increasing trend with the increase of FA content in films. For the films with FA:MA as 25:75 a bandgap of 1.28 eV was recorded, while for films with FA:MA as 50:50 and 75:25, bandgaps of 1.30 eV and 1.33 eV was recorded respectively. The morphological study of these mixed cation perovskite films revealed that films having lower FA content had few pin holes and low coverage, whereas films with higher FA content, (FA)₀.₇₅(MA)₀.₂₅SnI₃ and FASnI₃ was pin hole free and had complete coverage.

When devices were fabricated incorporating these mixed cations perovskite films a low average PCE of 3.61% ± 0.32% was obtained for MASnI₃ films. Moreover, with increasing FA content an increase in FF and Voc was observed, with the best average PCE of 7.48%±0.52% recorded for devices based on (FA)₀.₇₅(MA)₀.₂₅SnI₃ perovskite films. The best device based on (FA)₀.₇₅(MA)₀.₂₅SnI₃ perovskite films gave maximum efficiency of 8.12% with a JSC of 21.2 mA.cm⁻², a Voc of 0.61 V and a FF of 62.7%. This outstanding performance was attributed to the pin hole free and complete coverage of (FA)₀.₇₅(MA)₀.₂₅SnI₃ perovskite film. This combination of cations in perovskite significantly reduced the carrier recombination rate as was proved from transient state PL spectra and electrochemical impedance spectroscopy (EIS) of these films. (FA)₀.₇₅(MA)₀.₂₅SnI₃ had the highest PL lifetime of 3.07 ± 0.1 ns compared to other mixed cations perovskite films. At high applied voltages the value of R∞ recorded from EIS was also the largest for this combination among all perovskite films proving the effectiveness of reducing carrier recombination rate through cation mixing. These devices had a very high reproducibility with considerable stability. Under inert environment these PSCs retained 80% of their initial efficiency for more than 400 h.

To further improve coverage of (FA)₀.₇₅(MA)₀.₂₅SnI₃ perovskite films and increase the crystallite size Ozaki et al., [108] reported a hot antisolvent treatment (HAT) along with annealing in DMSO vapors. Pin hole free films with complete coverage were obtained when antisolvent was preheated to 65 °C before dripping (in this case chlorobenzene). A large density of perovskite nucleation sites were formed in the case of preheated antisolvent dripping technique, resulting in a pin hole free full coverage films. Whereas, films without HAT resulted in poor coverage, and had pin holes after annealing. When films were annealed in a mild DMSO vapor-enriched environment the quality of perovskite further increased and average crystallite size increased from 237 nm to 440 nm. Combining both of these optimizing strategies Ozaki et al., [108] were able to achieve a best PCE of 7.2%.

By employing solvent engineering technique, Yan et al., [109] were able to achieve efficiency of 9.06%. Different anti solvents such as toluene (TL), chlorobenzene (CB) and diethyl ether (DE) were used for perovskite film production. For optimum performance, SnF₂ was added to suppress Sn²⁺ oxidation and mixture of DMF as well as DMSO was used as a solvent in the perovskite precursors. When films were prepared without anti-solvent dripping it affected both, their crystallinity and crystal orientation. The preferred orientation for perovskites without anti-solvent dripping was (120), while those prepared with anti-solvent dripping preferred (100) and (200) [109]. A morphological study of (FA)₀.₇₅(MA)₀.₂₅SnI₃ perovskite films prepared with and without anti-solvent dripping revealed that films produced without any anti-solvent treatment resulted in discontinuous films with several flower shaped grains as shown in Figure 12. This discontinuous film is resulted due to low number of nucleation sites. When anti-solvent treatment was applied number of
nucleation sites considerably increased and a much smoother full coverage film was formed. As can be seen from Figure 12 with DE as anti-solvent higher number of pin holes are present, the number of pin holes dropped when TL was used. However, the best film having least number of pin holes was produced when CB was used as anti-solvent.

![Figure 12](image-url)  
**Figure 12.** Top-view (FA)0.75(MA)0.25SnI3 films deposited on ITO/PEDOT:PSS substrates as seen under SEM (a) without anti-solvent; (b) with DE; (c) with TL; and (d) with CB. Adapted with permission from [109]. Copyright © 2020, American Chemical Society.

Perovskite devices employing p-i-n architecture were fabricated based on these films using PEDOT: PSS as HTL and C60 as ETL. Films dripped by CB yielded the best PCE of 9.06%. Whereas films dripped with TL and DE gave PCE of 7.52% and 6.29% respectively. The high efficiency obtained from films dripped with CB was attributed to low charge carrier recombination rate resulted from pin hole free films with full coverage. At high applied voltages value of $R_{\text{rec}}$ recorded from EIS was also the largest for CB dripped films based devices proving the effectiveness of reducing carrier recombination rate through CB dripping. When tested for stability, CB dripped perovskite films based encapsulated devices retained almost 75% of their initial efficiency over a period of 30 days when stored in nitrogen glove box.

