

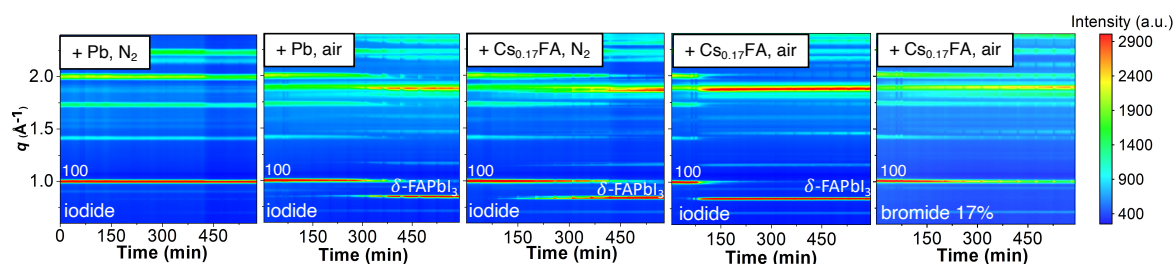
## Beyond humidity: the underlying phase transitions in cesium-formamidinium lead halide perovskites

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Lead halide perovskites have shown to be promising materials for solar cells, having achieved a maximum power conversion efficiency greater than 25%. However, lead halide perovskites are highly unstable under different environmental conditions such as humidity. The underlying phase transitions upon humidity in high-efficiency mixed cation compositions, such as cesium-formamidinium (Cs-FA) in  $(\text{Cs}_x\text{FA}_{1-x})\text{PbI}_3$ , are still unexplored. Given that compositional mixing has been a strategy to stabilize the crystal structure, it is paramount to unravel the degradation pathway of these materials to design robust and efficient materials. Herein, we did an *in-situ* humidity X-ray scattering study to unravel the intermediate and final degradation phases of Cs-FA lead halide perovskites.

Single cation FA and Cs lead iodide perovskites ( $\text{CsPbI}_3$ ,  $\text{FAPbI}_3$ ) suffer from phase instability at room temperature. The mixture Cs-FA has led to improved stability [1], but not when exposed to humidity. In this work, different humidity conditions were studied such as the humidity carrier gas, the material's stoichiometry, and the halide composition (Fig.1). The degradation kinetics were observed, demonstrating that humidity in air accelerated the formation of the hexagonal non-perovskite  $\delta$ - $\text{FAPbI}_3$  phase. Degradation was also faster for the off-stoichiometric composition with a 5 percent molar excess of the Cs-FA cation. Moreover, a different route was observed in the mixed iodide-bromide halide perovskites compared to the pure iodide one. Bromide hindered degradation and it transformed into other numerous non-perovskite hexagonal phases such as 4H and 6H [2]. Further, a comprehensive structural powder X-ray diffraction refinement was done by the Le Bail method.



**Figure 1.** In-situ X-ray scattering as a function of time for i) different humidity carrier gas ( $\text{N}_2$  or air), ii) stoichiometry (excess Pb or excess CsFA), and iii) halide composition (iodide or iodide-bromide) in a relative humidity of  $\sim 100\%$

The humidity degradation pathways of the high-efficiency Cs-FA lead halide perovskites were observed. The origins of the phase transitions of the perovskite go beyond humidity: the carrier gas and the elements present in the solid solution play an important role in determining the degradation kinetics. For this reason, it is needed to understand the role of oxygen in the acceleration of degradation. It is also essential to understand the mechanism of why the mixed halides prevent the degradation of lead halide perovskites.

- [1] J. W. Lee, D. H. Kim, H. S. Kim, S. W. Seo, S. M. Cho, and N. G. Park, "Formamidinium and cesium hybridization for photo- and moisture-stable perovskite solar cell," *Adv. Energy Mater.*, vol. 5, no. 20, 2015, doi: 10.1002/aenm.201501310.
- [2] P. Gratia *et al.*, "The Many Faces of Mixed Ion Perovskites: Unraveling and Understanding the Crystallization Process," *ACS Energy Lett.*, vol. 2, no. 12, pp. 2686–2693, 2017, doi: 10.1021/acsenerylett.7b00981.

J.H acknowledges support from the DAAD and GEM fellowship.