Effect of SnF_2 concentration on the optoelectronic and PV cell properties of CsSnBr_3

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Abstract

Lead-based halide perovskites have shown a dramatic improvement in photo-conversion efficiencies in the past decade. However, the toxicity of lead (Pb^{2+}) may present barriers or even prevent it from commercialization. On the other hand, Sn^{2+} is a potential candidate as a replacement of Pb^{2+} , while maintaining the perovskite crystal structure. However, Sn^{2+} suffers from easy oxidation to Sn^{4+} , resulting in Sn vacancy doping which limits the device efficiencies. It has been generally reported in earlier studies that addition of tin fluoride (SnF_2) restricts the oxidation of Sn^{2+} to Sn^{4+} , resulting in improvement in solar cell efficiencies. We report our findings on the role of SnF_2 concentration on the photovoltaic properties and energy level positions of cesium tin bromide (CsSnBr_3). The device properties were found to be affected strongly by SnF_2 concentration, which could not be explained simply by filling of Sn vacancies by excess tin. Observed changes in CsSnBr_3 energy levels also could not explain the improvement. Time-resolved surface photovoltage results are consistent with reduction in trap state density (assumed to be Sn^{4+}) upon SnF_2 addition, probably due to the reducing character of SnF_2 .

Keywords Lead free halide perovskite · Tin perovskite · Solar cell · Thin films · Devices

1 Introduction

Rapid rise in power conversion efficiencies (PCE) of lead-based halide perovskite photovoltaic (PV) cells have been witnessed by the research community [1–6]. Some specific compositions of perovskites have shown efficiencies beyond 23% [7]. However, Pb is well-known to be toxic and thus there is a popular fear of detrimental environmental effects in case of catastrophic device failure, something that may well restrict the commercialization of Pb-based solar cells. A strong effort has been made to replace lead (Pb^{2+}) by other less-toxic elements such as tin (Sn^{2+}) [8, 9], germanium (Ge^{2+}) [10], a combination of tin and germanium ($\text{Sn}^{2+}/\text{Ge}^{2+}$) [11], or a combination of bismuth/silver ($\text{Bi}^{3+}/\text{Ag}^+$) [12, 13].

Pure tin-based perovskites (ASnX_3) have been studied for PV applications [14, 15]. However, the efficiencies of tin perovskites are much lower than those of champion lead-based halide perovskite, as tin perovskites suffer from: (1) instability due to rapid $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$ oxidation, causing self-doping which likely increases charge scattering and decreases the charge diffusion length and (2) a high voltage loss, which may be due, either partly or to a large extent, to this self-doping [16].

In tin-based perovskite systems, it is commonly observed that cell efficiencies are improved by tin fluoride (SnF_2) addition. The first report we are aware of that used SnF_2 addition was for CsSnI_3 , where the halide perovskite (HaP) was used not (intentionally) as a light absorber but as hole transport material (HTM) [17].

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The role of the SnF_2 was not discussed in that paper and it was treated as a dopant. Kumar et al. added SnF_2 to CsSnI_3 , used as the light-absorbing HaP [18]. It was shown that, at an optimal concentration of 20%, SnF_2 reduced the hole concentration by ~ 2 orders of magnitude, and it was suggested that this was a result of a decrease in the concentration of Sn vacancies. Since then, most reported studies of pure Sn HaP cells have included SnF_2 in the preparation recipe, although there are several, mostly early reports where relatively good cells were obtained without using SnF_2 . We have reviewed the literature involving SnF_2 used in Sn HaP cells, including its effect not only by de-doping, but also on film morphology, preventing formation of unwanted crystal phases, modification of energy levels and HaP stability [19].

Only a small number of studies have studied the effect of varying concentration of SnF_2 on various properties of the Sn HaPs and their cells. The improvement of film morphology (less pinholes/exposed substrate) has been described by several groups with optimal SnF_2 concentrations of between 10 and 20 mol% [20–22]. Three studies showed that carrier densities dropped by 1–2 orders of magnitude with added SnF_2 ; for CsSnI_3 a weak dependence from 0 to 10 mol% and then a large drop between 10 and 20 mol% [18]; while for the same material, another study found a moderately large drop from 0 to 5 mol% SnF_2 and a similar relative drop from 5 to 20 mol% [23]; finally, for FASnI_3 , there occurred already a large drop for 5 mol% SnF_2 and only a relatively small difference for higher concentrations [21]. Cell-efficiencies for CsSnI_3 [18] and FASnI_3 [20] were optimal at ~ 20 mol% SnF_2 with both of them showing a strong improvement up to 20 mol% and a moderate decrease at 40 mol%. Zhao et al. reported an optimal efficiency for (FA, MA) SnI_3 with 10% SnF_2 but the differences between a minimum of 5 mol% and maximum of 20 mol% were not very large [22].