Kanatzidi and group applied a different approach to enhance overall performance and improve air stability of lead free Sn based perovskite solar cells. Perovskite devices based on hollow ethylenediammonium FASnI3 (en)FASnI3 were fabricated to achieve a PCE of 7.14% with enhanced air stability of more than 1000 h with proper encapsulation [110]. The incorporation of en in perovskite resulted in a novel 3D mixed cation perovskite (en)FASnI3, opening the door for tuning the bandgap without using solid solutions. This 3D hollow (en)FASnI3 was prepared by mixing stichometric amount of en and FAI in a solution of SnI2, followed by adding it to a mix solvent of hydroiodic acid (HI) and H3PO4. Initially en/FA ratio was kept at 0%, 10% and 25% to determine the optimum amount of en loading. The crystal structure of (en)FASnI3 retained the pseudocubic shape of pristine FASnI3 and orthorhombic unit cell with very minor change in the unit cell volume. It was assumed that to incorporate large sized en in 3D crystal structure other species, neutral or charged with proportionate size must be removed from crystal resulting in Schottky defects or point defects respectively.

To investigate the exact structure of this new mixed cation perovskite Kanatzidi and coworkers used many experimental techniques and theoretical calculations, all of which confirmed a hollow 3D structure with missing SnI2 neutral fragments. This resulted in narrowing of both, VB and CB hence increasing the bandgap of these (en)FASnI3 perovskites. Removal of SnI2 units from the crystal structure, the observed decrease in energy levels of VB maxima automatically enhanced the stability of devices based on these perovskites as it shifted the absolute work function to lower energies resulting in reduction of oxidation tendency. A bandgap of 1.4, 1.5 and 1.9 eV was reported for perovskite materials with 0, 10 and 25% of en loading, respectively. Films with 0% en loading showed...
a carrier lifetime of 0.19 ns whereas a carrier lifetime of 0.46 and 0.68 ns was calculated for 10 and 25% en loading respectively. Perovskite devices employing n-i-p architecture were fabricated using these \{en\}FASnI₃ perovskites. Device based on pristine FASnI₃ yielded a PCE of 1.40%, whereas devices based on 10 and 25% of en loading gave PCE of 6.94% and 2.34%, respectively.

The relatively poor performance of pristine FASnI₃ based device was attributed to poor coverage and a very high carrier recombination rate. While low efficiency of 2.34% in devices based on 25% en loading was caused by a very low J_sc resulted from a high bandgap of 1.9 eV. These results proved the optimum value for en loading to be 10% where the champion cell achieved a PCE of 7.14% with a J_sc of 22.54 mA.cm⁻², a V_OC of 0.480 V and a FF of 65.96% when measured under reverse voltage scan. When tested for stability the encapsulated devices retained 96% of their initial performance even after 1000 h which is a very encouraging prospect for the future of highly efficient and stable lead free tin based PSCs. Later Kanatzidis and group extended the same approach to fabricate highly efficient and stable \{en\}MASnI₃ and \{en\}CsSnI₃ perovskites \[111\]. The champion cell achieved a PCE of 6.63% for \{en\}MASnI₃ with 15% of en loading, while the best performance for \{en\}CsSnI₃ based solar cell was recorded for 10% of en loading with a PCE of 3.79%. This optimum en loading also significantly increased the air stability of both perovskites and PSCs based on them. Very recently Kanatzidis and group demonstrated the effective use of benzodithiophene (BDT)-based small organic molecules as hole transport materials for efficient lead free Sn based PSCs \[112\]. Efficiency of 7.59% was achieved for the champion device using these HTMs.

It was observed in the case of lead based perovskite devices that as the dimensionality of perovskite decreased the stability of device increased \[113,114\]. Keeping this in mind Kanatzidis and group reported 2D (BA)ₓ(MA)ₙ₋₁SnI₃₊₁ perovskites with enhanced moisture stability \[115\]. The optical band gaps of these 2D perovskites can be tuned from 1.83 eV (n=1) to 1.20 eV (n=∞), however for solar applications n=3 and n=4 were selected to have an optimal band gap of 1.50 and 1.42 eV respectively. To improve perovskite film morphology triethylphosphine (TEP) and SnF₂ was added to the precursor solution. Devices were fabricated using these perovskite films to test their performance and moisture stability. For value of n =3 a maximum PCE of 1.94% was obtained, while devices with n=4 yielded a PCE of 2.53 %. When compared for stability with MASnI₃ based devices, the encapsulated devices with n=4 retained almost 90% of their initial efficiency for more than one month while in the same period the encapsulated devices based on MASnI₃ completely degraded. This enhanced stability of 2D (BA)ₓ(MA)ₙ₋₁SnI₃₊₁ perovskites based solar cell is attributed to the formation of long chains of hydrophobic butyl ammonium in the perovskite resulting in protecting perovskite films.

