

# The Impacts and Origins of A-site Instability in Formamidinium-Cesium Lead Iodide Perovskite Solar Cells Under Extended Operation

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**Abstract**—Improved understanding of the origins of instability during photovoltaic operation of perovskite solar cell materials must be established to overcome barriers to commercialization. In this study, we analyze the microscopic mechanisms of degradation in high-performing methylammonium free (FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub>) perovskite solar cells (PSC) over 600 hours of operation under stressors inherent to PV operation, including heat, illumination, and a load while excluding atmospheric effects by testing in a water- and oxygen-free atmosphere. While the PSCs exhibit reasonable thermal stability, they show considerable performance loss under constant illumination or stable power output. Synchrotron-based nanoprobe X-ray fluorescence and X-ray beam induced current (XRF/XBIC) measurements reveal segregation of current-blocking Cs-rich phases during stress testing. The decrease in performance correlates with the resulting number density of the Cs-rich clusters, which varies by stress condition. These findings

unveil cation-dependent instability in FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub> perovskites and provide a framework for understanding the energy landscape in alloy perovskites to guide the engineering of long-lived halide perovskite devices.

**Index Terms**—Halide Perovskites, intrinsic stability, phase segregation, nano-XRF/XBIC

## I. INTRODUCTION

The performance of organic-inorganic halide perovskite solar cells (PSCs) has improved dramatically in the past decade, with the highest certified power conversion efficiency (PCE) of 25.2% using a polycrystalline perovskite absorber, [1] close to state-of-the-art crystalline silicon solar cells. Halide perovskites have the ABX<sub>3</sub> structure, and high-performing

perovskite absorbers are typically comprised of mixed MA/FA (methylammonium (MA<sup>+</sup>) and formamidinium (FA<sup>+</sup>) A-site cations and Br/I X-site anions. [2] Despite their impressive device performance, the stability of MA-containing and mixed Br/I perovskite is limited by light and heat exposure, due to the volatile nature of the MA molecule and light-induced phase segregation in mixed halide systems. [3], [4] Furthermore, the difficulty in homogenized mixing in micro- or nano- scale can lead to chemical heterogeneity in mixed halide perovskites. [6] Upon preparing absorber with simple composition, the photoactive black  $\alpha$ -phase of pure FAPbI<sub>3</sub> is not thermodynamically stable at room temperature and will spontaneously change to the photoinactive yellow  $\delta$ -phase in room temperature, [5] incorporation of Cs<sup>+</sup> on the A-site is found to stabilize the perovskite structure, yielding PSCs with initial efficiency above 20%. [7]

Although A-site alloying of MA-free PSCs have demonstrated high efficiency with enhanced thermal stability, [7] investigation of remaining degradation mechanisms in MA-free devices upon aging under operational conditions is needed. In particular, microscopic characterization of degradation may help elucidate reaction mechanisms. In this study, we monitor performance of high-performing MA-free (FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub>) PSCs over 600 hours of various environmental stressors, including dark, heat, illumination (at V<sub>oc</sub>) and stabilized power output (SPO, with fixed electric load). [8] Combining current density-voltage (J-V) measurement and synchrotron based X-ray fluorescence (XRF) mapping, we reveal that absorber degradation under prolonged testing is associated with formation of photoinactive Cs-rich clusters. The driving force of the phase segregation appears to be condition dependent, in which Cs clusters of different size and number density are observed. These findings reveal cation-dependent instability in FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub> perovskites and provide guidance for engineering long-lived halide perovskite devices.

## II. EXPERIMENTAL AND RESULTS

The devices, with a nominal absorber composition of FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub>, are fabricated adapting a previously reported method. [9] The devices have the conventional n-i-p architecture: ITO/SnO<sub>2</sub>/Perovskite/Spiro-ometad hole transport layer (HTL)/Au with the champion device achieving an initial PCE of 20.12%.

The devices are subjected to four distinct stress conditions: (1) 85 °C heating in the dark (labelled **Heat**), 1 sun illumination at near room temperature (35 ± 10 °C) at (2) open circuit condition (labelled **Light**) and (3) stabilized power output at the maximum power point at near room temperature (labeled **SPO**). The reference sample (labeled **Ref**) is (4) stored in the dark. All samples under stress conditions are maintained in an N<sub>2</sub> environment for a total time of 600 hours. The devices are unencapsulated throughout.

Operating perovskite solar cells are investigated by means of synchrotron-based nanoprobe X-ray fluorescence (n-XRF) with a 250 nm full-width half-maximum focused beam at 7 keV in a helium environment at beamline 2-IDD of the

Advanced Photon Source (APS) at Argonne national Laboratory. The *in-situ* n-XRF and XBIC (X-ray beam induced current) characterization was conducted using a similar setup as previous studies, [10] allowing collection of both elemental distribution (n-XRF) and XBIC simultaneously.

The nano-XRF maps reveal widespread phase segregation in the perovskite absorber for devices that were subjected to the stressing conditions (Ref, Heat, Light and SPO). The local Cs:I stoichiometry is homogeneous within Ref perovskite device but shows a clear phase separation in all stressed devices. The underlying degradation mechanism appears linked to the number of charge carriers (the injection level), resulting in a varying size and density of the Cs-rich clusters according to the stress condition. [8]

## III. CONCLUSION AND OUTLOOK

*In-situ* XRF/XBIC demonstrates its unique capability on revealing the chemical and electronic relationship in halide perovskites. From the XRF/XBIC data, either 1-sun illumination or heating like that present in the field is enough to induce degradation over hundreds of hours of operation by microscopic phase separation into an inactive Cs-rich secondary phase. This microscopic assessment reveals the cation-dependent instability in FA<sub>0.9</sub>Cs<sub>0.1</sub>PbI<sub>3</sub> perovskites, which provides additional guidance on designing the alloy perovskite devices with improved photo-stability.

## IV. ACKNOWLEDGEMENT

The work at UC San Diego was supported in part by the California Energy Commission (EPC-16-050) and the National Science Foundation under Grant No. DMR-1848371.

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