	Experiment title: Ion migration in perovskite x-ray detectors: simultaneous elemental mapping, XBIC and XEOL.	Experiment number: MA-4631
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Names and affiliations of applicants (* indicates experimentalists):

Matteo Verdi* (1,2), Dr. Laura Basiricò (1,2), Dr. Andrea Ciavatti* (1,2), Prof. Beatrice Fraboni (1,2), Prof. Federico Boscherini* (1)

(1) Department of Physics and Astronomy, University of Bologna, Vaile Berti-Pichat 6/2, Bologna 40127, Italy

(2) National Institute for Nuclear Physics – INFN section of Bologna, Bologna, Italy

Report:

During this experiment we successfully performed measurements on four samples of Methylammonium lead triiodide ($MAPbI_3$) nanocrystalline perovskite film x-ray detectors. All samples were deposited by bar coating on interdigitated gold contacts with channel length 5 µm, width 20 mm and thickness 5 µm. Two samples had a coating of the organic molecule [6,6]-phenyl-C61-butyric acid methyl ester fullerene (PCBM). Each sample consisted of two devices, thus a total of 8 working devices, previously tested in our home laboratories in Bologna, were available for the experiment. A sketch of the single device and a photo are reported in Figs.1a and 1b, respectively.

We used a photon energy of 17.5keV and the spot size on the sample was 50 × 58 nm. During the assigned shifts, we managed to acquire simultaneous X-ray Fluorescence (XRF) and X-ray Beam Induced Current (XBIC) maps. XRF was measured with two silicon drift detectors facing the sample surface while the XBIC signal was measured with a modulation technique by chopping the beam at 1 kHz and using a lock-in amplifier; measurements were performed at various values of the external bias voltage. An example of the typical XRF spectrum is reported in Fig. 1c.

The preliminary step in the measurements was to find the beam conditions which guaranteed the absence of beam – induced damage of the samples, detected as a time dependent change of the elemental distribution. Using these conditions we mapped Pb, I and Au using pixel sizes of 5 × 5 μm^2 or 10 × 10 μm^2; Au corresponds to the metal electrode, the position determines the direction of the electric field.

In Fig 1d we report an example of a Pb fluorescence map, in which it is possible to observe the perovskite nanocrystal grains and notice modulations of the intensity due to different thickness of the sample. An XBIC map of the same sample area is reported in figure 1e, in which it is also possible to see the signal produced by the metallic contact. The inset shows the fluorescence signal from Au. It is worth mentioning that there is no 1:1 correlation between the XRF and the XBIC maps. The difference is highlighted in Fig. 1f in which we overlayed the two maps for the same region: XBIC in green and XRF in purple. The overlap makes the grain boundaries stand out clarifying the position, dimension and orientation of the perovskite grains.

For both types of samples (with and without PCBM), we acquired maps in 10 different regions near the metallic contacts, with 0, 1 and 4 V bias. Detailed data analysis is able to correlate the X-ray generated current with the elemental distribution and morphology of the perovskite thin-film and the effect of the bias. In particular, we can evaluate the ion migration of the halide component and how the phenomenon changes with the applied bias, as well as how the metal contact is affected. We are also comparing the two types of samples to establish the effect of the semiconductor polymer on the perovskite charge transport properties. A paper reporting on these results is being prepared and will be submitted to Advanced Funcional Materials.
In this experiment we also tried to acquire XEOL maps but we did not succeed. Although a strong XEOL signal was visible at the first irradiation, its amplitude steeply decreased in few runs and became not detectable. This is probably due to photobleaching of the perovskite layer, an effect that degrade the perovskite photoemission even in absence of evident structural or compositional efects (not visible in XRF nor in XBIC maps). Nonetheless, the correlation of XEOL maps with compositional (XRF) and charge transport (XBIC) maps will be of great interest to unravel the effect of layer efficiency and stability in perovskite thin films, and it will be the target of future experiments as it requires high attention to obtain reliable measurements.