In 2017 Liao et al., \[116\] reported a 5.94% efficient and 100 h stable 2D (PEA)ₓ(FA)ₙ₋₁SnI₃₊₁ based perovskite solar cell. Very recently Liu et al., \[117\] demonstrated that different alkyl chain lengths have significant effects on crystal orientation and phase distribution in 2D perovskite films. Organic cations with short lengths of alkyl chains can increase dimensionality and can produce highly oriented crystal grains \[117\]. 2D/3D mixed cations (PEA:FA(1₋ₓ)SnI₃) Sn based PSC with a PCE of 6.98% was reported in 2018 by Xi et al., \[118\]. Incorporation of large PEA in perovskite structure significantly improved the PCE and stability of the 2D/3D mixed fabricated devices. A two-step fabrication route was used to prepare (PEA,FA)SnI₃ bulk heterojunction perovskites. First PEA molecules were evaporated to form PEA/FAI mixture on top of FAI films followed by evaporation of SnI₃ forming a 2D/3D perovskite. To find the best combination different amounts of PEA was evaporated such as 25, 50 and 75 mg. Devices were fabricated employing p-i-n planar heterojunction architecture with an ultrathin layer of LiF (3, 5 and 8 nm thick) deposited at ITO/PEDOT:PSS interface. This insulating LiF improved the hole extraction at ITO/PEDOT:PSS interface along with lowering the work function of PEDOT:PSS. The best performance was realized with 50 mg of PEAI evaporation along with keeping LiF thickness at 5 nm. The champion device provided a PCE of 6.98% with a J_sc of 20.07 mA.cm⁻², a V_OC of 0.47 V and a FF of 0.74. Shao et al., \[119\] reported a 9% efficient 2D/3D mixed highly crystalline FASnI₃ based perovskite solar cells. The perovskite films were prepared by mixing 0.08 M of 2D layered tin perovskite with 0.92 M of 3D FASnI₃ along 2-phenylethylammoniumiodide (PEAI).
Marshall and group reported a 3D mixed cation Cs$_{1-x}$Rb$_x$SnI$_3$ perovskite material for solar cell applications. By increasing the value of x open circuit voltage can be significantly increased in this type of perovskite material. However they observed that as the number of Rb atoms substituting Cs increased the stability of the perovskite decreased. The champion cell provided a PCE of 2.25% with 50% of Cs substituted by Rb and having 10 mol% of excess SnI$_2$ [120]. Ran et al. [121] reported a 2000 h stable perovskite device when stored in nitrogen filled glove box with a PCE of 6.08% by successfully doping Cs in FASnI$_3$ perovskite. Incorporating Cs into FASnI$_3$ improved the geometric symmetry of the crystal by inducing contraction of corner sharing SnI$_6$ octahedra. It also significantly enhanced the stability of perovskite by reducing Sn$^{2+}$ oxidation tendency. Compared to pristine FASnI$_3$, absorption edge in UV-Vis spectra and PL spectra of Cs$_x$FA$_{1-x}$SnI$_3$ films were considerably red shifted. This red shift is attributed to reduction of band gap resulted from the contraction of crystal lattice due to incorporation of Cs. Details of optimization can be read from the published report [121], where the best PCE of 6.08% is reported for device based on perovskite film having 8% of CsI doping. This enhanced efficiency is attributed to reduction of hole trap density, increase of carrier mobilities and reduction in bulk resistance for Cs$_x$FA$_{1-x}$SnI$_3$ films compared to pristine FASnI$_3$ films. The 8% doped CSI device showed an outstanding stability of 2000 h in nitrogen filled glove box by maintaining 90% of its initial performance in that time period. Compared with pristine MASnI$_3$ and FASnI$_3$ based devices Cs doped device had considerably improved stability both in nitrogen and in air.

Jokar et al. [122] reported addition of butylammonium iodide (BAI) and ethylenediammonium diiodide (EDAI$_2$) as additives in FASnI$_3$ based perovskite to achieve power efficiencies of 5.5% and 7.4% respectively. Addition of BAI in the FASnI$_3$ perovskite provided the benefit of lowering dimensionality of perovskite from 3D to a hybrid 2D/3D structure. Although this hybrid structure possessed advantages such as superior crystallinity and preferred crystallographic orientation, the surface was not pin hole free as was resulted from the slow nucleation and too rapid crystal growth rate. When BAI was replaced by di-ammonium cations a dense pin hole free perovskite film was produced as a result of the presence of two ammonium groups which increased interactions with Sn perovskite and ultimately controlling the crystal growth rate. These mixed cations perovskites were less likely to oxidize as compared to pristine FASnI$_3$ perovskites. Since, forming a compact layer and preventing water molecules to diffuse in the perovskite BAI successfully retarded the oxidation while in case of EDAI$_2$ the enhanced stability is attributed to it being a good reducing agent. Almost 90% of the initial efficiency was maintained by the encapsulated devices based on FASnI$_3$-BAI 15% for over 2000 h under inert environment. For devices based on FASnI$_3$-EDAI$_2$ 1% the efficiency gradually increased from its initial value of 6.3% to its maximum value of 8.9% after storing in nitrogen for 1462 h. This increase in performance is attributed to EDAI$_2$ slowly passivating the surface and gradually adjusting the crystal structure to its optimal phase near 1500 h [122]. Recently Weber et al., [123] reported a 4.63% efficient mixed cation perovskite device by mixing three different cations along with introducing bromide in the perovskite lattice. MA$_{0.75}$FA$_{0.15}$PEA$_{0.1}$Sn(Br$_{1-x}$I$_x$)$_3$ was used as perovskite layer having an optical bandgap of 1.29 eV.

