Recent Advances in Tin-based Hybrid Organic-Inorganic PSCs: Additives for Improved Stability and Performance

K Monga, R Rani, S Chaudhary*
Department of Applied Sciences, Punjab Engineering College (Deemed to be University) Chandigarh-160012, India

Kamilmonga.phdappsc20@pec.edu.in, shilpichaudhary@pec.edu.in

Abstract. Perovskite solar cells (PSCs) materials are progressing as potential candidates for the future generation of photovoltaics. Despite the most efficient photovoltaic performance, lead-based perovskite materials are not considered for commercialization due to the high toxicity of lead. One of the promising alternatives is tin (Sn)-based perovskites, which exhibits equivalent ionic size as lead and outstanding absorption properties. However, Sn-based perovskite materials have stability and low-performance issues because of the easy oxidation of Sn$^{2+}$ to Sn$^{4+}$ and fast crystallization. This paper gives a focused overview of the notable recent studies to address the stability and low-performance challenges of Sn-based hybrid organic-inorganic perovskite (Sn-HOIP) materials for solar cells by using functional additives. To date, the addition of SnF$_2$ additive in the methylammonium tin iodide-based PSCs has shown the highest efficiency of 7.78% and maintains 70% of original efficiency over 200-hours. In the case of formamidinium tin iodide-based PSCs, the addition of phenylhydrazine hydrochloride significantly increases the power conversion efficiency to 11.40% from 5.60% for a pristine device. However, further improvement in the stability and efficiency of Sn-based PSCs requires a molecular-level understanding of the role of existing and new candidates of additives tailored for evolving Sn-HOIP materials.

1. Introduction
The world energy consumption per capita and ever-increasing environmental deterioration demand for renewable energy sources. The deployment of solar cells is one of the promising technologies amid different renewable energy sources. It has been estimated that the one hour of continuous illumination of solar energy can fulfill the world’s annual energy requirements [1]. In 1839, the photovoltaic (PV) effect was discovered by Alexandre-Edmond Becqurel. In 1883, Charles Fritts creates the first working photovoltaic cell by sandwiched selenium between iron plates and gold layers but the efficiency was less than 1% [2]. In 1954, Chaplin et al., from Bell laboratories developed the first silicon cell with an efficiency of 6% which increase to 10% in a short period [3]. Presently employed monocrystalline silicon/polycrystalline silicon solar cells of efficiency $>$22% have a high cost, difficult preparation conditions, and harmful environmental pollution [4]. Thus, there is a demand to engineer high-efficiency, low price, and large-scale fabrication solar cells which are yet to be achieved. Currently, perovskite materials are picking up enormous interest among researchers because of their excellent performance and low raw cost [5]. The photovoltaics of lead (Pb) halide hybrid organic-inorganic perovskites (HOIP) materials have shown significant enhancement in the performance of...
solar cells as compared to semiconductor compounds due to their high absorption coefficient, low-temperature processing, tunable bandgap [1]. HOIPs normally have a general chemical formula, ABX₃; A = cation, B = divalent metallic cation, X = halogen anion. The A cation can be an organic ammonium group (CH₃NH₃⁺, CH(NH₂)₂⁺, etc.), and a divalent metal cation B can be replaced with Sn²⁺, Pb²⁺, Cu²⁺, etc., as shown in figure 1 [6].

Figure 1. Ideal perovskite structure (ABX₃)

So far, power conversion efficiency beyond 25% has been reported for Pb-based PSCs [7,8,9]. The commercialization of Pb-based PSCs and the issues related to toxicity and long-term stability has to be addressed [10]. In recent reports, Sn has been explored as a competent replacement of Pb because of the equivalent valency and comparable ionic radius as that of Pb and excellent optoelectronic properties. Thus, Sn can be used in place of Pb with insignificant perturbation in perovskite lattice. It may be pointed out that the Sn-based PSCs could not compete with Pb-based PSCs analogs because of the poor performance mainly related to the instability of the Sn²⁺ state, high crystallization rate, and defective thin film quality. The oxidized Sn²⁺ behaves as a p-type dopant, with a concentration of even less than 0.1% can have a significant effect on device performance [11]. All these issues hinder attaining the high value of open-circuit voltage (Vₖₒ) and fill factor (FF). To address these issues, researchers have investigated the use of different types of additives, which resulted in the change of crystallization rate, improved film quality, and stability of Sn-based PSCs. Recently, it has been demonstrated in various reports that the use of additives in Sn-based perovskites results in the enhanced photoelectrical performance, thus leading to increased values of Vₖₒ and FF [12, 22-38].

