Impact of SnF₂ Addition on the Chemical and Electronic Surface Structure of CsSnBr₃

Claudia Hartmann, Satyajit Gupta, Tatyana Bendikov, Xeniya Kozina, Thomas Kunze, Roberto Félix, Gary Hodes,* Regan G. Wilks, David Čahen,* and Marcus Bär*

1. INTRODUCTION

Lead-based halide APbX₃ perovskite (HaP) solar cells [with A = methyl ammonium (MA), formamidinium (FA) and/or cesium (Cs⁺), and X = I⁻, Br⁻, and/or Cl⁻] have shown a rapid increase in power conversion efficiencies (PCEs) over the past years, reaching efficiencies beyond 25%.

Yet, the toxicity of Pb and water-soluble Pb salts (PbX₂) that are products of degradation of HaPs raises environmental concerns, which might restrict the commercialization of Pb-based HaP cells. Therefore, special attention is currently paid to replace Pb with alternative less-toxic elements such as tin, germanium, or a combination of bismuth and silver, aiming for Pb-free HaPs.

In this paper, we consider Sn-based HaPs (in particular, CsSnBr₃). Although much less studied than Pb-containing HaPs, there is a significant body of work on these Sn-based materials and cells, some of which have been reviewed recently.

The optical band gap energies of Sn-based HaPs are lower than those of their Pb-containing counterparts (e.g., MASN₁₃ has a band gap of ~1.3 eV compared to ~1.6 eV for MAPbI₃) and are thus often closer to the optimal range for single-junction photovoltaic cells, calculated within the Shockley–Queisser model. However, so far the highest reported efficiency for these cells is 9.6%, which is more than 2.5 times lower than the best reported efficiencies for Pb-containing devices. Adding SnF₂ to the precursor solution of Sn-based HaPs enhances the device performance.

The underlying mechanism for the SnF₂-induced efficiency gain is, however, still not well understood. Thus, we aim at identifying the effect of adding SnF₂ to the precursor solution on the chemical and electronic structure of the resulting CsSnBr₃ thin-film solar cell absorbers, which are promising candidates for top cells in tandem devices. We find a beneficial effect of the addition of SnF₂ on the ability of CsSnBr₃ to cover the substrate. We identify SnIV-type tin and secondary Cs- and Br-derived species to be present in the studied CsSnBr₃ films and that their contribution decreases with addition of SnF₂.

Furthermore, an overall enrichment in tin and decreasing Br-derived species to be present in the studied CsSnBr₃ films and that their contribution decreases with addition of SnF₂.

ABSTRACT: We report on the chemical and electronic structure of cesium tin bromide (CsSnBr₃) and how it is impacted by the addition of 20 mol % tin fluoride (SnF₂) to the precursor solution, using both surface-sensitive lab-based soft X-ray photoelectron spectroscopy (XPS) and near-surface bulk-sensitive synchrotron-based hard XPS (HAXPES). To determine the reproducibility and reliability of conclusions, several (nominally identical prepared) sample sets were investigated. The effects of deposition reproducibility, handling, and transport are found to cause significant changes in the measured properties of the films. Variations in the HAXPES-derived compositions between individual sample sets were observed, but in general, they confirm that the addition of 20 mol % SnF₂ improves coverage of the titanium dioxide substrate by CsSnBr₃ and decreases the oxidation of SnII to SnIV while also suppressing formation of secondary Br and Cs species. Furthermore, the (surface) composition is found to be Cs-deficient and Sn-rich compared to the nominal stoichiometry. The valence band (VB) shows a SnF₂-induced redistribution of Sn Ss-derived density of states, reflecting the changing SnII/SnIV ratio. Notwithstanding some variability in the data, we conclude that SnF₂ addition decreases the energy difference between the VB maximum of CsSnBr₃ and the Fermi level, which we explain by defect chemistry considerations.

KEYWORDS: perovskites, CsSnBr₃, impact of SnF₂, chemical composition, photoemission, thin-film solar cells
to study the reproducibility (e.g., of sample preparation) as well as the impact of environmental (e.g., during transport) and handling (after sample preparation and before characterization) factors on the measured data.

2. RESULTS AND DISCUSSION

The impact of adding 20 mol % SnF₂ to the precursor solution on the chemical and electronic structure of the resulting Sn-based HAP was studied by lab-based soft X-ray photoelectron spectroscopy (XPS) and synchrotron-based hard X-ray photoelectron spectroscopy (XPS). XPS measurements were performed at the Weizmann Institute of Science (WIS) and at the Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB); all HAXPES measurements were carried out at the HiKE endstation located at HZB’s BESSY II KMC-1 beamline.17,18

All results are obtained on CsSnBr₃ films made by the same method as described in ref 19. In previous publications,19,20 using 20–30 mol % SnF₂ as an additive resulted in the best performing solar cells (best PCE reaching 2.5%).

Two types of samples, CsSnBr₃/compact TiO₂/FTO/glass (hereafter referred to as set A) and CsSnBr₃ + 20 mol % SnF₂/compact TiO₂/FTO/glass (hereafter referred to as set B), were studied. To study (and account for) any effects related to the reproducibility of sample preparation or handling and the stability of the films during transport from WIS to HZB, in total, five batches of two samples each (sets Aᵢ, Bᵢ, n = 1–5) were characterized by XPS at HZB and WIS and by HAXPES at HZB over the course of 4 months. Out of these five batches, two sets produced inconsistent results; neither A₁ nor B₁ had a detectable F 1s signal, which would have been expected for sample B₁. Both samples A₁ and B₁ had a measurable F 1s signal, which was supposed to be absent for A₁ (and attributed to cross-contamination during sample transport). Therefore, sample sets 2 and 4 were excluded from further detailed analysis, as they were not suitable for correlating our spectroscopic results with the addition of SnF₂ to the precursor solution. The remaining sample sets A₃,₅ and B₃,₅ show clear spectral differences in the HAXPES data (see Figure 1 and the Supporting Information, Figure S1). In the following, the photoemission (and here mainly the HAXPES) data of A₃ and B₃ are shown as examples and discussed; sample B₃ had the highest fluorine concentration of the remaining samples and, therefore, gives the largest contrast between the CsSnBr₃ sample that was prepared with and without 20 mol % SnF₂ being added to the precursor solution (see Figure S2).

