ESRF	**Experiment title:** Role of bismuth doping on the electronic bandgap of hybrid perovskites	**Experiment number**: A08-1-1085
Beamline: BM8	**Date of experiment**: from: 08/06/22 to: 10/06/22	**Date of report**: 26/4/23
Shifts: 12	**Local contact(s)**: Michela BRUNELLI	*Received at ESRF:*

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Report:

$Cs_3Cu_2I_5$ doped with BaI_2 was prepared by mechanochemical synthesis by mixing together simple iodides. The successful synthesis was checked with X-ray diffraction. Samples with 5% and 10% Ba with respect to Cs were succesfully measured and analyzed. Samples with 1% Ba were also measured, but the s/n ratio at the Ba K-edge proved unfeasible.

Pellets mixed with boron nitride were prepared under nitrogen in a glove box at the beamline to minimize exposure to air.

X-ray absorption spectra were recorded in transmission mode at the Cu K-edge and in fluorescence mode at the Ba K-edge using the multielement fluorescence detector. All measurements were collected at 80 K. All data reduction and analysis was carried out with Viper.

All measurements at the Ba K-edge proved extremely difficult because of the very high noise from iodine and cesium fluorescence lines. On the other hand, L-edges suffered from even worse interferences.

Several different atomic structures were calculated to generate the multiple scattering paths, starting from the ideal $Cs_3Cu_2I_5$ structure, and substituting either Cs or Cu with Ba. The atomic coordinates of 1 x 2 x 1 supercells containing one Ba atom were relaxed using QuantumESPRESSO, with a periodic DFT approach using the PBEsol functional and extrafine k-mesh. In particular, the possibililty that Ba^{2+} substitutes either Cs^{+} site in the structure was evaluated.

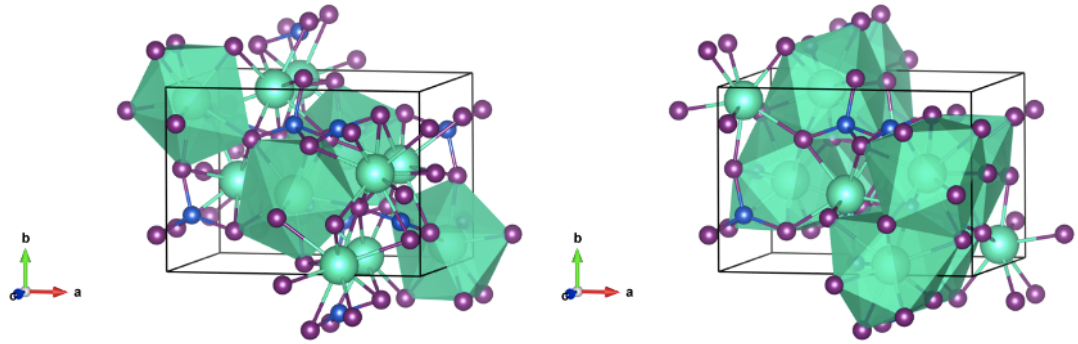

Figure 1 – Cs-I coordination polyhedra (green) in pure $Cs_3Cu_2I_5$. Two different polyhedra are present, one smaller (left) and one larger (right). Cu atoms in blue, iodine atoms in violet.

Data analysis is currently underway.

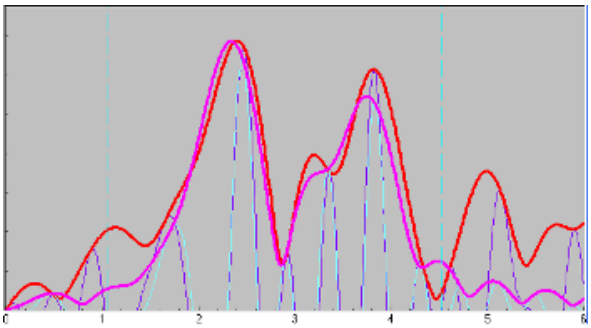

Figure 2 – FT data and model of 10%-doped sample at the Ba K-edge.