It was in 2019 when Jokar et al., [124] reported one of the most efficient and highly stable Sn based perovskite solar cell with a PCE of 8.5% recorded for fresh device. This extraordinary efficiency was achieved by incorporating a non-polar organic cation guanidinium (CH$_6$N$_3^+$, GA) in the perovskite crystal of FASnI$_3$ while simultaneously adding ethylenediammonium diiodide (EDAI$_2$) and SnF$_2$ to perovskite. Besides being a non-polar, Guanidinium has a size slightly larger (278 pm) than that of FA$^+$ (253 pm) [125]. When used in Sn based perovskite the GASnI$_3$ is reported to adopt a hexagonal shape with a bandgap of 1.9 and 2.1 eV for its 3D hexagonal and its 2D monoclinic structures respectively [126]. Perovskite films were prepared from precursor solutions of GAi and FAi with varying ratios and mixing them with equimolar SnI$_2$ solution. For enhancing performance and stability of perovskites, SnF$_2$ and EDAI$_2$ were also added in the mixture to obtain the final perovskite films of GA:FA$_{1-n}$Sn$_n$I$_3$–EDAI$_2$. As reported earlier by the same group incorporating trace amounts of EDAI$_2$ in FASnI$_3$ perovskite produced pin hole free, uniform and dense perovskite films simultaneously reducing tendency of Sn$^{2+}$ oxidation hence increasing
stability [122]. As the ratio of GA:FA increased the size of perovskite crystal also increased resulted from the larger size of the GA. Incorporation of GA into the perovskite crystal also caused expansion of unit cell hence, increasing the lattice parameters. Increasing GA proportion from 0 to 30, the absorption band edges of E1Gx perovskites correspondingly shifted towards smaller wavelengths. Whereas, bandgap energies increased from 1.44 eV for x=0 to 1.53 eV for x=30.

The optimal performance was recorded for device based on 20% GA and 1% EDAI2, represented as E1G20 this device yielded a champion PCE of 8.5% (8.3% certified). The efficiency continuously increased and reached 9.6% after 2000 h storage in nitrogen filled glove box. To test the champion device for stability, performance of device under three different test conditions were analyzed. For comparison device based on pristine FASnI3 and device based on perovskite having only EDAI2 mixed in FASnI3 (E1) was also tested under same conditions. As can be seen from Figure 13a the encapsulated E1G20 device remained stable for more than one h with negligible loss of PCE in air (RH= 50%) under continuous 1 Sun AM1.5G illumination. While under the same conditions encapsulated E1 device only sustained its maximum performance for 300 s and deteriorated quickly afterwards. When unencapsulated devices were stored in air (RH=60%) devices based on pristine FASnI3 lost their performance within two h, whereas E1G20 devices retained 80% of their initial performance for 96 h. The performance of E1G20 device was completely loss free for 170 h when was stored in air under 20% relative humidity as shown in Figure 13b. The same device when stored in nitrogen glove box for over 2000 h its PCE gradually increased with time from 7.3% to a maximum of 9.6%. Figure 13d represent the certified efficiency for E1G20 device.

Figure 13. (a) Stabilized PCE and Jsc of E1G20 and E1 (shown in the inset) devices taken at the position of maximum power under 1 sun irradiation from AM1.5G solar simulator for 3600 s; PCE of both devices E1 and E1G20 as a function of storage period in two environments: (b) un-encapsulated devices in ambient air with RH = 20% and 60%, (c) Nitrogen glove box, and (d) certified efficiency 8.30% for the E1G20 device in an ISO-approved PV Efficiency Verification Laboratory in Taiwan. Adapted with permission from [124]. Copyright © 2020, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fu et al., [127] used a similar strategy of adding NH3GACL to the perovskite film to passivate defects and decrease Sn2+ oxidation. Addition of NH3GACL in the perovskite also helped optimize the energy levels of the perovskite and favorably adjusted it to the charge transport layers that resulted in faster charge carrier dynamics. Devices fabricated from NH3GACL doped perovskites yielded a maximum PCE of 7.30% and were stable for more than 30 days when stored in nitrogen glove box. Very recently Kanatzidis and group reported a 9.61% efficient device by introducing 3-phenyl-2-propen-1-amine (PPA) in FASnI3 perovskite [128]. The incorporation of these conjugated organic cations in the perovskite lattice resulted in larger grain sizes, reduced density of traps, enhanced charge extraction and increased overall structural stability of the perovskite film.
Performance was optimized when the concentration of PPAI was kept at 15%. The champion cell yielded a \( V_{OC} \) of 0.56 \( V \), \( J_{SC} \) of 23.34 mA cm\(^{-2}\), FF of 73.5% and a PCE of 9.61% by reverse scan. Kanatzidis and group also demonstrated the large scale fabrication keeping the active area at 1 cm\(^2\) to achieve a maximum PCE of 7.08%. When these devices were tested for stability it was revealed that the un-encapsulated 15% PPAI devices retained almost 92% of their initial performance even after 60 days, while being kept in nitrogen glove box. Song and group reported an 8.07% efficient device using a technique of secondary crystallization for improved film quality and remarkably reduced Sn\(^{2+}\) oxidation [129]. When stored in Nitrogen glove box, the un-encapsulated device retained 87% of its initial efficiency even after 1000 h.

