

Direct Evidence of Permanent Octahedra Distortion in MAPbBr₃ Hybrid Perovskite.

Andrea Bernasconi and Lorenzo Malavasi*

University of Pavia, Department of Chemistry, Pavia

E-mail: lorenzo.malavasi@unipv.it

Table 1: Rietveld refinement results of the sample as a function of temperature.

	373 K	300 K	250 K	200 K	150 K
Space group	Pm-3m	Pm-3m	Pm-3m	I4/mcm	I4/mcm
a (Å)	5.94042 (6)	5.926241 (5)	5.914877 (5)	8.332114 (11)	8.309553 (15)
c (Å)	n.p.	n.p.	n.p.	11.849089 (22)	11.848213 (28)
Pb U _{ISO} (Å ²)	0.0237 (3)	0.0196 (2)	0.0168 (2)	0.0142 (3)	0.0123 (3)
Br ₁ U _{ISO} (Å ²)	0.0826 (5)	0.0798 (5)	0.0807 (5)	0.0613 (9)	0.0572 (10)
Br ₂ U _{ISO} (Å ²)	n.p.	n.p.	n.p.	0.0519 (13)	0.0485 (13)
X Br ₁	n.p.	n.p.	n.p.	0.2213 (4)	0.21701 (4)
Y Br ₁	n.p.	n.p.	n.p.	0.2809 (5)	0.2839 (4)
R _{WP} (%)	17.0	17.1	17.6	17.1	20.3

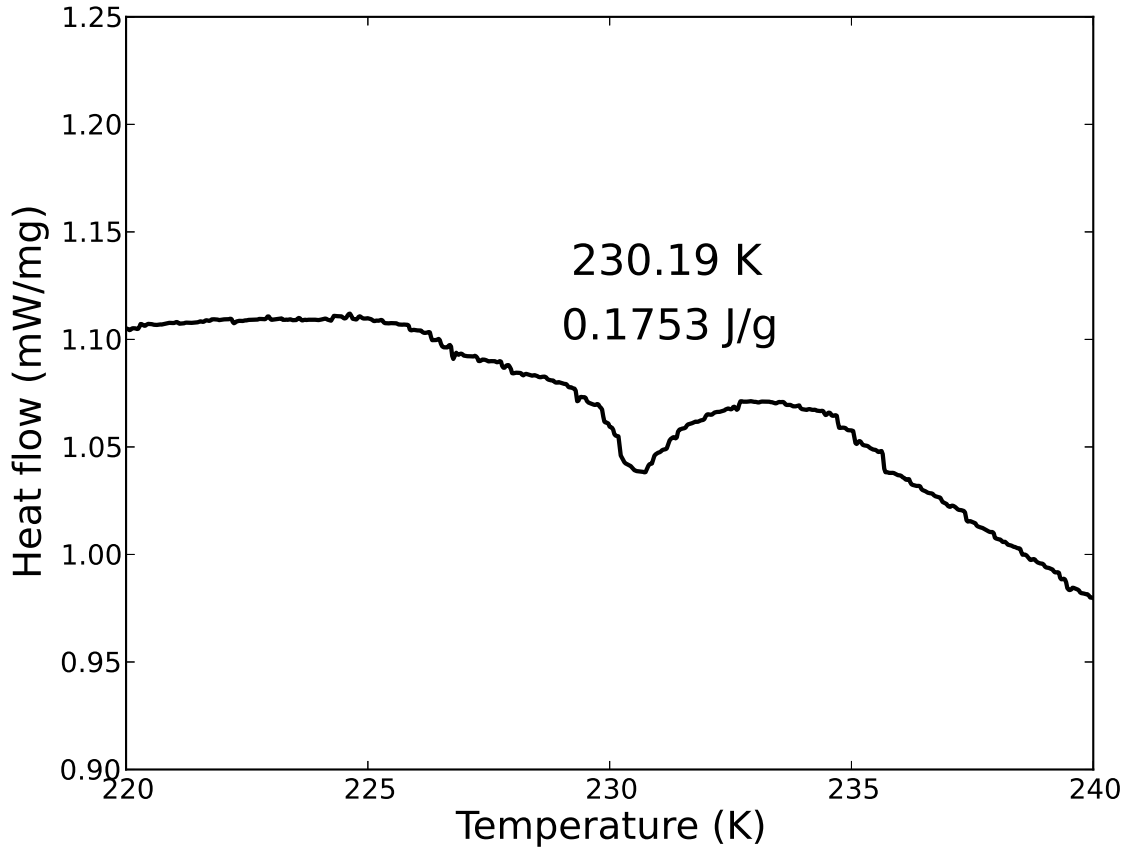


Figure 1: Differential Scanning Calorimetry curve of the sample. The cubic/tetragonal transition is displayed, whose temperature values has been determined by the onset method.

