Supporting Information

ELUCIDATING THE METHYLAMMONIUM (MA) CONFORMATION IN $MAPbBr_3$ PEROVSKITE WITH APPLICATION IN SOLAR CELLS

Carlos A. López,[a,b] María Victoria Martínez-Huerta,[c] María Consuelo Alvarez-Galván,[c] Paula Kayser [a], Patricia Gant[d], Andres Castellanos-Gomez[a], María T. Fernández-Díaz,[e] François Fauth,[f] and José A. Alonso[a]*

[a] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049 Madrid, Spain.

[b] INTEQUI, Universidad Nacional de San Luis, CONICET, Facultad de Química, Bioquímica y Farmacia, Chacabuco y Pedernera, 5700 San Luis, Argentine.

[c] Instituto de catálisis y Petroleoquímica, CSIC, Cantoblanco 28049 Madrid, Spain.

[d] Instituto Madrileño de Estudios Avanzados en Nanociencia (IMDEA Nanociencia), Campus de Cantoblanco, E-28049 Madrid, Spain.

[e] Institut Laue Langevin, BP 156X, Grenoble, F-38042, France.

[f] CELLS–ALBA synchrotron E-08290 Cerdanyola del Valles, Barcelona, Spain.

*Corresponding author: (ja.alonso@icmm.csic.es)

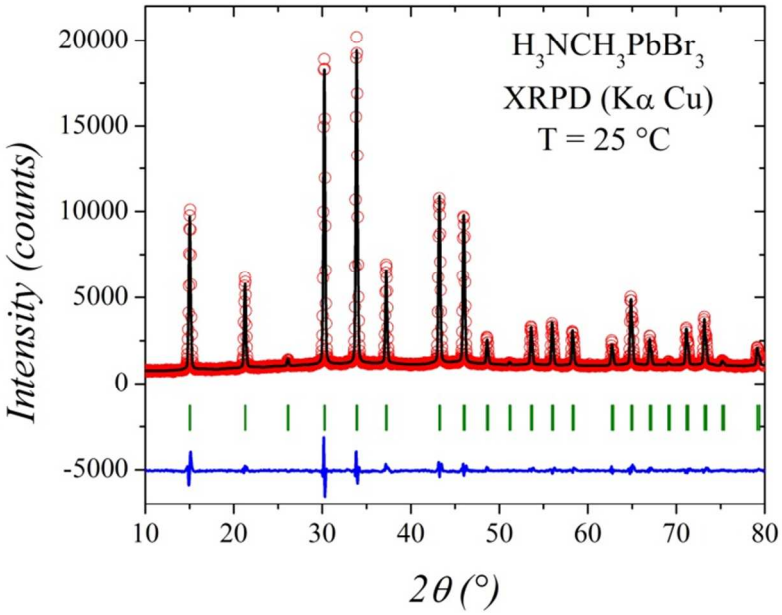


Figure S1. Observed (red circles), calculated (black line) and difference (blue line) laboratory X-ray diffraction pattern, at room temperature, refined in the cubic system, space group $Pm\bar{3}m$ using the Le Bail method.