Han et al., [130] reported a 10.81% efficient device by controlling FASnI\(_3\) nucleation at solution-air interface. A tailor made organic cation, pentafluorophen-oxyethylammonium iodide (FOEI) was introduced in the perovskite lattice, which reduced the surface energy of solution-air surface and enhanced the crystallization intensity of perovskite films by 20-fold. PSCs fabricated from these films provided a long term stability of 500 h under continuous 1 sun illumination. A unique blend of Sn triple-halide amorphous layer and Cs-formamidinium tin iodide polycrystals was reported by Liu et al., [131] very recently to achieve PCE of over 10% with a 1000 h stability. An amorphous-polycrystalline perovskite film composed of a Sn triple-halide amorphous layer and CsFASnI\(_3\) polycrystals was fabricated. The resulted structure proved very efficient in blocking moisture and oxygen resulting in elevated efficiency and enhanced stability. The champion device provided a PCE of 10.4% with a \( V_{OC} \) of 0.64 \( V \), a \( J_{SC} \) of 21.6 mA cm\(^{-2}\), and FF of 75.2%. The encapsulated device maintained over 95% of its initial PCE for more than 1000 h. Jiang et al., [132] reported an unprecedented \( V_{OC} \) of 0.94 \( V \) for PEA\(_x\)FA\(_{1-x}\)SnI\(_3\) based PSC, using indene-C\(_60\) bisadduct (ICBA) as ETL. The introduction of ICBA as ETL instead of commonly used PCBM considerably suppressed the iodide remote doping resulting in a higher \( V_{OC} \) and PCE. Champion device showed a PCE of 12.4% with shelf life of more than 3800 h.

Use of PEA\(^+\) or EADI\(^+\) is desirable to reduce trap density and enhance perovskite stability by improving crystal grain and orientation. However, doping optimized amount of Ge into the perovskite matrix is the latest focus of research [133,134]. The ab initio density functional theory (DFT) simulations performed on mixed elements Ca/(Ge, Sn) and Sr/(Ge, Sn) perovskites revealed that they have higher stability than Pb based perovskite deives [135]. Hayase and group introduced Ge in the perovskite lattice to significantly reduce trap density and suppress Sn vacancies. When 7.5% mol of Ge was added, the total trap density of the perovskite was doubly reduced to \( 4.14 \times 10^{20} \) cm\(^{-3}\) and PCE of 7.45% was realized [136]. Because of the double positive effects of both PEA\(^+\) and Ge\(^+\) on the stability of the perovskite, the un-encapsulated device retained 70% of its PCE for 3 h under continuous 1 Sun illumination in ambient conditions.

To further increase the stability of mixed perovskite devices Chen et al., [134] replaced FA with Cs. Devices fabricated with CsSn\(_{0.5}\)Ge\(_{0.5}\)I\(_3\) perovskites yielded a PCE of 7.11%. This perovskite had remarkable stability because of a stable native-oxide layer that formed on its surface when the perovskite got exposed to air. This stable native-oxide layer had completely encapsulated the surface of the perovskite which resulted in more than 500 h operational stability under continuous 1 Sun illumination in inert environment [134]. Although remarkably stable, these devices showed low PCE as compared to organic cation based perovskites. Very recently Hayase and group reported the most efficient Sn based PSC with a PCE of more than 13% [137]. To achieve such an outstanding PCE they used two different strategies of efficiency enhancement simultaneously. First of which involved the addition of metals to suppress Sn oxidation, while the second involved the addition of A cite cations to control perovskite crystallization. An optimized concentration of EAI was added to the perovskite lattice to favorably align energy bands between the perovskite and charge transport layers. To remove any iodide deficiency in the film GeI\(_2\) doping was performed, which combined with EAI addition reduced the trap density of the perovskite by 1 order of magnitude. In addition by controlling the amount of EAI in the perovskite lattice the tolerance factor close to 1 was achieved. This proved that this method can be successfully used to produce considerably stable crystal structures.
When devices were fabricated from GeI₂ doped perovskite employing p-i-n architecture (FTO/PEDOT:PSS/GeI₂ doped Sn-perovskite/C₆₀/BCP/Ag/Au), PCE of 13.24% was achieved with a J_Sc of 20.32 mA.cm⁻², a V_OC of 0.84 V and a FF of 78% [137]. This is the highest value of PCE reported for Sn based perovskites till date. Table 7 show the progress in performance mixed cation devices has made so far. Table 7 and Table 8 prove the importance of these devices in search of environment friendly highly efficient PSCs.