PSCs commonly consist of a transparent electrode (fluorine-doped tin oxide (FTO) and indium–tin oxide (ITO)), electron transport layer (ETL, e.g., Phenyl-C₆₁-butyric acid methyl ester (PCBM)), hole transport layer (HTL, e.g.poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS)), active perovskite film, and metallic electrodes (Ag and Au) [13]. In general, the active layer materials used in Sn-HOIP devices are methylammonium tin iodide (MASnI₃) and formamidinium tin iodide (FASnI₃). Although the ionic size of methylammonium (MA) is smaller than formamidinium (FA), which causes easy migration of MA ions results in very high hole density [14]. MA-based PSCs undergoes an early phase transition at 56 °C as compared to FA-based device, which does not show any phase transition until 150 °C [15, 16]. Also due to the larger size of FA, FA-based devices have a larger bandgap of 1.41 eV as compared to MA-based devices of bandgap 1.23 eV, so power conversion efficiency (PCE) of FA-based PSC is more as compared to MA-based PSCs [17,18]. Figure 2 shows the energy level band diagram of MASnI₃ and FASnI₃, Sn-HOIP respectively.
In this review, different functional additives resulting in the improved performance and stability of Sn including Sn-halides and their co-working, Lewis base, thiocyanates, hydrazine, and some other notable additive materials have been discussed, as categorized in figure 3. Further, a summary is given for the effect of additives on the stability, $V_{oc}$, $J_{sc}$, FF, and PCE of Sn-based PSCs. It can be concluded from the recent studies that the additives are promising candidates to enhance the overall performance of the Sn-based PSCs. Moreover, there is plenty of room for the development of suitable functional additives by exploring the underlying mechanism of reported additives to further enhance the stability and the PCE of Sn-based PSCs.

![Figure 2. Band energy diagram of (a) MASnI$_3$ and (b) FASnI$_3$Sn-HOIP [19, 20]](image)

In this review, different functional additives resulting in the improved performance and stability of Sn including Sn-halides and their co-working, Lewis base, thiocyanates, hydrazine, and some other notable additive materials have been discussed, as categorized in figure 3. Further, a summary is given for the effect of additives on the stability, $V_{oc}$, $J_{sc}$, FF, and PCE of Sn-based PSCs. It can be concluded from the recent studies that the additives are promising candidates to enhance the overall performance of the Sn-based PSCs. Moreover, there is plenty of room for the development of suitable functional additives by exploring the underlying mechanism of reported additives to further enhance the stability and the PCE of Sn-based PSCs.

![Figure 3. Types of additives used in Sn-based hybrid organic-inorganic perovskite (Sn-HOIP)](image)

2. Roles of additives in Sn-based PSCs devices

The low stability and PCE of Sn-HOIP are mainly related to the oxidation of Sn$^{2+}$ and fast crystallization rate along with poor coverage and morphology of Sn-based perovskite materials. Sn$^{2+}$ can be easily oxidized to Sn$^{4+}$ to form SnO$_2$ when exposed to air which is considered as one of the main disadvantages of this type of perovskite material. Also, the hole concentration of Sn-based perovskites is too high approximately $10^{16}$ - $10^{18}$ cm$^3$ which means more Sn$^{4+}$ content [21]. Numerous studies have reported that both these issues of low PCE and oxidation of Sn$^{2+}$ can be resolved by the addition of additives in Sn-based perovskites [22-25, 27-38]. In the following section, we are going to...
discuss the functional additives, which are proven to increase the stability and other device parameters of Sn-HOIP.

2.1. Tin fluoride (SnF₂)
SnF₂ is the most effective and generally used additive material, among all the additives for the Sn-HOIP solar cells. The addition of SnF₂ additives can suppress the oxidation of Sn²⁺ into Sn⁴⁺ and also improves film quality. Overall, the use of SnF₂ as an additive in Sn-HOIP solar cells has displayed an increase in the V<sub>oc</sub>, FF, efficiency, and device stability [22-24]. In a study by Xiao et al. (2017), SnF₂ has been used as an additive into MASnIBr₂-based PSCs, where SnF₂ can act as heterogeneous nucleation sites resulting in the improvement of perovskite film morphology and device performance (V<sub>oc</sub> and FF) [22]. They explored the role of different concentrations of SnF₂ additive for the fabrication of uniform MASnIBr₂ thin films. Figure 4 shows the SEM image of the MASnIBr₂ thin film with the addition of different concentrations of SnF₂ additive. It can be observed from figure 4 (a, e) that the pristine MASnIBr₂ film had poor coverage with significant features from mesoporous TiO₂ layers below clearly revealed. With the addition of 20 mol% SnF₂, the MASnIBr₂ film displays relatively more coverage and better uniformity than the pristine film, figure 4 (b). On increasing the concentration of SnF₂ to 30 mol%, the MASnIBr₂ film resulted in uniform morphology with the increase in grain size as shown in figure 4 (c, f). However, further increase of SnF₂ concentration to 40 mol%, the MASnIBr₂ film exhibits poor morphology (needle-like structures) with the non-uniform covering of the film as shown in figure 4 (d). It has been concluded that the optimum addition (30 mol%) of SnF₂ into the MASnIBr₂ film leads to the uniform morphology with the increase in grain size, thus a decrease in carrier recombination. Finally, a stable PCE of 3.70 % was achieved along with V<sub>oc</sub> = 0.45 V, J<sub>sc</sub> = 13.77 mA/cm<sup>2</sup>, FF = 59.58 % with addition of 30 mol % of SnF₂ as compared to pristine device of PCE = 0.08%, V<sub>oc</sub> = 0.19 V, J<sub>sc</sub> =1.37 mA/cm<sup>2</sup> and FF = 40.27% [22].