The objective of the present study was to investigate (1) the impact of SnF_2 concentration on PCE of CsSnBr_3 based solar cells, (2) depth-dependent compositional homogeneity of CsSnBr_3 (with and without SnF_2). Furthermore, analysis of time-resolved surface photovoltage (SPV) analysis revealed that SnF_2 reduces trap state concentration.

2 Results and discussions

All the results presented below, are on CsSnBr_3 films made by the same method as described in our previous paper [14] and detailed in the Supplementary Information (SI). In brief, CsBr , SnBr_3 and SnF_2 were dissolved in DMSO and the solution was filtered immediately before use.

2.1 Effect of SnF_2 concentration on cell properties

In our previous paper on CsSnBr_3 [14] cells made without SnF_2 and those made with 20 mol% SnF_2 were compared, where 20 mol% represents the mole% excess of Sn in the deposition solution compared to the stoichiometric composition. In this paper, that study has been extended to find out how the cell photovoltaic properties depend on the SnF_2 concentration and how critical the concentration is. The cells were prepared, as our previous paper [14], by deposition of CsSnBr_3 on FTO glass/dense TiO_2 /mesoporous TiO_2 , and completed with spin-coated spiro-OMeTAD as hole transport material (HTM), followed by evaporated Au as a contact (details in the SI).

The results of the best cells for each SnF_2 concentration are presented in Table 1 and the J–V characteristics of the best cell (with 30 mol% SnF_2) are shown in Fig. 1. The J–V characteristics of the cells from Table 1 are shown in the SI, Figures S1 to S10. A statistical distribution of cell efficiencies (16 cells for each concentration) is shown in Fig. 2 and the data of the various PV parameters of all these cells are given in the SI, Table S1 (A to J) along with their average parameters (except for the completely shorted ones which were excluded from this averaging).

Relatively good cells were obtained using between 20 mol% and 30 mol% SnF_2 with the best overall at 30 mol%. Within this range, open circuit voltage (V_{OC}) was similar in both cases, the fill factor (FF) was a little larger for the 30 mol% ($< 10\%$) and the main variation was in the short circuit current (J_{SC}) ($\sim 25\%$ increase for 30 mol% SnF_2) with an increase in overall efficiency of $\sim 40\%$ for the

Table 1 Photovoltaic parameters for best CsSnBr_3 cells made with different concentrations of SnF_2 , defined as excess Sn (mole%) compared to the SnBr_2 concentration in the deposition solution ($[\text{SnBr}_2] = [\text{CsBr}]$)

Mol% of SnF_2 added	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
0	0.4	0.1	35	0.01
1	1	0.12	33	0.035
5	3.7	0.12	36	0.16
10	7.55	0.3	49	1.11
20	9.1	0.41	56.5	2.1
30	11.4	0.39	57	2.5
40	10.3	0.34	45	1.6
60	9.0	0.3	38	1.0
80	3.3	0.13	27	0.11
No SnF_2 but 25 mol% SnBr_2	1.1	0.13	38	0.055

All data here and elsewhere in the paper are averages between forward and reverse scans unless specifically noted otherwise

Scan direction	V_{OC} (Volt)	J_{SC} (mA cm ⁻²)	FF (%)	PCE (%)
FWD	0.38	11.4	61.2	2.67
REV	0.4	11.4	52.3	2.4

Fig. 1 J–V characteristics of the best performing CsSnBr₃ (with 30 mol% SnF₂) cell in the dark and under illumination. PV parameters of the cells are tabulated at the bottom. FWD forward, REV reverse

30 mol% SnF₂ cells (based on a comparison of all cells—SI Table S1). Cells using 10 mol% SnF₂ were substantially poorer, with a drop in all parameters and about 50% of the efficiency of the cells in the 20–30 mol% range and a much sharper drop for 5 mol% SnF₂. On the higher SnF₂

concentration side, for 40 mol% SnF₂, the drop was appreciable but more modest (~70% of the 30 mol% SnF₂) and with a drop mainly in V_{OC} and FF. Between 60 and 80 mol% SnF₂, the performance again dropped drastically with most of the 80 mol% SnF₂ cells exhibiting complete shorting.