Table 2: PDF refinement results of the sample as a function of temperature in the 10-50 Å range.

	373 K	300 K	250 K	200 K	150 K
Space group	Pm-3m	Pm-3m	Pm-3m	I4/mcm	I4/mcm
a (Å)	5.9391 (10)	5.9242 (9)	5.9133 (8)	8.3342 (52)	8.3103 (38)
c (Å)	n.p.	n.p.	n.p.	11.8288 (77)	11.8251 (56)
Pb U_{ISO} (Å ⁻²)	0.0136 (6)	0.0114 (5)	0.0101 (4)	0.0096 (5)	0.0091 (5)
Br ₁ U_{ISO} (Å ²)	0.0599 (24)	0.0586 (22)	0.0594 (20)	0.0311 (3)	0.0296 (4)
Br ₂ U_{ISO} (Å ²)	n.p.	n.p.	n.p.	0.0243 (3)	0.0227 (3)
X Br ₁	n.p.	n.p.	n.p.	0.2119 (1)	0.2101 (1)
Y Br ₁	n.p.	n.p.	n.p.	0.2881 (1)	0.2899 (1)
R _W (%)	26.3	25.8	26.1	20.3	19.3

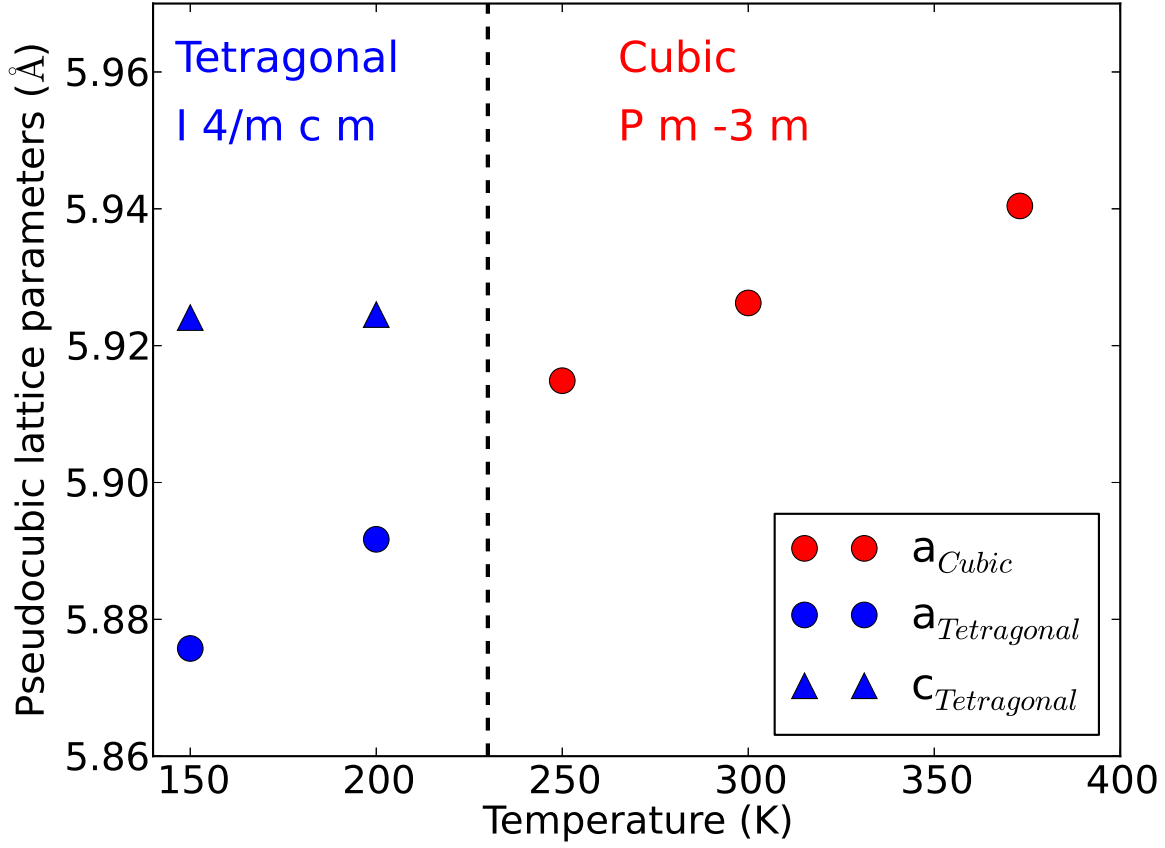


Figure 2: Pseudocubic lattice parameter evolution after Rietveld refinement.

Table 3: PDF refinement results of the sample at the different temperatures in the 1-10 Å range with the orthorhombic Pnma space group.