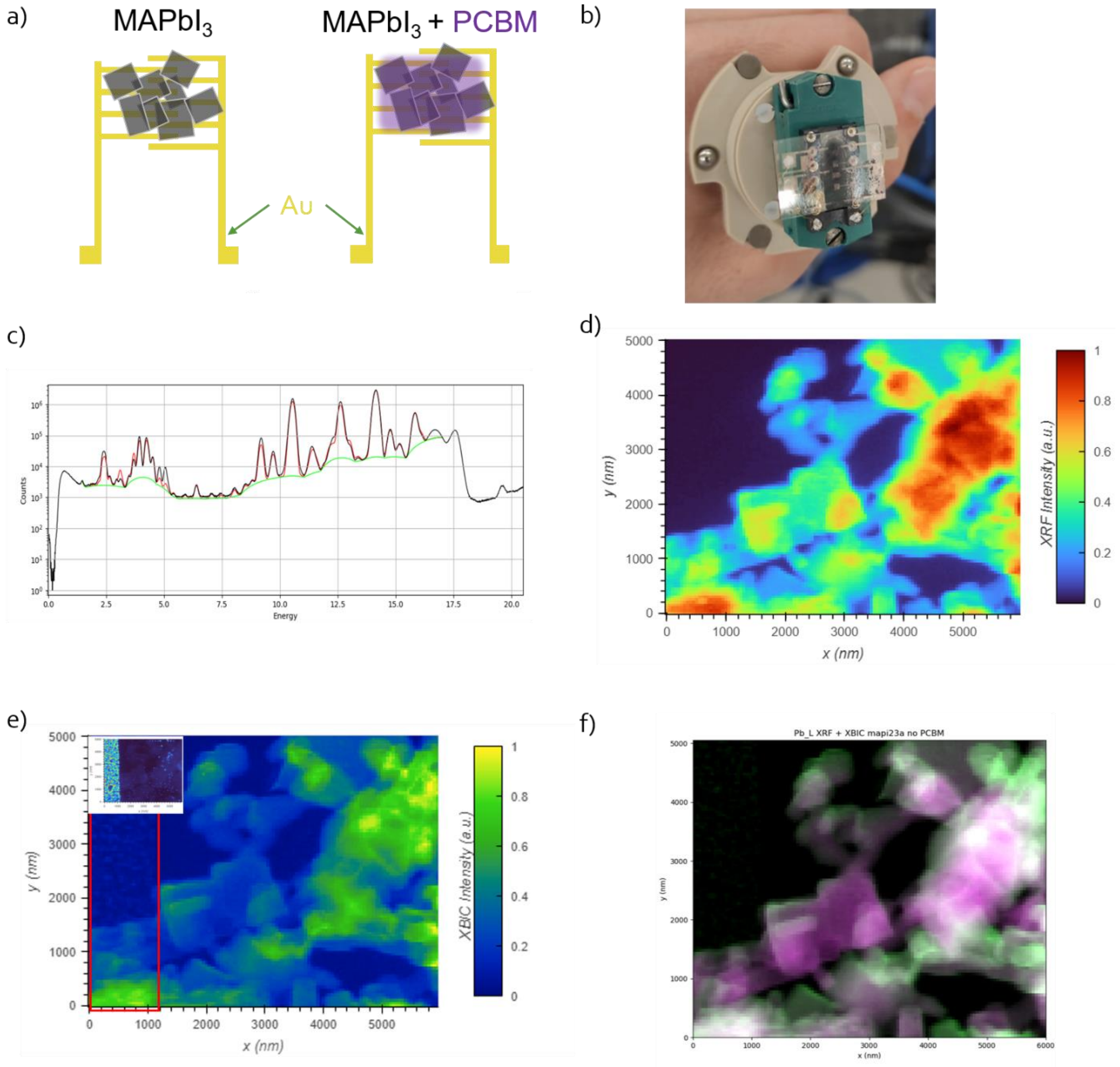

Figure 1: a) Schematics of the two types of sample analyzed durign the experiment. b) Picture of the sample mounted on the sample holder. The black perovskite is visible on top of the gold metal contacts. c) Example of a typical XRF spectrum. d) 5x6 μm^2 map of the Pb XRF signal e) XBIC map acquired in the same region. The inset reports the Au XRF in the same region. The red rectangle highlights the position of the metal contact underneath the perovskite layer. f) Overlap of the XRF and XBIC signals.