# Experimental report

14/12/2020

**Proposal:** **5-21-1131** **Council:** 10/2019

**Title:** Crystal structure features of $CH_3NH_3PbI_{3-x}Br_x$ hybrid perovskites prepared by ball milling: a route to more stable materials

**Research area:** Materials

**This proposal is a new proposal**

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**Samples:** $CH_3NH_3PbI_{3-x}Cl_x$

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D2B | 2 | 2 | 21/01/2020 | 23/01/2020 |
| D20 | 0 | 1 | 10/01/2020 | 11/01/2020 |

## Abstract:

The optoelectronic properties of hybrid organic-inorganic perovskites are suitable for efficient photovoltaic devices. For $MAPbI_3$ (MA: $CH_3NH_3$) an adequate direct bandgap of ~1.6 eV permits a broad light absorption range. However, the sensitivity to humidity is a serious drawback. Here we found that $MAPbI_{3-x}Br_x$ (x= 0.0, 1.0), prepared by ball milling, exhibit a much superior stability, showing no signs of degradation after several months exposed to humid air. Preliminary SXRD data unveiled some peculiar structural features that may account for the improved stability. Whereas $MAPbI_3$ prepared from solution chemistry is defined in I4/mcm s.g., our material from mechanosynthesis crystallizes in the acentric I4cm s.g. with an off-centering ferro-electric component along the c-axis, and distinct tilting angles. The orientation of the organic MA units may play an important role in the properties, given the degrees of freedom for internal motion of MA groups within the $PbX_6$ network. Here we aim at finding the structural reasons for the superior chemical stability; among other, we expect from difference Fourier synthesis to determine the orientation of $MA^+$ units and its T evolution.

Hybrid organic-inorganic perovskites, and in particular methyl-ammonium (MA) lead halide $CH_3NH_3PbX_3$ (X = I, Br, Cl) compounds, have attracted wide interests in recent years due to their applications in optoelectronic devices [1-2]. While methyl-ammonium lead iodide ($MAPbI_3$) remains the most widely studied perovskite due to its ability to absorb broadband light below its bandgap of 1.6 eV, the degradation in a humid atmosphere has remained a major obstacle for commercialization. $MAPbBr_3$ is a promising alternative to $MAPbI_3$ with a large band-gap of 2.2 eV, which gives rise to a high open circuit voltage (Voc ≈ 1.2–1.5 V) [3]. Thus, a good compromise between both materials can be found in the solid solution $CH_3NH_3PbI_{3-x}Br_x$.

However, the crystal structure of these fascinating materials is still, partly unknown. As in conventional $ABX_3$ (X= halogens) perovskites, B cations are located in the vertices of a cubic unit cell, with X anions at the center of the edges and the large A cations in the center of the cube. In the case of $CH_3NH_3PbI_3$ the organic A cation ($CH_3NH_3^+$) is partly delocalized or resonant between preferred conformations, as determined by NMR and neutron diffraction in deuterated samples [5,6]. As conventional perovskites, the methylammonium lead halides are described to show tilting transitions, also adopting the most conventional symmetries and space groups, such as the orthorhombic *Pnma*, tetragonal *I*4/*mcm* or the cubic Pm-3m, where the structure optimizes the hydrogen bonding between the methyl-ammonium and the framework [5].

In this work, two hybrid perovskites of the family $MAPbX_3$ have been successfully prepared by mechano-chemical synthesis in inert atmosphere: $MAPbI_3$ and $MAPbI_2Br$. They have demonstrated to exhibit a superior chemical stability towards humidity than specimens prepared by solution chemistry. The samples were measured at D2B at RT, and then at selected temperatures below RT; the structural evolution was carefully followed in D20. Despite the presence of hydrogen in these non-deuterated samples, very good quality diffraction patterns were acquired, thanks to the high flux and resolution of the mentioned diffractometers.

For $CH_3NH_3PbI_3$, in the temperature range 100-298 K a tetragonal *I4/mcm* to orthorhombic *Pnma* phase transition was identified, in agreement with previous reports. Neutrons permitted determining the configuration of the organic $CH_3NH_3^+$ units within the perovskite cages, showing a progressive evolution within the stability ranges of the tetragonal and orthorhombic phases. A conspicuously smaller unit-cell volume was found in comparison with samples obtained from traditional solvent-induced crystallization, which is related to the superior compactness of the $PbI_6$ framework, with a less defective nature. It seems that the robustness of the crystal strongly relies on the $PbI_6$ framework, and this is solidly built by mechano-chemical synthesis.

In the *I*4/*mcm* space group (RT crystal structure), the covalent framework $PbI_6$ was defined by placing Pb at 4*c* (0,0,0) sites, I at 4*a* (0,0,1/4) and 8*h* (*x*,*x*+½,0) Wyckoff sites. The organic cation is disordered around the 4*b* site (0,1/2,1/4) and the centre of the MA unit is displaced from the geometrical centre of this cage. In order to simulate the delocalization of this organic cation, the C and N atoms were placed at random in two positions at the 16*l* (*x*,*x*+½,*z*) site and six H atoms in the 32*m* (*x*,*y*,*z*) site. Figure 1a shows the Rietveld plot at 298 K. Figure 2a shows a schematic view of the tetragonal crystal structure where the configuration of the $CH_3NH_3^+$ unit is highlighted, and Figure 2b illustrates the four-fold possibilities of orientation of the MA units.

