

# Influence of Bromine and Camphorsulfonic Acid on the Crystallization Dynamics and Long-Term Performance of Organic-Inorganic Perovskites

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In recent years, halide perovskites have gained increasing attention due to their significant potential applications, notably in photovoltaic cells, as well as in light sources and X-ray detectors. However, their degradation over time, particularly when exposed to light, oxygen, and humid air, coupled with issues concerning reproducibility in their technology, currently hinders their market introduction. Consequently, numerous studies worldwide are dedicated to understanding the degradation mechanisms of perovskites and enhancing the stability of their performance. It has been found that alterations in perovskite composition or the addition of extra components in precursor solutions, among other factors, influence perovskite aging. Here, we investigated the crystallization and long-term performance of methylammonium lead iodide (MAPI) and MAPbI<sub>0.85</sub>Br<sub>0.15</sub> (MAPIB) perovskites. Additionally, we examined the impact of adding camphorsulfonic acid (CSA) to the precursor solutions. CSA, being a Lewis base, is known to enhance the performance of solar cells [1]. Grazing-incidence wide-angle X-ray scattering and photoluminescence (PL) spectroscopy were employed for in situ characterization of the crystallization process, while X-ray diffraction was utilized to monitor the aging of the perovskites. Scanning electron microscopy, energy-dispersive X-ray spectroscopy (EDS), and X-ray photoemission spectroscopy (XPS) were used to analyze the morphology and chemical composition homogeneity. We observed that during perovskite formation, the addition of antisolvent to the liquid perovskite precursor resulted in the emergence of Bragg peaks corresponding to the transition phase of the DMSO solvent complex [2]. These peaks were stronger in MAPIB than in MAPI, suggesting enhanced ordering of this transition phase in the presence of Br-containing molecules, consistent with the theoretically predicted lower formation energy for Br compounds. Subsequent heating facilitated the crystallization of the respective perovskites, with stronger texturization observed in the case of MAPIB, likely resulting from better ordering of its transition phase. For both perovskites, PL exhibited higher energy at the beginning of crystallization compared to that at the end, attributed to weakening quantum confinement of the growing nanograins. The evolution of the full width at half-maximum (FWHM) of both the PL band and diffraction peaks during crystallization indicated the homogenization of the growing MAPI grains. In contrast, the larger FWHM and the lack of tendency to decrease over time for MAPIB suggested an increase in chemical inhomogeneity already at the crystallization phase, a finding further confirmed by PL and EDS measurements. Comparative analysis of XPS and other results revealed higher Br concentrations in regions closer to the surface. Additionally, during the aging process, a gradual enrichment in Br content was observed in MAPIB, reaching up to 55% within 100 days, with iodine creating PbI<sub>2</sub> degradation product. Our findings suggest stronger bonds of bromine than iodine in the crystallized perovskite, resulting in improved solar cell parameters with the addition of Br. However, bromide-iodide perovskites exhibit compositional changes starting from the initial crystallization stages due to the lower stability of iodine within the mixed-halide perovskite network.

[1] A. Wincukiewicz et al. Moll. 27, 7850 (2022) [2] S. Pratap et al. Nature Comm. 12 (2021).