

# Accelerated Stability Testing of Perovskite Photovoltaic Materials Reveals Dependence on the Halide Composition

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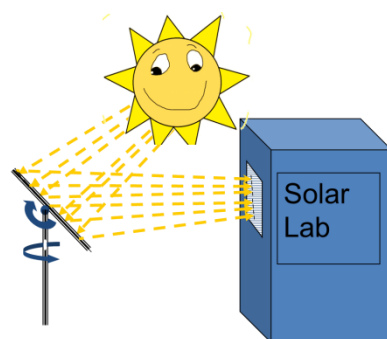
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A significant challenge for the commercialization of perovskite-based PV is combining high efficiency and long-term stability. Accelerated stability tests can be used to rapidly characterize new PV materials and promote the development of stable and efficient devices. We recently demonstrate a methodology for stability testing using concentrated sunlight that allows independent control of light intensity, the sample temperature and environment.<sup>1</sup> Such accelerated stability studies of perovskite thin films showed that encapsulated MAPbBr<sub>3</sub> films were more stable than MAPbI<sub>3</sub> films following exposure to concentrated sunlight of 100 suns (1 sun = 100 mW/cm<sup>2</sup>). Joint analysis of light absorbance and XRD data suggests that decomposition occurs via crystallization of PbI<sub>2</sub> during exposure of MAPbI<sub>3</sub> film. Heating was found to accelerate photo-degradation, however heat only (in the dark) did not induce decomposition of the perovskite films. The improved stability of MAPbBr<sub>3</sub> films was related to differences in Br-related bond strengths and in the perovskites' crystalline forms: The Pb-Br bond was previously calculated to be stronger and shorter compared to the Pb-I bond. The MAPbBr<sub>3</sub> is cubic at room temperature, whereas MAPbI<sub>3</sub> is in tetragonal crystal arrangement in a distorted 3-D perovskite structure. Since cubic structures may be denser than tetragonal ones, they are expected to be less prone to attack. In addition, hybrid halide perovskites are expected to be stabilized by halogen-(amine) hydrogen bonds. The increased

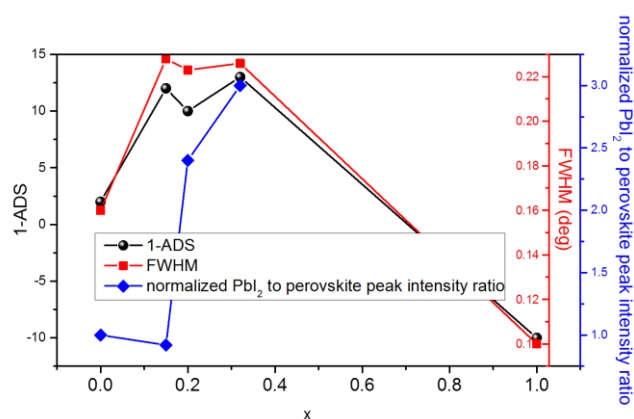


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<sup>1</sup> I. Visoly-Fisher, A. Mescheloff, M. Gabay, C. Bounioux, L. Zeiri, M. Sansotera, A. E. Goryachev, A. Braun, Y. Galagan, E.A. Katz, *Sol. Ener. Mater. & Sol. Cells* 134 (2015), 99–107.

strength of the H-Br bond compared to the H-I bond, resulting from larger Br electronegativity, can further contribute to the relative stability of MAPbBr<sub>3</sub>.<sup>2</sup>

Tuning the energy band gap, hence the absorption spectrum, by changing the halide anion composition, is an important advantage of these perovskites. We postulated that combining the better photovoltaic performance of MAPbI<sub>3</sub> with the added stability of its bromide counterpart, by using mixed compositions of MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub>, would yield an optimized PV material. However, we found that MAPbI<sub>3</sub> and MAPbBr<sub>3</sub> are more stable than mixed halide compositions, under both concentrated sunlight and 1-sun exposures. The photolysis decomposition of the mixed halide perovskites is suggested to proceed via formation of MAI, PbI<sub>2</sub> and a Br-richer mixed halide perovskite as a first step, which is followed by further MAI decomposition into volatile species and iodine. The degradation in absorption and decomposition were found to correlate with an increase in the Full Width at Half Maximum (FWHM) of the XRD peaks for mixed halide perovskites compared to MAPbI<sub>3</sub> and MAPbBr<sub>3</sub>. The FWHM of XRD peaks is inversely related to the crystal coherence length, therefore the observed FWHM increase indicates that the mixed halide perovskites contain more structural defects and/or grain boundaries compared to pure halide perovskites. The decreased grain sizes in the mixed halide films have been confirmed by Scanning Electron Microscopy. Both the smaller grain size and the enhanced decomposition rate of the mixed halide perovskite films can be explained by the presence of halide ions with different sizes, distorting the octahedral structure of [PbI<sub>6</sub>]<sup>4-</sup> and inducing a corresponding strain amplification in the pseudo-cubic structure of the MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> solid solutions.<sup>3</sup> The role of grain boundaries in the photochemical degradation of perovskite PV materials should be further investigated.



<sup>2</sup> R. K. Misra, S. Aharon, B. Li, D. Mogilyanski, I. Visoly-Fisher, L. Etgar, E. A. Katz, *J. Phys. Chem. Lett.* 6 (2015), 326–330.

<sup>3</sup> R. K. Misra, L. Ciammaruchi, S. Aharon, D. Mogilyanski, L. Etgar, I. Visoly-Fisher, E. A. Katz, submitted.