SUPPORTING INFORMATION

for

Phase Diagram and Dielectric Properties of $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$

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Experimental Methods:

(i) *Synthesis of Samples:* $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ samples (for $x = 0.05, 0.075, 0.10, 0.125, 0.15, 0.175, 0.2, 0.3$ and 0.4) were synthesized from the precursor solution containing methyl ammonium iodide (MAI), formamidinium iodide (FAI) and lead iodide (PbI_2) in appropriate proportions.

Synthesis of precursors: MAI was prepared from methyl amine and concentrated HI (57% in water) taken in an equimolar quantity, which were then mixed and stirred for 2 hour at 0 °C. The resultant mixture was distilled at 50-60 °C for 4-5 hours to remove the solvent and as a result white precipitate was obtained. The precipitated solid (i.e. MAI) was repeatedly washed with diethyl ether to remove excess HI present in the sample. The precipitate was recrystallized in ethanol and this recrystallized MAI again was washed with diethyl ether. After sufficient washing, the obtained clean white solid was dried under vacuum and stored

under inert atmosphere. It was used as it is; for further synthesis procedures. FAI was prepared by following the above procedures by taking equimolar amount of formamidinium acetate and concentrated HI (57% in water).

Single crystal and polycrystalline $MA_{1-x}FA_xPbI_3$ samples: As obtained MAI, FAI and PbI_2 were used as precursors for synthesizing series of $MA_{1-x}FA_xPbI_3$ samples. MAI (1-x moles), FAI (x moles) and PbI_2 (1 moles) were stoichiometrically mixed in γ -Butyrolactone (GBL) to make 1M solution. This mixture was heated at 60 °C with constant stirring for 30-40 min to dissolve the precursors completely and thus a clear solution was obtained. This solution was drop-casted on clean glass slides, which was already kept at 105 °C, heated for 20 min at this temperature to evaporate all the solvent. The resulting black powders and few small crystals obtained on glass slide were scrapped off, collected and stored separately in N_2 atmosphere for powder and single crystal XRD measurements respectively.

(ii) Temperature Dependent Powder and Single Crystal XRD Measurement: The powder X-Ray Diffraction data were collected on phase pure samples at specific temperatures (mentioned as cyan dot in the phase diagram) in Bruker D8 Advance X-Ray diffractometer by using Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) equipped with a PheniX Oxford closed cycle helium cryostat. The PheniX is uniquely designed for powder diffraction data collection at very low temperatures in reflection geometry with good temperature stability of 0.1 K. The measurement was carried out in cooling cycle starting from 295 K down till 15 K. Profile fitting of PXRD patterns at selected temperatures are carried out by using JANA2006.¹ The single crystal XRD data at different temperatures were collected on selected compositions in Oxford Xcalibur diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) to determine the cation orientations and the space group of the system in respective regions found in the phase diagram namely cubic, tetragonal, large-cell cubic and orthorhombic phases. The single crystals were smeared with paraton-N oil to avoid exposure to moisture and then mounted on

a Hampton cryo-loop. The crystal was maintained at the desired temperature under a nitrogen gas stream from the Oxford cryo-systems open-flow cryostat (COBRA) using liquid nitrogen. Data collection, data reduction and numerical absorption corrections were performed by using CrysAlisPro² software suite. The structure solution and refinement were accomplished by using SHELXS and SHELXL^{3,4} included in the WinGX suite⁵. Profile refinement for the XRD pattern at different crystallographic phases for all compositions have been shown in Figures S1 - S9 and respective refinement parameters are included in the Tables S1 - S9. All temperature dependent XRD pattern collected for various compositions are represented in Figures S10 – S18.

(ii) *Dielectric Measurement:* The samples were ground and approximately 85 mg powder was pressed under hydrostatic pressure of around 1.5 N/mm² to make pellets of 6 mm diameter. The pellets were annealed at 50-60 °C for 2 hour to get better connectivity in the grains. Silver paste was used to make electrode on both the faces of the pellet and the temperature dependent dielectric measurements were carried out in a closed cycle helium cryostat (Cryo Industries Inc.) using a Keysight E4990A Impedance Analyzer. The measurements were performed in the frequency range of 1 kHz - 1 MHz by cooling the sample from room temperature down to 12 K, in steps of 0.5 K with a scan rate of 0.5 K/min. The measurements were also done in the heating cycle to check the reproducibility. The results from both the cycles overlapped except some hysteresis of few K found at phase transition temperatures indicative of the transition being first order in nature.