Note that all HAXPES measurements are used in quantification and mostly mean values are considered when discussing the data and drawing conclusions. Because of the higher surface sensitivity of the XPS data (e.g., the inelastic mean free path (IMFP) of Cs 3d photoelectrons excited with Al Kα (1486.58 eV) and a kinetic energy of 762.58 eV is approximately 2 nm) compared to the HAXPES measurements (e.g., the IMFP of Cs 4d photoelectrons excited with 2 keV and a kinetic energy of 1927.6 eV is approximately 4 nm), the latter will be significantly less affected by surface effects (e.g., contamination and/or oxidation), and thus, we will mainly use the HAXPES data for discussion. However, in order to compare the impact of the duration between sample deposition and characterization and/or the impact of transport, we will also use and refer to the measured XPS data.

Figure 1 shows the shallow core levels of the CsSnBr₃/compact TiO₂ samples for which no (sample A₀ "CsSnBr₃") and 20 mol % SnF₂ (sample B₀ “CsSnBr₃ + 20 mol % SnF₂”) was added to the precursor solution. All expected core levels originating from CsSnBr₃ (i.e., Cs 4d, Cs 5p, Br 3d, and Sn 4d) and, for sample A₀, also lines attributed to the compact TiO₂ substrate (i.e., Ti 3s, Ti 3p, and O 2s) can be identified in the spectra. In contrast to sample A₀, no substrate-related lines can be observed in the spectrum of sample B₀ (CsSnBr₃ + 20 mol % SnF₂), suggesting that the SnF₂ additive increases the absorber coverage of the compact TiO₂ substrate, which is further supported by scanning electron microscopy top view images on a similar prepared sample set complementing the HAXPES data (see Figure S3 in the Supporting Information). This improvement of coverage and morphology has also been observed by Koh et al., describing an improved surface coverage of the mesoporous TiO₂ substrate by FASnI₃, manifested as a reduced number of pinholes and voids compared to the pure halide perovskite film.21 Similar observations were made by Liao et al.22 for CsSnI₃ prepared with SnF₂: a larger crystallite size was observed compared to that prepared without SnF₂.22 Furthermore, a similar reduction of the density of pinholes was found for a low-dimensional form of FA−Sn−I.23 A systematic study of the CsSnI₃ morphology by Marshall et al.24 showed that actually the excess of Sn (mostly independent of the used anions: F, Cl, Br, and I) is responsible for the improved coverage. While each SnX₂ salt gave a somewhat different morphology, SnF₂ led to the best coverage and smoothest films.25

The peak shapes of the Sn 4d, Br 3d, and Cs 4d lines vary between the spectra of A₀ and B₀, indicating the presence of multiple chemical species, which is confirmed by curve fit analysis and discussed in detail below [the complete fit results and more details can be found in the Supporting Information (Figures S4–S6, including related discussion and Experimental Section)].

Figure 2 shows the Sn 4d spectra (along with the O 2s and Cs 5s lines) of samples A₀ and B₀, including curve fit results. For the Sn 4d signal, satisfactory fits of the spectra can be obtained by using two peak doublets, indicating the presence of (at least) two distinct Sn species in both samples. Note that

**Figure 1.** HAXPES spectra of the shallow core-level energy region of CsSnBr₃ prepared without (sample A₀, “CsSnBr₃”, black line) and with 20 mol % SnF₂ (sample B₀, “CsSnBr₃ + 20 mol % SnF₂”, red line) in the precursor solution. Spectra are shown after background subtraction and normalization to the Sn 4d peak height; vertical offset is added for clarity.
CsSnBr₃ samples have been reported to be sensitive to X-rays, but no evidence is found for a (hard) X-ray induced formation of metallic Sn—as previously reported in ref 19 for lab-based XPS measurements—in our HAXPES data. If metallic Sn (Sn⁰) were present, the Sn 4d component would be located in approximately the same energy region as the O 2s/Cs 5s peaks, and, because there is no indication of Sn⁰ signal in the Sn 3d HAXPES spectra of the same samples (see Figure S8, left panels), this can be excluded. However, accompanying XPS measurements of a CsSnBr₃/compact TiO₂/FTO/glass sample (sample A_WIS) at WIS do show a metallic Sn contribution to the Sn 3d core level, which is not seen when SnF₂ is added to the precursor solution (see Figure S8, right panels). Possible explanations for this difference would be (i) modification of the chemical structure of the CsSnBr₃ samples during transport from WIS to HZB despite being shipped, stored, and handled in inert gas atmosphere or (ii) a spontaneous degradation occurring during the longer time between deposition and characterization (ranging from 2 days to >1 month, see Table S1). The most likely chemical reaction would be the oxidation of (metallic) tin (because of the presence of residual oxygen atoms in the inert gas atmosphere) to a Sn–O₂ species, with SnO₂ being the most stable [i.e., Sn would change its oxidation state from 0 (if metallic tin is inherently present in CsSnBr₃) or from +2 (in case that the metallic tin signal detected in the WIS XPS measurements is due to X-ray irradiation) to +4]. Indeed, Sn⁴⁺ (tin in the oxidation state of +4) derived contributions can be identified in the respective HAXPES shallow core-level spectra. Note that the significantly larger lifetime broadening of the Sn 3d leads to considerable ambiguity in the respective curve fitting results, and thus, we focus on the Sn 4d signal to differentiate between Sn²⁺ and Sn⁴⁺. In sample A₃, the main and secondary Sn 4d₅/₂ fit peak components are found at a binding energy (BE) of (25.6 ± 0.1) and (26.4 ± 0.1) eV, respectively. For sample B₃, they are located at (25.4 ± 0.1) and (26.1 ± 0.1) eV. Hence, for the CsSnBr₃ + 20 mol % SnF₂ sample, we find a core-level shift in the range of (−0.2 to −0.3) eV. Based on the BE positions, we attribute the main and secondary spectral contributions to the Sn 4d spectra to Sn²⁺ (tin in the oxidation state of +2) and Sn⁴⁺, that is, Sn as in CsSnBr₃ and a Sn component that is oxidized, relative to CsSnBr₃ (e.g., SnO₂). Note that SnBr₃, if present, would also contribute to the Sn 4d Sn⁴⁺ component. The average HAXPES-derived Sn⁴⁺/Sn⁴⁺ ratio increases from 1.8 ± 0.5 (for samples without SnF₂ additive) to 3.1 ± 1.6 (see Table 1); that is, the oxidation of Sn is suppressed when SnF₂ is added to the precursor solution.

