$CsSnBr_3$ - a Completely Pb-free Inorganic Halide Perovskite for Long-term Solar Cell Application: *Insights into SnF_2 Addition Effects*

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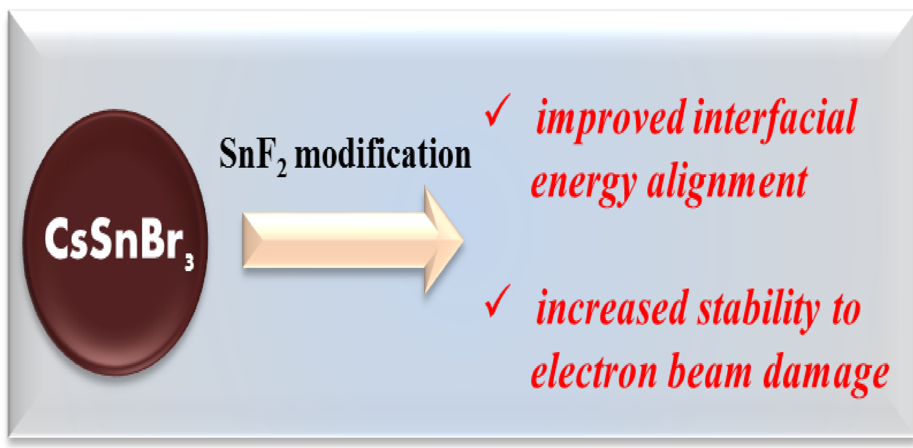
Background

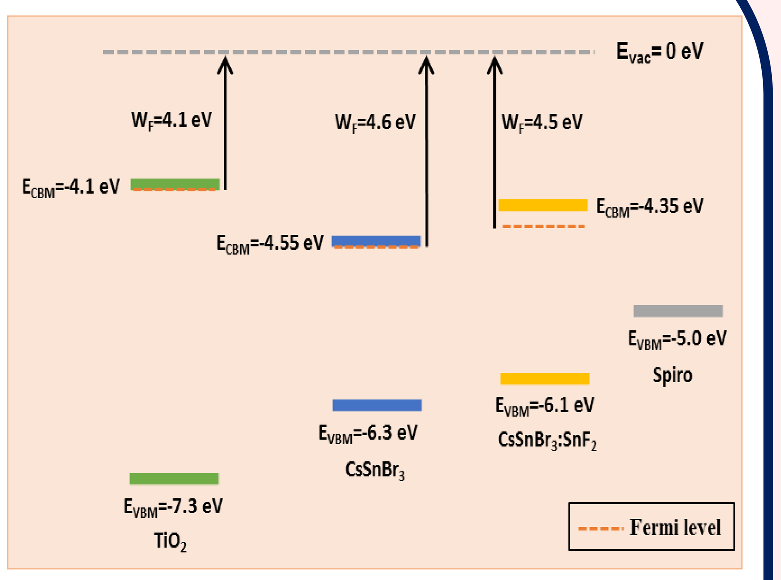
Solar cells based on 'halide perovskites' (HaPs), have demonstrated unprecedented high power conversion efficiencies (> 21%). However, the toxicity (esp. its public perception) of lead, used in the most studied cells, may affect its large-scale production. We explore an all-inorganic, completely Pb-free HaP for opto-electronic applications.

Here, the roles of SnF_2 on the properties of $CsSnBr_3$ with a direct ~1.75 eV optical bandgap were studied, using UV photoemission and X-Ray photoelectron spectroscopies (UPS, XPS).



Band alignment-UPS

Results of UPS measurements reveal a significant electron injection barriers (0.45 eV for pristine $CsSnBr_3$ and 0.25 eV for SnF_2 modified $CsSnBr_3$) between the conduction band minimum (CBM) of the perovskite and CBM of the TiO_2 layer (in UHV).