Figure S1. Powder XRD pattern and profile refinement for MA_{0.95}FA_{0.05}PbI₃ at (a) 295 K, (b) 130 K and (c) 15 K. Details of refinement parameters are given in Table S1.

Table S1. Fitting parameters for FA_{0.05}MA_{0.95}PbI₃ sample obtained from profile refinement

Composition	MA _{0.95} FA _{0.05} PbI ₃			
Temperature	295K (Single phase)	130K (Multi-phase)		15K (Single Phase)
Crystal system	Tetragonal	Tetragonal (Phase-1)	Orthorhombic (Phase-2)	Orthorhombic
Space group	<i>I4/mcm</i>	<i>I4/mcm</i>	<i>Pnma</i>	<i>Pnma</i>
a(Å)	8.86083(16)	8.79161(39)	8.86274(22)	8.84186(24)
b(Å)	8.86083(16)	8.79161(39)	12.61363(27)	12.5970(28)
c(Å)	12.63719(22)	12.66423(88)	8.59362(23)	8.56419(24)
V(Å ³)	992.20(18)	978.85(81)	960.69(11)	953.89(53)
χ ²	1.56	1.35		1.76
R _P	6.73	5.83		7.44

Figure S2. Powder XRD pattern and profile refinement for $\text{MA}_{0.925}\text{FA}_{0.075}\text{PbI}_3$ at (a) 295 K, (b) 120 K and (c) 15 K. Details of refinement parameters are given in Table S2.

Table S2. Fitting parameters for $\text{MA}_{0.925}\text{FA}_{0.075}\text{PbI}_3$ sample obtained from profile refinement

Composition	$\text{MA}_{0.925}\text{FA}_{0.075}\text{PbI}_3$			
Temperature	295K (Single phase)	120K (Multi-phase)		15K (Single Phase)
Crystal system	Tetragonal	Tetragonal (Phase-1)	Orthorhombic (Phase-2)	Orthorhombic
Space group	$I4/mcm$	$I4/mcm$	$Pnma$	$Pnma$
a(Å)	8.87250(16)	8.78498(25)	8.86450(24)	8.83494(73)
b(Å)	8.87250(16)	8.78498(25)	12.61481(28)	12.59348(10)
c(Å)	12.64340(28)	12.67204(66)	8.596653(23)	8.56284(71)
V(Å ³)	995.30(35)	977.98(58)	961.31(79)	952.72(23)
χ^2	1.39	1.46		1.53
R _P	6.88	6.46		6.74

Figure S3. Powder XRD pattern and profile refinement for $\text{MA}_{0.9}\text{FA}_{0.1}\text{PbI}_3$ at (a) 295 K, (b) 150 K, (c) 130 K, (d) 110 K and (e) 15 K. Details of refinement parameters are given in Table S3.

Table S3. Fitting parameters for MA_{0.9}FA_{0.1}PbI₃ sample obtained from profile refinement

Composition	MA _{0.9} FA _{0.1} PbI ₃						
Temperature	295K (Single phase)	150K (Multi-phase)		130K (Single phase)	110K (Multi-phase)		15K (Single phase)
Crystal system	Cubic	Tetragonal (Phase-1)	Cubic (Phase-2)	Cubic	Cubic (Phase-1)	Orthorhombic (Phase-2)	Orthorhombic
Space group	<i>I4/mcm</i>	<i>I4/mcm</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Pnma</i>	<i>Pnma</i>
a(Å)	8.88533(17)	8.79708(18)	12.47523(48)	12.43300(23)	12.42632(29)	8.596097(25)	8.84299(28)
b(Å)	8.88533(17)	8.79708(18)	12.47523(48)	12.43300(23)	12.42632(29)	12.61242(27)	12.59522(31)
c(Å)	12.63297(28)	12.67490(33)	12.47523(48)	12.43300(23)	12.42632(29)	8.863799(22)	8.572983(27)
V(Å ³)	997.362(36)	980.90(40)	1941.54(71)	1921.89(36)	1918.79(44)	960.99(32)	954.85(59)
χ^2	1.36	1.77		1.83	1.32		1.52
R _p	6.37	8.36		8.73	6.35		7.47

Figure S4. Powder XRD pattern and profile refinement for $\text{MA}_{0.875}\text{FA}_{0.125}\text{PbI}_3$ at (a) 310 K, (b) 250 K, (c) 150 K, (d) 120 K, (e) 100 K and (f) 15 K. Details of refinement parameters are given in Table S4.