For A₃ and B₃, the O 2s signal (see Figure 2) at (21.8 ± 0.1) and (21.4 ± 0.1) eV can be attributed to oxygen from (primarily) the TiO₂ substrate as it mainly scales with the intensity of the Ti-related shallow core levels. The near-vanishing of the O 2s signal corroborates the increased coverage of the TiO₂ substrate when SnF₂ is added to the precursor solution (see discussion in conjunction with Figure 1). Note that the observed changes in the O 2s signal can, to some extent, also be ascribed to an increased presence of SnO₃-type Sn⁴⁺ for the SnF₂-free CsSnBr₃ sample as suggested above. Because Sn⁴⁺-derived states will act as deep defects in CsSnBr₃, a Sn⁴⁺-related O 2s signal could, in that respect, also be considered as an indirect probe for the presence of defects. The peaks at (23.2 ± 0.1) and (23.3 ± 0.1) eV belong to the Cs 5s states.

Relative to the respective Sn 4d line intensity, the Cs 5s intensity of sample B₃ is significantly decreased compared to that of sample A₃, indicating a lower Cs/Sn ratio when SnF₂ is added to the precursor solution; the decrease exceeds the expected impact of the additional Sn from the 20 mol % SnF₂ added to the precursor solution of B₃ (see Table 1 and discussion below). Figure 3 shows the Br 3d spectra of samples A₃ and B₃, including curve fit results. As for the Sn 4d spectra above, the

Table 1. Average Compositions Calculated from the HAXPES Data Shown in Figures 2−4 and in Figures S4−S6 of CsSnBr₃ Samples Deposited without (A) and with (B) SnF₂ Being Added to the Precursor Solution in Comparison to the Expected Nominal Composition

| Sample(s) A (CsSnBr₃) | Cs/Sn | Br/Sn | F/Sn | Sn(II)/Sn(IV) | Br(m)/Br(s) | Cs(m)/Cs(s) |
|-----------------------|-------|-------|------|---------------|-------------|-------------|
| nominal               | 1.00  | 3.00  | N/A  | N/A           | N/A         | N/A         |
| HAXPES                | 0.5 ± 0.2 | 2.0 ± 0.6 | N/A | 1.8 ± 0.5     | 1.8 ± 0.2   | 2.8 ± 0.9   |
| Sample(s) B (CsSnBr₃ + 20 mol % SnF₂) | nominal | 0.83  | 2.50  | 0.33           | N/A         | N/A         |
| HAXPES                | 0.3 ± 0.1 | 1.3 ± 0.1 | 0.2 ± 0.1 | 3.1 ± 1.6    | 4.0 ± 1.4   | 22.6 ± 24.5 |

The ratios represent the average of the derived compositions of sample sets A₁,₃,₅ and B₁,₃,₅, and the stated error margins represent the standard deviation from the average. The Cs/Sn, Br/Sn, and F/Sn ratios are derived considering the total intensity (i.e., main + secondary contribution) of the respective photoemission lines. Obtained from laboratory XPS data.
The background intensity at BEs around 74.9 eV, attributed to Br, is not straightforward, as Cs oxide-related Cs 4d lines with a BE of 75.5 ± 0.1 eV for A3 and 75.4 ± 0.1 eV for B3. Attributing the main Cs contribution to the Cs 4d line in our study is also related to a chemical environment best described by Cs "oxide" (see also discussion in conjunction with Figures S6 and S7).

Based on Figures 2−4, a correlation can be drawn between the addition of SnF2 to the precursor solution and the formation of secondary (oxidized) Sn, Br, and Cs species in Sn-based HaP thin films: the presence of SnF2 (20 mol %) in the precursor solution seems to generally prevent the formation of (oxidized) secondary phases. This is most obvious from the calculated mean Sn(II)/Sn(IV), Br(m)/Br(s), and Cs(m)/Cs(s) ratios derived from the HAXPES measurements, see Table 1, and supported by the additional data sets A1,5 and B1,5 (Figures S4−S6). The only exception is the chemical environment of Sn for sample set 5 (see Figure S4), which may be related to it having the lowest F (and thus presumably insufficient SnF2) content, hypothetically opening a route for additional oxidation of the sample during transport. Moreover, the Cs content for sample B3 is comparably low (see Table S1).

The observed decrease of SnIV due to the addition of SnF2 to the precursor solution has also been observed by Koh et al. Using XPS, they found that much less SnIV is formed (at the FASnI3 surface) if the precursor solution contained SnF2 compared to the case where no SnF2 was added to the precursor solution. At the same time, they reported an enhanced PCE for a solar cell based on the HaP that was prepared from a precursor solution that contained 20 mol % SnF2. The oxidation of Sn (and its prevention) is of central importance for Sn-based HaPs since the presence of SnIV will create deep defects that may act as charge carrier recombination centers, which, because of the resulting increase in doping density, will decrease the space charge layer width. If the doping is high enough, this will hinder charge separation. Both effects (creation of deep defects and decreasing space charge layer width) will limit cell efficiency.