![Figure 4. (a–d) SEM images of active film with different concentrations of SnF₂ additive: a) 0, b) 20, c) 30, and d) 40 mol%. 4 (e, f) Cross-section SEM images of active film with concentration of 0 and 30 mol% SnF₂ [22]. Copyright, Advanced Optical Materials](image-url)

To address the poor quality of perovskite films, Wang et al. (2020) used SnF₂ as an additive during the fabrication of MASnI₃ film using an ion-exchange/insertion approach [23]. They found that the addition of solid-state SnF₂ (10 mol%) and gaseous methylammonium iodide during the fabrication of
MASnI$_3$ film through ion exchange/insertion approach, not only resulted in pinhole-free perovskite film of MASnI$_3$ but also suppresses oxidation of Sn$^{2+}$ into Sn$^{4+}$. The suppression of oxidation of Sn$^{2+}$ was observed from XPS results, Figure 5. It is clear from XPS results that ion-exchange/insertion approach based MASnI$_3$ film has less content of Sn$^{4+}$ (Figure 5 (a)) in comparison to the controlled one-step solution approach based MASnI$_3$ film, Figure 5 (b). Furthermore, they reported that the reaction time of the ion-exchange/insertion approach also influences device parameters. For optimum reaction time of 60 min, highest PCE of 7.78% along with $V_{oc} = 0.57$ V, $J_{sc} = 20.68$ mA/cm$^2$, FF = 66% was achieved as compared to pristine device (without addition of SnF$_2$) of PCE = 1.62%, $V_{oc} = 0.32$ V, $J_{sc} = 12.36$ mA/cm$^2$ and FF = 41% [23].

Figure 5. (a) XPS image of MASnI$_3$ perovskite film fabricated via (a) ion exchange/insertion approach, and (b) controlled one-step solution approach with addition of 10 mol% of SnF$_2$ additive [23]. Copyright, Advanced Sciences

2.2. Tin halide Co-working additives

The use of Sn halide as an additive in Sn-HOIP solar cells has displayed excellent improvement in the performance of PSCs. However, excessive use of Sn-halide as an additive leads to phase separation effect thus, the inferior performance of Sn-HOIP. So, studies have demonstrated that a second additive along with Sn-halide can suppress phase separation caused by Sn halides and synchronously result in better $V_{oc}$ and FF compare to Sn halide as additive [24,25,26]. Obila et al. (2021) used anilinium hypophosphite (AHP) as an additive along with SnF$_2$ in Sn-based PSCs [24]. The addition of AHP passivates the defects and suppresses phase degradation caused by the addition of SnF$_2$ by making complex between AHP and SnF$_2$ as confirmed by XRD spectra in figure 6 as the film is more stable with high peak intensity at different intervals of time. Perovskite device show champion efficiency of 6.87% along with $V_{oc} = 0.48$V, $J_{sc} = 25.21$ mA/cm$^2$ and FF = 57.16% as compared to pristine device of PCE = 4.74%, $V_{oc} = 0.44$ V, $J_{sc} = 25.38$ mA/cm$^2$ and FF = 43.08%. AHP additive device shows 97% of its original PCE after 720 hours when kept in the glove box [24].

Figure 6. XRD patterns of FA$_{0.5}$MA$_{0.45}$PEA$_{0.05}$SnI$_3$ films at different intervals of time (with and without the addition of AHP additive) [24]. Copyright, Royal Society of Chemistry
Even though the addition of Sn-halide is one of the crucial approaches to suppress the oxidation of Sn\(^{2+}\), it hinders the charge movement across active (perovskite) layers [25]. Thus, to address the stability of tin halide PSCs, Wang et al. (2020) used gallic acid (GA) along with SnCl\(_2\) as an additive into the perovskite film of FASnI\(_3\) to enhance the morphology and device parameters of PSCs [25]. They found that the addition of SnCl\(_2\) suppresses the oxidation of Sn\(^{2+}\) into Sn\(^{4+}\), but excess of SnCl\(_2\) degrades film morphology and reduces device parameters. By the addition of a second additive GA, film morphology is improved by the formation of the SnCl\(_2\)-GA complex on perovskite grains. This complex suppresses the oxidation of Sn\(^{2+}\) and very few defects were generated in the perovskite film of FASnI\(_3\). By the addition of optimized concentration (1 mol%) of GA into the perovskite film of FASnI\(_3\), PCE of 9.03% along with \(V_{oc}=0.64\) V, \(J_{sc}=19.75\) mA/cm\(^2\), FF = 71.4% is achieved as compared to pristine device of PCE = 3.38%, \(V_{oc}=0.33\) V, \(J_{sc}=19.33\) mA/cm\(^2\), FF = 53%. The unencapsulated device retains 80% of the initial PCE after storage in an ambient atmosphere with a relative humidity of 20% for 1000h. Also, the encapsulated device shows no degradation when stored in the N\(_2\) atmosphere for 1500h [25]. They have shown that the air-stable Sn-based PSCs can be obtained and the device efficiency can be relatively maintained over 80% after 1000 h exposure to air, which is even better than some lead-based PSCs.

