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Challenges in tin perovskite solar cells

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Abstract:

Perovskite solar cells are the rising star of third-generation photovoltaic technology. With a power conversion efficiency of 25.5\%, the record efficiency is close to the theoretical maximum efficiency for a single-junction solar cell. However, lead toxicity threatens commercialization efforts and market accessibility. In this context, Sn-based perovskites pose themselves as a safe alternative. Nevertheless, the efficiency of Sn-based devices falls far behind the efficiency of Pb-based counterparts.

This concise review sheds light on the challenges that the field faces toward making Sn-based perovskites the perovskite photovoltaic benchmark. We identified four key challenges: materials and solvents, film formation, Sn (II) oxidation, and energy bands alignment. We illustrate every single challenge and highlight the most successful attempts to overcome them. Finally, we provide our opinion of the most promising trends in the future of the field.
1. Motivation

Exploring the photoactive properties of halide perovskites started twenty years ago as a scientific curiosity, and it resulted in a novel type of photovoltaics and optoelectronics. Perovskite solar cells (PSCs) grabbed the attention of the photovoltaics community due to their ease of fabrication, optimum optoelectronic properties, low cost, materials abundance, and increasing power conversion efficiencies (PCEs) that quickly increased from 3.8% in 2009 to 25.5% in 2021. These advantageous characteristics encouraged an unprecedented number of researchers to work on developing PSCs. With the inherited knowledge and techniques from previously developed technologies, especially silicon and organic photovoltaics, notable progress has been made in the last ten years to overcome the hurdles that face industrialization and commercialization of PSCs. It is the first time an emerging technology has quickly overtaken older technologies like dye-sensitized solar cells (DSSC) and compete with other commercially available technologies such as crystalline silicon solar cells, cadmium telluride (CdTe), and copper indium gallium selenide (CIGS) in terms of power conversion efficiency (PCE).

However, long-term stability and lead toxicity still hinder PSCs from accessing the market, at least in the visual perspective. The toxicological nature of lead increases fears of environmental implications that could hinder PSCs' investments and market adoption. This perspective made the replacement or reduction of lead in PSCs a core activity of several research groups. Nevertheless, the current record efficiencies rely on lead as the metallic component inside the perovskite crystal.

According to the US Environmental Protection Agency (EPA), the maximum allowed lead concentrations are 0.15 µg m⁻³ and 0.15 µg L⁻¹ in air and water, respectively. The directives adopted by the European Union against the use of lead limit its concentration in electronic devices to less than 0.1% of the weight of each homogeneous material inside the device. However, current state-of-the-art lead-based perovskite materials exceed this threshold by at least ten folds taking into consideration the high water solubility of lead compounds used in PSCs. As a backup strategy, the photovoltaics community started looking for a lead-free perovskite technology in order to lower or even eliminate lead from PSCs completely.
Applying the perovskite dimensionality rules, we realize that very limited metal ions could form a high-performing and environmentally-friendly perovskite structure, such as Bi/Sb-based halides, a semi-perovskite structure, double perovskites, and Sn/Ge-based perovskites. Sn attracted the most attention among these candidates as it fulfills the charge balance, coordination, and ionic size prerequisites. Tin perovskites carry many environmental advantages over lead perovskites. Tin could be more toxic to living organisms than lead when leaked to the environment. However, it is less bioavailable due to the lower water solubility of oxygenated Sn compounds.

Tin perovskites show exciting electrical and optoelectronic properties enabling them to excel lead perovskites in terms of photovoltaic performance. The outer electronic configuration of tin is very similar to that of lead (ns² np⁴), and the atomic size of both elements is comparable (1.49 Å for Pb(II) and 1.35 Å for Sn (II)). However, the atomic number of lead is higher than tin, thanks to the relativistic effect. Compared to lead perovskites, tin perovskites show a very sharp absorption edge with a direct bandgap ranging from 1.35 to 1.4 eV, close to the Schockly-Quisser limit with an estimated theoretical efficiency of above 30% (e.g., 33.7 % at 1.34 eV). Tin perovskites also show higher charge mobilities, higher external photoluminescence quantum yield (PLQY). These properties would enable Sn-based perovskites to overcome their Pb analogs in terms of efficiency while already showing very promising applications for quantum dots, sensors, detectors, and transistors.

