Electronic Supplementary Information

Phase Behaviour and Composition in the Formamidinium-Methylammonium Hybrid Lead Iodide Perovskite Solid Solution

O. J. Weber, B. Charles and M. T. Weller

Department of Chemistry and Centre for Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath. BA2 7AY. UK. E-mail: m.t.weller@bath.ac.uk.

Contents

Table S1 Reactant quantities used for crystal synthesis via precipitation from hydroiodic acid (method HI)

	Ratios		Weights (g)			Volume HI (ml)
Sample	**MA**	**FA**	**MAI**	**FAI**	**$Pb(CH_3CO_2)_2 \cdot 3H_2O$**	**1 molar**
1	1	0	0.2564	0	0.6119	1.6130
2	0.9	0.1	0.2303	0.0277	0.6106	1.6096
3	0.8	0.2	0.2043	0.0552	0.6093	1.6062
4	0.7	0.3	0.1784	0.0827	0.6080	1.6029
5	0.6	0.4	0.1526	0.1100	0.6068	1.5996
6	0.5	0.5	0.1269	0.1373	0.6055	1.5962
7	0.4	0.6	0.1013	0.1644	0.6043	1.5929
8	0.3	0.7	0.0758	0.1914	0.6030	1.5896
9	0.2	0.8	0.0504	0.2182	0.6018	1.5864
10	0.1	0.9	0.0252	0.2450	0.6005	1.5831
11	0	1	0	0.2717	0.5993	1.5798

Table S2 Reactant quantities used for crystal synthesis via Inverse solubility (method IS)

0.001	**mol**	**1 M solutions in 1 mL γ-butyrolactone**							
Ratio MA/FA	**9:1**	**8:2**	**7:3**	**6:4**	**5:5**	**4:6**	**3:7**	**2:8**	**1:9**
	wgt / g								
MAI	0.1431	0.1272	0.1113	0.0954	0.0795	0.0636	0.0477	0.0318	0.0159
FAI	0.0172	0.0344	0.0516	0.0688	0.0860	0.1032	0.1204	0.1376	0.1548
PbI2	0.4610	0.4610	0.4610	0.4610	0.4610	0.4610	0.4610	0.4610	0.4610

Table S3 Lattice Parameters and Cell Volumes at 300K of $FA_xMA_{1-x}PbI_3$ crystals grown via inverse solubility (IS) method.

x in $FA_xMA_{1-x}PbI_3$	Reduced lattice parameter / Å	Cell Volume / Å^3
0.1	6.3047(15)	249.946(14)
0.2	6.3102(15)	251.267(1)
0.3	6.3122(2)	251.501(17)
0.4	6.3199(3)	252.42(2)
0.5	6.3319(15)	253.859(1)
0.6	6.3333(3)	254.03(2)
0.7	6.3479(2)	255.795(18)
0.8	6.3543(2)	256.573(2)
0.9	6.3486(2)	255.878(15)

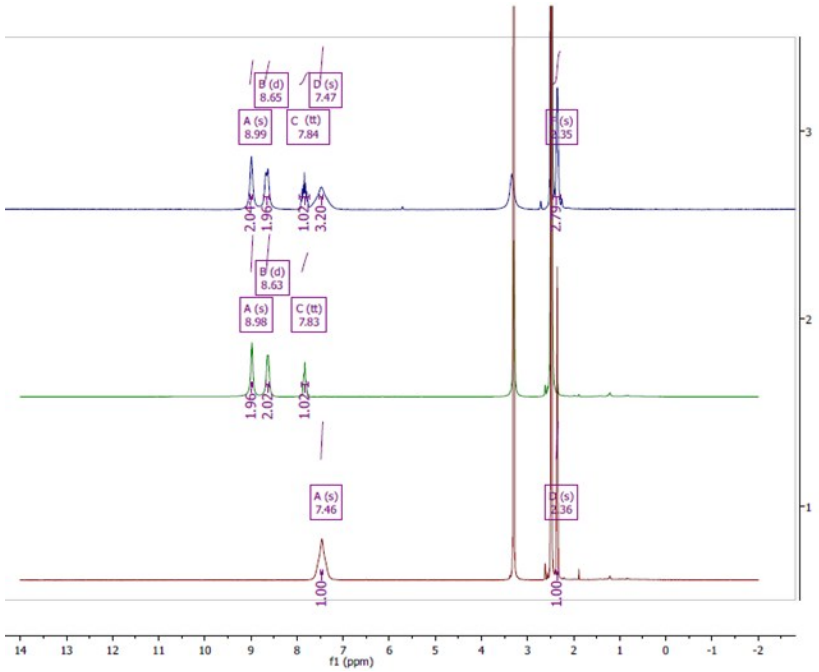

Figure 1 ^{1}H NMR in d_6-DMSO of 1) $MAPbI_3$ (HI), 2) $FAPbI_3$ (HI) and 3) $FA_{0.5}MA_{0.5}PbI_3$ (IS).