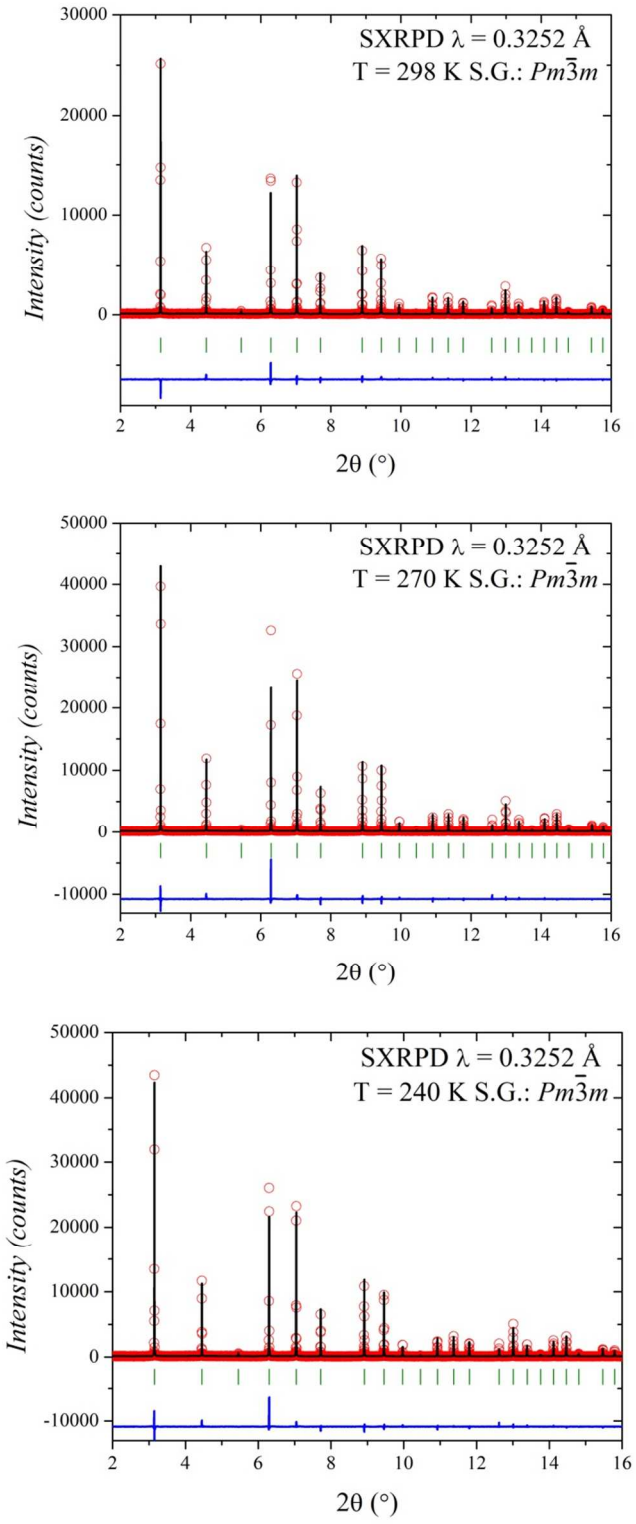


Figure S2. Observed (red circles), calculated (black line) and difference (blue line) synchrotron X-ray diffraction patterns at 298, 270 and 240 K, refined in the cubic system, space group $Pm\bar{3}m$.