Currently, tin perovskites still lie in the back behind Pb-based counterparts in terms of efficiency due to several causes. First, Sn(II) oxidation to Sn(IV), which causes self-p-doping and devastates the performance of the devices. Second, fast crystallization dynamics, Sn-based perovskites crystallize very fast compared to Pb-based perovskites, which results in nonuniform crystallization, smaller perovskite domains, pinholes, and a considerable amount of defects. Third, energy band alignment, most of the charge transport layers are designed primarily for Pb-based perovskites, but when used blindly for Sn-based perovskites, we find energy bands mismatch, which is very harmful to the overall performance of Sn-perovskite devices.
**Chronological Overview:**

The first successful attempt to synthesize Sn-based perovskites dates back to 1974 by Scaife and co-workers, where they synthesized and characterized the all-inorganic CsSnX$_3$, where X$_3$ is Cl$_3$, BrCl$_2$, Br$_3$, Br$_2$I, BrI$_2$, and I$_3$. Five years later, Parry and co-workers prepared and studied the optoelectronic properties of the same all-inorganic Sn-based perovskite materials. However, hybrid Sn perovskites were never reported until 1988 when Yamada and co-workers prepared and investigated phase transition properties of MASnBr$_3$ (MA = CH$_3$NH$_3$)$^{30,31}$ From the mid-90s till 2001, Mitzi and co-workers studied the dimensionality and structure engineering of different structures of layered perovskites$^{35}$. In addition, they reported more detailed studies on the thermal, optical, magnetic, and electrical properties of layered Sn-based perovskites$^{31,36}$. It was also reported that the conductivity of such layered perovskites varies with the thickness or the number of perovskite layers; in other words, its electric behavior changes from semiconducting to metallic with increasing the number of perovskite layers$^{37,38}$. Furthermore, they exploited the optoelectronic properties, low cost, and low-temperature
processability of Sn-based perovskites by demonstrating them as a semiconducting channel in thin-film field-effect transistors; this was the first reported electronic application of a hybrid lead-free tin-based halide perovskite material.\(^{39,40}\)

Sn-based perovskite materials started to attract the interest of the photovoltaic community, especially after 2009 when Chung and co-workers reported the first solar cell based on MAPbI\(_3\) and MAPbBr\(_3\) perovskites photoactive materials.\(^1\) The first report about Sn perovskites was published in 2012 by Chung and co-workers, where they employed CsSnI\(_3\) doped with SnF\(_2\) as a hole transporting material (HTM) in a DSSC using dye N719 as the solar absorber, and they achieved a PCE of 10.2% (8.51% with a mask).\(^{41}\) Later on, in the same year, Shum and co-workers employed CsSnI\(_3\) with a bandgap of 1.3 eV as an independent light absorber in a Schottky solar cell and achieved a PCE of 0.9%.\(^{42}\) In 2013, the PV community started to reinvestigate and exploit the optoelectronic properties of Sn-based perovskites as a potential candidate for solar light harvesting.\(^{43,44,45,46}\) The first promising efficiencies were reported in 2014 when Snaith and co-workers reported a PCE of 6.4% based on MASnI\(_3\) as light absorber.\(^{17}\) Four days later, Hao and co-workers reported an efficiency of around 5.7% utilizing MASnI\(_3\) and MASnI\(_3\)·Br\(_3\) as photoactive absorber materials.\(^{18}\) These initial results gave the solar cells community a sense of trust in Sn-based materials as potential nontoxic contenders for the rocketing Pb-based perovskites.\(^{47,48,49}\)