	150K	200K	250K	300K	373K
a (Å)	8.134 (9)	8.140 (12)	8.150 (14)	8.157 (18)	8.166 (16)
b (Å)	11.777 (11)	11.783 (17)	11.797 (19)	11.815 (18)	11.833 (20)
c (Å)	8.577 (13)	8.626 (19)	8.660 (19)	8.688 (20)	8.731 (15)
Pb U_{ISO} (Å ⁻²)	0.0050 (5)	0.0056 (6)	0.0065 (8)	0.0078 (10)	0.0097 (15)
Br ₁ U_{ISO} (Å ²)	0.0108 (18)	0.0132 (21)	0.0152 (26)	0.0177 (35)	0.0176 (48)
Br ₂ U_{ISO} (Å ²)	0.0014 (10)	0.0017 (10)	0.0024 (12)	0.0032 (16)	0.0041 (26)
X Br ₁	0.2990 (25)	0.2970 (26)	0.2939(29)	0.2914(32)	0.2622 (31)
Y Br ₁	0.0236 (10)	0.0254 (11)	0.0269 (13)	0.0278 (14)	0.0341 (14)
Z Br ₁	0.7042 (24)	0.7074 (28)	0.7118 (31)	0.7154 (36)	0.7395 (37)
X Br ₂	0.9872 (16)	0.9862 (19)	0.9854 (22)	0.9839 (23)	0.9772 (22)
Z Br ₂	0.4885 (17)	0.4880 (19)	0.4882 (22)	0.4882 (23)	0.4874 (24)
R _W (%)	22.6	21.5	21.4	21.3	20.1

