

# **Formation of a mixed valence Sn<sub>3</sub>F<sub>8</sub> phase explains the SnF<sub>2</sub> stabilizing role in tin-halide perovskites**

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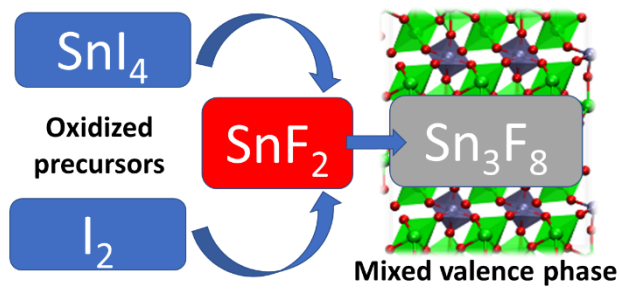
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## Abstract

$\text{SnF}_2$  is a common additive stabilizing tin halide perovskites. We propose that this is due to formation a mixed valence  $\text{Sn}_3\text{F}_8$  phase which sequesters oxidized species from the reaction environment.

## TOC graphics

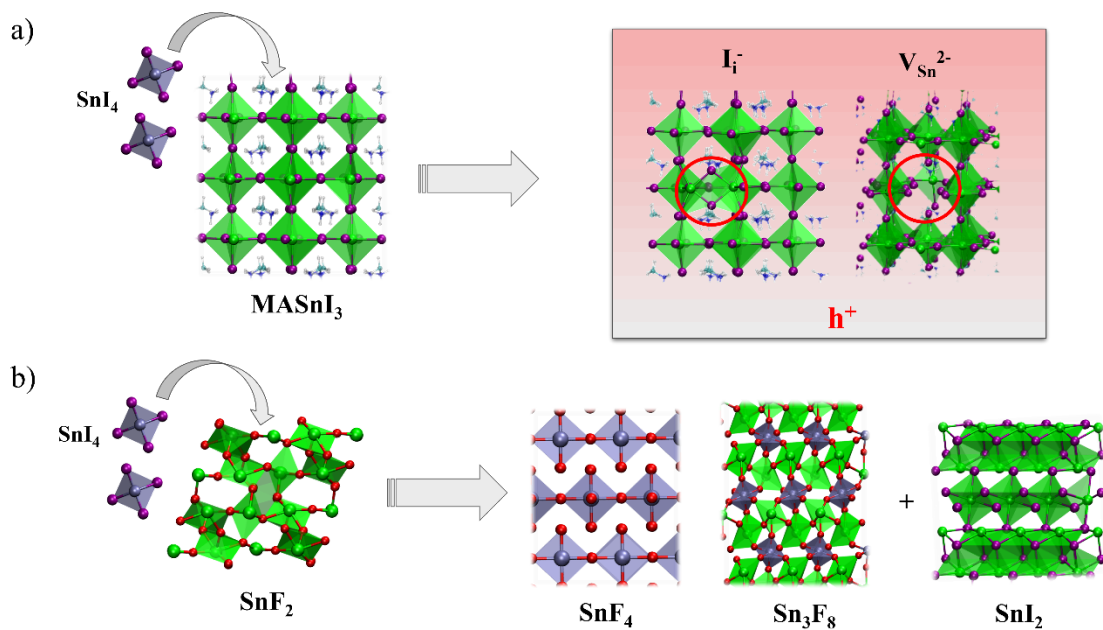


With lead-halide perovskite solar cells heading towards commercialization, tin halide perovskites (THPs) still show an immense development potential. Besides the lower toxicity of tin vs. lead, THPs may represent alternative low-band gap materials for both standalone and tandem devices.<sup>1-3</sup> Sn-Pb alloying is also considered promising to obtain intermediate band gap materials useful in all perovskite tandem solar cells.<sup>4-6</sup> The facile oxidation of Sn(II) to Sn(IV) seriously limits the material stability and, consequently, the efficiency of THP-based solar cells. Interestingly, Sn(IV) species, such as SnI<sub>4</sub>, are not thermodynamically stable in the perovskite bulk, but they spontaneously tend to release holes to the THP valence band, leading to p-doping.<sup>7</sup> Sn(IV) species are, however, stable at the perovskite surface or grain boundaries where they constitute electrons traps, with Sn(IV) formation being promoted by surface tin vacancies.<sup>7</sup> Clearly, preventing the presence of Sn(IV) species in the THP precursors is mandatory to avoid p-doping and incorporation of oxidized species. Improving the thin film quality together with a proper surface passivation strategy may further decrease the likelihood of Sn(IV) formation during the operational device lifetime.