2.3. Lewis bases
Another functional additive to overcome the problem of stability of Sn-HOIP is the addition of a lewis base, which can decrease strength or reaction between FAI and SnI\(_3\). Zhu et al. (2017) use trimethylamine (TMA) as an additive [27]. The TMA reacts with Sn-halide and forms a lewis acid-base bond. Further due to the weak interaction of TMA with Sn-halide as compared to FA and the large size of TMA, they used a two-step method to fabricate Sn-based PSCs. Then FASnI\(_3\) solution can be formed by the replacement of FA ions in place of TMA, which removes the problem of rapid crystallization of the film. Hence by forming lewis acid-base adduct TMA help in the formation of compact FASnI\(_3\) film with large grain size and also reduce Sn\(^{4+}\) content and reduces oxidation of Sn\(^{2+}\) as confirmed in XPS spectra shown in figure 7. By addition of TMA PCE of 7.09% along with \(V_{oc}=0.47\) V, \(J_{sc}=22.45\) mA/cm\(^2\) and FF = 67.80% is reached as compared to pristine device of PCE = 4.20% \(V_{oc}=0.40\) V, \(J_{sc}=17.89\) mA/cm\(^2\) and FF = 58.80% [27].

Figure 7.XPS spectra of Sn 3d of pristine, and with the addition of TMA in perovskite films [27].Copyright, Advanced Materials

Wu et al. (2019) use 2- cyano-3-[5-[4-(diphenylamine)phenyl]-2-thienyl]-propenoic acid (CDTA) as an additive for FASnI\(_3\) based PSCs to optimize the crystallization process of the perovskite layer [28]. Addition of \(\pi\)-conjugated lewis base CDTA makes FASnI\(_3\) perovskite stable due to its hydrophobic nature by suppressing their degradation in air and moisture. The film shows a pinhole-free and stable structure with an increase in carrier recombination time. The concentration of 0.5% CDTA addition
improves the morphology of FASnI$_3$ film but an increase in a concentration above this leads to smaller grain size and more pinholes in PSCs. The device with the addition of CDTA maintains 90% of its initial efficiency after operating 1000h in air. A stable PCE of 10.17% is reached along with $V_{oc} = 0.63$ V, $J_{sc} = 21.22$ mA/cm$^2$, FF = 74.7% after addition of 0.5% CDTA as compared to pristine device of PCE = 6.46%, $V_{oc} = 0.50$ V, $J_{sc} = 19.89$ mA/cm$^2$, FF = 64.80% [28].

2.4. Thiocyanate type additives

Thiocyanate has been reported to effectively slow down the crystallization process and also save Sn$^{2+}$ from oxidation during the film fabrication process. As there is a strong interaction between metallic and thiocyanate ion as compared to between iodine and metallic ion, firstly thiocyanate ion makes adduct with metallic ion and get replaced by iodine ion to make two-step process. To improve PCE and other photovoltaic parameters Kim et al. (2018) used formamidinium thiocyanate (FASCN) as an additive into quasi 2D FASnI$_3$ Sn-HOIP [29]. By substitution of FASCN, the oxidation of Sn$^{2+}$ into Sn$^{4+}$is suppressed and the crystallinity of Sn-halide perovskite is increased, as shown in figure 8 with the low peak of Sn$^{4+}$ in FASCN added device. By addition of 5 mol% of FASCN in active film, PCE reached to 8.17% along with $V_{oc} = 0.53$ V, $J_{sc} = 21.8$ mA/cm$^2$, and FF = 66.50% as compared to pristine device of PCE = 5.74% with $V_{oc} = 0.48$ V, $J_{sc} = 18.5$ mA/cm$^2$ and FF = 57.20%. The photovoltaic device retains 90% of its original PCE over 1000h when placed in N$_2$ filled glove box [29].

![Figure 8. XPS spectra of Sn-based PSCs (a) pristine and (b) with additive (FASCN 5 mol%)](image)

Copyright, Journal of Materials Chemistry A

In an attempt to suppress the oxidation of Sn$^{2+}$ and to improve the film morphology of the active layer Heo et al. (2020) used lead thiocyanate (Pb(SCN)$_2$) as an additive in FASnI$_3$ Sn-HOIP [30]. By addition of 0.25 mol% of Pb(SCN)$_2$ a maximum PCE of 8.44% is achieved along with $V_{oc} = 0.68$, $J_{sc} = 17.02$ mA/cm$^2$, FF= 73% as compared to pristine device of PCE = 1.67%, $V_{oc} = 0.42$ V, $J_{sc} = 6.93$ mA/cm$^2$, FF = 58%.They have concluded that the addition of an excess of Pb(SCN)$_2$ increases the roughness of the active film and generates pinholes, resulting in a decrease of photovoltaic parameters along with PCE [30].