| Year | Device architecture | Perovskite Film Fabrication technique /Perovskite Film | J_Sc (mA.cm⁻²) | V_OC (V) | FF | EFF (%) | Ref. |
|------|---------------------|--------------------------------------------------------|---------------|--------|----|---------|-----|
| 2017 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | Spin Coating using DMSO as solvent + Annealing / (FA)(MA)_xSnI₃+SnF₂ | 21.2 | 0.61 | 0.627 | 8.12 | [107] |
| 2017 | FTO(c-TiOₓ/mp-TiO₂)-Perovskite/PTAA/Au | Spin Coating using DMF + DMSO as solvent + Annealing / {en}FASnI₃ + SnF₂ | 22.54 | 0.480 | 0.6596 | 7.14 | [110] |
| 2017 | FTO(c-TiOₓ/mp-TiO₂)-Perovskite/PTAA/Au | Spin Coating using DMF + DMSO as solvent + Annealing / {en}MASnI₃ + SnF₂ | 24.28 | 0.428 | 0.6372 | 6.63 | [111] |
| 2017 | FTO(c-TiOₓ/mp-TiO₂)-Perovskite/PTAA/Au | Spin Coating using DMF + DMSO as solvent + Annealing / {en}CsSnI₃ + SnF₂ | 25.07 | 0.280 | 0.5382 | 3.79 | [111] |
| 2017 | FTO(c-TiOₓ/mp-TiO₂)-Perovskite/PTAA/Au | Spin Coating using DMSO as solvent/(BA)ₓ(MA)₁₋ₓSnI₃ + SnF₂ + triethylphosphine (TEP) | 24.1 | 0.229 | 0.457 | 2.53 | [115] |
| 2017 | ITO/NiOₓ/Perovskite/PCBM/Al | Spin Coating using DMF + DMSO as solvent / (PEA)(FA)nSnI₃n+1 + SnF₂ | 14.44 | 0.59 | 0.69 | 5.94 | [116] |
| 2018 | ITO/LiF/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | two-step film fabrication protocol / (PEA,FA)SnI₃ | 20.07 | 0.47 | 0.74 | 6.98 | [118] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Al | Spin Coating using DMF + DMSO as solvent + Anti solvent dripping + Annealing/ (PEA)(FA)xSnI₁₋ₓ | 24.1 | 0.525 | 0.71 | 9 | [119] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Ag | Spin Coating using DMF + DMSO as solvent + Hot antisolvent treatment+Annealing in DMSO vapor atmosphere/ (FA)(MA)_xSnI₃ + SnF₂ | 19.4 | 0.55 | 0.67 | 7.2 | [110] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C₆₀/BCP/Al | Spin Coating using DMF + DMSO as solvent + Antisolvent dripping / FAₓMAₓSnIₓ + SnF₂ | 24.3 | 0.55 | 0.673 | 9.06 | [109] |
| 2018 | ITO/Perovskite/PC₆₁BM/BCP/Al | Spin Coating using DMF as solvent/CsxRb₁-xSnI₃ + Excess SnI₃ | 8.11 ± 0.53 | 0.48 | ± 0.46 ± 0.05 | 1.81 ± 0.30 | [120] |
| Year | Device Configuration | Processing Method | Power Conversion Efficiency | Fill Factor | Open Circuit Voltage | Short Circuit Current | Steady State Efficiency |
|------|----------------------|-------------------|-----------------------------|-------------|----------------------|----------------------|------------------------|
| 2018 | ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag | Spin Coating + Annealing / Cs:FAx:FA5SnI5 | 20.70 | 0.44 | 0.668 | 6.08 | [121] |
| 2018 | ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag | Spin Coating using DMSO as solvent + Antisolvent dripping/FASnI3–yEDAI2+SnF2 | 21.3 | 0.538 | 0.718 | 8.9 | [122] |
| 2019 | FTO/mp-TiO2/Perovskite/BDT-4D/Au | Spin Coating using DMSO as solvent + Antisolvent dripping/FASnI3–SnF2 | 22.41 | 0.497 | 0.682 | 7.59 | [112] |
| 2019 | ITO/PEDOT:PSS/Perovskite/PC60BM/Al | Spin Coating using DMF + Antisolvent dripping/FASnI3 + SnF2 | 23.34 | 0.56 | 0.735 | 9.61 | [128] |
| 2019 | ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag | Secondary crystallization growth (SCG) technique/FA0.75MA0.25SnI2.75Br0.25 | 22.3 | 0.52 | 0.695 | 8.07 | [129] |
| 2019 | ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag | Spin Coating using DMSO + DMF as solvent + Antisolvent dripping + Annealing/FASnI3–FOEI | 21.59 | 0.67 | 0.75 | 10.81 | [130] |
| 2019 | ITO/PEDOT:PSS/Perovskite/PCBM/PEI/Ag | Spin Coating using DMSO + DMF as solvent + Antisolvent dripping + Annealing/ NH2GACl+FASnI3+SnF2 | 19.30±0.35 | 0.54±0.02 | 0.681±0.084 | 7.10±0.2 | [127] |
| 2020 | FTO/c-TiO2/mp-TiO2/perovskite/PTAA/Au | Ba0.55FA0.4SnI3.60 | 22.02 | 0.439 | 0.433 | 4.12 | [117] |
| 2020 | ITO/PEDOT:PSS/Perovskite/C60/BCP/Ag | Spin Coating using DMSO as solvent + Antisolvent dripping of CB + Annealing/FASnI3–FOEI | 21.59 | 0.67 | 0.75 | 10.81 | [130] |
| 2020 | ITO/PEDOT:PSS/Perovskite/PCBM/BCP/Ag | Spin Coating using DMSO as solvent + Antisolvent dripping of CB + Annealing/ CsFASnI3 | 21.6 | 0.64 | 0.752 | 10.4 | [131] |
| 2020 | ITO/PEDOT/Perovskite/ICBA/BCP/Ag | Spin Coating using DMSO + DMF as solvent + Antisolvent dripping of toluene + Annealing/ PEA:FAx:SnI3:SCN | 17.4 | 0.94 | 0.75 | 12.4 | [132] |
| 2020 | FTO/PEDOT:PSS/Perovskite/C60/BCP/Ag/Au | Spin Coating using DMSO as solvent + Antisolvent dripping of CB + Annealing/ FAx:PEAx:Sn:Ge-I3 | 21.92 | 0.46 | 0.73 | 7.45 | [136] |
| 2020 | FTO/PEDOT:PSS/perovskite/C60/BCP/Ag/Au | Gel: doped (FAx:EAx):yEDAI2+SnF2 | 20.32 | 0.84 | 0.78 | 13.24 | [137] |
### Table 8. Stability of Mixed Cation tin halide(s) based perovskites.