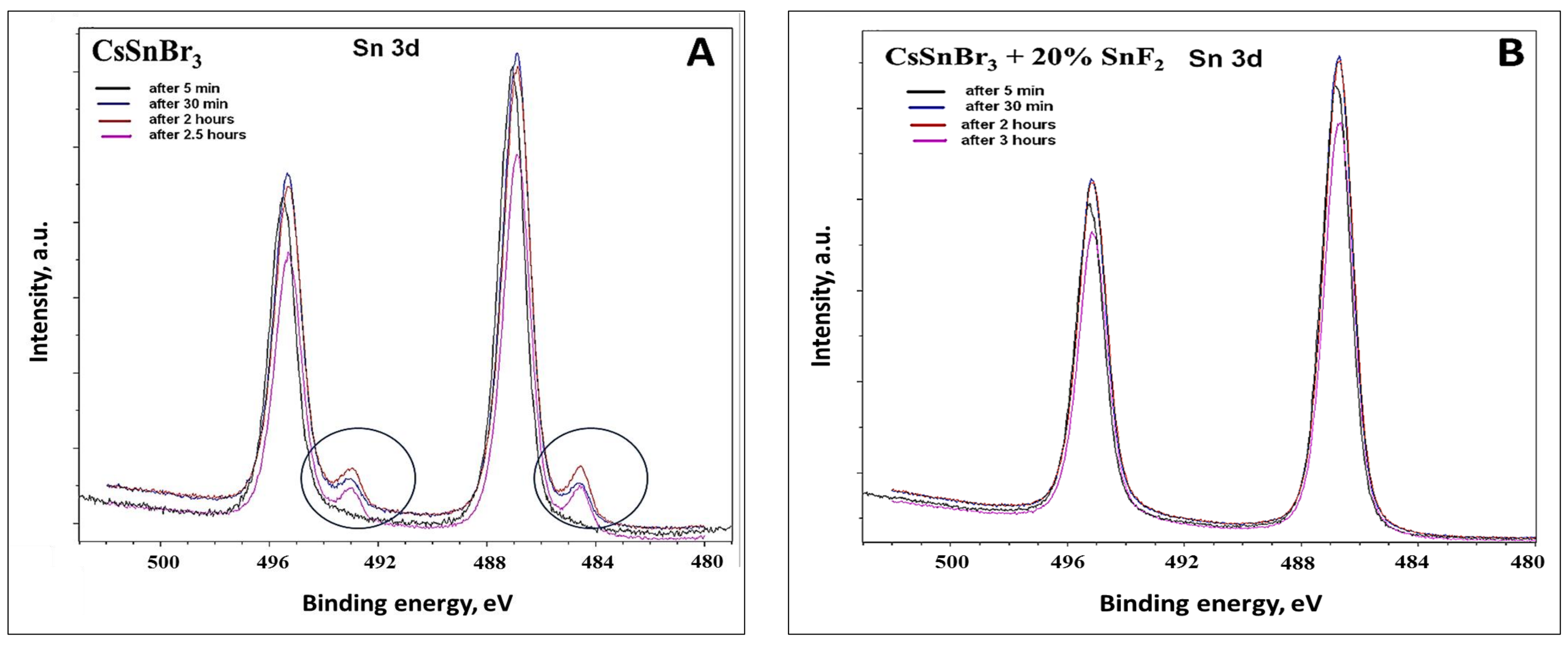


✓ → *high recombination of the photoexcited charge carriers with the photogenerated holes during illumination!*

Large voltage loss across perovskite/HTM (spiro) interface.

✓ → *explains most voltage loss in Sn HaP solar cells!*

Stability under X-irradiation



Time-dependent XPS analysis shows that pristine $CsSnBr_3$ is susceptible to beam-damage (metallic tin formation is observed within ~0.5 h of continuous X-irradiation; *Fig. A*).

