



	Experiment title: Suppression of phase transitions in mixed cation halide perovskites MA/EAPbI₃	Experiment number: No 91951 CH-6376
Beamline:	Date of experiment: from: 26.10.2022 to: 28.10.2022	Date of report: 25.01.2023
Shifts: 6	Local contact(s): Andrew Fitch	<i>Received at ESRF:</i>

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Report:

In the course of experiment several samples obtained from the grinded single-crystals were measured. Data were collected for similar compositions as it occurred that some diffractograms revealed another phase, possibly coming from the partial decomposition of the single crystals or from radiation damage. Nevertheless, we were able to collect the data sufficient enough to answer the questions concerning the temperature and composition induced polymorphism in MA_{1-x}EA_xPbI₃. Additionally, we collected diffraction data for three new organic-inorganic materials which will help determine the temperature induced polymorphism in these materials. The summary of materials measured is shown in Table 1.

Table 1. The summary of compounds measured during the experiment.

Composition	T_c (K, from DSC)	T(K) of experiment
MA _{0.85} EA _{0.15} PbI ₃	274/272; 139/134	LP 90-290; 80
MA _{0.63} EA _{0.37} PbI ₃	215/217K	LP* 110-290; 80, 240,
MA _{0.915} EA _{0.085} PbI ₃	295/293; 148/143	LP 90-290K; 90, 160
MA _{0.78} EA _{0.22} PbI ₃	226/225; 135/127	LP 95-320; 80
MA _{0.62} EA _{0.38} PbI ₃	213/215;	LP 95-320
MA _{0.79} EA _{0.21} PbI ₃	244; 135	LP 95-320
MA _{0.92} EA _{0.08} PbI ₃	296/294; 149/144	LP 85-320
MA _{0.63} EA _{0.37} PbI ₃	212/214	LP 100-290
AZIRPbBr ₃	247/262; 142/145	90, 170
FA ₅ Bi ₂ Br ₁₁	140	160, 90
Pyrr ₃ Bi ₂ I ₉	223; 193; 133	90, 145, 200, 295

- Shorter measurements for lattice parameters

The SRD data collected during the 91951 experiment confirm the influence of EA doping on structural properties of the mixed $\text{MA}_{1-x}\text{EA}_x\text{PbI}_3$ system. For low concentrations of EA ($<10\%$) the diffractograms are characteristic of pure MAPbI_3 , and the phase transitions from cubic ($Pm\bar{3}m$) \rightarrow tetragonal ($I4/mcm$) \rightarrow orthorhombic ($Pnma$) phases are signified by characteristic splitting of diffraction peaks. For moderate amounts of EA the structural distortions are suppressed resulting in lower separation of diffraction peaks. Finally for the highest concentrations of EA the cubic phase is suppressed to the lowest temperature and below T_c a new phase is stabilized.

All diffracted peaks of the LT phase of $\text{MA}_{0.62}\text{EA}_{0.38}\text{PbI}_3$ may be indexed using tetragonal primitive cell with $a=8.9357(9)\text{\AA}$, $c=12.606(4)\text{\AA}$, which is a new tetragonal phase in $\text{MA}_{1-x}\text{EA}_x\text{PbI}_3$ system. Figure 1 shows the diffractograms for 8,5% and 38% EA concentration. The low-temperature orthorhombic phase is suppressed in the latter composition. Figure 2 shows selected peaks collected at the lowest temperatures (90K) for three different compositions.