| Year | Device architecture | Testing environment | Stability | Ref. |
|------|---------------------|---------------------|-----------|------|
| 2017 | FTO/c-TiO₂/mp-TiO₂-{(BA)₂(MA)₂SnI₃ + SnF₂ + triethylphosphine (TEP)/PTAA/Au | Encapsulated devices under inert environment | Retained almost 90% of initial efficiency after 720 h | [115] |
| 2017 | ITO/PEDOT:PSS/(FA)ₓ(MA)₁₋ₓSnI₃ + SnF₂/C₆₀/BCP/Ag | Encapsulated devices stored in inert environment | Retained almost 80% of initial efficiency after 400 h | [107] |
| 2017 | FTO/c-TiO₂/mp-TiO₂-{en}FASnI₃ + SnF₂/PTAA/Au | Encapsulated devices when stored | Retained almost all of their initial performance after 1000 h | [110] |
| 2018 | ITO/PEDOT:PSS/ FA₀.₇₅MA₀.₂₅SnI₃ + SnF₂/C₆₀/BCP/Al | Encapsulated devices stored in inert environment | Retained almost 75% of their initial efficiencies after 720 h | [109] |
| 2018 | ITO/PEDOT:PSS/ CsₓFA₁₋ₓFASnI₃/C₆₀/BCP/Ag | Encapsulated devices stored in inert environment | Remained stable for almost 2000 h | [121] |
| 2018 | ITO/PEDOT:PSS/ FASnI₃₋ₚEDAI₂+SnF₂/C₆₀ /BCP/Ag | Encapsulated devices | Efficiency remained stable for 1 h | [122] |
| 2019 | ITO/PEDOT:PSS/ GAₓFA₁₋ₓSnI₃₋ₚEDAI₂+SnF₂/C₆₀ /BCP/Ag. | Encapsulated device under 1 Sun illumination in ambient condition (RH=50%) | Retained 80% of its initial PCE after 96 h | [124] |
| 2019 | ITO/PEDOT:PSS/ PPAₓFA₁₋ₓSnI₃/C₆₀/BCP/Ag | Un-encapsulated device stored in ambient condition (RH=60%) | Retained 100% of its initial PCE after 170 h PCE increased from 7.3% to 9.6% after 2000 h | [124] |
| 2019 | ITO/PEDOT:PSS/ PPAₓFA₁₋ₓSnI₃/C₆₀/BCP/Ag | Un-encapsulated device stored in inert environment | Retained 90% of its initial PCE after 1440 h | [128] |
6. Conclusion and outlook

