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## FUNCTIONAL DEVICES BASED ON CsSnI<sub>2</sub>Br<sub>4</sub> PEROVSKITE SEMICONDUCTOR MATERIAL USING ELECTRO-PRINTING- TECHNOLOGY

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## Functional devices based on CsSnI<sub>2</sub>Br<sub>4</sub> Perovskite semiconductor material using electro-printing-technology

### Introduction

Inexpensive mass printing of semiconductor functional devices such as photovoltaic cells, diodes, transistors, LEDs etc., for smart packaging applications has a potential of a considerable market size, and is a desirable goal. This goal could not be achieved with traditional crystalline or even polycrystalline Silicon or similar semiconductor materials.

Originally, hybrid halide perovskites with the general formula of ABX<sub>3</sub> are structural analogs of the natural mineral CaTiO<sub>3</sub>, while A is a monovalent, organic or alkali metal cation, M is a divalent p-block metal (typically Pb, Sn, and Ge), and X is a halide anion [1].

During the past ten years, a power conversion efficiency (PCE) of hybrid halide perovskite photovoltaic cells based on MAPbX<sub>3</sub> (X = I, Br) has soared from 3.8% in 2009 [2] to over 22%. Lead halide MAPbI<sub>3</sub> perovskite - exhibited a skyrocketing certified PCE state-of-the-art 22.1% [3]. Realizing the highest-performing solution-processed solar cell on record, rivaling commercial crystalline silicon solar cells in efficiency. This high conversion efficiency indicates that functional devices of any sort can be "printed" using LEP technology.

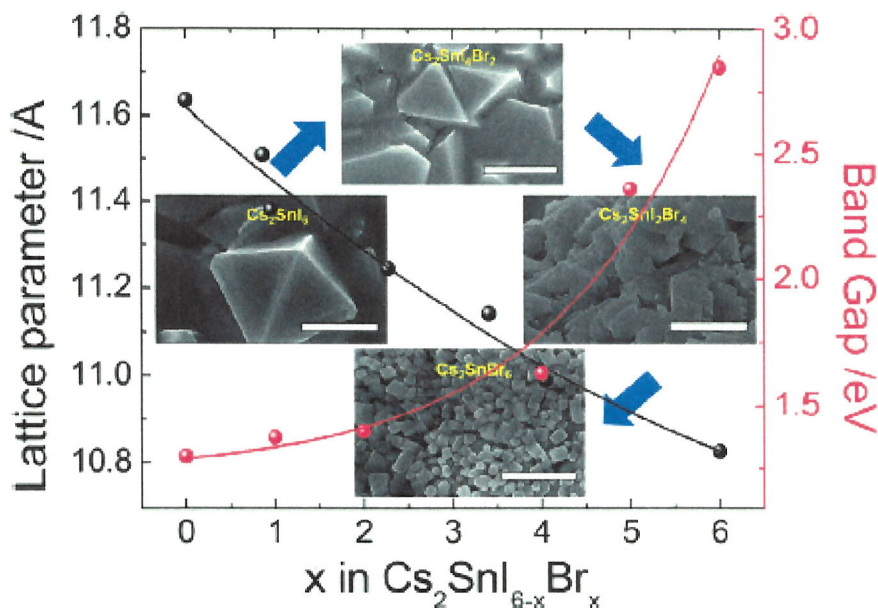
Perovskites possesses many ideal semi-conducting properties. Thanks to its electronic configuration, 3D lead MAPbI<sub>3</sub> the archetypal hybrid halide perovskite, such as a direct bandgap ( $E_g$ ) of 1.53 eV, [4] small exciton binding energies (37 or 45 meV), [5-7] long charge carrier diffusion lengths over 3.5  $\mu\text{m}$ , [8, 9] and excellent charge carrier mobilities [10-11]. These properties permit charge carriers to hop over large potential barriers when moving from one particle to another on the chaotically organized particles in LEP printed ink layer. This property is the main reason that prohibited crystalline/polycrystalline Silicon like materials from being printed on foldable substrates.

Toxicity issue of the lead, however, prohibits its use for commercial printing. Second best alternative to Lead, Tin-halide perovskite materials are a viable for lead-free, high-efficiency active layers for photovoltaic cells. These however suffer from two issues. The first is its lower PCE when compared with Lead based materials. The other issue is stability over time. In our laboratory we have synthesized formamidinium tin iodide (FASnI<sub>3</sub>) demonstrating poor stability rapid spontaneous disintegration even when immersed in oil.

Substitution of Pb with Sn in the lattice reduces toxicity but compromises the air stability of these materials. Use of tetravalent rather than divalent tin can help solve this issue. The deficient perovskite Cs<sub>2</sub>SnI<sub>6</sub> consists of air-stable tetravalent Sn<sup>4+</sup> and has a similar crystal structure to CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The main difference between the two is that, in Cs<sub>2</sub>SnI<sub>6</sub>, Sn<sup>4+</sup> cations only occupy half of the perovskite heavy-metal centers, whereas in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, every heavy-metal center is occupied creating a 3D network of vortex-sharing [PbI<sub>6</sub>]<sup>4-</sup> octahedra. The latter

leads to formation of isolated  $[\text{SnI}_6]^{2-}$  octahedra in the crystals of  $\text{Cs}_2\text{SnI}_6$ .

