Solution Phase Halide Exchange and Targeted Annealing Kinetics in Lead Chloride Derived Hybrid Perovskites

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Supplemental Information

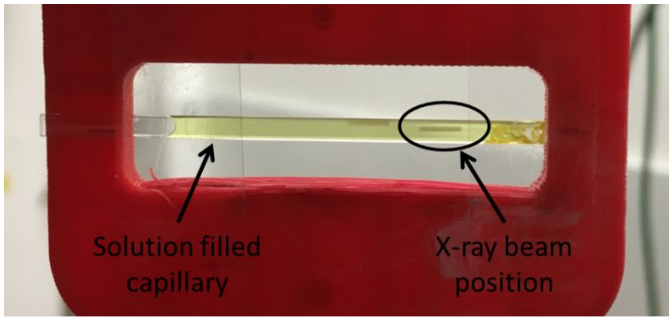


Figure S1 – Picture of solution filled rectangular capillary used for EXAFS measurements. The capillary was filled with solution and mounted in air before being placed in a helium purged atmosphere for measurement. The X-ray beam position and relative size can be seen by the dark grey region on the capillary. This is caused by the generation of color centers in the glass capillary. No beam induced changes to the solution were observed during measurement.

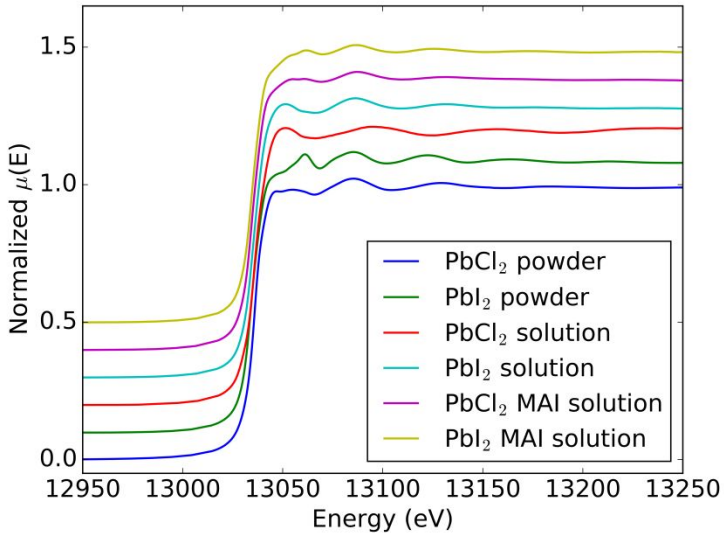


Figure S2 – X-ray absorption near edge structure (XANES) for the Pb L_{III}-edge for the samples considered in this work.

EXAFS of $PbCl_2$ powder:

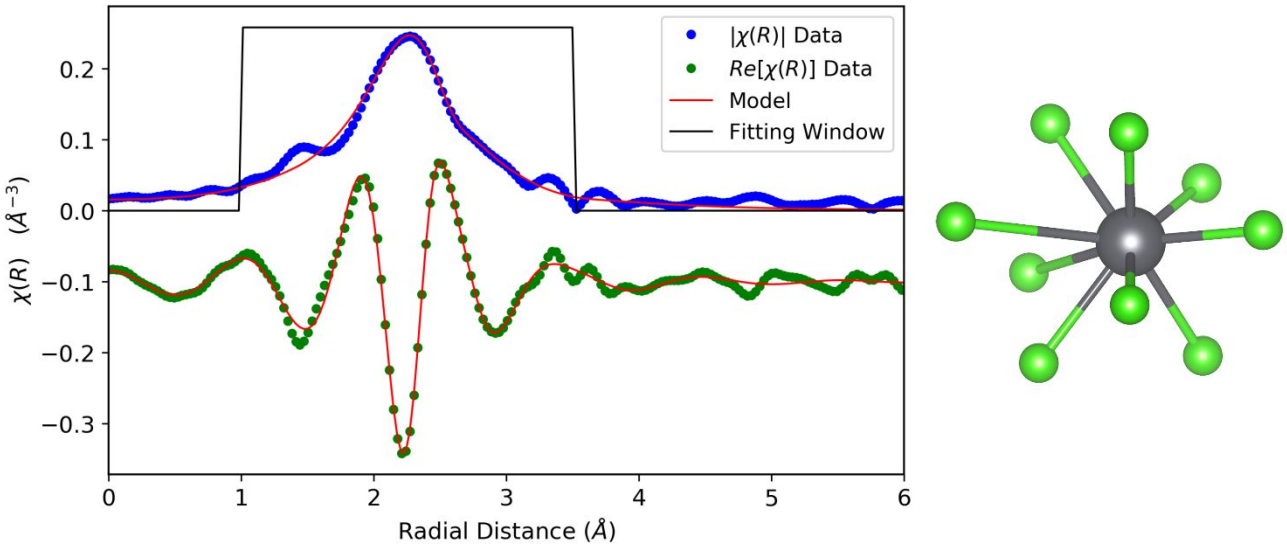


Figure S3 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for $PbCl_2$ powder (left) and schematic of local coordination of Pb species with 9 Cl atoms (right).

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
Cl1	2	0.65±0.26	0.0132±0.0027	-2.59±2.40	0.046±0.035	2.784	2.830±0.035
Cl2	5	0.65±0.26	0.0279±0.0101	-2.59±2.40	-0.072±0.100	3.01780	2.980±0.100
Cl3	2	0.65±0.26	0.0406±0.0288	-2.59±2.40	-0.072±0.079	3.67460	3.60217±0.079

EXAFS fitting summary:

k range: 3-14

Number of variables: 8

$\chi^2 = 1305.98$

$\chi^2_{Reduced} = 140.08$

R-factor = 0.0170

EXAFS of PbI_2 powder:

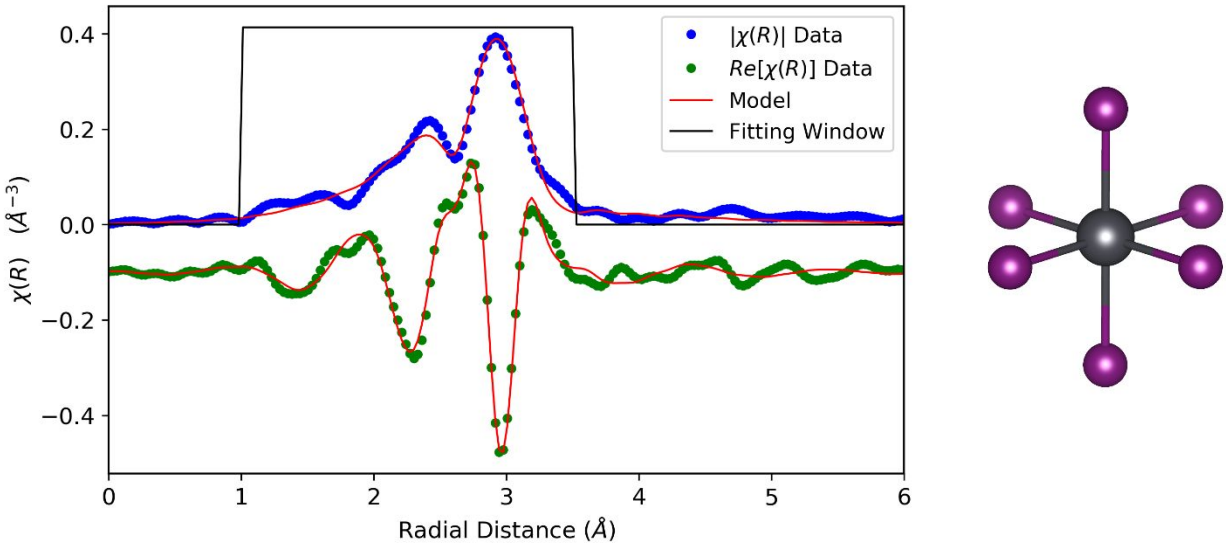


Figure S4 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for PbI_2 powder (left) and schematic of local coordination of Pb species with 6 I atoms (right).

