

Degradation of methylammonium-free mixed-cation perovskites under thermal and moist conditions investigated with multiple photoelectron spectroscopic techniques

Suresh Maniyarasu^{1,2}, Jack Chun-Ren Ke^{1,2}, Ben F. Spencer^{2,3,4}, Alex Walton^{2,5}, Andrew G. Thomas^{2,3,4} and Wendy R. Flavell^{1,2,3}

¹Department of Physics and Astronomy, University of Manchester, UK, ²Photon Science Institute, University of Manchester, UK, ³The Henry Royce Institute, University of Manchester, UK, ⁴Department of Materials, University of Manchester, UK, ⁵Department of Chemistry, University of Manchester, UK.

X-ray photoelectron spectroscopy (XPS), and in particular, near-ambient pressure XPS (NAP-XPS) allows us to study surface reactions in atmospheric (gaseous) conditions. These measurements may be further complemented using hard X-ray photoelectron spectroscopy which probes materials from the surface into the bulk region (up to hundreds of nm from the surface) due to an increased inelastic mean free path [1]. The combination of these techniques provides unique insights into the chemical composition of materials.

The stability of perovskite-based solar cells has recently been improved when alkali metal cations (caesium- (Cs^+) and rubidium- (Rb^+)) are added as an absorber material [2]. Understanding the nature of these alkali cations is therefore of high interest. Here, the degradation of two perovskite compositions ($\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ and $(\text{FACs})_{0.9}\text{Rb}_{0.1}\text{PbI}_3$) was investigated using three XPS techniques. Heat-induced degradation was assessed at two temperatures (100 °C and 150 °C) in ultra-high vacuum conditions, and moisture-induced degradation was investigated in the presence of 9 mbar of water vapour using NAP-XPS. The chemical composition as a function of depth was measured using angle-resolved HAXPES using a novel laboratory-based 9.25 keV source. HAXPES of deeper core levels (e.g. Cs 2p and Rb 2p) enables a greater sensitivity to these dilute elements compared to XPS.

We demonstrate that $\text{FA}_{0.9}\text{Cs}_{0.1}\text{PbI}_3$ decomposes with formation of metallic lead (Pb^0) upon heating via loss of iodine, however, $\text{FA}_{0.85}\text{Cs}_{0.1}\text{Rb}_{0.05}\text{PbI}_3$ exhibits the formation of an RbPbI_3 phase which suppresses this degradation. Interestingly, no changes in the chemical composition were measured under humid conditions, which indicates that thermal stress has a larger impact upon the perovskite degradation than humidity. HAXPES measurements demonstrate the distribution of the alkali metal cations in the surface layer. These combined measurements provide insight into the degradation mechanisms involved, and may therefore provide insights into the design of more stable perovskite solar cells.

[1] B. F. Spencer, *et al.*, *Applied Surface Science* **541**, 148635 (2020).

[2] B. Philippe, *et al.*, *Chemistry of Materials* **29**, 3589 (2017).