2.5. Hydrazine type additives

Hydrazine-based additives have been proven popular for increasing the stability of Sn-based perovskites. It reduces Sn$^{4+}$ back to Sn$^{2+}$. This type of additive effectively increases the efficiency and stability of the perovskite along with the improvement of $V_{oc}$, $J_{sc}$ and FF. To remove defects caused by oxidation of Sn$^{2+}$ into Sn$^{4+}$ Li et al. (2019) used trihydrazinedihydriodide (TD) as an additive for FASnI$_3$, Sn-HOIP [31]. It also reduces Sn$^{4+}$ content back into Sn$^{2+}$ due to its reductive property and improves the morphology of the active layer. The device with 3 mol% of TD along with 10 mol% SnF$_2$ shows better photovoltaic properties due to the reduction of Sn$^{4+}$ content in the active film. The addition of more TD (5%) reduces photovoltaic properties due to reduced carrier transport properties
by excess addition of TD additive. Device with 3 mol% of TD achieved PCE of 8.48% along with $V_{oc} = 0.54$ V, $J_{sc} = 22.12$ mA/cm$^2$ and FF = 71% as compared to pristine device of PCE = 0.21%, $V_{oc} = 0.07$ V, $J_{sc} = 10.71$ mA/cm$^2$ and FF = 29% [31].

To enhance the photovoltaic property of FASnI$_3$ based PSCs Kayesh et al. (2018) added hydrazinium chloride (N$_2$H$_5$Cl) along with SnF$_2$ as an additive [32]. The Cl$^-$ anion act as nucleation sites that form the intermediate phase and generate FaSnI$_3$ film with larger grain size. The hydrazine in N$_2$H$_5$Cl stops Sn$^{4+}$ formation while controlling the growth of the film. This increases stability and efficiency of Sn-based perovskite reached to 5.40% along with $V_{oc} = 0.45$ V, $J_{sc} = 17.63$ mA/cm$^2$ and FF = 67.30% as compared to pristine device of PCE = 2.50% with $V_{oc} = 0.29$ V, $J_{sc} = 15.06$ mA/cm$^2$ and FF = 55.90% [32]. Further, Wu et al. (2020) used hydrazine monohydrobromide (N$_2$H$_5$Br) in FASnI$_3$ for the reduction of Sn$^{4+}$ content [33]. This increases the crystallization process and also adjusts the bandgap between the active layer and the transport layer, which is more suitable for the removal and transfer of charged particles from the perovskite layer. In figure 9 XPS spectra shows that by the addition of 0.02M of N$_2$H$_5$Br the Sn$^{4+}$ content in perovskite film decreases as compared to pristine device, which leads to photovoltaic efficiency of 7.81% with $V_{oc} = 0.53$ V, $J_{sc} = 24.19$ mA/cm$^2$, and FF = 60.10% as compared to pristine device of PCE = 5.60%, $V_{oc} = 0.43$ V, $J_{sc} = 24.89$ mA/cm$^2$ and FF = 51.90% [33].

![Figure 9. XPS spectra](image-url)

Figure 9. XPS spectra (a) without addition and (b) with addition of N$_2$H$_5$Br additive (0.02M) in FASnI$_3$ film [33]. Copyright, Organic Electronics

### 2.6. Other types of additives

In addition to the solid additive, Meng et al. (2020) used liquid formic acid (LFA) as an additive into Sn-HOIP [34]. Its main advantage as it escapes easily as compared to other solid additives and no residue left of it. By the addition of the LFA additive, Sn$^{4+}$ content is decreased and further stops oxidation of Sn$^{2+}$, which was confirmed using XPS measurements. It mainly reduces trap density by reduction of Sn$^{4+}$ and forms a high crystallization perovskite film. Then finally it reached PCE of 10.37% along with $V_{oc} = 0.63$ V, $J_{sc} = 22.25$ mA/cm$^2$ and FF = 74.2% as compared to pristine device of PCE = 6.48%, $V_{oc} = 0.55$ V, $J_{sc} = 18.10$ mA/cm$^2$ and FF = 64.70% [34].

To passivates, grains of the perovskite film Tai et al. (2018) report greater air stability of FASnI$_3$ Sn-HOIP by addition of hydroxyl benzene sulfonic acid (HBSA) or its salt along with SnCl$_2$ work as a dual additive [35]. The Addition of these types of additives helps in the removal of phase change induced by SnCl$_2$ by the formation of SnCl$_2$-additive adducts. Further, this HBSA group works as a hydrophobic group to shield the perovskite layer from damage and preventing oxidation of Sn$^{2+}$. They use three types of additives namely 2-aminophenol-4-sulfonic acid (APSA), phenolsulfonic acid (PSA), and the potassium salt of hydroquinone sulfonic acid (KHQSA) for their work and get PCE of 4.67%, 4.33%, and 5.73% respectively as compared to without additive of efficiency only 2.21%. With the addition of these types of additives, the photovoltaic device maintained 80% of initial efficiency after 500h without encapsulation when exposed to the air [35].
Apart from the above additives, Wang et al. (2020) used phenyl hydrazine hydrochloride (PHCl) as an additive into FASnI$_3$ Sn-HOIP which enhances the photovoltaic property by reducing Sn$^{4+}$ content and prevent further degradation of perovskite film [36]. PHCL consists of two groups firstly phenyl group which shields the perovskite material film from side effects caused by the effect of air and water on it and secondly hydrazine group which reduces Sn$^{4+}$ ions, increases efficiency and stability of the photovoltaic. In figure 10 (a-d) SEM images show that the photovoltaic with the addition of 5 mol% of PHCl shows better morphology, however, pinholes start generating when the concentration of PHCl reached 10 mol%. In figure 10 (e) PCE of 11.40% with negligible J-V hysteresis is achieved in forward scan with the addition of 5 mol% of PHCl as an additive along with $V_{oc} = 0.76$ V, $J_{sc} = 23.50$ mA/cm$^2$, FF = 64% as compared to pristine device of PCE = 5.60%, $V_{oc} = 0.49$ V, $J_{sc} = 19.70$ mA/cm$^2$, FF = 59%. In figure 10 (f) unencapsulated Sn-HOIP with the addition of 5 mol% PHCl shows almost the same PCE after 110 days when stored in N$_2$ filled glove box [36].