In early 2016, Lee and co-workers reported FASnI\(_3\)-based PSC (FA = NH\(_2\)CH = NH\(_2\))^+ utilizing SnF\(_2\)-pyrazine complex to guarantee a uniform dispersion of SnF\(_2\) to avoid perovskite phase separation; an efficiency of 4.8% was achieved, and the encapsulated cells maintained 98% of its initial efficiency for 100 days.\(^{50}\) Later on, Liao and co-workers achieved a PCE of 6.22% based on inverted planar FASnI\(_3\) utilizing solvent engineering method.\(^{51}\) In 2017, the PSCs community witnessed remarkable achievements regarding both efficiency and stability of Sn-based PSCs, most of which were based on inspired techniques from Pb-based PSCs such as cation mixing, incorporating low dimensional perovskites, and utilizing hollow and mixed 2D-3D perovskites.\(^{54,55}\) Such practices led to a jump in the PCE from 6% in 2016 to around 9% and significantly enhanced stability.\(^{54}\) Zhao and co-workers adopted the cation mixing strategy to improve cell efficiency; by optimizing the ratio of FA\(^+\) and MA\(^+\) cations mixture, a PCE of 8.12% was obtained along with improved perovskite film morphology.\(^{52}\) Shao and co-workers mixed 92% of highly crystalline 3D FASnI\(_3\) with 8% of 2D Sn-based materials as potential nontoxic contenders.
perovskites in a p-i-n planar device; this increased the PCE to 9% with negligible hysteresis, low shunt losses, and very low trap-assisted recombination. In early 2018, Ran and co-workers reported a 2D-3D heterojunction Sn-based PSC using phenylethylammoniumiodide (PEAI) as a 2D and FASnI₃ as 3D perovskite materials; a PCE of 6.98% was obtained. At the same time, Liu and co-workers improved the morphology of perovskite layers by using hot antisolvent and annealing under a low partial pressure of DMSO. Both groups reported a PCE of around 7%. In 2019, PCEs of Sn-based PSCs continued to surge, approaching the 10% threshold through two different approaches. Jokar and co-workers reported the first approach by using bulk organic molecules such as ethylenediammonium diiodide (EDAI₂) and butylammonium iodide (BAI) to improve film morphology and improve crystallinity in addition to surface passivation, and they achieved a PCE of 8.9%. Later on, the same group used guanidinium cation GA⁺ as a nonpolar organic cation mixed with FA⁺ cation in a ratio of 20:80 respectively in addition to 1% ethylenediammonium diiodide (EDAI₂) as an additive to suppress Sn(II) oxidation to Sn(IV) and passivate surface defects; 9.6% was achieved after storage in glovebox environment for 2000 h; this gradual increase in efficiency was attributed to slow surface passivation and crystal relaxation. The second approach was reported by Wang and co-workers. They grew a parallel-orientated 2D PEA₂SnI₄ on the surface of 3D FASnI₃, using the pseudohalogen NH₄SCN as a structure regulator. This hierarchical 2D-quasi-2D-3D Sn-based perovskite structure delivered a PCE of 9.41% with improved air stability and high reproducibility. In 2020, Nishimura and co-workers achieved a PCE of 13.24% by partially substituting FA⁺ with ethylammonium (EA⁺), which enhanced film morphology and charge extraction. Recently, two high efficiencies were reported, 13.4% using phenylhydrazine with FA as mixed cations and a mixture of halogens Cl⁻ and Br⁻ as mixed anions by Wang and co-workers; while the record efficiency in tin perovskites is 14.63% using one-step synthesis of SnI₂-solvent adduct. In terms of stability, Liu and co-workers reported FASnI₃ layers prepared via templated crystal growth with a PCE of 11.22% and decent stability of over 1000 h of light soaking while retaining 95% of the initial efficiency. These improvements and efficiencies approaching 15% were possible through the big effort of the community. And, despite of all the strategies implemented, Sn-based PSCs must still face important challenges if they are to reach the expected performance. The photovoltaic parameters of the best performing tin-based perovskite devices in recent years is summarized in table 1.
In this review, we discuss the bottlenecks that hinder Sn-based PSCs from achieving efficiencies comparable to those of Pb-based PSCs.\(^6^6\) First, we discuss the effect of solvents and materials on the performance and stability of the devices and the recent efforts to find new solvent systems for FASnI\(_3\).

Second, we discuss the film formation and crystallization dynamics in Sn-based perovskites and talk about the most effective tries to make oriented and highly crystalline films. In particular, we discuss the use of 2D/3D mixed perovskites to make highly efficient Sn-based PSCs. After that, we discuss the oxidation of Sn(II) to Sn(IV) and the most successful attempts to quench it. Finally, we discuss energy band alignment and its effect on charge extraction and overall device efficiency.

### Table 1: Summary of the evolution of tin-based perovskite solar cells.

<table>
<thead>
<tr>
<th>Tin Perovskite</th>
<th>Year</th>
<th>Photovoltaic Parameters</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MASnI(_3)</td>
<td>2014</td>
<td>V(<em>\text{oc}) 0.88, J(</em>\text{sc}) 16.8, FF 42, PCE 6.4</td>
<td>[17]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2016</td>
<td>V(<em>\text{oc}) 0.46, J(</em>\text{sc}) 22, FF 61, PCE 6.2</td>
<td>[51]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2017</td>
<td>V(<em>\text{oc}) 0.53, J(</em>\text{sc}) 24.1, FF 71, PCE 9.0</td>
<td>[56]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2018</td>
<td>V(<em>\text{oc}) 0.58, J(</em>\text{sc}) 21.3, FF 72, PCE 8.9</td>
<td>[59]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2018</td>
<td>V(<em>\text{oc}) 0.61, J(</em>\text{sc}) 22, FF 70, PCE 9.4</td>
<td>[61]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2019</td>
<td>V(<em>\text{oc}) 0.62, J(</em>\text{sc}) 21.2, FF 73, PCE 9.6</td>
<td>[60]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2020</td>
<td>V(<em>\text{oc}) 0.84, J(</em>\text{sc}) 20.3, FF 78, PCE 13.2</td>
<td>[62]</td>
</tr>
<tr>
<td>FASnI(_3)(_2)Br</td>
<td>2020</td>
<td>V(<em>\text{oc}) 0.81, J(</em>\text{sc}) 23, FF 72, PCE 13.4</td>
<td>[63]</td>
</tr>
<tr>
<td>FASnI(_3)</td>
<td>2021</td>
<td>V(<em>\text{oc}) 0.91, J(</em>\text{sc}) 20.6, FF 77, PCE 14.6</td>
<td>[64]</td>
</tr>
</tbody>
</table>

#### 2. Precursors & Solvents:

To find the main reason behind the low efficiency in Sn-based halide perovskites\(^6^7\), we have to take a step backward and follow up the processing steps from the beginning. We should start with the materials we use to prepare the precursor solutions. For example, commercially available reagents may contain a small but effective amount of Sn(IV) (<0.1%), which is enough to convert ASnX\(_3\) film into a p-type material, with devastating effects on the photovoltaic performance of devices\(^6^8\).