A control experiment was carried out using 25 mol% SnBr₂ instead of SnF₂ (the last row in Table 1). This was based on the principle of excess Sn filling Sn vacancies. While a very small improvement was found, it was negligible compared to that obtained from the same concentration of SnF₂. Marshall et al. [24] showed that there were differences in the improvement of CsSnI₃ cells when different Sn halides were added in excess. However, the differences were not as extreme as for CsSnBr₃ and even without the excess Sn, the CsSnI₃ cells were far better than our bromide cells without added Sn. Thus, we conclude that the effect of excess Sn and the way it is introduced can be very specific to individual perovskites. However, it is clear that, in the experiments carried out here, the presence of the F was important and just adding excess Sn (as SnBr₂) only resulted in a much smaller improvement.

2.2 Trap state analysis using time-resolved surface photovoltage (TR-SPV)

SPV and TR-SPV analyses are commonly used to understand properties of samples and sample interfaces, such as work-function, built-in potential (in a complete cell or partial cell) and conductivity type. In SPV, the contact potential difference of the sample surface is measured with respect to a standard of known work function (WF), which gives the sample surface WF. Illumination can

Fig. 2 Statistical distribution of cell efficiencies with varying concentrations of SnF₂ (or SnBr₂ in the leftmost box). The red markers are described by the left efficiency axis and the black markers by the right efficiency axis. The circled numbers at the top of some of the columns give the number of completely shorted cells (efficiency=0) for the relevant SnF₂ concentrations. Two large cells were made for each concentration and from each of these, 8 separate gold contacts were evaporated to give a total of 16 cells for each concentration. The triangles and the circles represent cells made from the two different large cells

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change this contact potential difference due usually to changes in band bending. If charges are trapped, this will affect the band bending, since one charge is localized in the sample. The rate at which these trapped charges fill or, more particularly empty, is determined largely by the depth of the traps in the energy gap.

An important difference was observed in the TR-SPV of CsSnBr₃ films on TiO₂ without and with SnF₂ (20 mol%), shown in Fig. 3. For the pure CsSnBr₃ (Fig. 3a), the response, both for light on and off, was slow (minutes for light 'on' and ~ 20 min for 'off'). For the sample with SnF₂ (Fig. 3b, CsSnBr₃:SnF₂), the response times were much shorter (a few seconds for both 'on' and 'off'). The slow response time of the pure CsSnBr₃ suggests slow (deep) trap filling and emptying. Such traps are absent (or at least greatly reduced) in the CsSnBr₃:SnF₂ as evidenced by the much faster response. Thus, we conclude that deep traps normally present in the CsSnBr₃ are removed or strongly reduced by SnF₂. One source of such traps could be the Sn (IV) which is known to be reduced in concentration by SnF₂.

2.3 Chemical composition—differences between the surface and bulk

X-ray photoelectron spectroscopy (XPS) was used to probe chemical composition at and near the surface with emphasis on the F concentration and distribution. For this investigation, pure CsSnBr₃ and CsSnBr₃ + 20 mol% SnF₂ (on PEDOT:PSS/ITO substrates) were compared. Both Br and Cs were strongly depleted on the surface and thus the F concentration was compared to that of Sn.

From the results in Table 2, we see that the F concentration is close to the expected stoichiometric value (F:Sn = 0.33) and while there is a moderate increase after 10 nm, the decrease again at 50 nm back to the surface value suggests no important depth dependence of the F concentration, i.e. it is reasonably homogeneously distributed through the depth of the film, in agreement with Ref. [18]. Note that Ref. [23] suggests distribution

Table 2 XPS analyses of F/Sn ratios of 20 mol% SnF₂ (~250 nm thick) CsSnBr₃ deposited on PEDOT:PSS/ITO substrates at the surface and after sputtering to ~10 nm and ~50 nm depth (depth numbers should be taken as a guide rather than accurate numbers)

Material	Ratio of elements	Sputtering depth		
		Initial	> 10 nm sputtering	> 50 nm sputtering
CsSnBr ₃ + (20 mol% SnF ₂)	F/Sn (theoretical ratio = 0.33)	0.3	0.42	0.34

of F throughout the sample but probably some concentration at grain surfaces. Since all these conclusions of F distribution (including in this study) can only be taken as approximations, we consider that there is no real difference between all these studies, i.e., approximately homogeneous distribution but with possibility of some concentration at grain surfaces.