To increase stability and photovoltaic performance of 3D Sn-HOIP Ke et al. (2017) introduced ethylenediamine (EN) additive into FASnI$_3$Sn-HOIP and reached a PCE of 7.14% [37]. [EN]-FASnI$_3$ with Schottky defect structure exhibit low carrier trap density, long carrier lifetime and tunable bandgap ranging from 1.4 to 1.9 eV, which results in $V_{oc} = 0.48$ V, $J_{sc} = 22.54$ mA/cm$^2$ and FF = 65.96% as compared to pristine device of PCE = 1.40% with $V_{oc} = 0.15$ V, $J_{sc} = 23.76$ mA/cm$^2$ and FF = 38.24 %. Device retains 96% of original PCE more than 1000 h with encapsulation [37]. Also, they use MASnI$_3$ in place of FASnI$_3$ results in better band alignment, By the effect of EN, film formation was improved and decrease in value of trapped states which results in stability of perovskite and efficiency reached 6.63% along with $V_{oc} = 0.42$ V, $J_{sc} = 24.28$mA/cm$^2$, FF of 63.72% as compared to pristine device of PCE = 0.17%, $V_{oc} = 0.04$ V, $J_{sc} = 23.76$ mA/cm$^2$ and FF = 38.24% [38].

In summary, the SnF$_2$ additive has shown the best photovoltaic parameters for methyl ammonium tin iodide-based PSCs. Further, for formamidinium tin iodide-based PSCs, the phenyl hydrazine hydrochloride has proven to be the best additive so far with a power conversion efficiency of 11.40%. Overall, Table 1 summarizes all the device parameters with and without the addition of additives in Sn-based PSCs.
### Table 1 Sn-based perovskite device structure, stability, PCE, $V_{oc}$, $J_{sc}$, FF with (W) additive and without (WO) Additive

| Additives | Device Structure | PCE (WO) | $V_{oc}$ (V) (WO) | $J_{sc}$ (mAcm$^{-2}$) (WO) | FF (%) (WO) | FF (%) (W) | Reference |
|-----------|-----------------|----------|-------------------|-----------------------------|------------|------|----------|
| SnF$_2$   | FTO/c-TiO$_2$/m-TiO$_2$/MASnI$_3$/Spriro-OMeTAD/Metal electrode | 0.08     | 3.70              | 0.19                        | 0.45       | 1.37 | 13.77    | 40.27     | 59.58          | [22] |
| SnF$_2$   | ITO/PEDOT:PSS/MA/PCBM/Ag | 1.62     | 7.78              | 0.32                        | 0.57       | 12.36| 20.68    | 41.00     | 66.00          | [23] |
| AHP       | Glass/ITO/PEDOT: PSS/FA$_2$$_3$MASn$_3$/PEA$_3$Sn$_3$/PCBM/Ag | 4.74     | 6.87              | 0.44                        | 0.48       | 25.38| 25.21    | 43.08     | 57.16          | [24] |
| SnCl$_2$  | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/PCBM/BCP/Ag | 3.38     | 9.03              | 0.33                        | 0.64       | 19.33| 19.75    | 53.00     | 71.40          | [25] |
| SnCl$_3$  | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/PCBM/BCP/Ag | 4.20     | 7.09              | 0.40                        | 0.47       | 17.89| 22.45    | 58.80     | 67.80          | [27] |
| TMA       | ITO/SnO$_2$/C$_{60}$/FA$_2$$_3$SnI$_3$/Spriro-OMeTAD/Metal | 6.46     | 10.17             | 0.50                        | 0.63       | 19.89| 21.22    | 64.80     | 74.70          | [28] |
| CDTA      | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Ag | 5.74     | 8.17              | 0.48                        | 0.53       | 18.5 | 21.8    | 57.20     | 66.5           | [29] |
| FASCN     | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Ag | 5.60     | 7.81              | 0.43                        | 0.53       | 24.89| 24.19    | 51.90     | 60.10          | [30] |
| Pb(SCN)$_2$ | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Cu | 4.80     | 10.37             | 0.55                        | 0.63       | 18.10| 22.25    | 64.70     | 74.20          | [31] |
| TD        | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Ag | 2.21     | 4.67              | 0.25                        | 0.44       | 15.09| 15.97    | 54.70     | 65.60          | [32] |
| N$_2$H$_2$Cl | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/PCBM/Ag | 2.50     | 5.40              | 0.29                        | 0.45       | 15.06| 17.63    | 55.90     | 67.30          | [33] |
| N$_2$H$_2$Br | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/PCBM/Ag | 5.60     | 7.81              | 0.43                        | 0.53       | 24.89| 24.19    | 51.90     | 60.10          | [34] |
| LFA       | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Ag | 6.48     | 10.37             | 0.55                        | 0.63       | 18.10| 22.25    | 64.70     | 74.20          | [35] |
| PSA       | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/PCBM/Ag | 2.21     | 4.67              | 0.25                        | 0.44       | 15.09| 15.97    | 54.70     | 65.60          | [36] |
| APSA      | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/PCBM/Ag | 2.21     | 4.33              | 0.25                        | 0.45       | 15.09| 14.91    | 54.70     | 63.80          | [37] |
| KHQA      | ITO/NO$_2$/FA$_2$$_3$SnI$_3$/PCBM/Ag | 2.21     | 5.73              | 0.25                        | 0.53       | 15.09| 16.56    | 54.70     | 65.20          | [38] |
| PHCl      | ITO/PEDOT: PSS/FA$_2$$_3$SnI$_3$/C$_{60}$/BCP/Ag | 5.60     | 11.40             | 0.49                        | 0.76       | 19.70| 23.50    | 59.00     | 64.00          | [39] |
| EN        | FTO/c-TiO$_2$/m-TiO$_2$/FA$_2$$_3$SnI$_3$/PTAA/Au | 1.40     | 7.14              | 0.15                        | 0.48       | 23.76| 22.54    | 38.24     | 65.96          | [40] |
| EN        | FTO/c-TiO$_2$/m-TiO$_2$/MASnI$_3$/PTAA/Au | 0.17     | 6.63              | 0.04                        | 0.42       | 23.76| 24.28    | 38.24     | 63.72          | [41] |
3. Conclusions
Sn-based perovskite materials have achieved rapid development due to their environment-friendly nature and excellent optoelectronic properties. However, Sn-based perovskite solar cells exhibit low $V_{oc}$ and FF resulting in poor device efficiency because of the combined effect of poor film quality, low crystallinity, fast crystallization rate, and oxidation of Sn$^{2+}$. Out of numerous efforts which have been implemented to resolve these problems, the additive-based approach has a great impact to improve the overall performance of Sn-based PSCs.