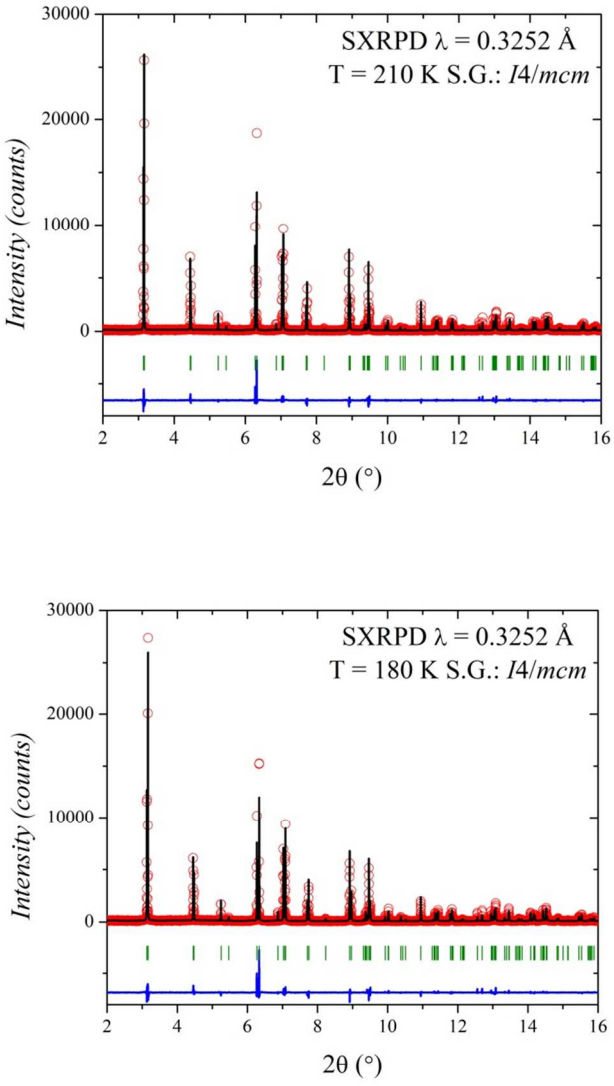


Figure S3. Observed (red circles), calculated (black line) and difference (blue line) synchrotron X-ray diffraction patterns at 210 and 180 K, refined in the tetragonal system, space group *I*4/*mcm*.

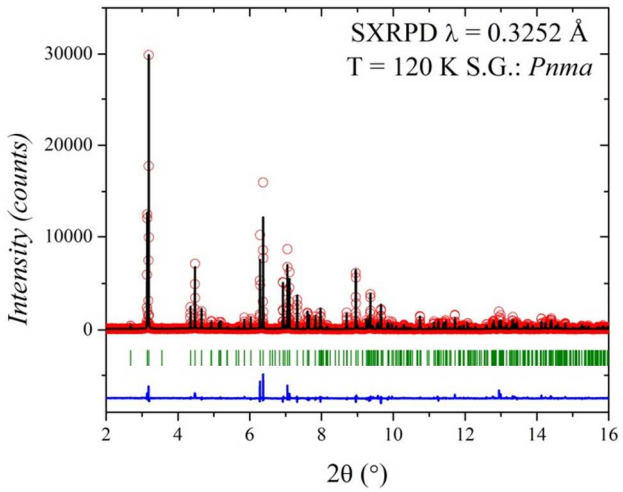


Figure S4. Observed (red circles), calculated (black line) and difference (blue line) synchrotron X-ray diffraction patterns at 120 K in the orthorhombic system, space group *Pnma*.

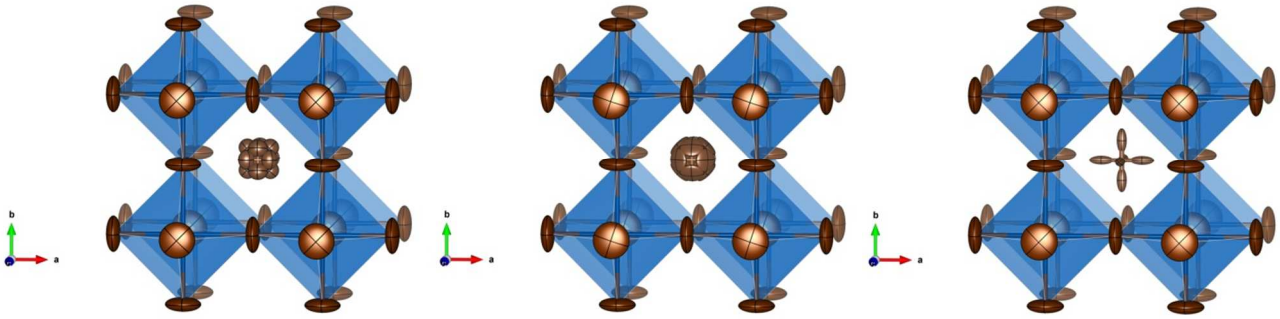
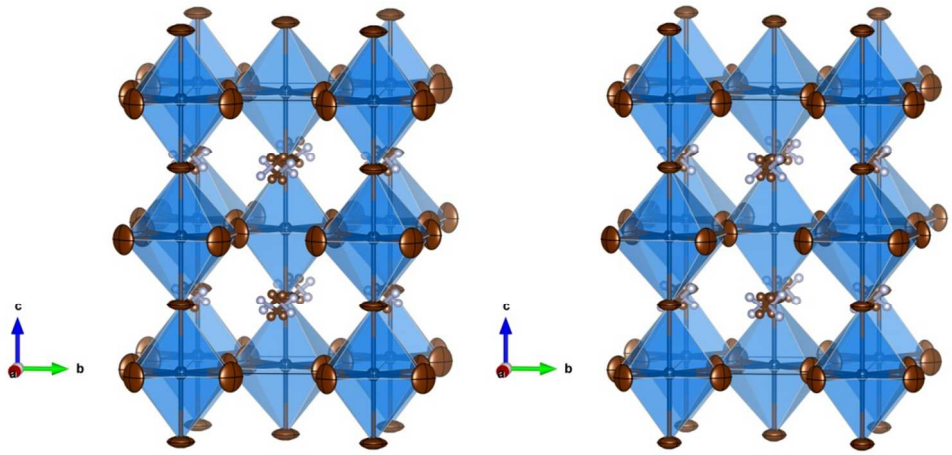