Since the pioneering paper by Kanatzidis and coworkers in 2012,<sup>8</sup> SnF<sub>2</sub> has been added to the perovskite precursors to limit THP oxidation. The impact of SnF<sub>2</sub> on the perovskite properties is twofold, leading to improved film quality and alleviated p-doping and Sn(IV) formation.<sup>9</sup> While the stronger S-F bonds in place of Sn-I bonds may induce retarded crystallization and overall film quality improvement, the role of SnF<sub>2</sub> in improving THP optoelectronic properties has been mainly ascribed to the realization of a tin-rich environment, leading to suppressed tin vacancy formation and associated p-doping.<sup>2</sup> SnF<sub>2</sub>, however, was also shown to stabilize precursor solutions against Sn(IV) formation,<sup>10</sup> coherent with SnF<sub>2</sub> being regarded as a reducing agent.<sup>8</sup> The question now is: *how can SnF<sub>2</sub> stabilize SnI<sub>2</sub> against oxidation and, consequently, stabilize the perovskite?* The oxidation potential of tin should be formally the same in SnI<sub>2</sub> and SnF<sub>2</sub>, being it referred to the solvated metal ion.

Here we employ state of the art Density Functional Theory (DFT) calculations to evaluate the possible reactions occurring upon  $\text{SnF}_2$  addition to the perovskite precursors, with emphasis on the interaction with oxidized species. Our results show that  $\text{SnF}_2$  may sequester  $\text{Sn(IV)}$  and  $\text{I}_2$  from the reaction environment by forming a thermodynamically stable mixed valence phase, thereby explaining its reducing action.

The incorporation of  $\text{Sn(IV)}$  into the tin perovskite bulk mainly leads to the release of the two holes into the VB of the material and to the parallel formation of acceptor defects compensating the process, specifically iodine interstitials ( $\text{I}_i^-$ ) and tin vacancies ( $\text{V}_{\text{Sn}}^{2-}$ ), see Figure 1a. This process has been modelled in the prototype  $\text{MASnI}_3$  perovskite exposed to  $\text{SnI}_4$  by reactions R1 and R2 (Table 1), which are thermodynamically driven by the high stability of  $\text{I}_i^-$  and  $\text{V}_{\text{Sn}}^{2-}$  defects in  $\text{MASnI}_3$  leading to heavily p-doped materials.<sup>11</sup>



**Figure 1.** Schematics of reactions involving  $\text{SnF}_2$ ,  $\text{SnI}_4$  and  $\text{MASnI}_3$ . a)  $\text{SnI}_4$  is incorporated into the  $\text{MASnI}_3$  perovskite, leading to the formation of  $\text{I}_i^-$  and  $\text{V}_{\text{Sn}}^{2-}$  defects and p-doped materials. b)  $\text{SnI}_4$  is incorporated into  $\text{SnF}_4$  and  $\text{Sn}_3\text{F}_8$  phases.

The beneficial impact of SnF<sub>2</sub> in the perovskite stability can be ascribed to its capacity of sequestering Sn(IV) species from the reaction precursors, hence limiting its incorporation into the perovskite. This process is simulated through reactions R3 and R4 in Table 1. The Sn(IV)/Sn(II) exchange between the SnI<sub>4</sub> and SnF<sub>2</sub> phases mainly proceeds with the formation of the Sn(IV) SnF<sub>4</sub> and the Sn(II)/Sn(IV) Sn<sub>3</sub>F<sub>8</sub> mixed-valence phase.<sup>12</sup> DFT results show that both these reactions are thermodynamically favored over the incorporation of SnI<sub>4</sub> into MASnI<sub>3</sub>, *i.e.* reactions R1 and R2, confirming that SnF<sub>2</sub> is able to suppress this detrimental process.