Assignments:

$MAPbI_3$ ^{1}H NMR (300 MHz, d6-DMSO) δ 2.36 (3H, s, CH_3), 7.46 (3H, NH_3).
$FAPbI_3$ ^{1}H NMR (300 MHz, d6-DMSO) δ 7.83 (1H, tt, CH), 8.63 (2H, d, NH_2), 8.98 (2H, s, NH_2).
$FA_{0.5}MA_{0.5}PbI_3$ ^{1}H NMR (300 MHz, d6-DMSO) δ 2.35 (3H, s, CH_3), 7.46 (3H, NH_3), 7.83 (1H, tt, CH), 8.63 (2H, d, NH_2), 8.97 (2H, s, NH_2).

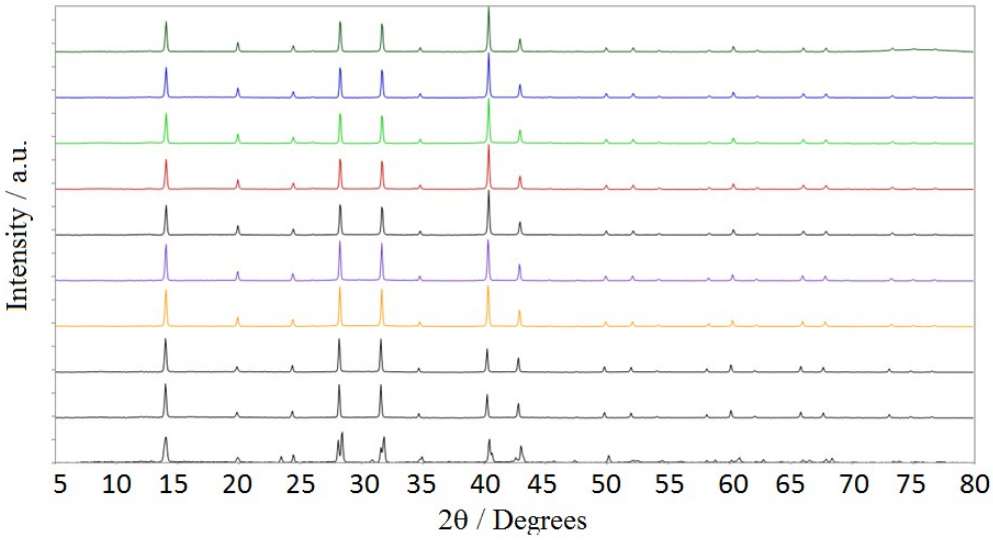

Figure 2 Powder X-ray diffraction patterns of HI method $MAPbI_3$ (bottom) $FA_xMA_{1-x}PbI_3$ $0 \leq x \leq 1$ in x = 0.1 increments to the top.