Compounds based on  $\text{Cs}_2\text{SnX}$  ( $X = \text{I}_{6-x}\text{Br}_x$ ) for a range of  $x$  provides a variety of bandgaps from 1.3 eV to 2.9 eV with  $x < 3$  being suitable for solar cell design. The Sn in this compound is in the  $4^+$  oxidation state, and thus it is much more stable with respect to oxidation and more resistant to hydrolysis during processing and device operation. Lee et. [13] has fabricated and characterized a series of  $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$  films and have demonstrated that the most stable material is  $\text{Cs}_2\text{SnI}_4\text{Br}_2$  showing 2% CE for over 2 months. Fabrication technology used in that paper is aiming for thin film technology. Because of stoichiometric and lattice constant matching, the higher the  $X$  the smaller is the average of particle size in the film. At  $x=4$  the size is several hundred nanometers. See the figure. This value is suitable for HP-Indigo liquid electro printing (LEP) technology. It can make ink from particles in the size of several hundred nanometers to several microns. But the making of this microcrystalline  $\text{Cs}_2\text{SnI}_4\text{Br}_4$  must be reconsidered.



The change in the lattice constant and the shift in the optical band gap both indicate the solid-solution nature of the  $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$  system (inset: the surface morphologies of different compounds (SEM scale bar is 1  $\mu\text{m}$ ) from [13]).

	Band gap ( $E_g$ )	VOC (V)	$J_{sc}$ ( $\text{mA}/\text{cm}^2$ )	FF (%)	Eff (%)
$\text{Cs}_2\text{SnI}_4\text{Br}_2$	1.40	0.563	6.225	57.7	2.025
$\text{Cs}_2\text{SnI}_2\text{Br}_4$	1.63	0.575	3.413	54.8	1.081

Table shows the results for  $\text{Cs}_2\text{SnI}_{6-x}\text{Br}_x$  photovoltaic cells of Lee et al., Ref [13].

## Synthesize

For this work, synthesis of lead free Cs<sub>2</sub>SnI<sub>2</sub>Br<sub>4</sub> perovskite crystalline powder with prospects of enhanced stability is performed. We adopt the procedure described by Dolzhanov et. al. [14] synthesizing Cs<sub>2</sub>SnI<sub>6</sub> nanocrystals (NC) to synthesized Cs<sub>2</sub>SnBr<sub>6</sub> NC.

Using a method modified from the synthesis of CsPbX<sub>3</sub> nanocrystals, on the basis of the reaction  $4\text{CsOA} + 2\text{SnBr}_4 \rightarrow \text{Cs}_2\text{SnBr}_6 + 2\text{CsBr} + \text{Sn}(\text{OA})_4$  a typical synthesis, 117 mg (0.187 mmol) of SnBr<sub>4</sub> was added to 10 mL of octadecene (ODE) in a 25 mL three-neck round bottom flask. We heated the mixture to 80 °C under vacuum (<0.1 Torr) for 15 min and then switched the system to a nitrogen atmosphere. After resetting the temperature of the solution to the desired temperature (80, 100, 120, 150, 190, or 220 °C, depending on the desired size of the NC), we quickly injected 0.2 mL of prepared cesium oleate (CsOA) solution in ODE to the mixture. A black suspension formed immediately after the injection, and the reaction was quenched right away by cooling the mixture to room temperature with a cold-water bath. We collected the product by centrifuging the suspension at 7000 rpm for 5 min. The black pellet was resuspended in 5 mL toluene and was centrifuged again to remove leftover ODE and byproducts of the reaction.

Finally, the nanocrystals were resuspended in 2 mL of toluene to make a ~10 mg/mL suspension. Unlike the synthesis of lead-halide perovskite NCs, our synthetic procedure for Cs<sub>2</sub>SnBr<sub>6</sub> NCs requires no surfactants, such as stearic or oleic acid or oleylamine, to dissolve the Sn precursor. SnBr<sub>4</sub> is nonpolar enough that it dissolves in pure ODE at 60–80 °C. In fact, the addition of these surfactants interrupts the reaction between SnBr<sub>4</sub> and CsOA by forming stable carboxyl complexes of Sn<sup>4+</sup>. Within these complexes, shows an X-ray diffraction (XRD) pattern of a film of Cs<sub>2</sub>SnBr<sub>6</sub> NCs, synthesized at 190 °C and deposited on glass. The pattern indicates that the film consists of primarily Cs<sub>2</sub>SnI<sub>6</sub> (blue reference curve) with minor (3 wt %) contamination.

Currently we are working to improve the process and optimize ink preparation making it suitable for LEP printing.

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