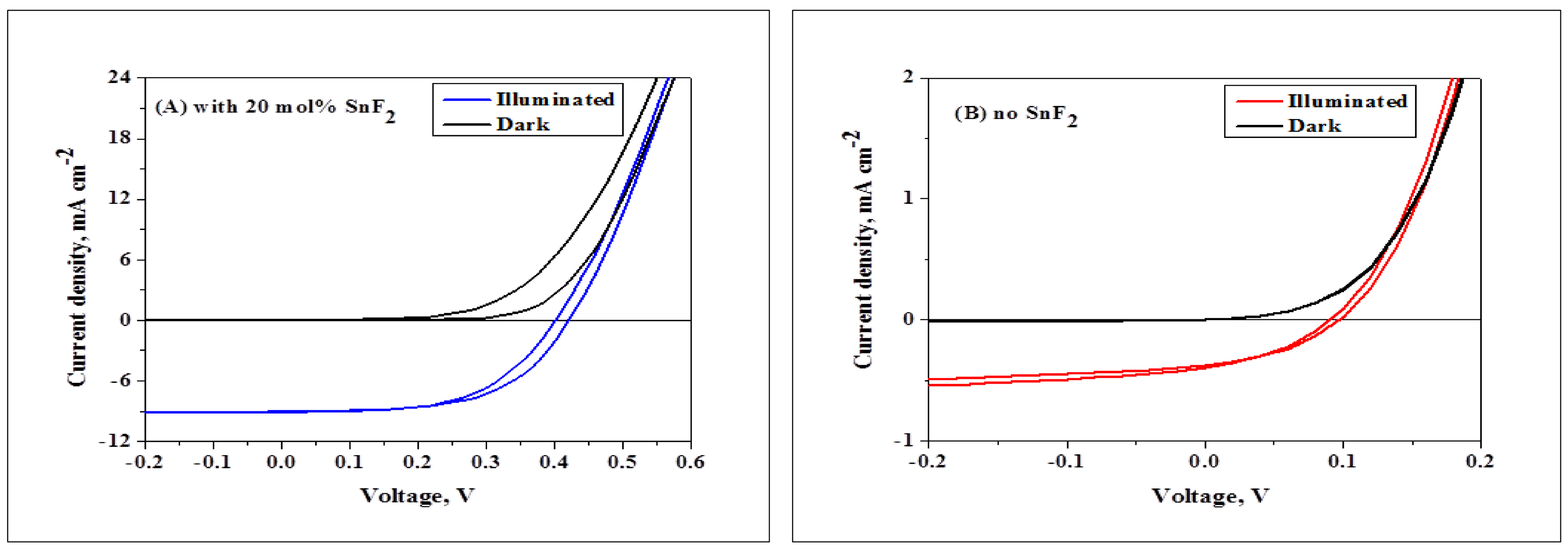
Addition of 20 mol% of SnF_2 improves HaP stability to such extent that no beam damage is observed after 2.5 h of continuous X-irradiation (*in vacuo*) - *Fig. B*.

Acknowledgements

This research was supported by the Israeli Ministry of National Infrastructures, Energy and Water Recourses as part of an ERA-net project and by the Israel Ministry of Science and Technology's China-Israel program.

J -V Analysis

Best performing devices: (measured at simulated AM1.5G)