Figure S5. Thermal evolution of the crystal structure in the cubic system (at 298, 270 and 240 K, from left to right), where the main change is due to methylammonium orientation.



220 K **180 K**

Figure S6. Crystal structures in the tetragonal system at 220 and 180 K.

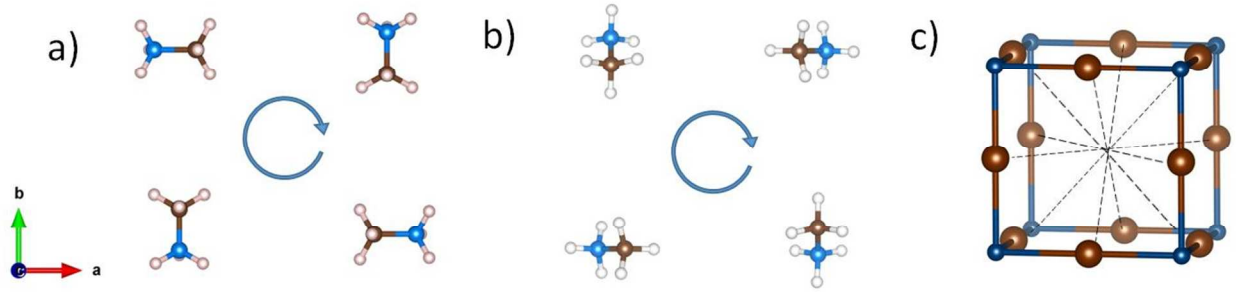


Figure S7. Schematic view of different orientations of MA contained in a) (001) plane and b) at 45° of (100) plane at room temperature, deduced from NPD at RT. The dashed lines in c) indicate the directions [110] that contain the MA figures in a) and b).

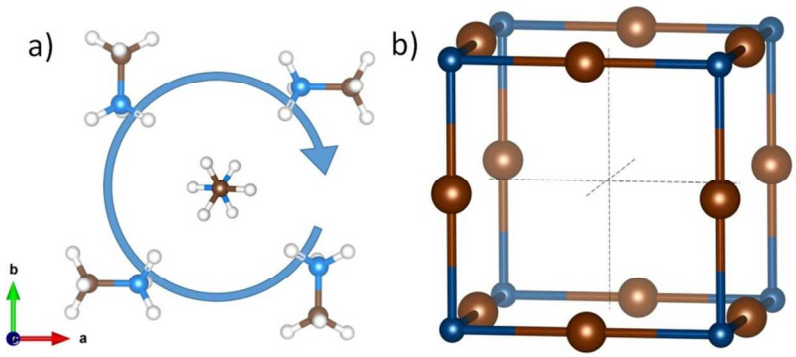


Figure S8. a) Schematic view of different orientations of MA at 240 K deduced from SXRPD. The dashed lines in c) indicate the [100] directions that contain the MA figures in a).