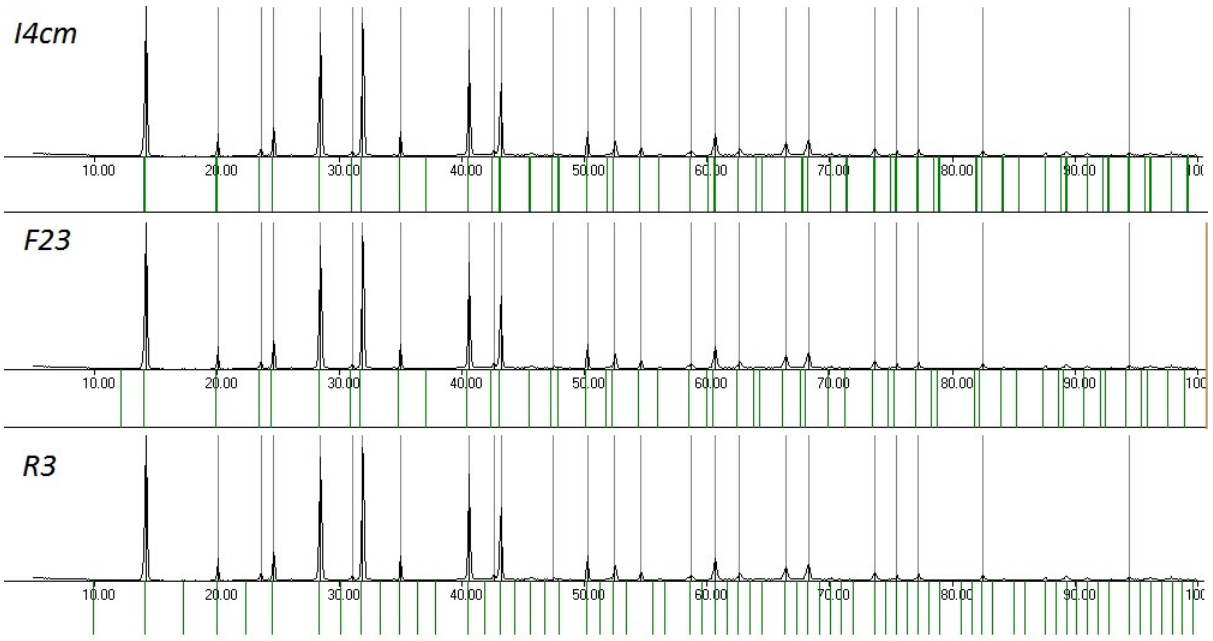

Figure 3 $FA_{0.1}MA_{0.9}PbI_3$ (HI) PXD pattern (black lines), peaks used for unit cell refinement (grey lines) and calculated peak positions (green lines) from CELREF for *I4cm* a= 8.89 c= 12.61, *F23* a = 12.6 and *R3* a = 8.91.

