

Investigating the Effects of X-Ray Irradiation on Triple Cation Perovskites: Degradation Kinetics and Lattice Reorganization

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Abstract

Accurate and reliable characterization of perovskites is crucial nowadays, due to the numerous applications of this material, whether in photovoltaics or in detection systems. Some conventional laboratory-based or synchrotron-based characterizations require the exposure of perovskites to a flow of X-Rays, such as during X-ray diffraction spectroscopy (XRD) or X-ray photoelectron spectroscopy (XPS). Therefore, it is important to fully understand the complex behavior of perovskites under continuous X-ray irradiation, and this is even more complex for metal halide perovskite. Numerous studies have been reported, indicating the degradation of perovskites during photoemission spectroscopy within synchrotron sources, where the X-ray fluence is relatively high¹. In this work, we dig deeper into this behavior by going softer, and we study the chemical evolution of a triple cation double halide perovskite $\text{Cs}_{0.05}(\text{MA}_{0.14}\text{FA}_{0.86})_{0.95}\text{Pb}(\text{I}_{0.84}\text{Br}_{0.16})_3$ layer directly inside the XPS spectrometer. XPS is thus used as both the perturbation source (10^{13} ph/cm²/s) and the analytic technique to detect chemical changes.

The chemical evolution of the perovskite layer was monitored inside the XPS X-ray spot of 400 μm , by proceeding to consecutive XPS acquisitions at the same position (under UHV), without stopping the X-ray source, for an irradiation duration reaching 16h. As the exposure time increased, we noticed a loss of volatile organic cations, the formation of Pb^0 and a decrease of the iodine content, indicating a chemical degradation of the surface. Furthermore, two main degradation pathways were identified with a significant kinetic change at 8h. During the initial hours, we detect minor changes in the surface chemistry, while at higher X-ray dose, the evaporation of the organic cations and the formation of an iodine-poor perovskite compound is observed.

To determine if the overall perturbation observed inside the 400 μm spot was spatially homogeneous or not, we developed an original approach based on spatially resolved XPS measurements. Smaller spot sizes ($\sim 50\mu\text{m}$) were sequentially aligned along the diagonals of the spot enabling to discretize the chemistry from side to side of the irradiated zone, showing that the atomic ratios significantly change between inside and outside (dark and light orange area on Figure 1). An additional study is hence under investigation to better understand the chemical variations occurring during the first hour of exposure.

A second brief study was carried out by exposing a perovskite layer to 12h of X-Rays from an XRD spectrometer. Although no modification in the crystal structure was noticed by XRD characterization, a chemical degradation of the perovskite was detected when the sample was analyzed afterward by XPS. The effect of the X-rays in this case were slightly different since the layer was not only exposed to the X-rays, but also to oxygen from the XRD chamber bringing interesting additional information in terms of degradation mechanism.

These findings provide valuable insight on the impact of X-rays on perovskite layers during characterizations using X-ray based techniques, which helps adapting analysis procedures and identifying measurement artefacts.

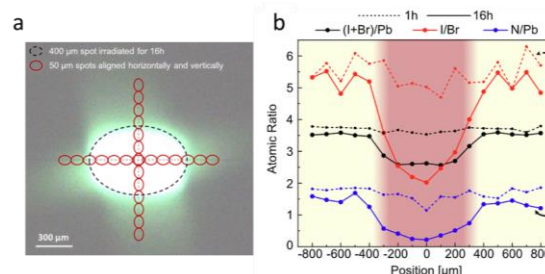


Figure 1. a) Schematic representation, and b) Atomic ratio variation for the spatially resolved XPS

References

1. S. Svanström, A. G. Fernández, T. Sloboda, T. Jesper Jacobsson, H. Rensmo, U. B. Cappel, *Physical Chemistry Chemical Physics*, **2021**, 23, 12479.