

## The Critical Roles of SnF<sub>2</sub> in the Optoelectronic Properties of Lead-Free Tin Halide Perovskites

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Lead-based halide perovskites (APbX<sub>3</sub>) have shown a dramatic improvement in efficiencies in the past few years. Due to toxicity issues of lead, tin-based halide perovskites are being studied. It is observed that tin fluoride (SnF<sub>2</sub>) addition can generally improve the device properties of tin-based halide perovskites. This effect is thought to be due to suppression of Sn(II)→ Sn(IV) oxidation, Sn(II)→Sn (0) reductions, and /or a decrease in Sn vacancy concentration. All these effects will change the doping, but in opposite directions. Here we report on the role of SnF<sub>2</sub> concentration on various properties of cesium tin bromide (CsSnBr<sub>3</sub>)-based halide perovskite, such as energetics (work function -  $W_F$  and ionization energy,  $I_E$ , X-ray beam damage and device properties. We find that the SnF<sub>2</sub> concentration strongly influences the device properties (open circuit voltage- $V_{OC}$ , short circuit current- $I_{SC}$ , fill factor- $FF$  and photoconversion efficiency- $\eta$ ) but not the work function ( $W_F$ ) or ionization energy. By monitoring the XPS signals over time as a function of SnF<sub>2</sub> concentration, we find that pristine CsSnBr<sub>3</sub> (without SnF<sub>2</sub> added) is highly susceptible to X-ray beam damage if deposited on titania (TiO<sub>2</sub>), gold (Au) or poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) substrates, but is stable if deposited on ZnO substrates. About 5 mol% of SnF<sub>2</sub> was sufficient to protect the perovskite from beam damage on all the substrates, possibly because of a SnF<sub>2</sub>-induced change in the Sn<sup>2+</sup>/Sn<sup>0</sup> electrochemical potential that makes that process energetically less probable. For solar cells adding ~20 mol% of SnF<sub>2</sub> was found to be optimum for device performance. Time-resolved surface photovoltage (SPV) results are consistent with SnF<sub>2</sub> addition reducing trap state concentration. Apart from that, we found that SnF<sub>2</sub> (1) improves conduction band-alignment of the perovskite with TiO<sub>2</sub>, at their interface in a solar-cell (2) making the perovskite somewhat less 'n-type', compared to highly n-doped pristine CsSnBr<sub>3</sub>.