Study of structural changes induced by light soaking in mixed-halide perovskites

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The organometal mixed-halide perovskites ABX_3, where typically A stands for cation like organic $MA^+ = CH_3NH_3^+$, $FA^+ = CH(NH_2)_2^+$ and/or inorganic Cs^+, B stands for Pb_2^+ and/or Sn_2^+, and X stands for halide anion I^-, Br^- and/or Cl^-, are for their inexpensive manufacturing and very favorable optoelectronic properties materials, well-suited for multi-junction solar cells. Unfortunately, mixed-halide perovskites suffer from a partial de-mixing (phase segregation) during light soaking called the Hoke effect. This operational instability has an unpleasant influence on their absorption spectrum and further optoelectronic properties. Despite intense research, there is still no clear consensus on the origin of the halide ions migration and the forces acting against a concentration gradient. To manufacture reliable long-term operating devices, it is crucial to understand and fully eliminate this effect.

In our contribution we used the combination of *in operando* and *in situ* X-ray scattering techniques, to link the evolution of the phase composition, internal strain propagation, and domain morphology to photoelectrical properties, mainly the energetic positions of PL peaks, absorptance measured by photothermal deflection spectroscopy, the concentration of deep defects accessed by FTPS, carrier lifetime extracted from PL spectroscopy and device operation through J-V measurements. The internal strain-field originating from halide-composition inhomogeneity and the halide migration was modelled by kinetic simulations. The model based on numerical solution of phenomenological Cahn-Hilliard formalism was developed and the results of numerical simulation were compared with experimental results obtained from X-ray scattering and optoelectronic measurements. In Fig. 1 the integrated intensity of the 220 diffraction maximum of $FA_{0.83}Cs_{0.17}Pb(I_{0.85}Br_{0.15})_3$ of single-crystalline sample before, during, after and long after the light illumination is shown. After illumination, the sample begins to relax; however, this relaxation is incomplete, as the diffraction maximum remains broader even after an extended relaxation period. When the cycle of illumination and relaxation is repeated multiple times - effectively increasing the total illumination time, broadening in the direction of lower Q also becomes apparent. The broadening toward higher Q suggests the creation of regions or domains with smaller lattice parameters, which correlates with an increased Br concentration. These observations highlight the complex interplay between illumination, compositional changes, and structural relaxation within the sample.

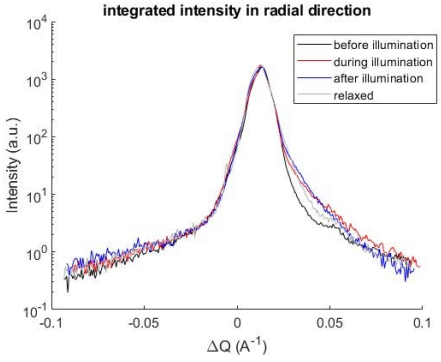

Figure 1. Intensity of the 220 diffraction maximum of $FA_{0.83}Cs_{0.17}Pb(I_{0.85}Br_{0.15})_3$ before, during, after and long after the *light illumination.*

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