Therefore, analyzing the purity of raw materials is necessary to guarantee that Sn(IV) is not present as an initial component, minimizing the incorporation of oxidised species and alleviating self-p-doping. Furthermore, it is also vital for perovskite film formation, as we will explain in a latter section\(^6^9\).
Several researchers placed great importance on materials purification, and different approaches were reported. Ozaki and co-workers followed a chemical purification strategy in which they formed a tin halide-solvent complex \([\text{SnX}_2(S)_n]\) where S is a solvent (S = DMF and DMSO)\(^{71,70}\). In the beginning, they characterized SnI\(_2\) using \(^{119}\text{Sn}\) magic-angle spinning (MAS) NMR spectroscopy, thermogravimetric analysis (TGA), and Karl Fischer titration. They found that SnI\(_2\) contains around 10% of SnI\(_4\) and about 10 000 ppm of water, although the bottle was labeled 99.99% purity. \(^{119}\text{Sn}\)-NMR spectra in figure 2a show a peak at -1742 ppm, which is attributed to the SnI\(_4\). TGA confirmed the same results as 10.1% weight loss was observed at ~ 150 °C, which corresponds to the sublimation of SnI\(_4\) (figure 2b), while SnI\(_2\) sublimes at 330 °C. Next, Ozaki and co-workers utilized the difference...
in sublimation temperature between SnI₂ and SnI₄ to purify SnI₂ using the vacuum sublimation technique where SnI₄ sublimes then condensate as an orange powder at ~ 150 °C\(^7\). \(^{119}\)Sn-NMR and TGA analysis of the purified SnI₂ using the vacuum sublimation method are shown in figure 2c, d. They recrystallized SnI₂ in DMF and DMSO to remove any SnO₂ residuals from the vacuum sublimation step for further purity. SnI₂ from the first step was dissolved in DMF and DMSO, then toluene or dichloromethane was poured gently into the solution, which converted into needle crystals of \([\text{SnI}_2(\text{DMSO})]\), \([\text{SnI}_2(\text{DMSO})_2]\) and \([\text{SnI}_2(\text{DMF})]\) as determined by single-crystal XRD (figure 2e, f). The purity of these crystals was confirmed using elemental analysis and \(^{119}\)Sn MAS NMR spectroscopy and found to be stable under an inert atmosphere and could be used conveniently as a pure starting reagent for tin perovskites. The authors merged these purifying techniques with other film formation methods and additives to achieve a PCE of ~12% for FASnI₃.

Figure 3: Oxidative effect of DMSO, (a) FASnI₃ solutions in DMSO and DMF before and after ageing for 5 h at 120 °C\(^7\). Reproduced with permission Copyright 2020, American Chemical Society. (b) Mechanism of Sn(II) oxidation by DMSO. (c) \(^{13}\)C-NMR spectra of FASnI₃ heated at 100
°C for 30 min. the green arrow indicates the DMS-related peak\textsuperscript{73}. Reproduced with permission.

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Solvents have a very strong influence on the perovskite film crystallization and, hence, on the device performance\textsuperscript{74,75}. Nevertheless, in Sn-based PSCs, solvents have a much more profound influence due to the sensitivity of Sn(II) towards oxidation\textsuperscript{76}. In parallel, Sargent group and our group independently found that DMSO was undergoing a redox reaction with Sn(II), oxidizing it to Sn(IV)\textsuperscript{72,73}. Solid-state \textsuperscript{119}Sn-NMR analysis of the received SnI\textsubscript{2} did not show any Sn(IV) peaks, implying no content of it or a concentration lower than the measurement detection limit of 1.5 wt%. By exposing the same sample to air, the Sn(IV) signal appeared and increased with exposure to air. After that, fresh precursor solutions of FASnI\textsubscript{3} were prepared and characterized for the presence of Sn(IV). Fortunately, there was no Sn(IV) at room temp, but after heating the solutions at 100 °C for 30 minutes to simulate the conditions of the film formation, the color of the DMSO-based FASnI\textsubscript{3} changed to dark red, and Sn(IV) peaks were detected in the \textsuperscript{119}Sn-NMR spectrum\textsuperscript{73}. To further understand the oxidation mechanism of Sn(II) to Sn(IV), \textsuperscript{13}C-NMR and \textsuperscript{1}H-NMR analyses were performed for the organic species in the precursor solution (DMSO, FAI, and MAI). \textsuperscript{1}H-NMR showed a peak at ~ 1.9 ppm for both MA\textsuperscript{+} and FA\textsuperscript{+} containing solutions, this peak matches with the expected peak of dimethylsulphide (DMS) which confirms the same finding reported earlier by Saidaminov and co-workers. The same peak was found in the \textsuperscript{13}C-NMR spectrum, which confirms the formation of DMS as a product of the Sn(II) oxidation reaction (Figure 3b). Previous results confirms the occurrence of a redox reaction between DMSO and Sn(II) which is promoted in the presence of the acidic environment\textsuperscript{77,78} (Figure 3c).
Figure 4: (a) 16 nonsulfoxide solvents that formed stable perovskite solution divided into groups according to the functional group. (b) SEM images of DEF:DMPU film. (c) J-V curves of FASnI$_3$ without any additives in DEF:DMPU against DMSO$^{79}$. Reproduced with permission Copyright 2021, American Chemical Society.

