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# White light-induced halide segregation in triple-cation mixed halide perovskites studied by in-situ fast scanning nano-XRF at the NANOSCOPIUM beamline, Synchrotron SOLEIL

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**Abstract.** In-situ study of the variation of the chemical composition of triple-cation mixed halide perovskites  $\text{Cs}_{0.05}(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$  under visible light illumination performed by Fast Scanning Nano Hard X-ray Fluorescence Imaging revealed the migration and irreversible phase separation of halide ions into micro-meter sized clusters.

## 1. Introduction

Organic-inorganic halide perovskites have recently attracted tremendous attention as a promising material for low-cost preparation and high efficient photovoltaic and light-emitting devices due to their unique opto-electronic properties. Indeed, their gap of ~1.5 eV allows high absorption of the visible spectrum, and they also present long carrier diffusion length and small exciton binding energy [1,2]. To date, various combinations, and ratios of monovalent organic or inorganic cations (formamidinium FA ( $\text{NH}_2\text{CH}=\text{NH}_2^+$ ), Methylammonium MA ( $\text{CH}_3\text{NH}_3^+$ ), Cs, and Rb) and halide anions (I and Br) have been optimized for bandgap tuning as well as a means of improving efficiency and stability of perovskite photovoltaic devices [3]. (Cs, FA, MA)Pb(I, Br)<sub>3</sub> triple-cation based mixed-halide perovskites (TC-MHP) have been found more suitable than other systems for solar cell application due to their higher stability. However, even such most advanced perovskite materials suffer from instabilities of the bandgap in certain conditions, especially due to the migration of halide ions in operating conditions [4,5]. In recent years, it was indeed commonly reported that light-induced phase segregation takes place in mixed halide  $\text{MAPb}(\text{I}_{1-x}\text{Br}_x)_3$  and  $\text{CsPbBr}_3\text{I}_{1-x}$  perovskites due to migration of iodine ions and causes a red-shift in the photoluminescence (PL). In a recent PL experiment performed on TC-MHP thin films  $(\text{MA}_{0.17}\text{FA}_{0.83})_{0.95}\text{Cs}_{0.05}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ , we also observed a red-shift of the PL emission attributed to iodide and bromide ions migration when the sample is illuminated with a continuous wavelength of 454 nm laser excitation. In order to have an insight into the variation of the composition of triple-cation mixed halide perovskites and the migration process of its components nano x-ray fluorescence (XRF) imaging is an ideally adapted tool due to its multi-elemental nature and the possibility of performing quantitative studies. In this study we have profited the fast-scanning multi-scale XRF imaging possibility offered by the Nanoscopium beamline to obtain elemental distribution maps down to 100 nm spatial resolution in *in situ* conditions during white light illumination and the following relaxation process in a statistically significant manner [6]. The study of nanoscale variation of halide ion distribution was of particular importance, as iodine is known to migrate easily in certain conditions.



## STUDY OF THE MIGRATION OF HALIDE IONS IN triple-cation mixed halide perovskites at the NANOSCOPIUM beamline of synchrotron SOLEIL

### 2. Experimental

Several TC-MHP polycrystalline films, with average grain sizes smaller than 200nm have been investigated. Reference marks on the sample surface permitted to localize the region to be studied and to correct for eventual drifts during sequential XRF imaging. The samples have been kept in dark before the experiments. The samples were mounted on the CX3 station of Nanoscopium. A special attention has been taken to assure the measurement conditions without any parasitic visible light arriving at the samples. 18.35 keV excitation energy was chosen for the XRF measurements in order to excite simultaneously the K-edge of Br (13.474 keV), L-edges of Iodine (5.188-4.852-4.557 keV) include the Cs (5.714-5.359-5.012 keV) and Pb (15.861-15.200-13.035 keV) edges. The beam was focused to ~100 nm with a KB mirror optics, which was the highest spatial resolution required for XRF mapping. With fast continuous mapping 40 ms/pixel dwell time was sufficient to obtain elemental maps with good contrast. This permitted to measure a sequential series of XRF maps of  $10\ \mu\text{m} \times 10\ \mu\text{m}$  areas in “normal” conditions and  $40\ \mu\text{m} \times 40\ \mu\text{m}$  regions with 150 nm pixel-size using white light excitation in *in-situ* conditions. Semi-quantitative stoichiometry of the initial composition of the triple-cation mixed halide perovskites, which cannot be determined precisely based only on the fabrication process, was determined by the PyMCA software [7] after calibration with an appropriate standard and using the self-absorption correction option of PyMCA with the known sample thickness. The power density of the white light was  $5\ \text{mW}/\text{cm}^2$  with a spectrum showing intense peaks around 150 nm wavelength (blue).