In this review, we have discussed the major outcomes of the functional additive-based approach in Sn-based PSCs to improve PCE and other device parameters. We have discussed the effect of SnF$_2$, Sn halide co-working additive, Lewis acid, thiocyanate, hydrazine, and some other types of additives which have shown some significant improvement in band alignment of Sn-HOIP. The highest PCE of 7.78% is achieved in MA-based PSCs by the addition of SnF$_2$ and PC of 11.40% is achieved in FA-based PSCs by the addition of PHCl as an additive and the device shows the same PCE after 110 days when stored in N$_2$ filled glovebox as an additive. Although a number of the research group have shown the remarkable increase in the device parameters of the Sn-based PSCs by using various additives, there is plenty of scope for the development of suitable targeted functional additives by investigating the underlying mechanism of reported additives to enhance the PCE of Sn-based PSCs.

Acknowledgments

We would like to acknowledge the grant from the Science & Engineering Research Board (SERB), Department of Science and Technology (DST) under Start up Research Grant, Government of India (SRG/2020/000777). The authors also acknowledge the Punjab Engineering College (Deemed to be University) for research initiation grant No. PEC/DSR&IC/4636 for the financial support.

References
[1] Roy P, Sinha N.K, Tiwari S and Khare A 2020 Sol. Energy 198 665-88
[2] Chandrasekaran J, Nithyaprakash D, Ajjan K. B, Maruthamuthu S, Manoharan D and Kumar S 2011 Renew. Sust. Energ. Rev. 15 1228-38
[3] Goetzberger A, Luther J and Willike G 2002 Sol. Energy Mater. Sol. Cells. 74 1-11
[4] Zhou D, Zhou T, Tian Y, Zhu X and Tu Y 2018 J. Nanomater. 1-15
[5] Fagioliari L and Bella F 2019 Energy Environ. Sci 12 3437-72
[6] Yi Z, Ladi N.H, Shai X, Li H, Shen Y and Wang M 2019 Nanoscale Adv 1 1276-89
[7] Almora O, Viaillant-Roca L and Garcia-Belmonte G 2017 Rev. CubanaFis. 34 58-68
[8] Yoo J.J, Seo G, Chua M.R, Park T.G, Lu Y, Rotermund F, Kim Y-K, Moon C-S, Jeon N-J, Correa-Baena J-P, et al., 2021 Nat. Comm. 590 587-93
[9] Green M, Dunlop E, Hohl-Ebinger J, Yoshita M, Kopidakis N and Hao X 2020 Prog Photovolt Res Appl. 29 3-15
[10] Snaith H.J 2013 Phys. Chem. Lett. 4 3623-30
[11] Gao F, Li C, Qin L, Zhu L, Huang X, Liu H, Liang. L, Hou Y, Lou Z, Hu Y and Teng F 2018 RSC Adv 8 14025-30
[12] Wang T and Yan F 2020 Chem. - Asian J. 15 1524-35
[13] Chen J and Park N-G 2019 Adv. Mater. 31 1803019
[14] Wang F, Ma J, Xie F, Li L, Chen J, Fan J and Zhao N 2016 Adv. Funct. Mater. 26 3417-23
[15] Baikie T, Fang Y, Kadro J.M, Schreyer M, Wei F, Mhaisalkar S.G, Graetzel M and White T.J 2013 J. Mater. Chem. A1 5628-41