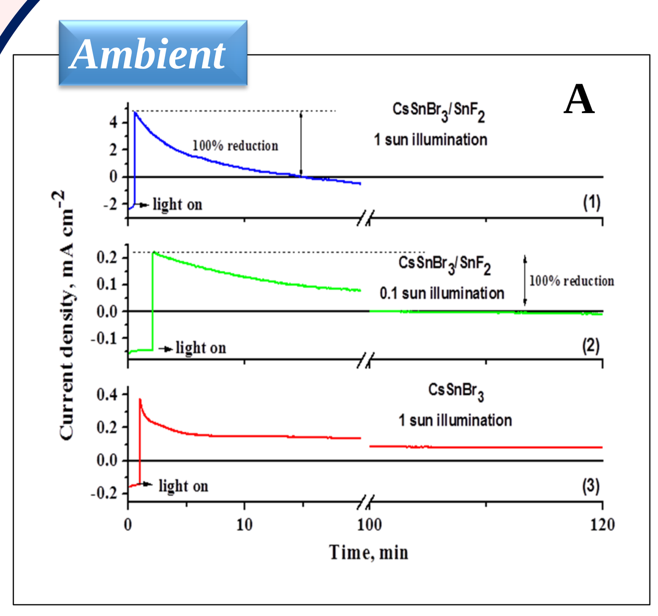


Scan direction	V_{OC} (Volt)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
FWD	0.4	9.1	56	2.04
REV	0.42	9.1	57	2.17

Scan direction	V_{OC} (Volt)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
FWD	0.1	0.4	33	0.01
REV	0.1	0.4	38	0.01

~200 times increase in power conversion efficiency (PCE) and large improvement in all PV parameters are observed with 20 mol% of SnF_2. *We are studying possible causes for this behavior, such as, reduction in background carrier density due to lower doping and/or decreased trap density.*

Operational stability-close to max. power point

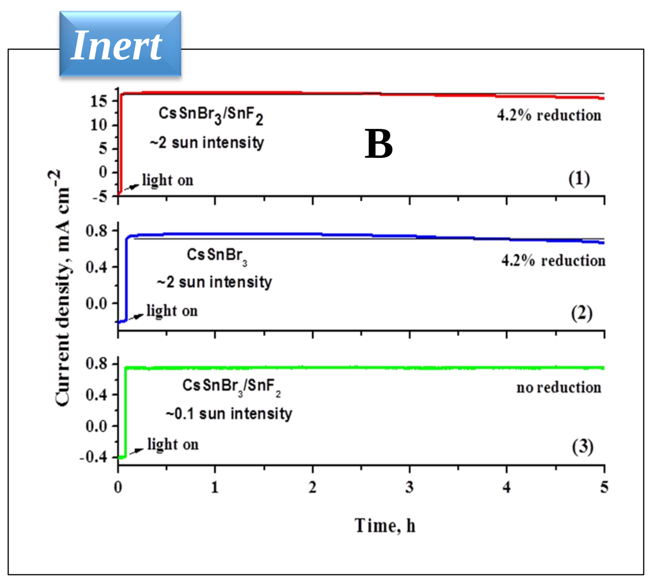


Strong reduction in the photocurrent density (*Fig. A (1)* and *(3)*) of the cell is observed, when measured in ambient atmosphere (~65% RH with 1 sun intensity).

✓ → *coupled effect of moisture-mediated decomposition and oxygen-mediated oxidation of Sn^{2+} to Sn^{4+}.*

If such an experiment ($CsSnBr_3$ with 20 mol% SnF_2) is performed at lower light intensity (~0.1 sun), the decay rate in photocurrent is ~6 times slower (*Fig. A (2)*).

✓ → *role of photogenerated charges in instability, possibly by influencing the moisture and/or O_2-mediated degradation rate.*



Devices maintain most of their initial photocurrent, if measured in inert atmosphere (with white LED, ~2 sun intensity) (*Fig. B (1) and (2)*), and are stable for 5 h.

✓ *If the device with SnF_2 was illuminated with low-intensity white light (~0.1 sun LED light) to give a current density, comparable to that of cells made without SnF_2, no reduction in photocurrent was observed (Fig. B (3)).*

Conclusions

The presence of SnF_2 with $CsSnBr_3$: *(1)* improves band-alignment at the perovskite cell interfaces, *(2)* increases the stability to X-ray beam damage, compared to pristine $CsSnBr_3$ and *(3)* somewhat improves cell stability under operating conditions.

The operational instability in ambient air and relative stability under inert conditions suggests that, with suitable encapsulation, tin HaP-based solar cells may become useful, either/both as stand-alone modules or as part of larger cell systems.