Table S4. Fitting parameters for MA_{0.875}FA_{0.125}PbI₃ sample obtained from profile refinement

Composition	MA _{0.875} FA _{0.125} PbI ₃							
Temperature	310K (Single phase)	250K (Single phase)	150K (Multi-phase)		120K (Single phase)	100K (Multi-phase)		15K (Single phase)
Crystal system	Cubic	Tetragonal	Tetragonal (Phase-1)	Cubic (Phase-2)	Cubic	Cubic (Phase-1)	Orthorhombic (Phase-2)	Orthorhombic
Space group	<i>Pm-3m</i>	<i>I4/mcm</i>	<i>I4/mcm</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Pnma</i>	<i>Pnma</i>
a(Å)	6.30304(12)	8.85399(16)	8.80089(32)	12.44843(16)	12.43350(70)	12.42186(25)	8.86514(30)	8.85655(48)
b(Å)	6.30304(12)	8.85399(16)	8.80089(32)	12.44843(16)	12.43350(70)	12.42186(25)	12.61891(34)	12.61487(60)
c(Å)	6.30304(12)	12.66350(26)	12.66076(48)	12.44843(16)	12.43350(70)	12.42186(25)	8.600199(31)	8.59131(49)
V(Å ³)	250.41(51)	992.73(34)	980.6465(53)	1929.05(91)	1922.12(10)	1916.73(39)	962.09(27)	959.86(14)
χ^2	1.77	1.34	1.68		1.81	1.78		1.96
R _p	6.58	6.67	6.49		6.82	6.71		7.30

Figure S5. Powder XRD pattern and profile refinement for $\text{MA}_{0.85}\text{FA}_{0.15}\text{PbI}_3$ at (a) 295 K, (b) 220 K, (c) 170 K, (d) 120 K and (e) 15 K. Details of refinement parameters are given in Table S5.

Table S5. Fitting parameters for MA_{0.85}FA_{0.15}PbI₃ sample obtained from profile refinement

Composition	MA _{0.85} FA _{0.15} PbI ₃						
Temperature	295K (Single phase)	220K (Single phase)	170K (Multi-phase)		120K (Single phase)	15K (Multi-phase)	
Crystal system	Cubic	Tetragonal	Tetragonal (Phase-1)	Cubic (Phase-2)	Cubic	Cubic (Phase-2)	Orthorhombic (Phase-1)
Space group	<i>Pm-3m</i>	<i>I4/mcm</i>	<i>I4/mcm</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Im-3</i>	<i>Pnma</i>
a(Å)	6.29922(9)	8.84675(19)	8.81457(35)	12.46748(22)	12.44343(22)	12.40334(31)	8.58265(31)
b(Å)	6.29922(9)	8.84675(19)	8.81457(35)	12.46748(22)	12.44343(22)	12.40334(31)	12.59596(36)
c(Å)	6.29922(9)	12.66227(31)	12.66381(49)	12.46748(22)	12.44343(22)	12.40334(31)	8.84513(28)
V(Å ³)	249.95(37)	991.01(40)	983.93(54)	1937.92(93)	1926.728(35)	1908.17(10)	956.22(64)
χ^2	1.49	1.83	1.84		1.72	1.58	
R _P	6.39	7.44	7.54		7.08	6.47

Figure S6. Powder XRD pattern and profile refinement for MA_{0.825}FA_{0.175}PbI₃ at (a) 295 K, (b) 230 K, (c) 190 K and (d) 15 K. Details of refinement parameters are given in Table S6.

Table S6. Fitting parameters for MA_{0.825}FA_{0.175}PbI₃ sample obtained from profile refinement

Composition	MA _{0.825} FA _{0.175} PbI ₃				
Temperature	295K (Single phase)	230K (Single phase)	190K (Multi-phase)		15K (Single phase)
Crystal system	Cubic	Tetragonal	Tetragonal (Phase-1)	Cubic (Phase-2)	Cubic
Space group	<i>Pm-3m</i>	<i>I4/mcm</i>	<i>I4/mcm</i>	<i>Im-3</i>	<i>Im-3</i>
a(Å)	6.30213(86)	8.84934(16)	8.82535(15)	12.50214(39)	12.39421(18)
b(Å)	6.30213(86)	8.84934(16)	8.82535(15)	12.50214(39)	12.39421(18)
c(Å)	6.30213(86)	12.66186(26)	12.67016(27)	12.50214(39)	12.39421(18)
V(Å ³)	250.30(34)	991.56(34)	986.84(33)	1954.13(58)	1903.96(28)
χ ²	1.64	1.32	1.24		1.37
R _P	6.85	6.88	6.31		6.97

Figure S7. Powder XRD pattern and profile refinement for $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$ at (a) 295 K, (b) 220 K and (c) 15 K. Details of refinement parameters are given in Table S7.