The large performance difference between Sn- and Pb-based HaPs is generally associated with the much easier oxidation of SnII to SnIV compared to the oxidation of PbII to PbIV. Even under carefully controlled conditions, it is difficult (in particular, for wet-chemical synthesis routes) to completely prevent exposure to oxygen, and probably mainly for this
reason—and in contrast to Pb-based HaPs—some degree of oxidation of Sn-based HaPs is likely to occur during preparation. Thus, it is difficult to completely avoid the presence of Sn\textsuperscript{IV}-related deep defects during the preparation process, but their formation can be significantly suppressed by adding excess Sn\textsuperscript{II} (in the form of SnF\textsubscript{2}) during HaP preparation.\textsuperscript{22}

From the fits of the HAXPES data in Figures 2–4 and S4–S6, the elemental ratios were calculated by correcting the areas of Sn 4d\textsubscript{5/2}, Br 3d\textsubscript{5/2}, and Cs 4d\textsubscript{5/2} by the photoionization cross section of the respective photoemission line.\textsuperscript{33,34} Table 1 summarizes the averaged HAXPES-derived elemental ratios for sample sets A\textsubscript{1.3,3} (CsSnBr\textsubscript{3}) and B\textsubscript{1.3,3} (CsSnBr\textsubscript{3} + 20 mol % SnF\textsubscript{2}) and the nominal compound composition, as expected from the reagent concentrations. The ratios for the individual batches and the respective ratios for the accompanying XPS analysis at WIS can be found in the Supporting Information (see Table S1). We observe that for sample sets A and B, the HAXPES-derived compositions significantly deviate from the expected values and that there is also variation between the individual samples within one sample set. However, the smaller standard deviations for the average compositions derived for the samples of CsSnBr\textsubscript{3} + 20 mol % SnF\textsubscript{2} than for those without SnF\textsubscript{2} (Table 1) indicate a reduced variation of the experimental data between sample sets upon addition of SnF\textsubscript{2}. Most striking in the comparison with the nominal (and assumed bulk) Cs/Sn = 1 (0.83) and Br/Sn = 3 (2.5) is the suppression of the secondary Cs and Br species and the Sn\textsuperscript{II} to Sn\textsuperscript{IV} oxidation (see discussion). The variation between batches and the respective ratios for the accompanying XPS analysis at WIS can be found in the Supporting Information (see Table S1). A decreased presence of the oxidized Sn\textsuperscript{IV} oxidation and Cs de

### Table 1

| Sample Set | Cs/Sn | Br/Sn | Cs(\textit{m})/Cs(\textit{s}) | Sn/SnF\textsubscript{2} |
|------------|-------|-------|-----------------------------|-------------------------|
| A          | 1.05±0.01 | 3.04±0.03 | 1.00±0.01 | 0.48±0.03 |
| B          | 1.21±0.02 | 2.55±0.03 | 1.33±0.02 | 0.61±0.03 |

The addition of SnF\textsubscript{2} to the precursor solution seems to affect the formation of Sn\textsuperscript{IV} oxidation and related formation of Sn vacancies. Kumar et al.\textsuperscript{33} proposed that SnF\textsubscript{2} addition to the precursor solution results in an increase of the defect formation energy of Sn\textsuperscript{IV} oxidation and the related formation of Sn vacancies. Therefore, we speculate that the addition of SnF\textsubscript{2} has a disproportionately large effect on the surface of the CsSnBr\textsubscript{3} + 20 mol % SnF\textsubscript{2} sample.

An interpretation of the elemental ratios of the secondary Cs and Br species and the Sn\textsuperscript{IV} component is less straightforward, mainly because of the large number of possible Sn\textsuperscript{IV} species [possible candidates are SnO\textsubscript{2}, Sn(BrO\textsubscript{3})\textsubscript{2} and/or Cs\textsubscript{3}SnBr\textsubscript{6}], and thus, we will refrain from doing so.

In order to decide whether the observed chemical structure variations between batches in each sample set is caused by (insufficient) reproducibility of sample preparation or by environmental and handling effects, more controlled in-system experiments (i.e., sample preparation and characterization in one system without intermediate air exposure) will be needed.

In order to shed some light on the underlying mechanism of the observed SnF\textsubscript{2}-induced effects on the chemical composition and layer morphology, we note that the quality of Sn-based perovskite films depends on various parameters. A central factor seems to be the ability to minimize the Sn\textsuperscript{II} → Sn\textsuperscript{IV} oxidation and the related formation of Sn vacancies. Kumar et al.\textsuperscript{33} proposed that SnF\textsubscript{2} addition to the precursor solution results in an increase of the defect formation energy of Sn vacancies in correspondingly prepared CsSnI\textsubscript{3} perovskites. Therefore, we speculate that this higher formation energy not only limits the presence of Sn vacancies but also prevents minimizes the accompanied creation of unwanted secondary species [in our case, the Sn\textsuperscript{IV}, Br(s) and Cs(s) components of the discussed Sn 4d, Br 3d, and Cs 4d shallow core levels], which might also benefit film morphology, that is, improving substrate coverage.

#### 2.1. Effect of SnF\textsubscript{2} on Electronic Structure

Based on the results of the chemical analysis of (the surface of) the CsSnBr\textsubscript{3} and CsSnBr\textsubscript{3} + 20 mol % SnF\textsubscript{2} samples, we will now discuss the electronic structure of this absorber class. The HAXPES VB spectra on a linear scale are presented in Figure 5 for samples A\textsubscript{1} and B\textsubscript{1} (see Figure S9 for the individual VB spectra and VB maximum (VBM) determination of all samples and Figure S10 for the VB spectra represented on a semilog scale).
The VBM region. Nishikubo et al.37 also found no VBM change
however, be scaled so that they appear to overlay each other in
previously, the VBM positions of
mixed chemical surface compositions discussed above.
VBM shift can, however, certainly be attributed to the di-
the disappearance or overshadowing of the small (average)
precursor solution. Based on the measurements shown here,
incomplete coverage (see discussion above).25
The feature at BE ϵeV (indicated by an arrow in the right
panel of Figure S9) can be ascribed to states with a strong Sn
characteristic, and a DOS increase in this region can be
observed in the spectra of the sample for which 20 mol % SnF2
was added to the precursor solution. This change is consistent
with the (observed) change in Sn-oxidation state;27,37 a
decrease in relative concentration of SnV with respect to SnII
results in a change in nominal electron configuration from 4d10
5s0 5p0 to 4d10 5s2 5p0 and, thus, a corresponding increase of
electron density in this spectral range.