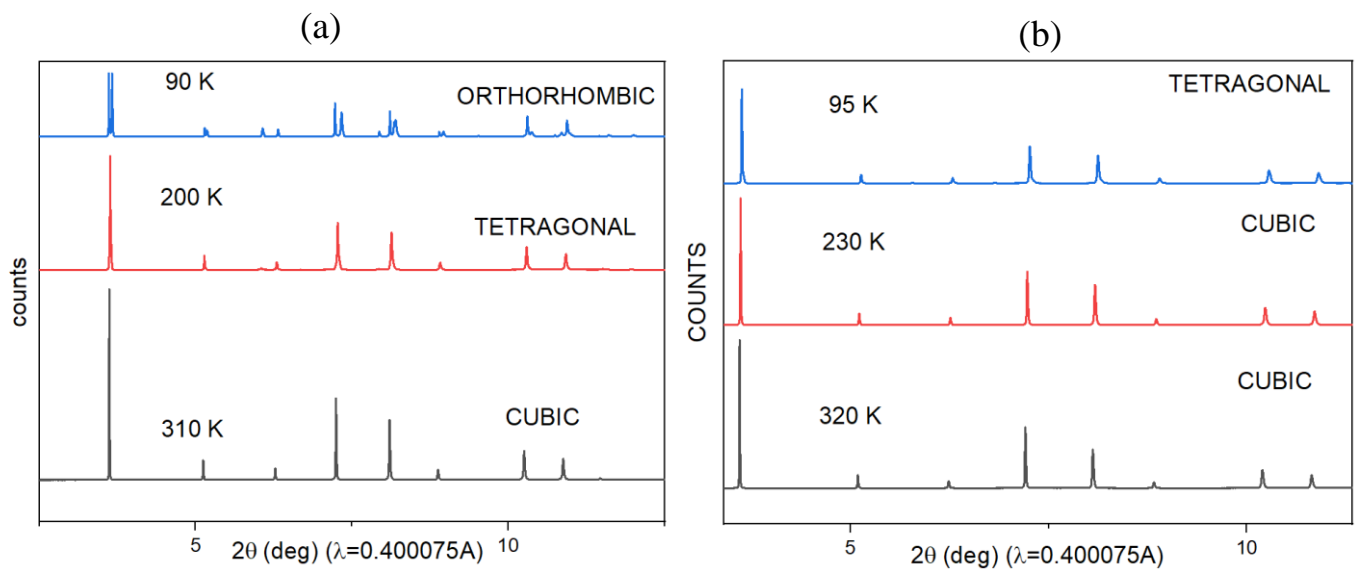


FIGURE 1 The diffractograms for (a) $\text{MA}_{0.915}\text{EA}_{0.085}\text{PbI}_3$ and (b) $\text{MA}_{0.62}\text{EA}_{0.38}\text{PbI}_3$ at selected temperatures

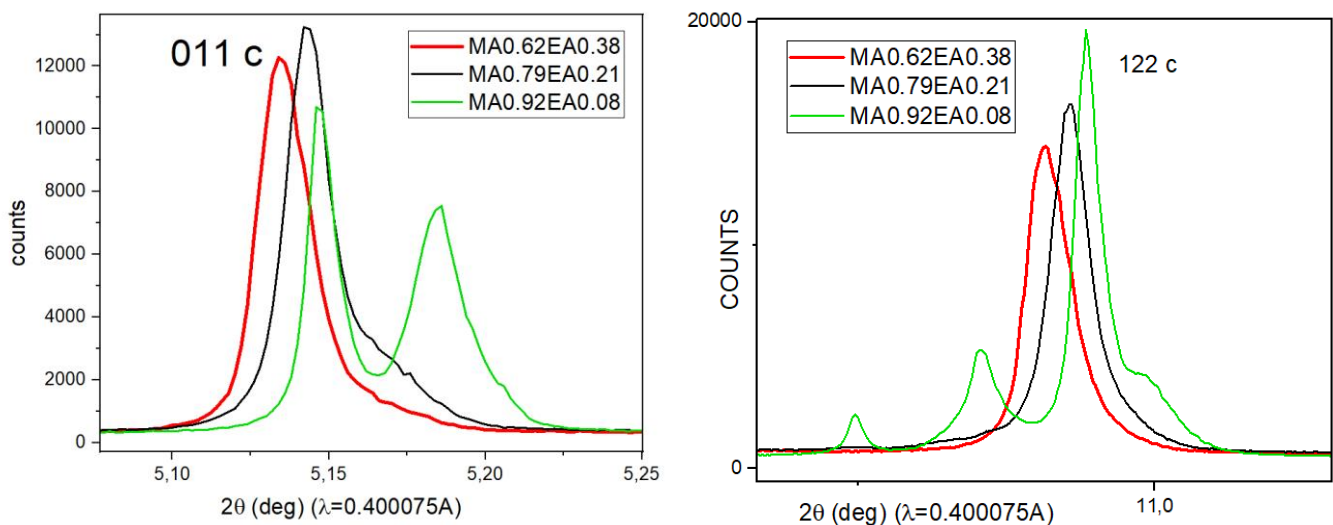


FIGURE 2 The suppression of structural distortion with increase in the EA content, $T=90\text{K}$.