Table S1. Crystallographic data for $MAPbBr_3$ from SXRPD data at room temperature (298 K). System: cubic, Space group: $Pm\bar{3}m$, a = 5.93076(2) Å.

Atom	x	y	z	Uiso*/Ueq	Occ
Pb	0	0	0	0.0236(5)	1
Br	0.5	0	0	0.098(2)	1
C	0.5	0.42(1)	0.42(1)	0.03(5)	0.0833
N	0.5	0.42(1)	0.42(1)	0.03(5)	0.0833

R_p: 12.3%; R_{wp}: 16.2%; R_{exp}: 14.2%; χ^2: 2.1; R_{Bragg}: 7.7%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0236(5)	0.0236(5)	0.0236(5)	0.00	0.00	0.00
Br	0.021(2)	0.136(3)	0.136(3)	0.00	0.00	0.00
C	0.04(9)	0.03(3)	0.03(3)	0.00	0.00	0.00(3)
N	0.04(9)	0.03(3)	0.03(3)	0.00	0.00	0.00(3)

Table S2. Crystallographic data for $MAPbBr_3$ from SXRPD data at 270 K. System: cubic, Space group: $Pm\bar{3}m$, a = 5.92382(3) Å.

	x	y	z	U_{iso}*/U_{eq}	Occ
Pb	0	0	0	0.0220(4)	1
Br	0.5	0	0	0.102(2)	1
C	0.5	0.404(3)	0.404(3)	0.0431(8)	0.0833
N	0.5	0.404(3)	0.404(3)	0.0431(8)	0.0833

R_p: 11.5%; R_{wp}: 15.0%; R_{exp}: 11.3%; χ^2: 2.6; R_{Bragg}: 5.7%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0220(4)	0.0220(4)	0.0220(4)	0.00000	0.00000	0.00000
Br	0.0200(2)	0.143(2)	0.143(2)	0.00000	0.00000	0.00000
C	0.062(2)	0.0337(4)	0.0337(4)	0.00000	0.00000	−0.03(2)
N	0.062(2)	0.0337(4)	0.0337(4)	0.00000	0.00000	−0.03(2)

Table S3. Crystallographic data for $MAPbBr_3$ from SXRPD data at 240 K. System: cubic, Space group: $Pm\bar{3}m$, a = 5.91685(3) Å.

	x	y	z	U_{iso}*/U_{eq}	Occ
Pb	0	0	0	0.0205(4)	1
Br	0.5	0	0	0.102 (2)	1
C	0.355(5)	0.5	0.5	0.03(2)	0.16667
N	0.355(5)	0.5	0.5	0.03(2)	0.16667

R_p: 11.4%; R_{wp}: 14.6%; R_{exp}: 11.2%; χ^2: 2.5; R_{Bragg}: 5.4%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0205(4)	0.0205(4)	0.0205(4)	0.00000	0.00000	0.00000
Br	0.020(2)	0.143 (2)	0.143(2)	0.00000	0.00000	0.00000
C	0.06(2)	0.01(1)	0.01(1)	0.00000	0.00000	0.00000
N	0.06(2)	0.01(1)	0.01(1)	0.00000	0.00000	0.00000

Table S4. Crystallographic data for $MAPbBr_3$ from SXRPD data at 210 K. System: tetragonal, Space group: I4/mcm, a = 8.33828(3), 11.8750(1) Å and V = 825.63(1) Å3.

	x	y	z	U_{iso}*/U_{eq}	Occ
Pb	0.00	0.00	0.00	0.0186(6)	1
Br1	0.00	0.00	0.25	0.064(3)	1
Br2	0.2791(3)	0.7791(3)	0.00	0.073(2)	1
N	0.578(4)	0.078(4)	0.274(6)	0.05(3)*	0.25
C	0.471(5)	−0.029(5)	0.209(5)	0.04(3)*	0.25