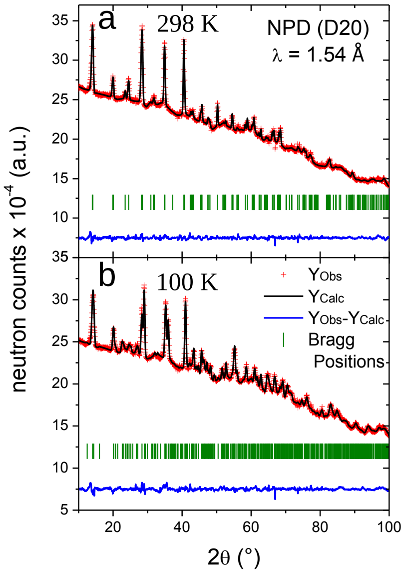

***Figure 1.*** *Observed (crosses) calculated (black line) and difference (blue line) profiles after the Rietveld refinement from NPD data at (a) 298 K and (b) 100K corresponding to tetragonal (I4/mcm) and orthorhombic (Pnma) symmetry, respectively.*

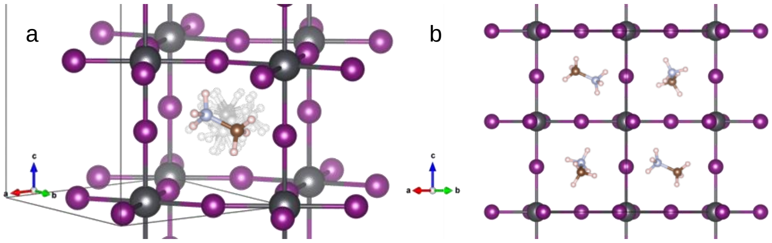

***Figure 2.*** *Two alternative views of the tetragonal structure observed at 298 K. (a) 3D view highlighting the octahedral tilting ($a^0a^0c^-$) and the superimposed $CH_3NH_3^+$ units, which are disordered in this temperature range (see text), (b) Idealized projection along [110] showing four possible configurations of the $CH_3NH_3^+$ unit in adjacent cages.*

The phase transition from the tetragonal to the orthorhombic phase of $MAPbI_3$ happens at 160 K. The 140 K and 100 K NPD patterns (illustrated in Fig. 1b) could thus be indexed in the orthorhombic symmetry, belonging to the *Pnma* space group. In this case, the Pb atoms are allocated in the 4*b* (0,0,1/2) site and the two types of iodide, I1 at 4*c* (*x*,1/4,*z*) and I2 at 8*d* (*x*,*y*,*z*) sites. The organic cation is around the 4*c* (1/2,1/4,1/2) position and the geometric centre of MA is displaced from this point. In the orthorhombic symmetry, the MA unit is not delocalized, and the C and N atoms were placed in 4*c* (*x*,1/4,*z*) sites and the H are distributed in both 4*c* (*x*,1/4,*z*) and 8*d* (*x*,*y*,*z*) sites. This model leads to a good starting point, which was improved from Difference Fourier Maps (DFM). The DFM displayed in Figure 3a and 3b reveal the presence of non-negligible negative densities between the H atoms, which can be explained considering that the MA molecule can also be rotated by 180° along the C–N axis.

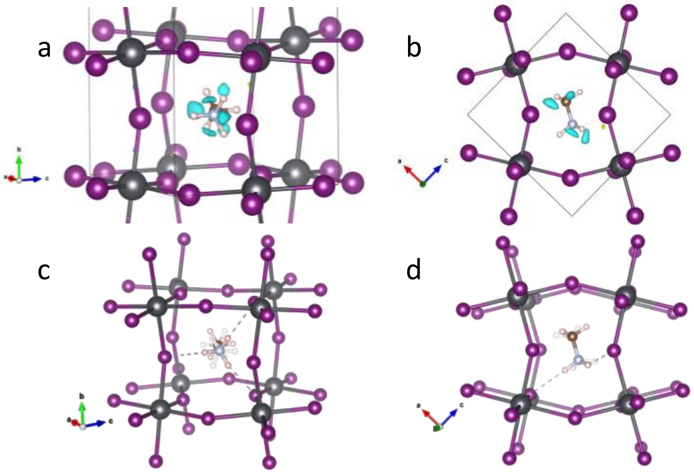

***Figure 3.*** *(top) Two views of the orthorhombic crystal structure of* $MAPbI_3$*, showing negative areas in the Difference Fourier Maps suggesting rotations of the MA molecule along the C-N axis (a) b-axis vertical (b) along b axis (bottom). Two views of the orthorhombic crystal structure of* $MAPbI_3$*, highlighting the H-bond interactions with adjacent I atoms (c) approximately along [101] direction, (d) along b axis; note the in-phase tilting of the* $PbI_6$ *octahedra.*

The C/N disorder totally disappears in the *Pnma* phase, which is driven by the formation of stronger N-H···I hydrogen bonds with the tilted corners of the octahedra. The Pb–I–Pb angles also decrease with temperatures, implying more pronounced tilting angles, as expected.

Regarding $MAPbI_2Br$, it is cubic in the 120 K-298 K range, suggesting that the anion disorder prevents the occurrence of phase transitions. In this case, the MA unit is aligned along the [111] direction in all the temperature range.

These results have been published in Scientific Reports, Ref [7]

## REFERENCES

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