	Experiment title: Low-temperature crystal structure of $Cs_2AgBiCl_6$ double perovskite	**Experiment number**: HC-4748
Beamline: ID28	**Date of experiment**: from: 06/10/2021 to: 08/10/2021	**Date of report**: 08/01/2022
Shifts: 6	**Local contact(s)**: Aleksandra Chumakova	*Received at ESRF:*

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Report:

Halide double perovskites $A^I_2B'B''X_6$ have been in the focus of research for several years now as these feature solar light conversion efficiency and moisture stability comparable to their hybrid lead analogues. In particular, $Cs_2AgBiBr_6$ and $Cs_2AgBiCl_6$ demonstrated remarkable stability [1], low carrier effective masses [2] and recombination lifetime [3] long enough for practical use.

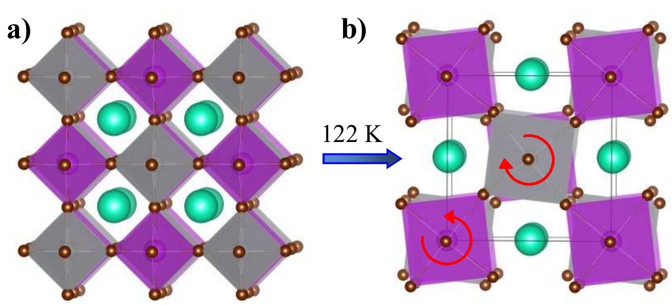

Fig. 1. a) Cubic (*Fm-3m*) to b) tetragonal (*I4/m*) phase transition in $Cs_2AgBiBr_6$ upon cooling. $BiBr_6$ and $AgBr_6$ octahedra are coloured violet and gray respectively, Cs are green.

From the structural viewpoint, both compositions adopt the same cubic double perovskite crystal structure (space group *Fm-3m*) in which Ag^+ and Bi^{3+} cations follow checkerboard ordering pattern on the B-sites. Large cuboctahedral voids in the extended tree-dimensional framework made up of corner-sharing octahedra are filled by Cs^+ cations. Doubling of the unit cell parameter with respect to that of the parent perovskite results from alternating $AgCl_6$ and $BiCl_6$ units in all three directions (**Fig. 1a**). $Cs_2AgBiBr_6$ has been recently shown [4] to undergo a second-order cubic to tetragonal phase transition at 122K resulting from the cooperative rotation of $AgBr_6$ and $BiBr_6$ octahedra about the tetragonal *c* axis in opposite senses (**Fig. 1b**). Our preliminary neutron diffraction data suggested a similar phase transition was likely to occur in $Cs_2AgBiCl_6$ on cooling below T_c=35K. However rather complex peak brodening pattern hindered unambiguous space group assignment from the powder data only and has been the motivating factor to resort to the single crystal measurements at ESRF.

Overall, the experiment HC-4748 was a success and we are grateful for the local contact's help and advise. A single crystal of $Cs_2AgBiCl_6$ was affixed to a copper pin prior to loading into the cryostat. The instrument was operated at λ=0.6968Å. The data were collected as a series of φ-scans covering the angular range of 360° across T_c on heating and cooling.

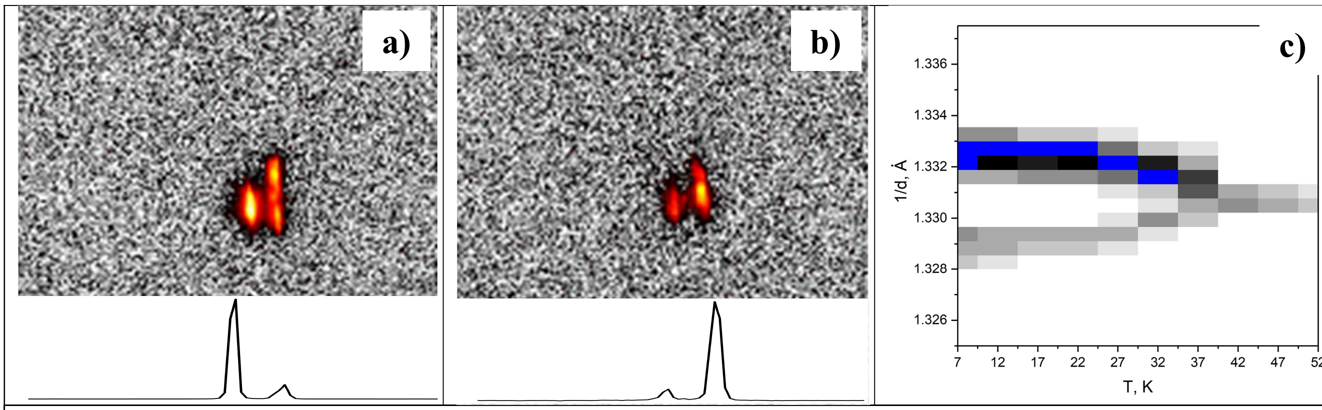

Fig. 2. Recorded intensity distribution around some point in reciprocal space at 7.5K and (**a**) φ = -126.75°, (**b**) φ = -126.5°. At the bottom of each image an intensity profile along x-axis is given highlighting the peak splitting as a function of 1/*d*. (**c**) Extracted intensity for a representative reflection as a function of 1/*d* and temperature across the phase transition.

As can be seen from **Fig. 2a,b** cooling below T_c leads to massive peak splitting due to the symmetry lowering and concomitant pseudo-merohedral twinning. The instrument resolution was high enough to capture the basic features of the peak splitting due to the symmetry decrease; however, most of the peaks in the low-temperature polymorph were quite broad probably due to the micro-twinning phenomenon, which hindered the direct search and refinement of the orientation matrix for each twin component. For this reason, the image analysis using the in-house software was carried out. As can be seen from **Fig. 2c**, the 2D intensity plots obtained allow for the straightforward extraction of the interplanar distances *d* for every group of reflections related by the twin operators and clearly show how each family of cubic crystal planes splits on cooling. This information was used to screen for the possible crystal systems that would explain the splitting pattern observed. At the moment, the singonies compatible with the observed splitting pattern have been identified and the unit cell parameter extraction as a function of temperature is in progress. The work carried out in this experiment will be published in an international journal.

References:

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[3] A. H. Slavney et al., *J. Am. Chem. Soc.*, **2016**, 138, 2138−2141
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