ESRF	**Experiment title:** Structure and Dynamics of Layered Hybrid Perovskites	**Experiment number**: CH-5239
Beamline: BM01	**Date of experiment**: from: 16/09/2017 to: 19/09/2017	**Date of report**: 1/3/2018
Shifts: 9	**Local contact(s)**: Dmitry Chernyshov	*Received at ESRF:*

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Report:

1. Introduction Hybrid perovskites, composed of an organic cation, inside a post transition metal halide framework, have emerged since 2009[2] as simple, low cost solar cell materials, with power conversion efficiencies that are competitive with silicon[3-8]. The most extensively studied 3D hybrid perovskite being $CH_3NH_3PbI_3$ ($MAPbI_3$), where advances in cell efficiency have been made despite of an incomplete understanding of the photovoltaic mechanism, which is in part due to a lack of clarity on its structure. Recently, we have shown that iodide ions (I-) in the methylammonium lead iodide perovskite ($MAPbI_3$), migrate via interstitial sites at temperatures above 280 K and undergoing a redox reaction to form diatomic molecular iodine. This redox couple (2I- → I2 +2e-) effectively forms an electron and hole pair. The actual formula of this compound is thus $MAPbI_{3-2x}(I_2)_x$ where x ~ 0.007 at room temperature. The aim of this experiment was to use maximum entropy method (MEM) analysis of single crystal x-ray diffraction data to study Ruddlesden-Popper layered hybrid lead iodide perovskites ($BA_2MA_{n-1}Pb_nI_{3n+1}$, n=1,2,3,4, ∞). However upon obserbation of significant diffuse scatteing from the n= ∞ compound of this series ($MAPbI_3$) the assigned beam time was devoted to further measuring this diffuse scatteirng as new observations only accessble from BM01 allowed for significant new insight into the complex structure of this compound.

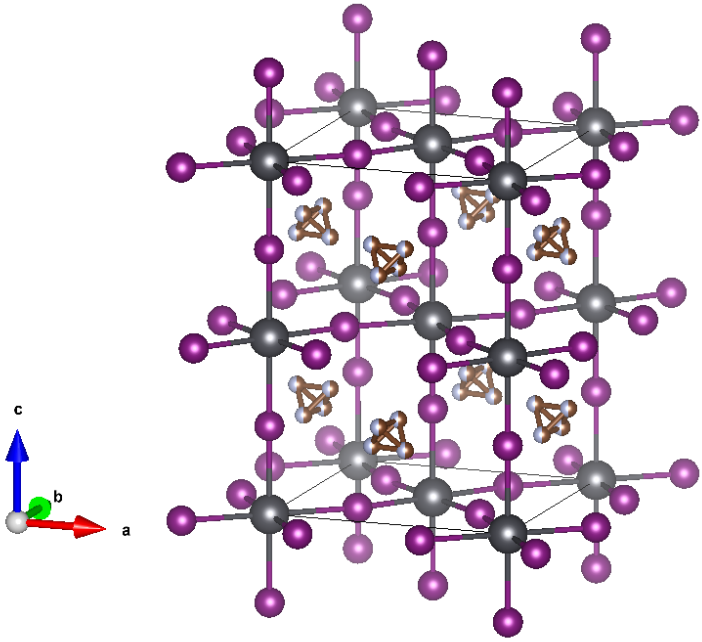

Figure 1. The structure of $MAPbI_3$ as solved from data collected at BM01.

2. Experiment To begin the detector was set up such that a single snapshot of the diffraction pattern of $MAPbI_3$ was taken at regular intervals while the temperature was varied from 350K down to 100K and backup again. This allowed us to determine our own phase transition temperatures for $MAPbI_3$ and quicly understand how the diffuse scattering evolves as a function of temperature. Fullsphere variable temperature single crystal diffraction patterns were taken for $MAPbI_{3\,I}$ at temperatures 100, 150, 160, 180, 220, 240, 330, 340 and 350K.

3. Results From the single snapshot diffraction measurements the average integrated intensity of those diffuse areas between peaks assosiated with all three structural phases (orthorhombic/tetragonal/cubic upon both cooling and heating. Allowing the intensity of diffuse scattering across both phase transitions to be determined using the Sleuth tool of the SNBL toolbox, appropriate temperatures for the full sphere single crystal diffraction measurments were also identified. Peak intensity analysis was performed highlighting the hysterisis in phase transition present in $MAPbI_3$.

The full sphere single crystal x-ray diffraction measurments were transformed into 3d reconstructions of reciprocal space via the SNBL toolbox for each temperature measurment. Initial analysis is underway through study of variations in the diffuse intensity across different temperature ranges highlighting complex structural dynamics across all phases of $MAPbI_3$, inorder to solve the origin of the diffuse scattering reverse monty carlo simulations will be implimented.