Figure 5. HAXPES spectra of the energy region near the VBM of
CsSnBr3 (A5) and CsSnBr3 + 20 mol % SnF2 (B5) samples, including
the VBM values (±0.10 eV) determined by linear extrapolation of the
leading edges on a linear scale. A vertical offset is added for clarity.

The VBM values derived by linear extrapolation for samples
A3 [(-1.11 ± 0.10) eV] and B3 [(-1.01 ± 0.10) eV] indicate a
small shift of the VBM toward Eb when SnF2 is added during
deposition, in agreement with ref 12. The averaged VB spectra
shown by the thick lines in the right panel of Figure S9 can,
however, be scaled so that they appear to overlay each other in
the VBM region. Nishikubo et al.17 also found no VBM change
of MA5SnI3 or FA5SnI3, independent of adding SnF2 to the
precursor solution. Based on the measurements shown here,
the disappearance or overshadowing of the small (average)
VBM shift can, however, certainly be attributed to the differing,
mixed chemical surface compositions discussed above.
Previously, the VBM positions of -1.7 and -1.6 eV19 for
similarly prepared CsSnBr3 and CsSnBr3 + 20 mol % SnF2
samples, respectively, have been reported. As these values
have been derived by ultraviolet photoelectron spectroscopy (UPS,
He I = 21.2 and He II = 40.8 eV), the discrepancy to the more
bulk-sensitive HAXPES (2 keV)-derived values of -1.11 and
-1.01 (±0.10) eV can be explained by an increased impact of
surface contaminants on the VBM determination and/or a
pronounced downward band bending (assuming p-type bulk
conductivity) toward the sample surface (see discussion
below). In addition, a certain impact of a low-excitation
energy-induced k-selectivity of the photoemission process
cannot be excluded. Furthermore, it has to be considered that
the top of the CsSnBr3 VB is formed by Sn 5s-derived states,36
to which HAXPES measurements are more sensitive than UPS
measurements (see the Supporting Information discussion
related to Figure S10 for details). Thus, the seemingly high
UPS-derived VBM values—also compared to the band gap of
CsSnBr3: 1.75 eV19—could be explained by the spectral onset
that is (at this excitation energy) dominated by Br 4p-derived
states. The thus presumably overshadowed “real” onset formed
by Sn 5s-derived states might mistakenly be interpreted as a
background when doing the linear approximation of the
leading edge. A solution for this issue could be the presentation
and evaluation of the VB spectra on a semilogarithmic scale as
suggested by Endres et al.38 The direct comparison of the
HAXPES VBM values determined by linear approximation of
the leading edge on a linear scale and the respective spectra
shown on a semilogarithmic scale are shown in Figure S10. As
the HAXPES spectra do have a significantly higher noise level
above the VBM than the UPS data (inherent to the experimental
setup, see the Supporting Information for more
details), it is not straightforward to use the semilogarithmic
HAXPES plots to derive VBM positions without respective
DOS calculations. However, the VBM values derived on a
linear scale mainly coincide within the experimental
uncertainty with the clear intensity drop of the semilogarithmic
HAXPES data, and thus, we conclude that in the case of
HAXPES for this Sn-based HaP, a semilog approach does not
lead to significantly different VBM values. Reasons for that
could be the relatively high photoionization cross section for s-
derived states when employing hard X-rays (instead of UV
light, see discussion above) and the higher DOS at the top of
the VB of CsSnBr3 compared to that of CsPbBr3,39 for which
the benefit of the semilog approach was demonstrated.38
Taking the CsSnBr3 bulk band gap of 1.75 eV (as derived by
UV–Vis spectrophotometry for similarly prepared samples19)
to account, the HAXPES-derived VBM positions may be
interpreted in terms of two scenarios. Assuming that there is
no (depth-dependent) chemical and electronic structure
profile (i.e., somewhat neglecting the finding of a Sn-rich
and Cs-/Br-poor CsSnBr3 surface), the VBMs (independent of
SnF2) indicate a very slight n-type (bulk) conductivity.
Assuming p-type conductivity in the bulk, the derived VBM
positions are in agreement with a conduction-type inversion at
the surface (for a p-type semiconductor, one would expect |VBM < ICBM = Eb – CBM, with CBM being the conduction
band minimum), most likely due to a high density of acceptor-
like surface states, causing a significant (downward) surface
band bending.

By focusing on each sample set (A3, B3) individually, we find
that in two (n: 3 and 5) of the three cases, we can observe a
SnF2-induced shift of the VBM toward Eb. The VBM (A3–
VBM (B3) shift of -0.18 eV (±0.14 eV) represents the upper
boundary in our case. In the first scenario (i.e., n-type bulk
conductivity), this shift indicates a decrease in the net n-type
doping concentration. For the second scenario (i.e., p-type
bulk conductivity), the VBM shift toward \( E_F \) would indicate a reduced downward surface band bending, for example, due to a reduced density of acceptor-like defect (surface) states and/or an increased p-type doping in the material bulk.

\( E_F \) being closer to the CBM than to the VBM, as well as the VBM shift, are—within experimental uncertainty—in agreement with previous UPS measurements\(^{19}\) (see discussion above) and with the core-level shifts discussed above. The fact that the VBM values derived by the more surface-sensitive UPS\(^{19}\) are farther from \( E_F \) than in the HAXPES measurements, supporting the second scenario (i.e., p-type bulk conductivity and downward surface band bending).