[16] Amat A, Mosconi E, Ronca E, Quarti C, Umari P, Nazeeruddin M.K, Grätzel M and Angelis F.D 2014 Nano Lett. 14 3608-16
[17] Koh T.M, Krishnamoorthy T, Yantara N, Shi C, Leong W.L, Boix P.P, Grimdsdale A.C, Mhaisalkar S.G and Mathews N 2015 J. Mater. Chem. A. 3 14996-00
[18] Stranks S. D, Eperon G. E, Grancini G, Menelaou C, Alcocer M. J, Leijtens T, Herz L. M, Petrozza A and Snaith H.J 2013 Science 342 341-44
[19] Ke W, Stoumpos C. C, Logsdon J. L, Wasielewski, Yan Y, Fang G and Kanatzidis M. G 2016 J. Am. Chem. Soc. 138 14998-03
[20] Zhao Z, Gu F, Li Y, Sun W, Ye S, Rao H, Li Z, Bian Z and Huang C 2017 Adv. Sci. 4 1700204
[21] Takahashi Y, Obara R, Lin Z-Z, Takahashi Y, Naito T, Inabe T, Ishibashi S and Terakura K 2011 Dalton Trans. 40 5563-68
[22] Xiao M, Gu S, Zhu P, Tang M, Zhu W, Lin R, Chen C, Xu W, Yu T and Zhu J 2017 Adv. Opt. Mater. 6 1700615
[23] Wang P, Li F, Jiang K-J, Zhang Y, Fan H, Zhang Y, Miao Y, Huang J-H, Gao C, Zhou X, Wang F, Yang L-M, Zhan C and Song Y 2020 Adv. Sci. 7 1703047
[24] Obila J. O, Lei H, Ayieta E. O, Ogachir A. A, Aduda B. O and Wang F 2021 New J. Chem.
[25] Wang T, Tai Q, Guo X, Cao J, Liu C-K, Wang N, Shen D, Zhu Y, Lee C-S and Yan F 2020 ACS Energy Lett. 5 1741-49
[26] Lee S. J, Shin S. S, Kim Y. C, Kim D, Ahn T. K, Noh J. H, Seo J and Seok S. I 2016 J. Am. Chem. Soc. 138 3974-77
[27] Zhu Z, Chueh C.C, Li N, Mao C and Jen A.K-Y 2017 Adv. Mater. 30 1703800
[28] Wu T, Liu X, He X, Wang Y, Meng X, Noda T, Yang X and Han L 2020 Sci. China Chem. 63 107-15
[29] Kim H, Lee Y.H, Lyu T, Yoo J.H, Park T and Oh J. H 2018 J. Mater. Chem. 6 18173-82
[30] Heo D.Y, Lee T.H, Iwan A, Kavan L, Omotava M, Majkova E, Kamaras K, Jang H. W and Kim S. Y 2020 J. Power Sources 458 228067
[31] Li F, Fan H, Zhang J, Huang J. H, Wang P, Gao C, Yang L. M, Zhu Z, Jen A. K. Y, Song Y and Jiang K. J 2019 Sol. RRL 3 1900285
[32] Kayesh M.E, Chowdhury T-H, Matsuishi K, Kaneko R, Kazaoui S, Lee J-J, Noda T and Islam A 2018 ACS Energy Lett. 3 1584-89
[33] Wu D, Jia P, Bi W, Tang Y, Zhang J, Song B, Qin L, Lou Z, Hu Y, Teng F and Hou Y 2020 Org. Electron. 82 105728
[34] Meng X, Wu T, Liu X, He X, Noda T, Wang Y, Segawa H and Han L 2020 J. Phys. Chem. Lett. 8 2965-71
[35] Tai Q, Guo X, Tang G, You P, Ng T-W, Shen D, Cao J, Liu C-K, Wang N, Zhu Y, Lee C-S and Yan F 2019 Angew. Chem. Int. Ed. 58 806-10
[36] Wang C, Gu F, Zhao Z, Rao H, Qin Y, Cai Z, Zhan G, Li X, Sun B, Yu X, Zhao B, Liu Z, Bian Z and Huang C 2020 Adv. Mater. 32 190723
[37] Ke W, Stoumpos C. C, Zhu M, Mao L, Spanopoulos I, Liu J, Kontsevoi O. Y, Chen M, Sarma D, Zhang Y, Wasielewski M. R and Kanatzidis M. G 2017 Sci. Adv. 3 e1701293
[38] Ke W, Stoumpos C.C. Spanopoulos, Mao L, Chen M, Wasielewski M.R and Kanatzidis M.G 2017 J. Am. Chem. Soc. 139 14800-06