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
I1	6	0.83±0.05	0.0152±0.0008	-2.20±0.41	-0.041±0.006	3.216	3.175 ±0.006

EXAFS fitting summary:

k range: 3-14

Number of variables: 4

$\chi^2 = 6921.96$

$\chi^2_{Reduced} = 589.54$

R-factor = 0.0228

EXAFS of $PbCl_2$ in DMF solution:

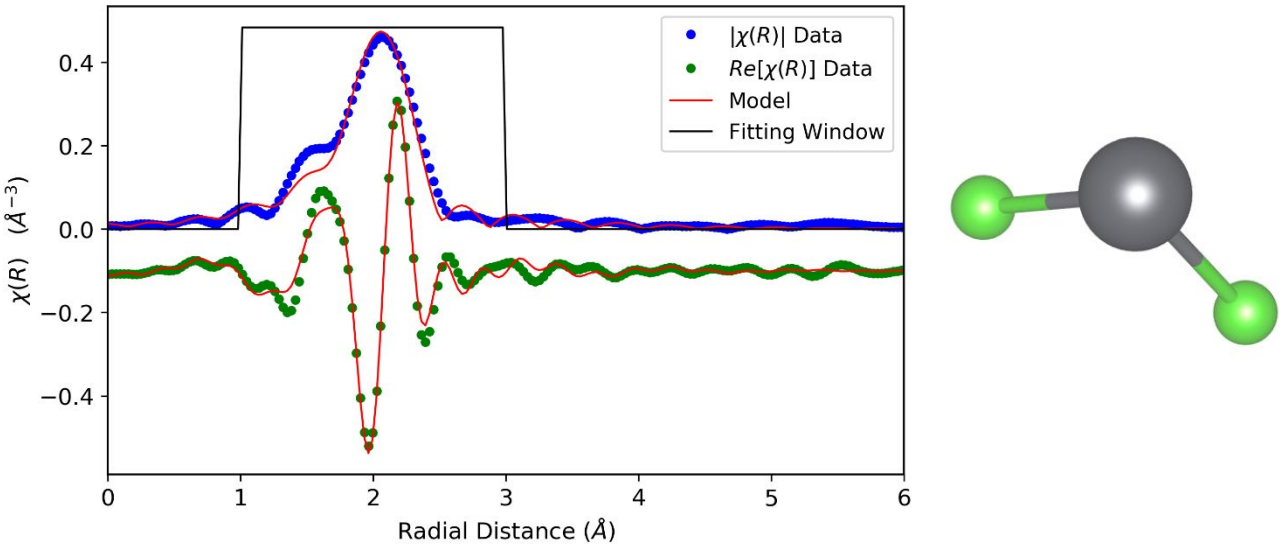


Figure S5 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for $PbCl_2$ dissolved in DMF (left) and schematic of local coordination of Pb species with 2 Cl atoms (right).

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
Cl1	2	0.73±0.18	0.0046±0.0014	-5.78±1.34	-0.212±0.011	2.784	2.571±0.011

EXAFS fitting summary:

k range: 3-11

Number of variables: 4

$\chi^2 = 3312.67$

$\chi^2_{Reduced} = 557.92$

R-factor = 0.0249

EXAFS of PbI_2 in DMF solution:

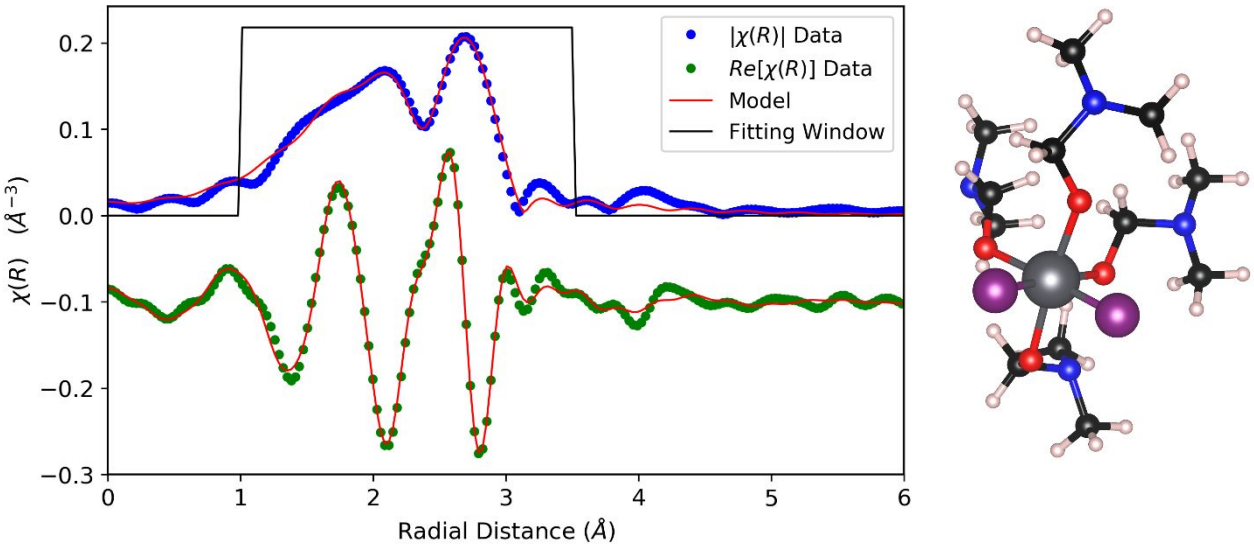


Figure S6 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for PbI_2 dissolved in DMF (left) and schematic of local coordination of Pb species with 2 I atoms and 4 DMF molecules (right).

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
I1	2	0.94±0.14	0.0136±0.0014	-5.81±1.03	-0.235±0.010	3.216	2.9810±0.010
O2	4	0.845±0.34	0.0307±0.0076	-5.81±1.03	0.012±0.026	2.431	2.443±0.100

EXAFS fitting summary:

k range: 3-11

Number of variables: 7

$\chi^2 = 458.11$

$\chi^2_{Reduced} = 82.14$

R-factor = 0.0108

EXAFS of 3:1 PbI_2:MAI in DMF solution:

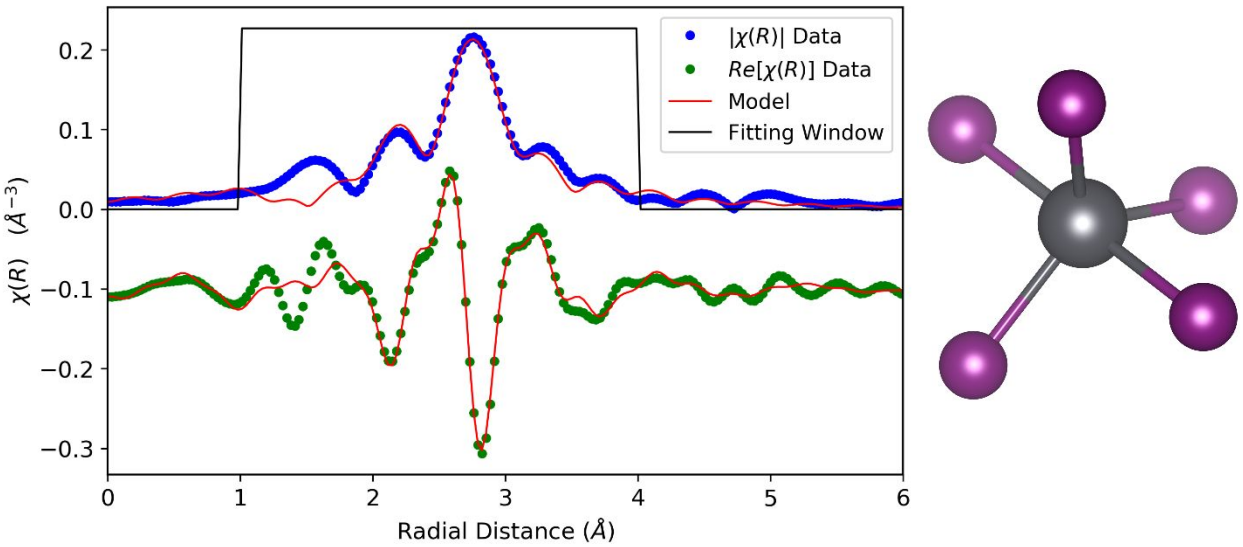


Figure S7 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for PbI_2 and MAI dissolved in a 3:1 molar ratio in DMF (left) and schematic of local coordination of Pb species with 5 I atoms total (right). Note, there is likely some DMF solvation but is too poorly defined for inclusion in the EXAFS fitting.

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
I1	2	0.80	0.0101±0.0195	3.22±2.47	-0.140±0.187	3.161	3.021±0.187
I2	3	0.74	0.0171±0.0651	3.22±2.47	-0.066±0.449	3.263	3.197±0.449

EXAFS fitting summary:

k range: 3-11

Number of variables: 7

$\chi^2 = 1109.56$

$\chi^2_{Reduced} = 198.95$

R-factor = 0.0693

Note – the correlation between S_o^2 for the two iodine paths is above 99%, making meaningful determination of the uncertainty for these parameters impossible.