We have previously shown how oxidation of \( \text{Sn}^{II} \) to \( \text{Sn}^{IV} \) in \( \text{CsSnBr}_3 \) can result in p-type doping.\(^{12}\) Other studies have also shown that inhibiting Sn-oxidation by using \( \text{SnF}_2 \) in the preparation leads to a reduction of the hole concentration in Sn-based HaPs by 1–2 orders of magnitude.\(^{23,24,32}\) Thus, in a simple picture, preventing this oxidation (by addition of \( \text{SnF}_2 \)) should result in a shift of the VBM away from \( E_F \) contrary to what we observe. Apparently, the \( \text{SnF}_2 \)-induced VBM shift toward \( E_F \) is mainly governed by the increase in Sn \( s^\text{xs} \)-derived DOS as a result of the change in Sn-oxidation state (i.e., the decrease of \( \text{Sn}^{IV} \)-derived defects) and corresponding electron configuration modification (see discussion above). However, assuming p-type bulk conductivity, one could also speculate that the VBM shift toward \( E_F \) may to some extent be due to a \( \text{SnF}_2 \) addition-induced reduction of the density of (acceptor-like) defect states at the surface, resulting in a less pronounced surface band bending. This conclusion is supported by refs\(^{24} \) and \(^{32} \) that correlate \( \text{SnF}_2 \) with the reduction of the density of (interband) defect states.

It has been reported\(^ {10} \) that any excess of \( \text{Sn}^{II} \) (from \( \text{SnX}_2 \) additives, \( X = \text{Cl}, \text{Br}, \text{I} \)) can result in an improved device performance, yet addition of excess \( \text{SnBr}_2 \) during \( \text{CsSnBr}_3 \) preparation has only a very small effect on performance compared to the improvement when using \( \text{SnF}_2 \).\(^ {23} \) Thus, on the one hand, the incorporation of excess Sn and its effect/benefits to the film properties can be specific to the individual perovskite; on the other hand, one could speculate that the results of this study w.r.t. the observed \( \text{SnF}_2 \) addition-induced chemical and electronic structure changes can, to some extent, also be transferred to these systems. However, detailed studies are required to conclusively answer this question.

### 3. CONCLUSIONS

The chemical and electronic structure of \( \text{CsSnBr}_3 \) thin-film solar cell absorbers and how it is impacted by the addition of 20 mol % \( \text{SnF}_2 \) to the precursor solution has been studied by lab-based soft (XPS) and synchrotron-based hard (HAXPES) X-ray photoelectron spectroscopy. To determine the reproducibility and reliability of the results, several of (nominally identically prepared) sample sets were investigated. Variations in the HAXPES-derived surface compositions between individual sample sets were observed. Despite such variability, we find that the addition of 20 mol % \( \text{SnF}_2 \) results in an improved coverage of the TiO\(_2\) substrate by \( \text{CsSnBr}_3 \), in agreement with earlier reports, a decrease in the oxidation of \( \text{Sn}^{II} \) to \( \text{Sn}^{IV} \), and a suppression in the formation of secondary Br and Cs species. Comparing HAXPES-derived compositions with the nominal compositions reveals an overall enrichment in tin and deficiency of cesium in the surface region, which is further enhanced by the addition of \( \text{SnF}_2 \) to the precursor solution. The HAXPES VB spectra show a \( \text{SnF}_2 \)-induced redistribution of Sn \( s^\text{xs} \)-derived DOS, reflecting the changing \( \text{Sn}^{II}/\text{Sn}^{IV} \) ratio. Furthermore, we suggest—despite some variation between sample batches—a VBM shift toward \( E_F \) upon \( \text{SnF}_2 \) addition to the precursor solution. This can be explained by a reduction of the density of acceptor-like (surface) defects, which results in a less pronounced surface band bending. Finally, the improvement of the performance of \( \text{CsSnBr}_3 \)-based solar cells, prepared with \( \text{SnF}_2 \), can likely be related to the reduction of \( \text{Sn}^{IV} \)-derived states, decreasing the density of deep defects in the \( \text{CsSnBr}_3 \) perovskite absorber (thus, effectively reducing the number of charge carrier recombination centers) and maintaining a moderate doping density that will result in a suitable space charge layer width (thus, maintaining sufficient charge separation).

### ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.9b22967.

Data analysis and description of the XPS and HAXPES spectra; complete set of shallow (\( \text{Cs} 4\text{d}, \text{Br} 3\text{d}, \text{and} \text{Sn} 4\text{d} \)) core-level HAXPES spectra as well as F 1s XPS, Cs 3d and Sn 3d HAXPES spectra, and XPS; Br 3d XPS spectra; and table of elemental ratios as well as VB spectra for all samples (PDF)

### AUTHOR INFORMATION

**Corresponding Authors**

Gary Hodes — Department of Materials & Interfaces, Weizmann Institute of Science (WIS), 7610001 Rehovot, Israel; Email: gary.hodes@weizmann.ac.il

David Cahen — Department of Materials & Interfaces, Weizmann Institute of Science (WIS), 7610001 Rehovot, Israel; Email: david.cahen@weizmann.ac.il

Marcus Bär — Interface Design, Energy Materials In-Situ Laboratory Berlin (EMILL), and Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (HI ERN), Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), 14109 Berlin, Germany; Department of Chemistry & Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, 91058 Erlangen, Germany; Email: marcus.baer@helmholtz-berlin.de

**AUTHORS**

Claudia Hartmann — Interface Design, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), 14109 Berlin, Germany; Email: orcid.org/0000-0002-8017-8116

Satyajit Gupta — Department of Materials & Interfaces, Weizmann Institute of Science (WIS), 7610001 Rehovot, Israel; Department of Chemistry, Indian Institute of Technology Bhubaneswar, Bhubaneswar, India

Tatyana Bendikov — Chemical Research Support Unit, Weizmann Institute of Science (WIS), Rehovot 7610001, Israel

Thomas Kunze — Interface Design, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH (HZB), 14109 Berlin, Germany
Author Contributions

C.H. and S.G. contributed equally to this work. The manuscript was written through contributions from all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

T.B. thanks Dr. Hagai Cohen for helpful discussions. G.H. and D.C. acknowledge support from the SolarERAnet program HESTPV, via the Israel Ministry of Energy. D.C. also thanks the Yotam project for partial support. (Part of) This research was carried out within the Helmholtz International Research School “Hybrid Integrated Systems for Conversion of Solar Energy” (HI-SCORE), an initiative cofunded by the “Initiative and Networking Fund of the Helmholtz Association”. C.H., X.K., T.K., RF, R.G.W., and MB also acknowledge the financial support by the Impuls-und Vernetzungsfonds of the Helmholtz-Association (VI-NG-423). The authors thank HZB for the allocation of synchrotron radiation beam time.