Table S7. Fitting parameters for MA_{0.8}FA_{0.2}PbI₃ sample obtained from profile refinement

Composition	MA _{0.8} FA _{0.2} PbI ₃			
Temperature	295K (Single phase)	220K (Multi-phase)		15K (Single phase)
Crystal system	Cubic	Cubic (Phase-1)	Tetragonal (Phase-2)	Cubic
Space group	<i>Pm-3m</i>	<i>Im-3</i>	<i>I4/mcm</i>	<i>Im-3</i>
a(Å)	6.30460(32)	12.53501(23)	8.85236(40)	12.39585(36)
b(Å)	6.30460(32)	12.53501(23)	8.85236(40)	12.39585(36)
c(Å)	6.30460(32)	12.53501(23)	12.64178(57)	12.39585(36)
V(Å ³)	250.59(13)	1969.58(36)	990.66(25)	1904.711(55)
χ^2	1.23	1.27		1.66
R _P	6.31	6.54		8.18

Figure S8. Powder XRD pattern and profile refinement for MA_{0.7}FA_{0.3}PbI₃ at (a) 295 K and (b) 15 K. Details of refinement parameters are given in Table S8.

Table S8. Fitting parameters for MA_{0.7}FA_{0.3}PbI₃ sample obtained from profile refinement

Composition	MA _{0.7} FA _{0.3} PbI ₃	
Temperature	295K (Single phase)	15K (Single phase)
Crystal system	Cubic	Cubic
Space group	<i>Pm-3m</i>	<i>Im-3</i>
a(Å)	6.31072(87)	12.44621(25)
b(Å)	6.31072(87)	12.44621(25)
c(Å)	6.31072(87)	12.44621(25)
V(Å ³)	251.32(35)	1928.02(39)
χ^2	1.37	1.83
R _P	6.14	7.75

Figure S9. Powder XRD pattern and profile refinement for MA_{0.6}FA_{0.4}PbI₃ at (a) 295 K and (b) 15 K. Details of refinement parameters are given in Table S9.

Table S9. Fitting parameters for MA_{0.6}FA_{0.4}PbI₃ sample obtained from profile refinement

Composition	MA _{0.6} FA _{0.4} PbI ₃	
Temperature	295K (Single phase)	15K (Single phase)
Crystal system	Cubic	Cubic
Space group	<i>Pm-3m</i>	<i>Im-3</i>
a(Å)	6.31543(11)	12.44621(25)
V(Å ³)	251.88(44)	1928.02(39)
χ^2	1.94	2.11
R _P	7.49	8.35

Figure S10. The plot shows powder XRD pattern for MA_{0.95}FA_{0.05}PbI₃ at different temperatures.

Figure S11. The plot shows powder XRD pattern for $\text{MA}_{0.925}\text{FA}_{0.075}\text{PbI}_3$ at different temperatures.

Figure S12. The plot shows powder XRD pattern for $\text{MA}_{0.9}\text{FA}_{0.1}\text{PbI}_3$ at different temperatures.

Figure S13. The plot shows powder XRD pattern for $\text{MA}_{0.875}\text{FA}_{0.125}\text{PbI}_3$ at different temperatures.

Figure S14. The plot shows powder XRD pattern for $\text{MA}_{0.85}\text{FA}_{0.15}\text{PbI}_3$ at different temperatures.

Figure S15. The plot shows powder XRD pattern for $\text{MA}_{0.825}\text{FA}_{0.175}\text{PbI}_3$ at different temperatures.

Figure S16. The plot shows powder XRD pattern for $\text{MA}_{0.8}\text{FA}_{0.2}\text{PbI}_3$ at different temperatures.

Figure S17. The plot shows powder XRD pattern for $\text{MA}_{0.7}\text{FA}_{0.3}\text{PbI}_3$ at different temperatures.

Figure S18. The plot shows powder XRD pattern for $\text{MA}_{0.6}\text{FA}_{0.4}\text{PbI}_3$ at different temperatures.

Figure S19. The plot shows the function $F(R)$ as a function of the photon energy, representing the absorption behaviour, obtained using the Kubelka-Munk formula from experimentally obtained diffuse reflectance spectra of $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ solid solution for different x values at RT.

Figure S20. The plot shows the room temperature photoluminescence (PL) spectra for $\text{MA}_{1-x}\text{FA}_x\text{PbI}_3$ solid solution for different x values. The PL was recorded with a 470 nm excitation source.

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