**Table 1.** Thermodynamics of incorporation of SnI<sub>4</sub> into the MASnI<sub>3</sub> bulk (R1-R2). Reactions of SnF<sub>2</sub> with SnI<sub>4</sub> through halide exchange reaction (R3) and the formation of the mixed valence Sn<sub>3</sub>F<sub>8</sub> phase (R4). Formation of Sn<sub>3</sub>F<sub>8</sub> from SnF<sub>2</sub> + SnF<sub>4</sub> (R5). I<sub>2</sub> reduction by SnF<sub>2</sub> to SnI<sub>2</sub> by formation of Sn<sub>3</sub>F<sub>8</sub>(R6). Calculations are carried out by the hybrid PBE0 functional including dispersion corrections through the DFT-D3 method, see Supporting Information.

Reaction	ΔE (eV)
R1. MASnI <sub>3</sub> + SnI <sub>4</sub> = MASnI <sub>3</sub> [2I <sub>i</sub> <sup>-</sup> + 2h <sup>+</sup> ] + SnI <sub>2</sub>	-0.37
R2. MASnI <sub>3</sub> + SnI <sub>4</sub> = MASnI <sub>3</sub> [V <sub>Sn</sub> <sup>2-</sup> + 2h <sup>+</sup> ] + 2 SnI <sub>2</sub>	-0.77
R3. 2 SnF <sub>2</sub> + SnI <sub>4</sub> = SnF <sub>4</sub> + 2 SnI <sub>2</sub>	0.35
R4. 4 SnF <sub>2</sub> + SnI <sub>4</sub> = Sn <sub>3</sub> F <sub>8</sub> + 2 SnI <sub>2</sub>	-0.70
R5. 2 SnF <sub>2</sub> + SnF <sub>4</sub> = Sn <sub>3</sub> F <sub>8</sub>	-1.05
R6. 4 SnF <sub>2</sub> + I <sub>2</sub> = Sn <sub>3</sub> F <sub>8</sub> + SnI <sub>2</sub>	-0.73

The thermodynamically most favorable process is the incorporation of Sn(IV) to form the Sn<sub>3</sub>F<sub>8</sub> phase, which is favored over SnF<sub>4</sub> formation, in agreement with experimental evidence showing that exposure of a SnF<sub>2</sub> solution to F<sub>2</sub> leads to the formation of Sn<sub>3</sub>F<sub>8</sub> and not to SnF<sub>4</sub>, as one may expect.<sup>12</sup> This is confirmed by our calculations, which show that a mixture

of  $\text{SnF}_2$  and  $\text{SnF}_4$  thermodynamically evolves to form the  $\text{Sn}_3\text{F}_8$  phase (R5). Formation of  $\text{Sn}_3\text{F}_8$  (R4) simultaneously releases Sn(II) species to the reaction environment, explaining the reducing action of  $\text{SnF}_2$ . Furthermore,  $\text{SnF}_2$  may “clean” the precursors from oxidizing  $\text{I}_2$  species, again by forming the  $\text{Sn}_3\text{F}_8$  phase (R6).

In conclusion, we have shown that the beneficial role of  $\text{SnF}_2$  as an additive to THPs resides in its capacity of retaining oxidized species, such as  $\text{SnI}_4$  and  $\text{I}_2$ , from the precursors by forming a thermodynamically stable mixed valence  $\text{Sn}_3\text{F}_8$  phase. We hope our results contribute fundamental understanding towards more stable THPs and prompt further studies to corroborate the proposed reaction mechanism.

## ACKNOWLEDGMENT

This work has received funding from the European Union’s Horizon Europe research and innovation programme under grant agreement No. 101082176 – VALHALLA and by the European Union - NextGenerationEU under the Italian Ministry of University and Research (MUR) National Innovation Ecosystem grant ECS00000041 - VITALITY. We acknowledge Università degli Studi di Perugia and MUR for support within the project Vitality.

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