In this comprehensive Review, we have summarized all the efforts made on enhancing the performance and stability of Sn based PSCs from the very first report in 2014 to reports published in 2020. Performance and stability of Sn based PSCs is largely depended on perovskite film quality, device architecture and fabrication technique. Optimizing film deposition technique, interface modification and cation substitution have attracted much attention in recent years. Band gap engineering and solvent engineering proved effective in elevating overall PCE and stability of PSCs. Although still lagging in both efficiency and stability when compared to conventional Pb based perovskites, the Sn based counterparts are progressing ever so rapidly. With excellent optical and electrical properties and recent demonstration of efficiency exceeding 13 % the prospect of these perovskites playing a leading role in the future PV market cannot be ruled out. PCE can be significantly improved from the current highest reported efficiencies of 7.78 % [60], 10.17 % [81], 4.81 % [37,90] and 13.24% for MASnX3, FASnX3, CsSnI3 and MCSnX3, respectively. As the theoretical maximum PCE calculated for MASnX3, FASnX3, CsSnI3 and MCSnX3 based PSCs is 19.9%, 26.9%, and 25.6% respectively [37]. Based on our thorough analysis, we will provide suggestions on ways to further elevate the PCE and improve stability of tin-based PSCs. Moreover, focusing the commercial applications of Sn based PSCs in building integrated photovoltaics (BIPVs), suggestions to enhance transparency of PSCs are also provided.

- Minimizing oxygen exposure. One of the major reasons for low performance is Sn$^{2+}$ oxidation. Reducing oxygen exposure during film growth by using techniques such as
reducing vapor atmosphere [50] and vacuum growth [129] can significantly improve both efficiency and stability by minimizing p-type doping and enhancing film quality.

- **Controlling perovskite crystallization.** To reduce density of trap states and optimize charge carrier dynamics different strategies can be used such as introduction of [poly(ethylene-co-vinyl acetate) [82], pentafluorophen-oxylethylammonium iodide (FOEI) [130] or triethylphosphine (TEP) [115] in the perovskite matrix.

- **Purification of Sn sources to prevent oxidation.** Any commercial SnX2 source contains Sn⁴⁺, even those with 99 % purity contain a significant concentration of oxidized Sn⁴⁺ resulting in poor performance and reproducibility issues [80]. Addition of tin powder can solve this problem by reacting with Sn⁴⁺ and reducing it to Sn²⁺ state.

- **Inverted p-i-n architecture should be preferred.** Better quality of perovskite film can be formed on HTLs by avoiding using salt-doped hole selective layers (HSLs), known to damage Sn perovskite [51,70]. Also p-i-n architecture can favorably align the energy levels of HTL and ETL with perovskite than when used in conventional n-i-p configuration.

- **Increasing Voc by optimizing energy levels.** While, the short circuit current (J_Sc) of the PSCs is approaching the theoretical limit, the open circuit voltage (Voc) emerges as a major limiting factor for overall performance of Sn based PSCs. Voc is reduced greatly due to the existence of severe recombination and mismatched energy levels in the device. New techniques of bandgap engineering must be explored along trying more suitable materials as HTL and ETL. For example, Jiang et al., [132] used indene-C₆₀ bisadduct (ICBA) as ETL instead of commonly used PCBM which considerably suppressed the iodide remote doping resulting in a record Voc of 0.94 V and PCE of 12.4 % with shelf life of more than 3800 h.

- **Regulating the A site cation to achieve a tolerance factor of nearly 1.** An inverse relation exists between tolerance factor and lattice strain of perovskite crystal. Optimizing A site cation with proper substitution is vital to achieve high performance and stability. Regulating A site cation can make the tolerance factor as close to one as possible, resulting in a stable perovskite structure. For example Nishimura et al., [137] partially substituted formamidinium cation with ethylammonium cation to achieve tolerance factor of 0.9985, achieving record PCE exceeding 13 %.

- **Doping Ge in Sn based PSCs.** Ge is known to passivate traps and stabilize the mixed 2D/3D perovskite lattice by simultaneously suppressing defect/trap states and Sn²⁺ oxidation [133,134]. The addition of an optimum amount of Ge to develop efficient and stable tin-based PSCs should be an efficient approach. Ge³⁺ oxidizes into Ge⁴⁺ resulting in a thin GeO₄ protecting layer encapsulating tin perovskite crystals. The highest PCE of 13.24 % reported for Sn based PSCs is achieved doping Ge in the perovskite lattice [137].

- **Enhancing transparency using bandgap engineering.** Halides (Cl, Br, I) play a major role in determining the bandgap of the perovskite. As the halide radii decrease, the bandgap of perovskite increases, allowing more light in the visible region to pass through the perovskite film. For example, the optical bandgap changed from 1.27 eV for pure CsSnI₃ to 1.37 eV for CsSnI₂Br, and from 1.65 eV for CsSnI₂Br₂ to 1.75 eV for CsSnBr₃. The increasing bromine content also induced a change in the color of perovskite films from black to light brown, increasing transparency [88].

- **Use of transparent contact.** Currently most of the fabricated devices use relatively thick (~70 nm or more) metal film as back contact which makes the design opaque. However, a fully semitransparent PSC can be achieved by using 2D structures, transparent conducting oxides (TCOs), graphene electrodes and metal nanowires etc.

Recent progress in the field confirms that Sn based PSCs has great potential for commercialization with very optimistic future prospects. Starting with a PCE of 5.73 % and a shelf life of 12 h, within few years the PCE has exceeded 13 % and stability reached 3800 h. With further research and resources directed in this field these nontoxic PSCs will be a major trend of the future.
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