EXAFS of 3:1 $PbCl_2$:MAI in DMF solution:

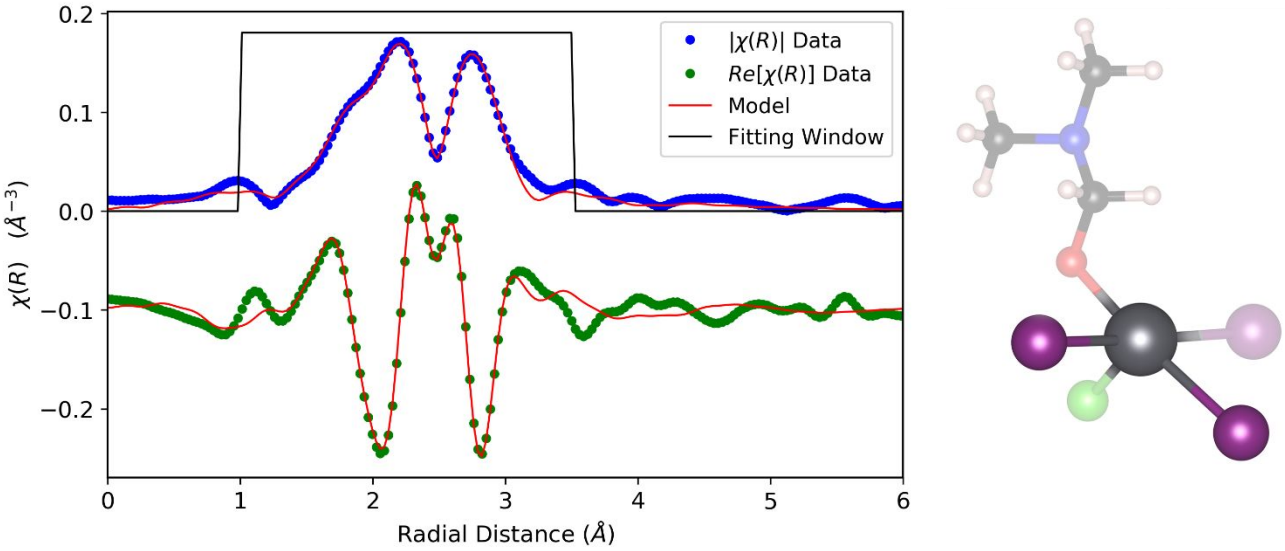


Figure S8 – Magnitude and real part of the Fourier transform of the Pb L_{III}-EXAFS for $PbCl_2$ and MAI dissolved in a 3:1 molar ratio in DMF (left) and schematic of local coordination of Pb species with ~2.5 I atoms, ~0.33 Cl atoms, and roughly half a DMF molecule (right). Note, partially occupied species are shown as partially transparent. Partial occupancy is a result of the volumetric averaging inherent to EXAFS such that, e.g., on average, 33% of Pb atoms are coordinated to a Cl atom.

Coordinating Atom	N	S_0^2	σ^2	E_0	ΔR	Reff	R
Cl1	0.33	0.837±0.641	0.0040±0.00656	-0.10±1.02	-0.070±0.019	2.784	2.714±0.019
I2	2.5	0.831±0.195	0.0177±0.0396	-0.10±1.02	-0.132±0.020	3.161	3.029±0.020
O3	0.4	0.842±0.683	0.0098±0.0124	-0.10±1.02	-0.061±0.050	2.431	2.370±0.050

EXAFS fitting summary:

k range: 2-12

Number of variables: 10

$\chi^2 = 3058.67$

$\chi^2_{Reduced} = 532.76$

R-factor = 0.0224

Structural refinements were performed using TOPAS-Academic. Structural models included a single lattice parameter, an independent isotropic thermal parameter for the Pb-atom, anisotropic thermal parameters for the I-atom, and the methylammonium was modeled as a rigid body with a C-N bond length of 1.48Å centered at fractional coordinates (0.5, 0.5, 0.5) with rotations allowed to freely refine. A single isotropic thermal parameter was used for all methylammonium atoms. The positions and thermal parameters for the methylammonium are expected to be unreliable due to disorder.