R_p: 11.6%; R_{wp}: 15.0%; R_{exp}: 12.1%; χ^2: 2.1; R_{Bragg}: 6.7%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0181(5)	0.0181(5)	0.0196(9)	0.00000	0.00000	0.00000
Br1	0.088(3)	0.088(3)	0.015(3)	0.00000	0.00000	0.00000
Br2	0.059(2)	0.059(2)	0.101(3)	0.045(2)	0.00000	0.00000

Table S5. Crystallographic data for $MAPbBr_3$ from SXRPD data at 180 K. System: tetragonal, Space group: I4/mcm, a = 8.31933(6), b = 11.8909(1) Å and V = 822.98(1) Å3.

	x	y	z	U_{iso}*/U_{eq}	Occ
Pb	0	0	0	0.0161(6)	1
Br1	0	0	0.25	0.049(2)	1
Br2	0.2858(3)	0.7858(3)	0	0.059(2)	1
N	0.577(4)	0.077(4)	0.287(5)	0.02(2)*	0.25
C	0.471(5)	−0.029(5)	0.218(6)	0.05(3)*	0.25

R_p: 12.0%; R_{wp}: 15.4%; R_{exp}: 12.0%; χ^2: 2.1; R_{Bragg}: 6.9%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0151(5)	0.0151(5)	0.0179(9)	0.00000	0.00000	0.00000
Br1	0.065(2)	0.065(2)	0.017(3)	0.00000	0.00000	0.00000
Br2	0.048(2)	0.048(2)	0.080(3)	0.034(2)	0.00000	0.00000

Table S6. Crystallographic data for $MAPbBr_3$ from SXRPD data at 120 K. System: orthorhombic, Space group: *Pnma*, a = 7.99820(6), b = 11.85699(8) Å, c = 8.57117(6) Å and V = 812.84(1) $Å^3$.

	x	y	z	U_{iso}*/U_{eq}	Occ
Pb	0	0	0.5	0.0083(7)	1
Br1	0.9694(6)	0.25	0.4871(8)	0.019(3)	1
Br2	0.2927(3)	0.0267(2)	0.7103(3)	0.022(2)	1
N	0.560(5)	0.25	0.594(5)	0.02533*	1
C	0.476(4)	0.25	0.429(4)	0.02533*	1

R_p: 12.0%; R_{wp}: 15.4%; R_{exp}: 12.0%; χ^2: 1.8; R_{Bragg}: 7.9%

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.0156(7)	0.0041(7)	0.0051(7)	−0.000(1)	0.000(1)	0.001(1)
Br1	0.039(4)	0.002(2)	0.016(3)	0.00000	0.003(3)	0.00000
Br2	0.027(2)	0.023(2)	0.018(2)	−0.003(2)	−0.010(2)	0.004(2)

Table S7. Crystallographic data for $MAPbBr_3$ from NPD data at room temperature (298 K). System: cubic, Space group: $Pm\bar{3}m$, a = 5.9259(4) Å.

		x	y	z	Uiso*/Ueq	Occ.
Pb	1*a*	0	0	0	0.025(2)	1
Br	3*d*	0.5	0	0	0.098(5)	1
C	24*i*	0.5	0.407(2)	0.407(2)	0.039(7)	0.08333
N	24*i*	0.5	0.407(2)	0.407(2)	0.039(7)	0.08333
H1	24*l*	0.5	0.414(9)	0.247(9)	0.06(1)*	0.08333
H2	48*n*	0.326(3)	0.326(3)	0.448(4)	0.06(1)*	0.16667
R_p: 1.3%; R_{wp}: 1.6%; R_{exp}: 1.7%; χ^2: 1.1; R_{Bragg}: 3.9%						
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb	0.025(2)	0.025(2)	0.025(2)	0.00000	0.00000	0.00000
Br	0.018(5)	0.138(5)	0.138(5)	0.00000	0.00000	0.00000
C	0.004(8)	0.057(7)	0.057(7)	0.00000	0.00000	0.003(6)
N	0.004(8)	0.057(7)	0.057(7)	0.00000	0.00000	0.003(6)