

LEAD-FREE ORGANIC-INORGANIC TIN HALIDE PEROVSKITES FOR PHOTOVOLTAIC APPLICATIONS

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Solar Photovoltaic (PV) technology is based on the conversion of solar radiation into electrical power. To do so, an active semiconducting material, with a proper bandgap value, must absorb the incident radiation and generate a hole–electron pair. The two opposite charges are then collected by two different electrodes, and will then recombine in an external circuit, generating power.

Halide Perovskites Solar Cells (PSC) are considered the most promising technology to deliver the next generation of photovoltaic, thanks to their high efficiency and flexibility together with a cheap production. Indeed, halide perovskite can be processed from inexpensive starting materials with deposition method already in use for organic electronics (i.e. spin coating, blade coating, vapour deposition). The term perovskite is given to all compounds, which have the general chemical formula AMX_3 . In Organic–inorganic metal tri-halide perovskites A is an organic or inorganic cation, M a divalent metal ion, and X a halide or any mixture thereof (see Figure 1). Choosing (or combining) the different constituents, make it possible to achieve a large variety of optoelectronic properties for this materials.

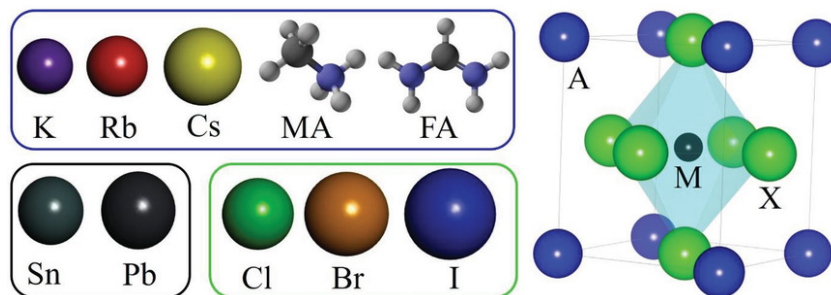


Figure 1: cations (in the blue box), metals (black box), and anions (green box) in an AMX_3 perovskite structure (right side). M. Saliba, *Adv. Energy Mater.* 2019, 9, 1803754

The efficiency of PSC have rapidly increased over the past decade, now reaching > 25% efficiency for single junction device and > 29% when used in tandem perovskites-silicon solar cells. However, the most efficient devices contain Lead (Pb), raising concerns regarding the sustainability of a potential large-scale commercialization of this technology.

Tin (Sn) its considered the most likely substitute of Pb, due to the similar ionic radius and belonging to the same group 14 of the period table. Moreover, tin halide perovskites have the optimal bandgap theoretically, between 1.1 and 1.4 eV, to reach the highest possible efficiency following the Shockley–Queisser (QS) limit (i.e., 33.7 % at 1.34 eV). However, it is known that Sn^{2+} is more prone to oxidation to Sn^{4+} , condition that is detrimental for the photovoltaic performances, both in terms of efficiency and stability.

Recently it has been demonstrated that the oxidation of Sn^{2+} can be already promoted in the solution of the precursors, before the formation of the perovskite thin film. In particular dimethyl sulfoxide (DMSO), which is the most common solvent in perovskites processing, is responsible for this oxidation.

Therefore, our activity focuses on the optimization and characterization of tin-based perovskite solar cell processed from DMSO free systems. The first period of this PhD project has been devoted to the optimization of the deposition protocol of $ASnI_3$ thin films on different substrates, exploring different solvents mixtures, different solution concentration and composition and processing parameters. Indeed, controlling the perovskite crystallization is crucial to obtain a uniform, smooth and pin-holes free film.

Future activities will be devoted to the optimization of the photovoltaic devices in their entirety, in particular to the optimization of the interfaces between the metal-organic perovskites and the selective contacts. Such interfaces can significantly limit the efficiency of the cell due to unwanted recombination phenomena by under-coordinated atoms at the perovskite/contacts interfaces. The strategy of passivation of the perovskite surface proposed by us exploits halogen bonds, one type of non-covalent interaction, between the halogen ions of perovskite and small organic molecules of halides, forming self-assembled monolayers (SAM). This strategy could also limit the exposure to external agents, and so limit the Sn²⁺ oxidation.

The effect of SAMs on the modulation of the energy level alignment of the device will be also investigated, employing molecules equipped with a spontaneous electric dipole.

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