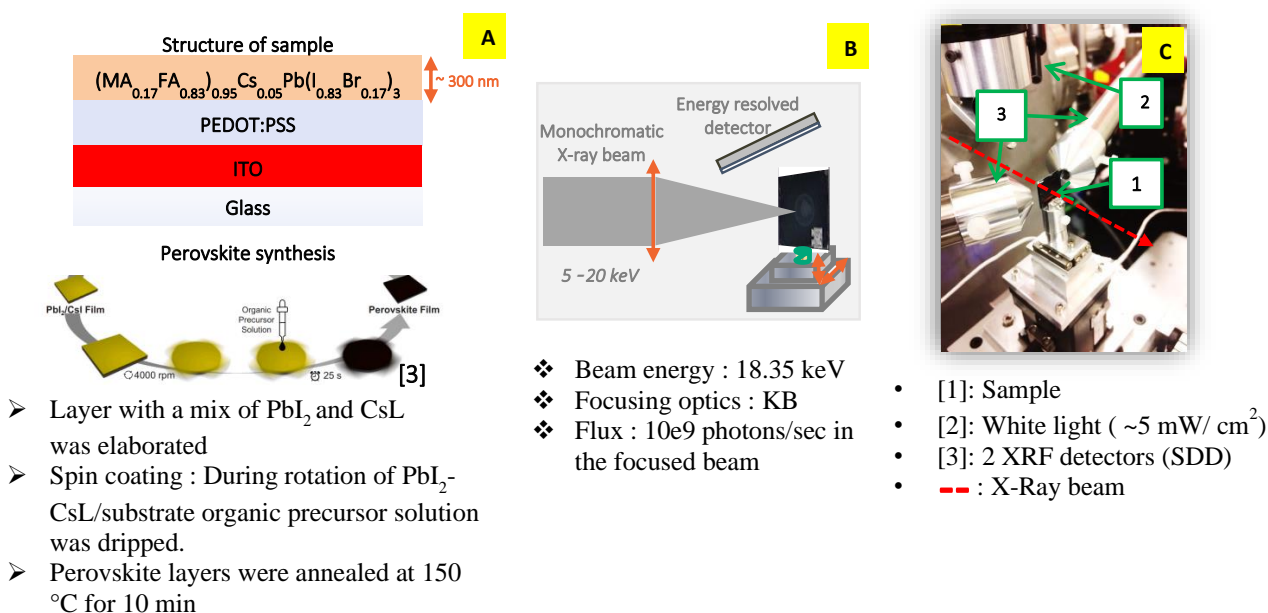


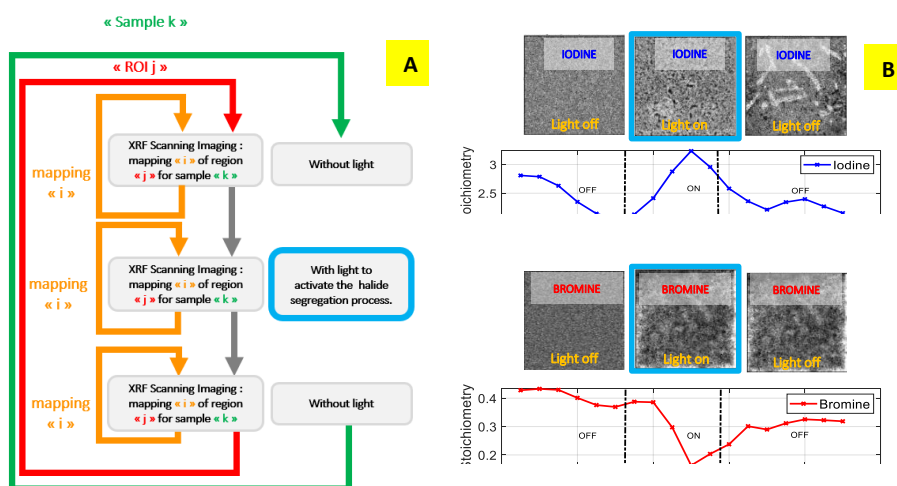
Figure1: A) Sample structure composed by 300 nm of triple cation mixed halides perovskite, PEDOT:PSS, ITO and substrate of glass. B) experimental conditions and C) photo of the experimental set-up.