Considering the negative impact of DMSO, so far the universal solvent for tin perovskites, on material stability, our group decided to replace it by new solvent combinations.$^{79}$ We targeted solvents with the ability to form a perovskite solution with a concentration over 1 M and stable after thermal soaking for at least 12 hours at 100 °C. For this, we screened most of the possible functional groups with particular attention to the dipolar aprotic solvents which could dissolve ionic molecules such as FAI and SnI$_2$ using their strong dipoles. Some solvents were excluded, such as strong acids, solvents with big aromatic structures commonly used as antisolvents, solvents with too low boiling point such as methylamine, and solvents with a high melting point. Out of 2000 suggested molecules, we tested 76
solvents for their solubility, stability, and ability to form a perovskite solution. Experimentally, we identified 12 solvents that could form a stable perovskite solution with six different functional groups with the amide group the mostly presented (Figure 4a). To ensure that these new precursors could form perovskite material, the easiest way was to drop-cast the precursor on a glass substrate, then anneal at 150 °C for 20 minutes with a thermal ramp of 12 °C/min. It was impressive that 15 out of 17 solvents (including DMSO and DMF) formed a black phase. XRD characterizations were done for the drop-casted films of the new solvents, and the resulted peak positions are in agreement with the standard positions of crystalline FASnI₃ films. However, some samples have low crystallinity, and some other samples have different phases; such optimizations can be dealt with in the film formation stage.

The ability of the new solvents to form a working perovskite device was also tested. A mixture of two solvents, namely N,N-Diethylformamide (DEF) and N,N’-Dimethylpropyleneurea (DMPU) in a 6:1 ratio achieved a PCE of 6.2% for FASnI₃ without the use of any additives. Meanwhile, additive-free DMSO samples achieved a PCE of only 3.84% (figure 4b, c). These results prove that finding a new stable solvent for processing Sn-based perovskites could be an entrance towards achieving highly efficient and durable tin-based PSC.

3. **Film Formation**:

The formation of high-quality perovskite films is a vital prerequisite to push the performance of PSCs forward. The perovskite film crystalline quality and morphology relate directly to the overall performance of the device. To make high-quality perovskite films, we have to understand and manipulate the mechanism of crystal formation that starts in the precursor solution and ends by the end of the annealing step. The perovskite crystallization process depends on several factors such as substrate nature, temperature, spin coating parameters, solvent, and antisolvent interaction. Film formation dynamics and crystallization kinetics in Sn-based perovskites are different from those of lead-based perovskites.

Although many reports focused on studying the crystallization dynamics and kinetics of Pb-based perovskites through in situ techniques, very few reports deal with the same point in Sn-based perovskites. Dong and co-workers studied the crystallization mechanism of tin perovskites using...
several techniques, offering essential insights that revealed the mechanism of structural revolution, material transformation, and crystallization dynamics in mixed 2D/3D Sn-based perovskites.\textsuperscript{85} They found that crystallization tends to start at the precursor/air interface, but in 3D Sn-based perovskites, the crystallization rate is comparable in bulk and at the precursor/air interface. Moreover, the addition of 2D molecules hinders the crystallization process in bulk, which allows uniform and highly oriented crystals with a similar structure to the 3D perovskites. The crystallization dynamics, in general, were found to be very fast compared to the lead-based counterpart.