■ REFERENCES

(1) Park, N.-G.; Grätzel, M.; Miyasaka, T.; Zhu, K.; Emery, K. Towards Stable and Commercially Available Perovskite Solar Cells. Nat. Energy 2016, 1, 16152.
(2) Mehmoond, U.; Al-Ahmed, A.; Afzaal, M.; Al-Sulaiman, F. A.; Daud, M. Recent Progress and Remaining Challenges in Organometallic Halide Based Perovskite Solar Cells. Renewable Sustainable Energy Rev. 2017, 78, 1–14.
(3) Asghar, M. I.; Zhang, J.; Wang, H.; Lund, P. D. Device Stability of Perovskite Solar Cells – A Review. Renewable Sustainable Energy Rev. 2017, 77, 131–146.
(4) www.nrel.gov/pv/assets/images/efficiency-chart.png (accessed 2020-02-28).
(5) Giustino, F.; Snaith, H. J. Toward Lead-Free Perovskite Solar Cells. ACS Energy Lett. 2016, 1, 1233–1240.
(6) Konstantakou, M.; Stergiopoulos, T. Critical Review on Tin Halide Perovskite Solar Cells. J. Mater. Chem. A 2017, 5, 11518–11549.
(7) Toshniwal, A.; Kheraj, V. Development of Organic-Inorganic Tin Halide Perovskites: A Review. Sol. Energy 2017, 149, 54–59.
(8) Stoumpos, C. C.; Frazer, L.; Clark, D. J.; Kim, Y. S.; Rhim, S. H.; Freeman, A. J.; Ketterson, J. B.; Jang, J. I.; Kanatzidis, M. G. Hybrid Germanium Iodide Perovskite Semiconductors: Active Lone Pairs, Structural Distortions, Direct and Indirect Energy Gaps, and Strong Nonlinear Optical Properties. J. Am. Chem. Soc. 2015, 137, 6804–6819.
(9) McClure, E. T.; Ball, M. R.; Windl, W.; Woodward, P. M. Cs2AgBiX6 (X = Br, Cl): New Visible Light Absorbing, Lead-Free Halide Perovskite Semiconductors. Chem. Mater. 2016, 28, 1348–1354.
(10) Filip, M. R.; Hillman, S.; Haghhighard, A. A.; Snaith, H. J.; Giustino, F. Band Gaps of the Lead-Free Halide Double Perovskites Cs2BiAgCl6 and Cs2BiAgBr6 from Theory and Experiment. J. Phys. Chem. Lett. 2016, 7, 2579–2585.
(11) Slavney, A. H.; Hu, T.; Lindenberg, A. M.; Karunadasa, H. I. A Bismuth-Halide Double Perovskite with Long Carrier Recombination Lifetime for Photovoltaic Applications. J. Am. Chem. Soc. 2016, 138, 2138–2141.
(12) Gupta, S.; Cahen, D.; Hodes, G. How SnF2 Impacts the Material Properties of Lead-Free Tin Perovskite. J. Phys. Chem. C 2018, 122, 13926–13936.
(13) Ke, W.; Stoumpos, C. C.; Kanatzidis, M. G. “Unloaded” Perovskites: Status Quo and Future Prospects of Tin-Based Perovskite Solar Cells. Adv. Mater. 2019, 31, 1803230.
(14) Hao, F.; Stoumpos, C. C.; Cao, D. H.; Chang, R. P. H.; Kanatzidis, M. G. Lead-Free Solid-State Organic-Inorganic Halide Perovskite Solar Cells. Nat. Photonics 2014, 8, 489–494.
(15) Shockley, W.; Queisser, H. J. Detailed Balance Limit of Efficiency of p-n Junction Solar Cells. J. Appl. Phys. 1961, 32, 510–519.
(16) Jokar, E.; Chien, C.-H.; Tsai, C.-M.; Fathi, A.; Diao, E. W.-G. Robust Tin-Based Perovskite Solar Cells with Hybrid Organic Cations to Attain Efficiency Approaching 10%. Adv. Mater. 2019, 31, 1804835.
(17) Gorgoi, M.; Svensson, S.; Schäfer, F.; Öhrwall, G.; Mertin, M.; Bressler, P.; Karis, O.; Siegbahn, H.; Sandell, A.; Rensho, M.; Doherty, W.; Jung, C.; Braun, W.; Eberhardt, W. The High Kinetic Energy Photoelectron Spectroscopy Facility at BESSY Progress and First Results. Nucl. Instrum. Methods Phys. Res., Sect. A 2009, 601, 48–53.
(18) Schaefer, F.; Mertin, M.; Gorgoi, M. KMC-1: A High Resolution and High Flux Soft X-ray Beamline at BESSY. Rev. Sci. Instrument. 2007, 78, 123102.
(19) Gupta, S.; Bendikov, T.; Hodes, G.; Cahen, D. CsSnBr3, A Lead-Free Halide Perovskite for Long-Term Solar Cell Application: Insights on SnF2 Addition. ACS Energy Lett. 2016, 1, 1028–1033.
(20) Gupta, S.; Hodes, G. Effect of SnF2 Concentration on the Optoelectronic and PV Cell Properties of CsSnBr3, SN Appl. Sci. 2019, 1, 1066.
(21) Tougaard, S. QUASES-IMFP-TPP2M; Quases-Tougaard Inc., 2002.
(22) Koh, T. M.; Krishnamoorthy, T.; Yantara, N.; Shi, C.; Leong, W. L.; Boix, P. P.; Grimsdale, A. C.; Mhaisalkar, S. G.; Mathews, N. Formamidinium Tin-Based Perovskite with Low Eg for Photovoltaic Applications. J. Mater. Chem. A 2015, 3, 14996–15000.
(23) Liao, W.; Zhao, D.; Yu, Y.; Grice, C. R.; Wang, C.; Cimaroli, A. J.; Schulz, P.; Meng, W.; Zhu, K.; Xiong, R.-G.; Yan, Y. Lead-Free Inverted Planar Formamidinium Tin Triiodide Perovskite Solar Cells Achieving Power Conversion Efficiencies up to 6.22%. Adv. Mater. 2016, 28, 9333–9340.
(24) Xing, G.; Kumar, M. H.; Chong, W. K.; Liu, X.; Cai, Y.; Ding, H.; Asta, M.; Grätzel, M.; Mhaisalkar, S.; Mathews, N.; Sum, T. C. Solution-Processed Tin-Based Perovskite for Near-Infrared Lasing. Adv. Mater. 2016, 28, 8191–8196.
(25) Liao, Y.; Liu, H.; Zhou, W.; Yang, D.; Shang, Y.; Shi, Z.; Li, B.; Jiang, X.; Zhang, L.; Quan, L. N.; Quintero-Bermudez, R.; Sutherland, B. R.; Mi, Q.; Sargent, E. H.; Ning, Z. Highly Oriented Low-Dimensional Tin Halide Perovskites with Enhanced Stability and Photovoltaic Performance. J. Am. Chem. Soc. 2017, 139, 6693–6699.
(26) Marshall, K. P.; Walker, M.; Walton, R. I.; Hatton, R. A. Enhanced Stability and Efficiency in Hole-Transport-Layer-Free CsSnI3 Perovskite Photovoltaics. Nat. Energy 2016, 1, 16178.
(27) De Padova, P.; Fanfoni, M.; Larciprete, R.; Mangiantini, M.; Priori, S.; Perfetti, P. A Synchrotron Radiation Photoemission Study of the Oxidation of Tin. Surf. Sci. 1994, 313, 379–391.
(28) National Institute of Standards and Technology. NIST X-ray Photoelectron Spectroscopy (XPS) Database [Online], available http://srdata.nist.gov/xps/Default.aspx (accessed 2020-02-03).
(29) Jung, M.-C.; Raga, S. R.; Qi, Y. Properties and Solar Cell Applications of Pb-Free Perovskite Films Formed by Vapor Deposition. RSC Adv. 2016, 6, 2819–2825.
(30) Spicer, W. E.; Lindau, I.; Su, C. Y.; Chye, P. W.; Pianetta, P. Core-level Photoemission of the Cs-O Adlayer of NEA GaAs Cathodes. *Appl. Phys. Lett.* 1978, 33, 934–935.

