

# Abstract

Halide perovskites promise various advantageous properties that are unique to this hybrid organic/inorganic material class, making them a topic of great interest in the field of solar cell applications. In the span of a handful of years, halide perovskites have proven their potential to achieve device efficiencies exceeding 20%, rivaling other thin film device technologies. However, there have been difficulties across research labs to fabricate this material in a reproducible fashion, leading to large variations in device efficiency and basic physical properties reported in the literature.

Consequently, in the first part of this work, an extensive study of the electronic structure of a large number of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  (MAPbI<sub>3</sub>) perovskite films produced with different preparation methods and by varying precursor ratios was done. Combined investigations using ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) reveal that variations in film stoichiometry lead to changes in the occupied density of states (DOS) close to the valence band (VB), and changes in the ionization energy (IE), which can be intentionally tuned by almost 1 eV. X-ray diffraction (XRD) measurements reveal that variations in film stoichiometry do not lead to the formation of separate phases, but the resulting interstitials are homogeneously distributed within the material. A clear correlation is found between the changes in DOS and the overall power conversion efficiency (PCE) of solar cells when the MAPbI<sub>3</sub> material, prepared with different PbI<sub>2</sub> to MAI stoichiometries, is implemented as the active layer.

In the past couple of years, increasing attention has been given to exploring the effects of the intentional addition of heterovalent and isovalent cations (to lead) on perovskite thin films. The controlled modification of perovskite films by doping and/or alloying could potentially play a key role in the future success of this material and its applications; not only for use in the field of photovoltaics but also for use in light-emitting diodes (LEDs), lasers, and photodetectors. However, challenges still remain to fundamentally understand the role of the extrinsically incorporated ions.

In this light, the second part of this work studies the introduction of various metal substituents (Sr, Bi, Cd, Cu, Sb, Co, Mn, Al, and In), heterovalent and isovalent to lead, into MAPbI<sub>3</sub>. The impact of the substituents on the electronic states and properties, structural, and optical properties of the MAPbI<sub>3</sub> film is shown. Photoelectron spectroscopy measurements show that In, Bi, Sb and Sr are successfully incorporated into the films in various oxidation states. However, the introduction of these metals does not result in obvious doping effects.

Notably, combined investigations show that the introduction of In and Bi result in the formation of a significant surface dipole (*ca.* 1000 and 400 meV respectively), with the formation of InI and BiI<sub>3</sub> layers on the perovskite film surface being the underlying reasons. The introduction of heterovalent metals result in the most significant changes in conductivity, with In resulting in an enhancement of *ca.* one order of magnitude, and Bi increasing the conductivity by *ca.* four times.