The attempts to optimize the quality of Sn-based perovskites films are numerous. Most of them rely on chemical additives that could form 2D perovskites on top of the regular 3D perovskite layer, usually known as Ruddlesden–Popper perovskites.\textsuperscript{86,61,87}

Figure 5: (a) proposed mechanism of action of TG-FASnI\textsubscript{3}. (b) SEM images of FASnI\textsubscript{3} (1) before and (2) after annealing; TG-FASnI\textsubscript{3} (3) before and (4) after annealing. (c) XRD patterns of FASnI\textsubscript{3} and TG-FASnI\textsubscript{3}. (d) PL spectra of FASnI\textsubscript{3} and TG-FASnI\textsubscript{3}. (e) TRPL of FASnI\textsubscript{3} and TG-FASnI\textsubscript{3}. (f)
J-V curves of FASnI3 and TG-FASnI3 in forward and reverse scanning. (g) Stability test of FASnI3 and TG-FASnI3 under simulated AM 1.5 G (100 mW cm\(^{-2}\)) operating at MPPT\(^{55}\). Reproduced with permission, Copyright 2020, The Royal Society of Chemistry.

Liu and co-workers reported a PCE of 11.22\% based on highly crystalline FASnI3 film with preferential orientation along the (001) plane\(^{65}\). They reported a solvent pretreatment method using a mixture of \(n\)-propylammoniumiodide (PAI) and DMSO (1:100 v/v). DMSO acts as a solvent to provide the liquid interface for nucleation. At the same time, PAI aggregates around the newborn nuclei of FASnI3 and forms a template that regulates the crystal growth and orients it along the (100) plane. PAI was used in a minimal amount compared to DMSO (1:100 v/v) as it is not considered as an additive to the precursor solution or co-solvent because it is not forming 2D perovskite that covers the surface of 3D perovskites. The mechanism of action of PAI is shown in figure 5a. SEM images in figure 5b indicate a big difference in the grain sizes between FASnI3 with and without PAI. The bigger the grain and the domains, the less the grain boundaries and the less the defects. In templated growth FASnI3 (TG-FASnI3), the defect density was lowered from 2.89\times10^{16} \text{cm}^{-3} to 5.41\times10^{15} \text{cm}^{-3}. XRD patterns in figure 5c show an increasing intensity of the 100 plane peak with increasing the concentration of PAI from 1 to 2 mg mL\(^{-1}\), while it decreases again after increasing the concentration to 5 mg mL\(^{-1}\), which indicates that the optimum concentration of PAI is around 2 mg mL\(^{-1}\). The effect of such a small quantity of PAI on the crystallization and the photovoltaic performance of FASnI3 was tremendous as shown in figure 5d-g. TG-FASnI3 shows an increase in PL intensity which confirms the low defect density and the longer carrier diffusion length than regular control FASnI3. The prepared devices based on TG-FASnI3 showed much better operational stability compared the to control devices. Figure 5g shows the results of maximum power point tracking (MPPT) of both devices encapsulated and stored in an N\(_2\) filled glove box. 95\% of the initial efficiency was maintained after 1000 h of operation, while the control devices lost around 60\% of their initial efficiency after 500 h.

Finally, one of the bottlenecks that face tin-based perovskites is the fast crystallization and low film quality compared to lead-based perovskites, which leads to a high defect density in the range of 10^{15}-10^{16}; while in lead-based perovskites 10^{13}-10^{14} \text{cm}^{-3}. This high defect density is one of the main reasons behind the low efficiency of tin-based perovskites\(^{88}\).
4. **Sn (II) Oxidation:**

Oxidation of Sn(II) is one of the bottlenecks to achieve good efficiency in Sn-based perovskites solar cells. Sn(II) is more vulnerable to oxidation which is electronically and chemically favorable. It has been revealed through theoretical calculations that tin oxidation is favorable at pristine surface and unfavorable in the bulk. Resultantly, bulk Sn(IV) changes into Sn(II), which releases two holes to the valence band and by p-doping the perovskite, this has been experimentally proved that tin vacancies lead to p-doping which limits the diffusion length.

Although Sn and Pb are present in the same group of the periodic table but it has been found that Sn 5s\(^2\) orbital has higher energy as compared to 6s\(^2\) of Pb which increase its contribution to the valence band edge. The electrons of 6s\(^2\) in Pb show inert pair effect due to lanthanide contraction but 5s\(^2\) lacks this phenomenon which ultimately makes Sn electrons loosely bound and easy to lose.

To stop the tin oxidation and to improve the stability of the perovskite films and devices, different \(\text{SnX}_2\) species have been employed in excess to stop p-doping. For the first time, Kumar and co-workers showed that the introduction of SnF\(_2\) in inorganic tin halide CsSnI\(_3\) reduces the Sn vacancies. Later on, they have also reported that by the introduction of SnF\(_2\) in FASnI\(_3\) film, the oxidation of Sn(II) has been effectively reduced, and there is an increase in the \(J_\infty\) values of the device. SnF\(_2\) has also been introduced in CsSnBr\(_3\) film, and it has been found that it suppresses the oxidation of Sn(II). In the most recent work on Sn halide perovskite-based devices, SnF\(_2\) has been used as an important dopant as it suppresses the oxidation of Sn(II), improves film morphology, and also improves \(J_\infty\). Other \(\text{SnX}_2\) species like SnCl\(_2\), SnBr\(_2\) and SnI\(_2\) improve film quality, device performances the energy alignments and also as surface passivation.