2.4 Energy levels as a function of SnF₂ concentration

In our previous paper [12], it was shown that the addition of 20 mol% SnF₂ to CsSnBr₃ shifted the energy bands upwards by ~0.2 eV and it was suggested that, since an energy barrier to electron injection from the perovskite to the TiO₂ ETM occurred (in a simple picture of non-interacting phases at the interfaces), and this barrier was reduced substantially by the upward band shift caused by the SnF₂, it was possible that this change in band positions due to the SnF₂ could explain, to a greater or lesser extent, the improvement in photocurrent obtained by adding the SnF₂. In addition, the upshifted valence band of the CsSnBr₃:SnF₂ could reduce the valence band offset between the CsSnBr₃ and the HTM which might reduce the V_{OC} loss at that interface. Since we noted in that paper that there was no difference in the band shift for SnF₂ concentrations between 5 mol% and 80 mol%, we were

Fig. 3 Time-resolved surface photovoltage of **a** CsSnBr₃ on FTO/dense TiO₂/mesoporous TiO₂; **b** as **a** but with CsSnBr₃ + 20 mol% SnF₂. (Measured using a gold probe). Note the very different time scales for the two samples

Fig. 4 Band positions of CsSnBr₃ on dense TiO₂ coated over FTO substrate with varying amounts of SnF₂ together with the WFs

also interested to know just what concentration of SnF₂ was sufficient to shift the bands. Figure 4 shows the band positions, measured by UPS, including WF and conduction band minimum (CBM) deduced from the measured valence band maximum (VBM) and the bandgap for 0 mol%, 1 mol% and 5 mol% SnF₂ concentrations.

The sample with 1 mol% SnF₂ shifted the bands upward by 0.12, approximately half the value using 5 mol% or more SnF₂. The location of the Fermi levels in the ≥ 5 mol% SnF₂ samples was 0.15 eV below E_C , while it was essentially at E_C for the pure and 1 mol% SnF₂ perovskites. In view of the fact that, the position of the Fermi level is derived from two measurements, the error in these measurements will be larger than for the WF and E_V measurements by themselves; therefore, we do not attempt to make any interpretation of the $E_F - E_C$ differences. However, the shifts in the energy bands are clear. We speculate that this could be explained by the creation of a dipole induced by SnF₂. Indeed, SnF₂ is a reducing agent (usually used in organic synthesis), which can donate electrons to the CsSnBr₃. Such electron transfer towards CsSnBr₃ would shift the energy levels towards the vacuum as observed.

If the effect of the various SnF₂ concentrations on the band positions (Fig. 4) are compared with the effect on the cell parameters (Table 1), it can be seen that, the values of J_{SC} , and only J_{SC} , increase as the SnF₂ concentration increases to 1 mol% and 5 mol%. While these changes are small in absolute terms, they are considerable in relative increases. It is only when 10 mol% SnF₂ is reached that not only J_{SC} , but the other cell parameters, FF and V_{OC} , also begin to increase, and the 1 mol% cell efficiency mark is passed. Thus, while we could rationalize the shift in energy levels with added SnF₂ to explain the increases in J_{SC} for the 1 mol% and 5 mol% SnF₂ cells, it is clear that these shifts contribute little to the efficiency increase with larger SnF₂ concentrations.

3 Conclusions

The effect of addition of SnF₂ to CsSnBr₃ used in PV cells has been studied. The cell efficiencies are strongly dependent on the concentration of SnF₂ relative to the SnBr₂ used. At low concentrations of SnF₂ (up to 5 mol%), only the J_{SC} increased while substantially above this concentration, all the cell parameters increased, up to a maximum at 20–30% with a gradual decrease up to $\sim 60\%$ and a strong decrease beyond that in all parameters.

The effect is largely dependent on the presence of F and not simply due to excess Sn filling Sn vacancies. While SnF₂ also shifts the energy bands upwards, the shift is independent of SnF₂ concentration above 5 mol% (for 1 mol%, the shift is ~ 0.1 eV and 0.2 eV for 5 mol% and above). However, this shift is not a major cause for the efficiency improvement since the band shift dependence on SnF₂ concentration does not correlate well with that of the cell performance. The F was distributed fairly evenly throughout the samples in agreement with previous reports. Time-resolved surface photovoltage measurements indicated a reduction in deep traps in the CsSnBr₃:SnF₂ compared to the SnF₂-free material, possibly due to prevention of formation, or reduction in concentration, of Sn⁴⁺ (assumed to be the trap source).

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Compliance with ethical standards

Conflict of interest The authors declare they have no conflict of interest.

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