Electronic Supplementary Information

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

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Table S1: Crystallographic data for $MAPbI_3$ phase in tetragonal system (*I*4/*mcm*) from SXRPD at lower temperatures.

a) T=180 K, a = 8.7865(1) Å, c = 12.6656(2) Å and V = 978.83(2) Å^3					
	x	***Y***	***z***	***Uiso*/Ueq***	***Occ***
Pb1	0	0	0	0.017(2)	1
I1	0	0	0.25	0.032(4)	1
I2	0.2994(3)	0.7994(3)	0	0.038(3)	1
C/N	0.949(3)	0.449(3)	0.218(4)	0.013*	0.25/0.25
R_p = 11.7%, R_{wp} = 14.9%, χ^2 = 1.28, R_{Bragg} = 5.78%					
Atomic displacement parameters (Å^2)					
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.017(2)	0.017(2)	0.017(3)	0	0	0
I1	0.043(3)	0.043(3)	0.009(4)	0	0	0
I2	0.028(2)	0.028(2)	0.059(4)	0.021(3)	0	0
b) T = 140 K, a = 8.7773(1) Å, c = 12.6627(2) Å and V = 975.56(2) Å^3					
	x	***y***	***z***	***Uiso*/Ueq***	***Occ***
Pb1	0	0	0	0.014(2)	1
I1	0	0	0.25	0.030(3)	1
I2	0.3007(3)	0.8007(3)	0	0.033(2)	1
C/N	0.937(3)	0.437(3)	0.221(4)	0.013*	0.25/0.25
R_p = 12.2%, R_{wp} = 15.5%, χ^2 = 1.73, R_{Bragg} = 5.01%					
Atomic displacement parameters (Å^2)					
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.010(1)	0.010(1)	0.022(3)	0	0	0
I1	0.045(3)	0.045(3)	0.003(1)	0	0	0
I2	0.023(2)	0.023(2)	0.054(3)	0.019(2)	0	0

Table S2: Crystallographic data for $MAPbI_3$ phase in cubic system ($Pm\bar{3}m$) from SXRPD at 393 K, a = 6.31065(3) Å and V = 251.318(2) Å^3

	x	*y*	*z*	*Ueq*	*Occ*
Pb1	0	0	0	0.0415(7)	1
I1	0.5	0	0	0.128(3)	1
C/N	0.5	0.41(1)	0.41(1)	0.05(6)	0.083/0.083
R_p = 10.0%, R_{wp} = 12.8%, χ^2 = 2.37, R_{Bragg} = 4.83%					
Atomic displacement parameters (Å^2)					
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0415(7)	0.0415(7)	0.0415(7)	0	0	0
I1	0.029(2)	0.178(3)	0.178(3)	0	0	0
C/N	0.00(6)	0.07(5)	0.07(5)	0	0	−0.05(6)

Table S3: Crystallographic data for $MAPbI_2Br$ phases in cubic system ($Pm\bar{3}m$) from SXRPD at 120 K.

a = 6.12035(8) Å and V = 229.260(5) Å^3					
	x	*y*	*z*	*Uiso*/Ueq*	*Occ. (<1)*
Pb1	0	0	0	0.0320(9)	1
Br1	0.5	0	0	0.148(4)	0.37
I1	0.5	0	0	0.148(4)	0.63
C1	0.568(3)	0.568(3)	0.568(3)	0.03(2)	0.12
N1	0.568(3)	0.568(3)	0.568(3)	0.03(2)	0.12
R_p = 11.4%, R_{wp} = 14.4% χ^2 = 1.07 R_{Bragg} = 9.8%					
Atomic displacement parameters (Å^2)					
	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0320(9)	0.0320(9)	0.0320(9)	0.00000	0.00000	0.00000
Br/I	0.019(3)	0.212(4)	0. 212(4)	0.00000	0.00000	0.00000
C1	0.03(2)	0.03(2)	0.03(2)	0.01(1)	0.01(1)	0.01(1)
N1	0.03(2)	0.03(2)	0.03(2)	−0.01(1)	−0.01(1)	−0.01(1)

EDX Results

The results derived from the compositional analysis of the samples are shown in figures S1 and S2 and in Table S4. For both samples, the EDX spectra show well defined peaks corresponding to lead, bromine and iodine. As observed, obtained weight % of these elements (Table S3) are in agreement with the nominal values. The slight difference between the experimental values and the nominal counterparts for $MAPbI_3$ sample may be explained by the extreme sensitivity of this perovskite to high energy electron beam radiation, being easily decomposed into PbI_2 during EDX analysis (S. Chen, et al., Atomic scale insights into structure instability and decomposition pathway of methylammonium lead iodide perovskite, Nat. Commun., 2018, 9(1), 4807).