### 3. Results

As a first step, we have collected successive XRF maps on  $10\ \mu\text{m} \times 10\ \mu\text{m}$  sample regions in usual XRF imaging conditions (without white light excitation) in the same measurement geometry as the following *in-situ* measurements. Each measurement sequence on a given sample region took several hours. Several regions have been measured on the very same sample to assure obtaining representative results. In the samples chosen for *in-situ* studies the initial sample composition was homogeneous at  $150\ \text{nm}$  length-scale, as indicated by the homogenous distribution of Cs, Br, Pb, and I. To minimize the eventual effect of X-rays on the samples, the beam shutter has been closed between taking successive images.

#### *In-situ* XRF imaging with a semi-automatic measurement sequence

The effect of white light illumination has been studied on intact sample areas outside of the previously measured by XRF imaging. We have developed a dedicated measurement sequence (see Fig. 2A) for the *in-situ* measurements in order to obtain directly comparable results on several sample areas of a given sample. This consists of taking several successive XRF images of the  $40 \times 40\ \mu\text{m}^2$  sample region in normal measurements conditions (before white light illumination), to follow the changes during white light illumination, and also after end of the illumination period. After the measurement sequence of a given sample region, the same measurement sequence has been performed at another distinct area at  $200\ \mu\text{m}$  distance. We have measured 5 regions per sample in *in-situ* conditions.



**Figure 2:** A) Scheme of the semi-automatic XRF imaging sequence used for the *in-situ* measurements used for study several areas of a sample that will eventually be replaced manually. Workflow shows for one sample “K” is mapped continuously for several times “I” in 5 different regions “j” following 3 measurement conditions: without light, with light to activate the halide segregation process and without light. B) Blue and red curves corresponding respectively to the stoichiometry of iodine and bromine evolution for fresh sample (K=1) in the first region (j=1) mapped several times (I=18 times) during 3 steps of measurements: without light, with light to activate the halide segregation process and without light

The distribution of Cs and Pb did not change during the white light illumination process. On the other hand, significant alteration has been triggered in the Iodine and Bromine of the perovskite by white light (figure 2B), which involves both stoichiometry and distribution changes. The overall Iodine abundance of the illuminated region started to increase immediately after the beginning of the white light illumination. This process was accelerating during the first hours of the illumination, then after reaching a sharp maximum, it decreases and stabilizes. At the end of the measurement sequence the Iodine

distribution evolved into a highly heterogeneous pattern showing elongated “worm-like” structures. Bromine shows a somehow similar dynamics in time. However, several significant differences can be detected between I and Br, one of the most striking is the inverse variation of the Br concentration starting with Br depletion and turning into Br re-accumulation. Also, a clearly detectable time lapse (~1.5-2 hours) occurs between the beginning of the white light illumination and the start of the decrease of the Br content. The abrupt change of the Br depletion process into Br re-accumulation occurs at the same point (time) of the measurement sequence as for Iodine. We can observe the appearance of Br-rich clusters with granular structure. We did not observe co-localization between the Iodine-rich and Bromine-rich clusters. Further measurements are needed to understand the evolution of the over-all Iodine and Bromine balance and migration process during the photo-induced process.

In order to check the eventual relaxation of the sample, the illuminated areas have been remeasured several days after the white light illumination. The samples have been kept in the experimental hutch in light-tight conditions after the end of the photo-induced experiments. These post-illumination experiments revealed no significant sample relaxation after several days and suggests that the cluster formation of Iodine and Bromine is irreversible. The mean composition of the clusters could be estimated by extracting their mean XRF spectra. This permitted to determine the local stoichiometry within the Iodine and Bromine rich clusters and to compare them to the initial sample composition.

#### 4. Conclusions

We performed direct measurement of the variation of the concentration and spatial distribution of halide ions in hybrid organic-inorganic perovskites during *in-situ* white line illumination thanks to the semi-automatic XRF nano-imaging, we implemented for these measurements. This is of prime importance to understand the local properties and their *in-situ* alteration of these promising materials for photovoltaics and to link them to macro-scale properties. The characterization by nano XRF allowed to study *in-situ* the steps of photo-induced alteration of the perovskite and to characterize the resulting irreversible changes in the concentration and spatial distribution of the main sample components. The concentrations of Iodine and Bromine evolved inversely during and after white-light illumination resulting in irreversible cluster formation. Other main components, Cs and Pb showed no significant photo-induced alteration neither in concentration nor in spatial distribution. These measurements reveal the high instability of the studied TC-MHP perovskite material for photo-illumination, which is a major bottleneck for practical photovoltaics applications.

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