EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

	Experiment title: Probing local structural disorder and its stabilizing effect in doped CsPbI3 perovskite using in situ XAFS	**Experiment number**: MA5686
Beamline: BM23	**Date of experiment**: from: 10/05/2023 to:16/05/2023	**Date of report**:
Shifts: 18	**Local contact(s)**: Puri	*Received at ESRF:*

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Report:

In the context of multi-junction solar cells, $CsPbI_3$ stands out as the preferred top absorber material. It boasts a direct bandgap of approximately 1.7 eV in its black perovskite phase (γ-$CsPbI_3$), which can be easily achieved through a low-temperature solution process. Notably, it offers greater chemical stability compared to its organic-inorganic counterparts. Despite its remarkable performance, its practical use is hindered by challenges related to phase stability. The solar-friendly black phase $CsPbI_3$, known as α, β, and γ, remains stable only at higher temperatures. At room temperature (RT), it tends to transform into a yellow, non-perovskite phase (δ) with a bandgap of 2.82 eV. Although the black phase may temporarily persist at RT, it ultimately transitions to the yellow phase within minutes, a process strongly dependent by the presence of oxygen, moisture or inert atmosphere. We believe that oxygen plays a key role in the stability of the black phase of perovskite, and it is therefore essential to study its properties and local structure as a function of these parameters.

XAS measurements were carried out on different samples of pure and doped $CsPbI_3$ perovskite powders at the BM23 beamline in transmission geometry and continuous scan mode, at Cs-K(35.9846 eV), I-K (33.1694 eV) and Pb-L_{III} (13.0352 eV) edges. Each spectrum was measured 2-3 times to improve the statistics.

The samples were prepared in inert atmosphere, grinding the $CsPbI_3$ perovskite with light absorber (BN), mixed powders were pressed in pellets and enclosed in the heating cell. We measured 12 (pure + doped) samples. For each sample, each edge was measured in the EXAFS region at RT, then the samples were heated (10 ^{o}C/min ramp) to about 350°C to get the black phase, and then cooled down at RT. XANES spectra were collected during the heating/cooling ramps and EXAFS spectra (2-3 scans) were measured after cooling down at RT. In some sample the thermal treatments were carried out in inert environment (under He flux gas) or in presence of oxygen (air) to correlate the effect of atmosphere on the phase stability, to the local structure.

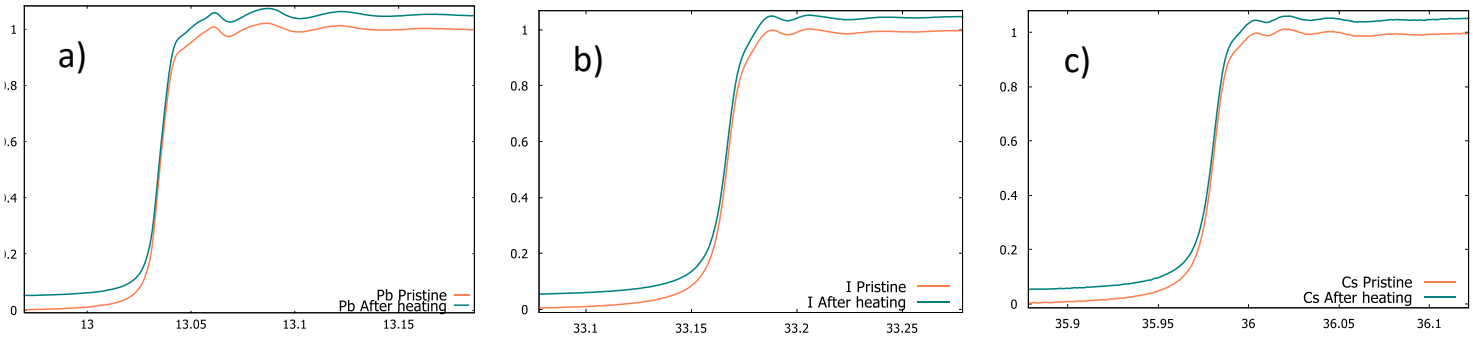

Figure 1:XANES regions of a) Pb-L_{III} edge, b) I-K edge, c) Cs-K edge.

Fig. 1 reports examples of normalized XANES spectra at the three different edges for representative sample (pure $CsPbI_3$) at RT (pristine) and after thermal (after heating) treatments. The XANES data are very similar indicating that the valence state, coordination chemistry and site geometries are preserved in the different phases. Further analysis in the EXAFS region permits to individuate and quantify changes in the neighbour distribution around the absorbers.

Fig. 2 shows preliminary results obtained analyzing the Pb-L_{III} edge EXAFS spectra measured for the pure sample treated under He atmosphere. From EXAFS data we see that temperature treatment induces a significant decrease in disorder of the Pb-I distribution. The best fit demonstrates a bimodal distribution of Pb-I bonds with two (approximately 4+2 neighbours) Pb-I shells.

The results of the Pb threshold analysis are included in a forthcoming publication. Further analysis is in progress.

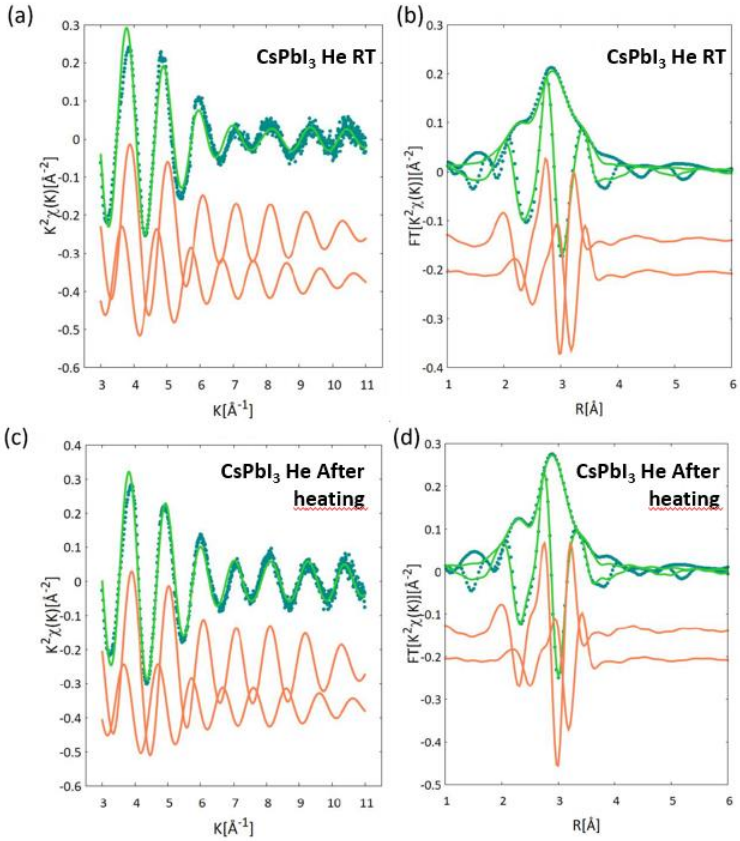

Figure 1: Pb-L_{III} edge EXAFS analysis. Panels a, c: k^2-weighted experimental EXAFS spectra (green dots) and best fit (green line) for the data measured at RT (a) and after thermal annealing (After-T). The Pb-I coordination is fitted with two contributions shown in the figure (orange curves, vertically shifted for clarity). Panels b,d: moduli of the k^2-weighted Fourier transforms (|FT|) of experimental data (green dots) and best fit curves (green lines). Imaginary part of the FT of experimental data, best fit, and partial contributions (shifted for clarity) are also shown for completeness.