Hydrazine and its derivatives were used by many researchers as a reducing material in Sn-based perovskites. Hydrazine in the vapor phase has been used in MASnI\(_3\) and CsSnI\(_3\) film formation and for device fabrication. The ratio of Sn(IV) to Sn(II) has been reduced by using hydrazine vapors. It has been found that hydrazine molecules release electrons which suppress the oxidation of Sn(II). By introducing, phenyl hydrazine hydrochloride salt (PHCl) in the FASnI\(_3\) film, Wang and co-workers reported 11.4% efficiency. It has been noticed that the molecule incorporates in the crystal lattice and improves the device performance. Similarly, by using 8 mol% trihydrazine dihydriodide (THDH)
into FASnI\textsubscript{3} solution, the oxidation of Sn(II) was suppressed, and the champion device efficiency was reported to be 8.50%. Another derivative of hydrazine 4-fluorobenzohydrazide (FBH) was introduced in FASnI\textsubscript{3}, and it significantly enhanced the efficiency as compared to the control device. The champion device efficiency was reported 9.03% by using FBH molecules\textsuperscript{101}. Lately, Wang and co-workers achieved a record efficiency of 13.4% (12.4% certified) through the introduction of synergistic effect between PH cation and halide anions\textsuperscript{63}.

T.Wang and co-workers introduced gallic acid (GA) as an antioxidant along with SnCl\textsubscript{2} for FASnI\textsubscript{3} films. By exploring the underlying chemistry of GA and tin precursor, they reported 9.03% efficiency\textsuperscript{102}. Kayesh and co-workers used 5-ammonium valeric acid (5-AVAI) to enhance the oxidation stability of FASnI\textsubscript{3} perovskite films. 5-AVAI not only suppresses the Sn(II) oxidation but also enhances the crystallinity by making a hydrogen bond with SnI\textsubscript{6}. The devices show improved stability with 7% efficiency\textsuperscript{103}.

The primary precursor used for tin halide perovskites is SnI\textsubscript{2}. It is oxidized by air. To make it more pure Sn metal power is used. Low purity has a high level of doping which ultimately decreases the efficiency. Huang and co-workers used tin powder to purify tin sources from Sn(IV) moieties, which has increased the device performance parameters\textsuperscript{104}. Recently, Nakamura and co-workers has reported a different technique to make Sn(IV) free device. They have produced Sn metal nanoparticles from SnF\textsubscript{2} over SnBr\textsubscript{2} and SnCl\textsubscript{2} by using 1,4-bis(trimethylsilyl)-2,3,5,6- tetramethyl-1,4-dihydropyrazine (TM-DHP) molecule. These Sn metal nanoparticles can reduce SnI\textsubscript{4} to SnI\textsubscript{2} to make it Sn (IV) free system. By using this technique, they have reported more than 11.2% certified efficiency\textsuperscript{105}.

5. **Device structure and energy alignment**:

In device operation, when light is shone on the device. Due to the low bandgap, the electrons from the valance band of the perovskite halide materials shifts to the conduction band and leave the hole vacancies in the valence band. These generated electrons and holes diffuse in the ETM and HTM and are finally collected at cathode and anode. These ETM and HTM materials should be efficient enough to transport the electrons and holes across the boundary. This phenomenon is only possible when the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the hole transport material and electron transport layer are well aligned with the conduction and the
valence band of the perovskite material. For better performance and stability of the devices, hole transport materials and electrons transport layers are chosen accordingly\textsuperscript{106}. Convensional HTMs in Sn-based perovskites were designed originally for Pb-based perovskites then tried for Sn-based devices after showing a good performance. However, the positions of energy bands in Sn-based perovskites are slightly different from those of Pb-based perovskites. This leads to mismatching in the alignment of the energy bands of the absorber material with charge transfer layers on both sides of the Sn-based absorber film\textsuperscript{107}. For instance, the conventional HTM used in inverted devices poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) has a work function of about -5.0 eV (higher than FASnI\textsubscript{3}) and 2,2′,7,7′-tetrakis[N,N-di(p-methoxyphenylamine)]-9,9-spirobifluorene (spiro-OMeTAD) has even more higher HOMO level that is -5.22 eV. Due to these poor energy alignments, Sn-based PSCs are unable to achieve their theoretical predicted efficiency. Initially, Noel and co-workers have reported Sn-based perovskite halide-based regular devices with efficiencies of greater than 6% under simulated full sunlight using MASnI\textsubscript{3} as a perovskite material. Later on, it was found that spiro-OMeTAD, which is used as hole transport material in regular structure devices, needs a dopant like lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI) and 4-tert-butylpyridine (tBP), which enhance its hole mobility. These dopants have a harmful effect on the perovskite layer\textsuperscript{108} in addition to that, it increases the rate of charge recombination by forming a bond between TiO\textsubscript{2} and Sn\textsuperscript{109}.