(31) Hrbek, J.; Yang, Y. W.; Rodriguez, J. A. Oxidation of Cesium Multilayers. *Surf. Sci.* 1993, 296, 164–170.

(32) Kumar, M. H.; Dharani, S.; Leong, W. L.; Boix, P. P.; Prabhakar, R. R.; Baikie, T.; Shi, C.; Ding, H.; Ramesh, R.; Asta, M.; Graetzel, M.; Mhaisalkar, S. G.; Mathews, N. Lead-Free Halide Perovskite Solar Cells with High Photocurrents Realized Through Vacancy Modulation. *Adv. Mater.* 2014, 26, 7122–7127.

(33) Trzhaskovskaya, M. B.; Nefedov, V. I.; Yarzhemsky, V. G. Photoelectron Angular Distribution Parameters for Elements Z=1 to Z=54 in the Photoelectron Energy Range 100–5000 eV. *At. Data Nucl. Data Tables* 2001, 77, 97–159.

(34) Trzhaskovskaya, M. B.; Nefedov, V. I.; Yarzhemsky, V. G. Photoelectron Angular Distribution Parameters for Elements Z=55 to Z=100 in the Photoelectron Energy Range 100–5000 eV. *At. Data Nucl. Data Tables* 2002, 82, 257–311.

(35) Sabba, D.; Mulmudi, H. K.; Prabhakar, R. R.; Krishnamoorthy, T.; Baikie, T.; Boix, P. P.; Mhaisalkar, S.; Mathews, N. Impact of Anionic Br\(^{-}\) Substitution on Open Circuit Voltage in Lead Free Perovskite (CsSnI\(_3\)-Br\(_x\)) Solar Cells. *J. Phys. Chem. C* 2015, 119, 1763–1767.

(36) Zheng, J.-C.; Huan, C. H. A.; Wee, A. T. S.; Kuok, M. H. Electronic Properties of CsSnBr\(_3\): Studies by Experiment and Theory. *Surf. Interface Anal.* 1999, 28, 81–83.

(37) Nishikubo, R.; Ishida, N.; Katsuki, Y.; Wakamiya, A.; Saeki, A. Minute-Scale Degradation and Shift of Valence-Band Maxima of (CH\(_3\)NH\(_3\))\(_2\)SnI\(_3\) and HC(NH\(_2\))\(_2\)SnI\(_3\), Perovskites upon Air Exposure. *J. Phys. Chem. C* 2017, 121, 19650–19656.

(38) Endres, J.; Egger, D. A.; Kulbak, M.; Kernre, R. A.; Zhao, L.; Silver, S. H.; Hodes, G.; Rand, B. P.; Cahen, D.; Kronik, L.; Kahn, A. Valence and Conduction Band Densities of States of Metal Halide Perovskites: A Combined Experimental–Theoretical Study. *J. Phys. Chem. Lett.* 2016, 7, 2722–2729.

(39) Mao, X.; Sun, L.; Wu, T.; Chu, T.; Deng, W.; Han, K. First-Principles Screening of All-Inorganic Lead-Free ABX\(_3\) Perovskites. *J. Phys. Chem. C* 2018, 122, 7670–7675.