Figure S1. EDX spectrum of $MAPbI_3$

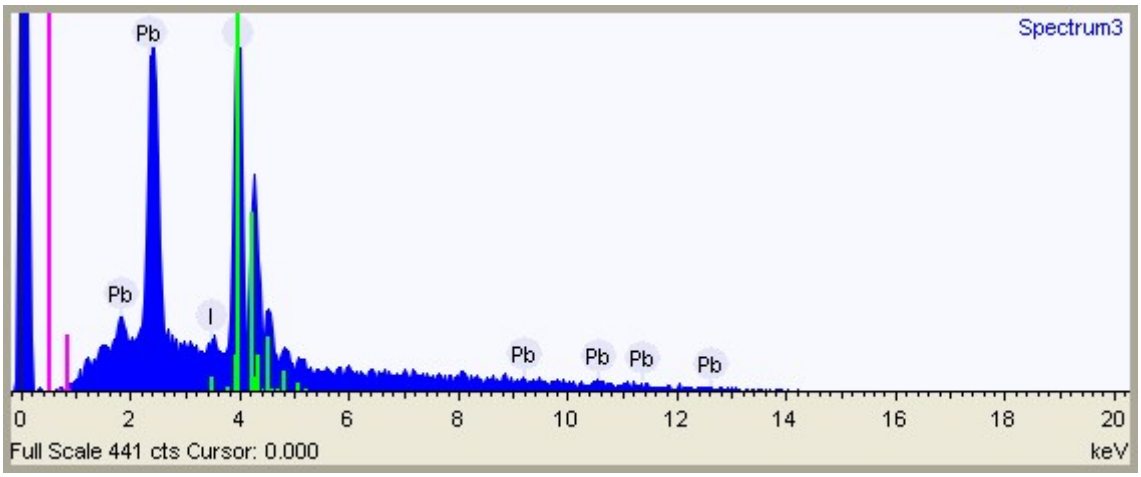

Figure S2. EDX spectrum of $MAPbI_2Br$

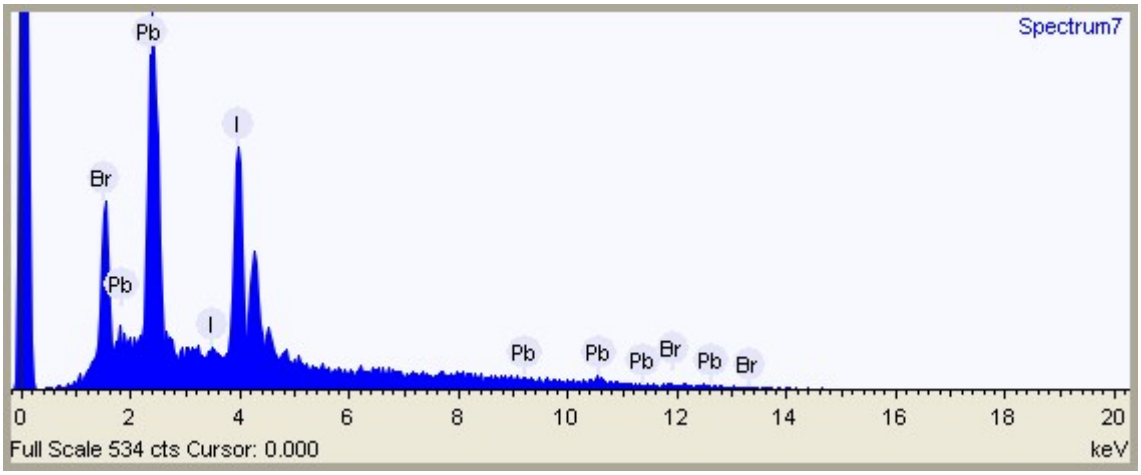

Table S4. Chemical composition by EDX and nominal values (% weight) for both $MAPbI_3$ and $MAPbI_2Br$ obtained by ball milling.

Sample	I (w. %)	I (w.%) nominal	Br (w. %)	Br (w.%) nominal	Pb (w. %)	Pb (w.%) nominal
$MAPbI_3$	66.8	64.8	---	---	33.2	35.2
$MAPbI_2Br$	46.5	46.9	15.2	14.8	38.3	38.3

Table S5. Chemical analysis of C, N, H for both $MAPbI_3$ and $MAPbI_2Br$ obtained by ball milling (calculated values in parenthesis)

Run	Weight (mg)	Carbon(%)	Hydrogen(%)	Nitrogen(%)
$CH_3NH_3PbI_2Br$	1.755	2.13	0.7	2.16
$CH_3NH_3PbI_2Br$	1.634	2.13	0.75	2.16
Average		2.13 (2.09)	0.72 (1.05)	2.16 (2.44)
$CH_3NH_3PbI_3$	1.883	2.05	0.78	2.02
$CH_3NH_3PbI_3$	1.578	2.09	1.12	1.97
Average		2.07 (1.94)	0.95 (0.97)	1.99 (2.26)

Table S6. X-ray fluorescence (TXRF) chemical analyses of the samples $MAPbI_3$ and $MAPbI_2Br$. Nominal values (%, weight) are shown in brackets

	mg Br / liter	% Br (wt.)	mg I / liter	% I (wt.)	mg Pb / liter	% Pb (wt.)
$MAPbI_3$			1074	62.8 (64.8)	635.3	37.2 (35.2)
$MAPbI_2Br$	288.3	14.5 (14.8)	827.0	41.5 (46.9)	875.0	44.0 (38.3)