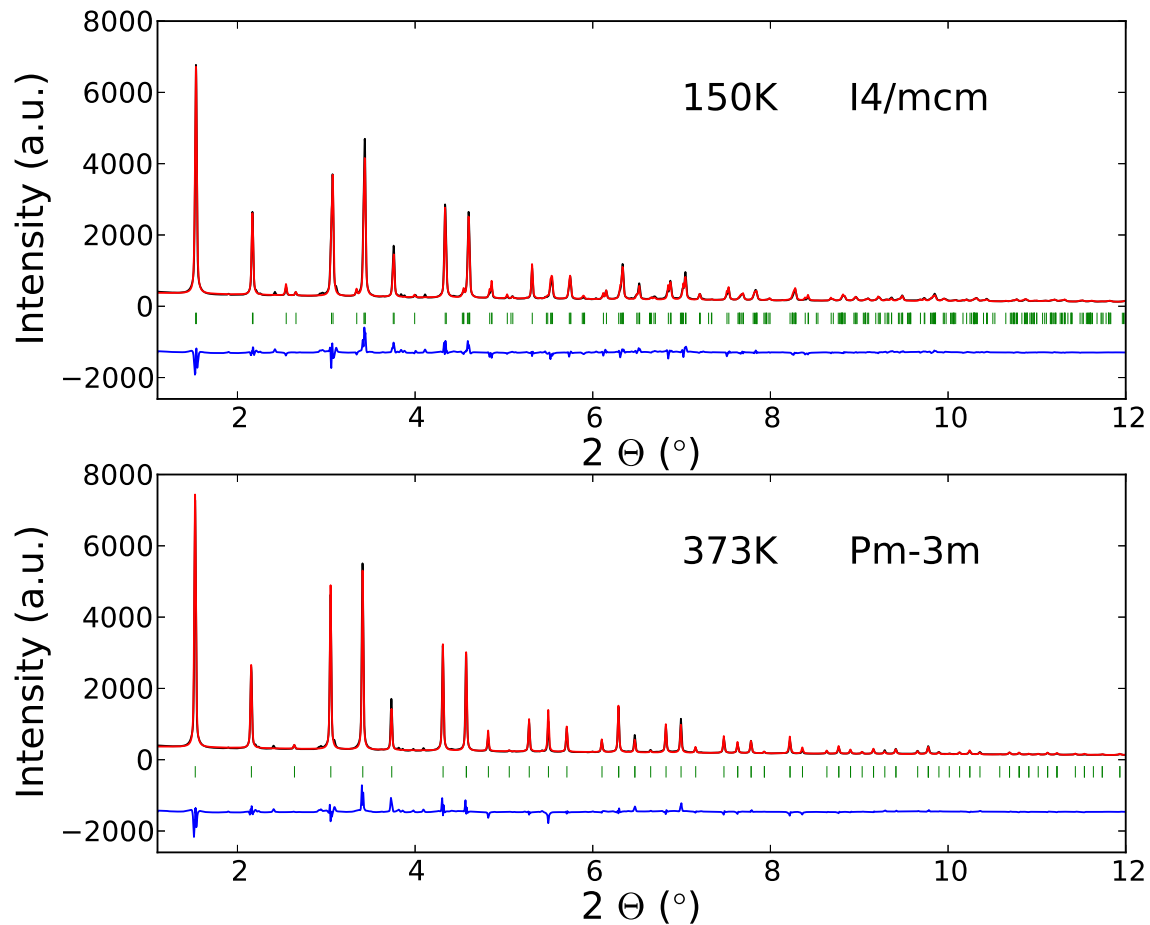


Figure 3: On the top, Rietveld refinement using the I4/mcm space group for the 150 K data. On the bottom, Rietveld refinement using the Pm-3m space group for the 373 K data. Black line represents the experimental data, red line represents the fit, blue line represents the difference between data and fit, and green lines represent the different hkl peak positions.

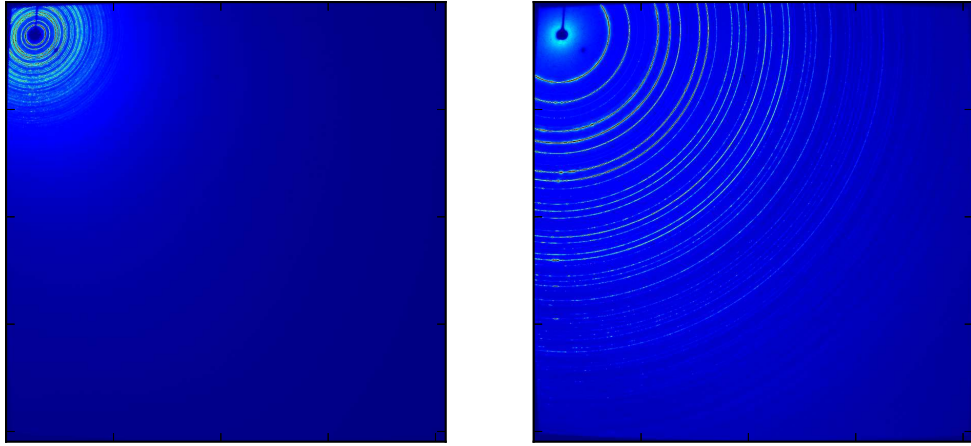


Figure 4: On the left side, MAPbBr₃ 2D image collected at 300K in near field configuration (i.e. for Pair Distribution Function approach). On the right side, MAPbBr₃ 2D image collected at 300K in high resolution configuration (i.e. for Rietveld approach).