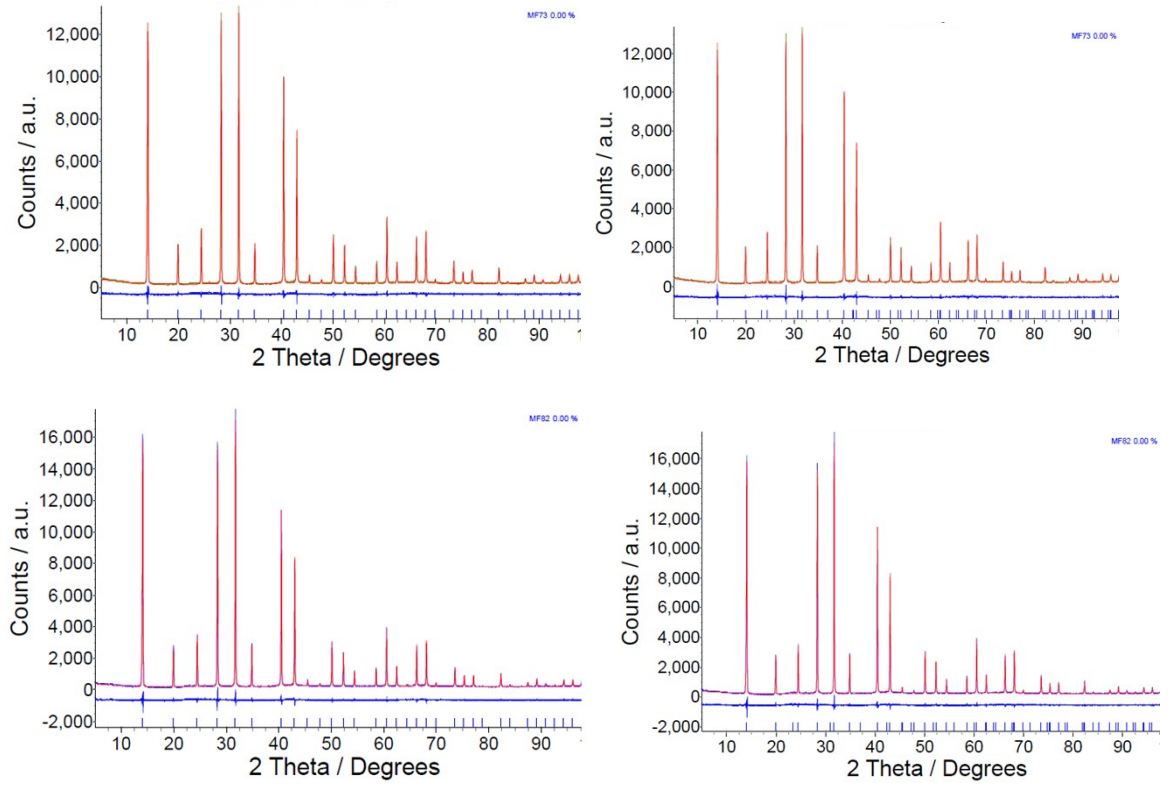

Figure 4 Pawley fits to PXD patterns of $FA_{0.3}MA_{0.7}PbI_3$, cubic *Pm-3m*, a ≈ 6.31 Å (top left) and tetragonal *I4cm* a≈ 8.90 Å, c ≈ 12.59 Å (top right). $FA_{0.2}MA_{0.8}PbI_3$ *Pm-3m* (bottom left) and *I4cm* (bottom right). Both samples were synthesised by the HI method. Difference profiles are plotted in blue and calculated peak positions are designated by pink ticks.

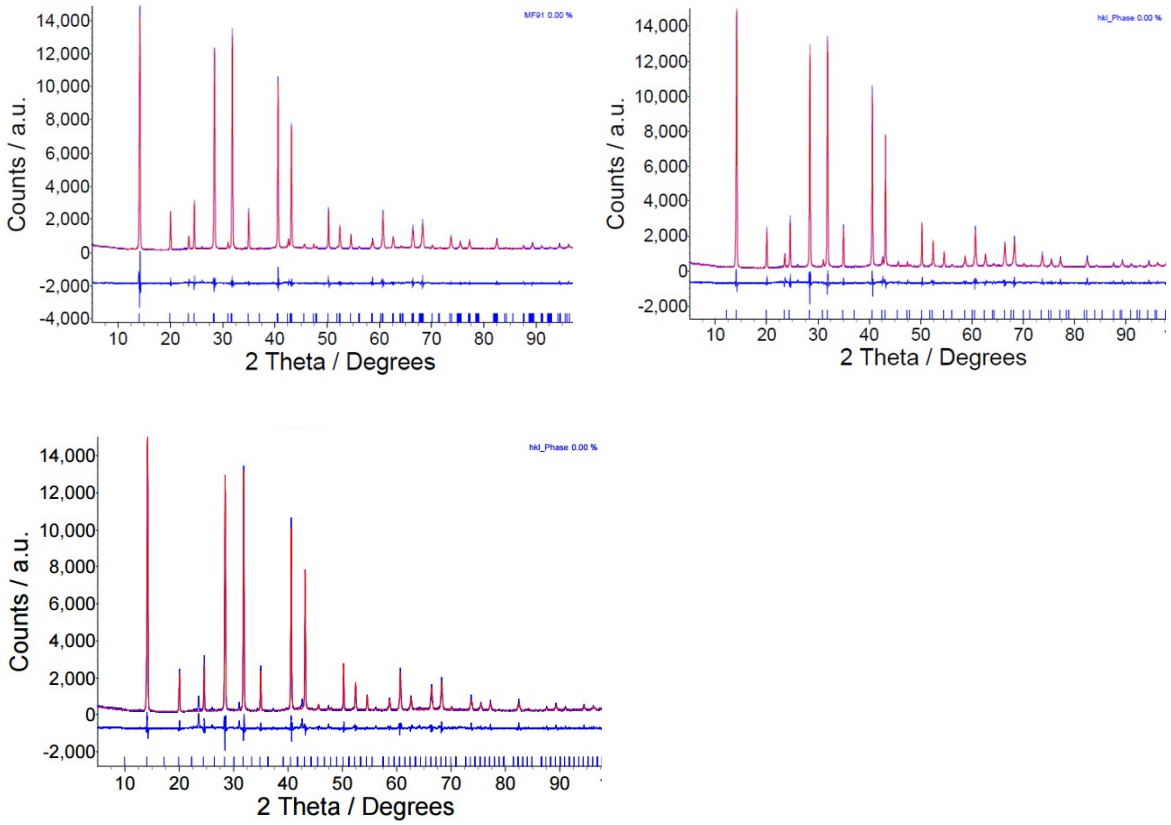

Figure 5 Pawley fits to the room temperature PXD pattern of $FA_{0.1}MA_{0.9}PbI_3$ for *I4cm*, a ≈ 8.91 Å c ≈ 12.59 Å (top left), *F23* a ≈ 12.6 Å (top right) and *Im-3* a ≈ 12.6 Å (bottom left).