Figure 6: (a) Band profiles for each ETL material and perovskite material obtained experimentally from the ionization potential, the electron affinity, and the work function. The dotted lines indicate the Fermi energy, and the vacuum level (EVAC) is plotted as zero. (b) Conduction band offset (CBO) at the ETL/perovskite layer interface when using each of the oxides. The CBO (ΔECBO) is defined as
the energy difference between the electron affinity of the ETL material and that of the perovskite material based on the perovskite material\textsuperscript{110}. Reproduced with permission Copyright 2020, American Chemical Society

After these experiences, the first inverted device reports with 3.30\% efficiency, which was a fabrication by using CsSnI\(_3\) as perovskite material, NiO\(_x\) as the hole transport layer, while PCBM and Al were used as ETL. By using PEDOT:PSS as HTL, Liao and co-workers reported 6.22\% efficiency\textsuperscript{51}. Later on, Liu and co-workers tuned the energy levels of PEDOT:PSS by using polyethylene glycol (PEG). Fullerene molecules are used as ETM in inverted devices. To know which derivative has the best energy alignment with Sn perovskites, C\(_60\), PCBM, and ICBA were used as ETL for FA\(_{0.9}\)PEA\(_{0.1}\)SnI\(_3\). Among all, ICBA with work function -3.73 and -5.73 has perfect energy alignment with perovskite and has a higher \(V_{oc}\) value as compared to others. Due to the dopant issues in spiro-OMETAD, Ke and co-workers reported dopant-free organic molecules tetrakis-triphenylamine (TPE) as HTM for Sn-based PSCs, and they reported 7.23\% champion device efficiency\textsuperscript{111}. Similarly, due to shortcomings of PEDOT:PSS, Cao and co-workers introduced copper thiocyanate (CuSCN) as HTM with FASnI\(_3\) based device and acquired 7.34\% efficiency\textsuperscript{112}. The conventional electron transport layer in Pb passed perovskites solar cell, have an energy mismatch with Sn halide-based perovskites solar cell. Yokoyama and co-workers used Nb\(_2\)O\(_5\) as electron transport material in place of TiO\(_2\) in a regular inverted device. It has been found that it decreased the conduction offset and interfacial charge recombinations\textsuperscript{110}.

This study reveals that the conduction band of Nb\(_2\)O\(_5\) is closest to zero for FASnI\(_3\) perovskite materials; this increases \(V_{oc}\) of Sn PSCs as compared to TiO\(_2\) and SnO\(_2\). To gain a good energy alignment, Cong and co-workers introduced an organic molecule poly[tetraphenylethene\(_3,3′-(((2,2\text{-diphenylethene}-1,1\text{-diyl})\text{bis}(4,1\text{-phenylene})\text{bis(oxy)})\text{bis}\left(N,N\text{-dimethylpropan-1-amine}\right)\text{tetraphenylethene}\) (PTN-Br) in FASnI\(_3\) to modify grain boundaries. It has the highest occupied molecular orbital (HOMO) energy level of \(-5.41\) eV, due to which it forms an energy alignment with Sn halide perovskites solar cell\textsuperscript{113}. Shuxia and co-workers reported an important work for tin and lead perovskites energy levels\textsuperscript{107}. These values are beneficial for making a new cascade route for electrons and holes.
6. Conclusion and outlook:

Sn-based PSCs carry enough optoelectronic properties to achieve the maximum theoretical efficiency of a single junction solar cell according to QS limit. We believe that it will also be a key component in the multi-junction solar cells industry. So far, an efficiency of 14.6% was achieved, which is 10% less than where it should be compared to Pb-based PSCs. However, to achieve such ambitious goals, Sn-based PSCs must come out of four bottlenecks, namely: (1) Pure starting chemicals and non-oxidising solvents, (2) better film formation dynamics, (3) Sn(II) oxidation suppression and (4) better energy bands alignment. To overcome these limitations, we need to focus on finding new, stable, and effective solvents for Sn-based PSCs. We also need to understand the Sn chemistry inside the precursor, and through film formation steps, customize new contact layers that have better matching with the energy bands of Sn-based compositions, and stabilizing Sn(II) through all the device making steps\textsuperscript{114}. Then we could provide a high protection and isolation level to devices under operation using modern encapsulation techniques\textsuperscript{115,116}.

Conflicts of Interest

There are no conflicts of interest to declare

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