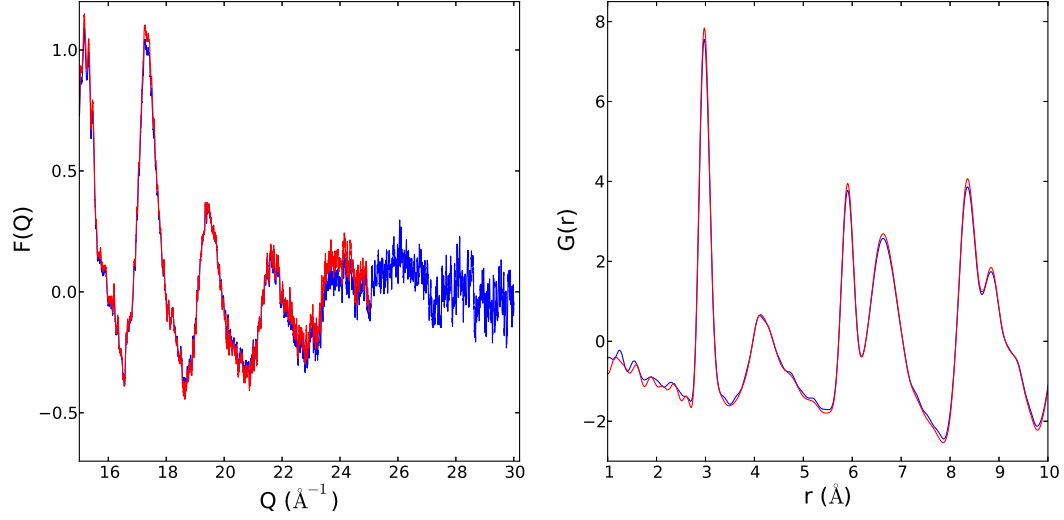


Figure 5: On the left, $F(Q)$ s of MAPbBr_3 obtained using a Q_{MAX} equals to $30.1 \text{ \AA}^{-1}$ (blue curve) and reducing the Q_{MAX} to $25 \text{ \AA}^{-1}$ (red curve). On the right, $G(r)$ of MAPbBr_3 obtained using a Q_{MAX} equals to $30.1 \text{ \AA}^{-1}$ (blue curve) and reducing the Q_{MAX} to $25 \text{ \AA}^{-1}$ (red curve). In both cases, curves refer to the temperature of 150 K.

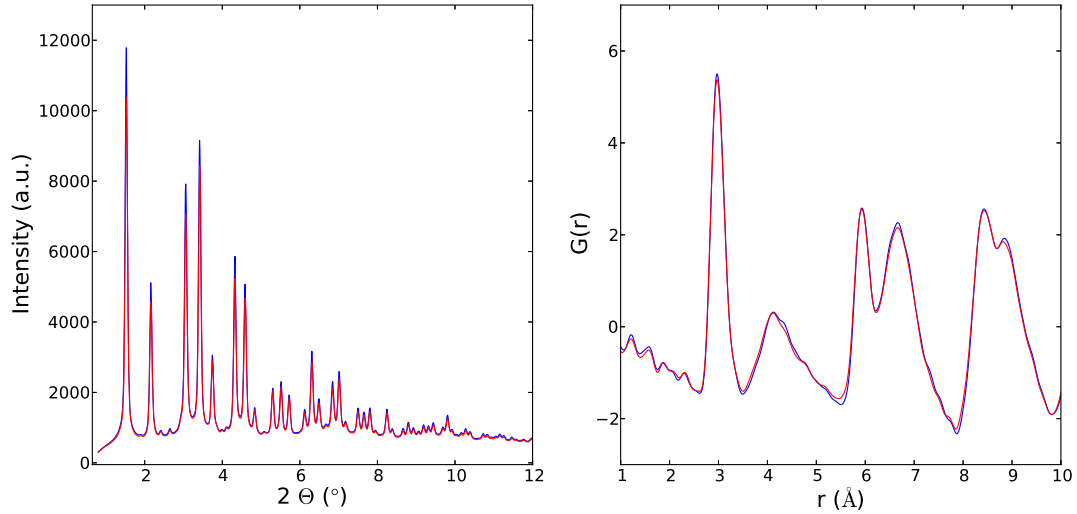


Figure 6: On the left, 2θ vs Intensity patterns of MAPbBr_3 collected at the beginning of the experiment (blue curve) and at the end of the experiment (red curve). On the right, $G(r)$ s of MAPbBr_3 collected at the beginning of the experiment (blue curve) and at the end of the experiment (red curve).