Integrated diffraction patterns and corresponding fits are shown for the fully annealed films at 100°C roughly 5 minutes following full conversion to the perovskite phase. Allowed peak positions are shown as tick marks at the bottom of the plots. Crystal structures are shown with thermal ellipsoids at a 50% level with methylammonium atoms removed for clarity.

Refinement of perovskite annealed from 3MAI + $PbCl_2$ precursor solution

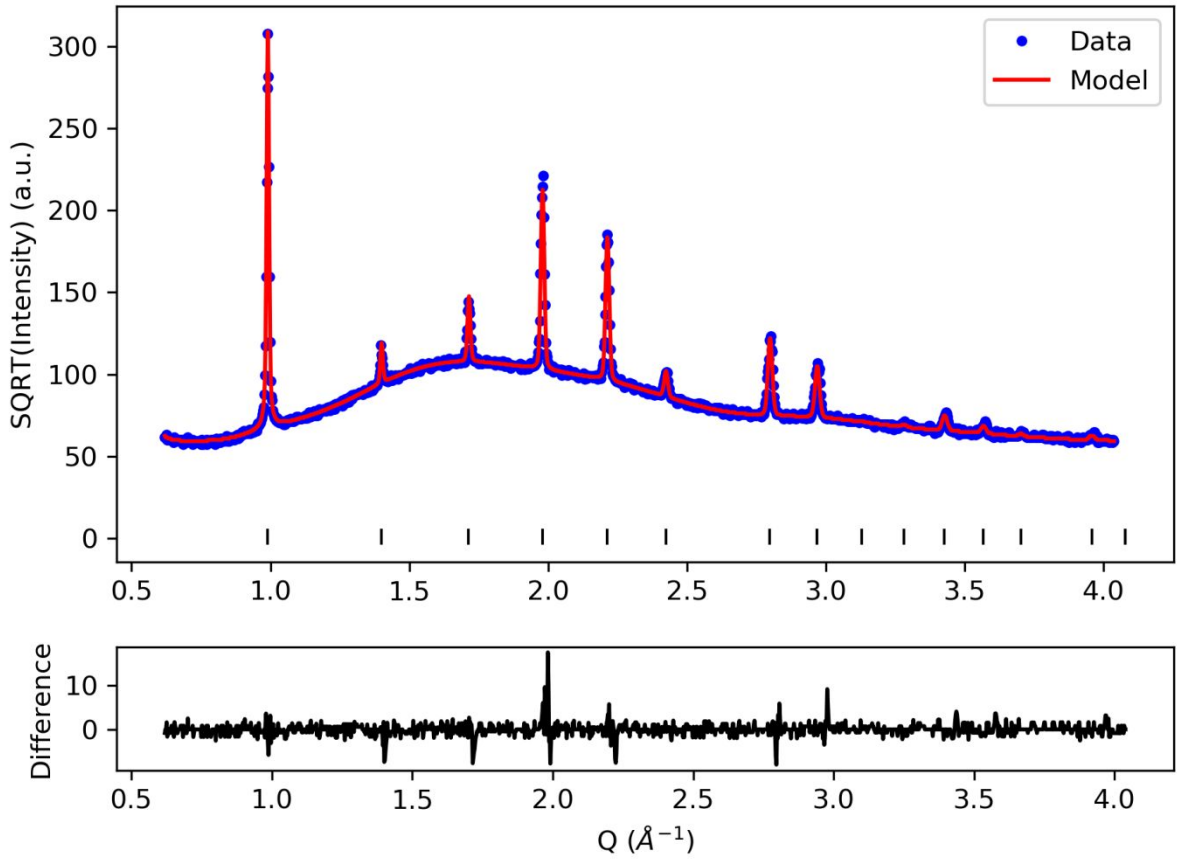
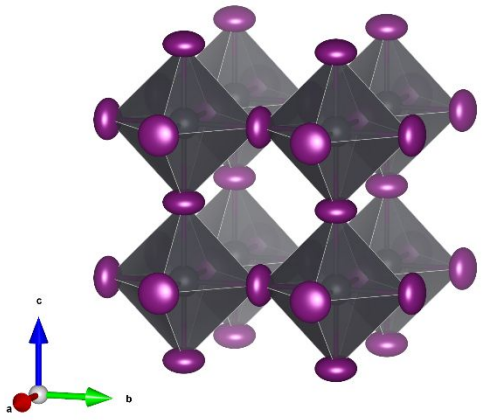


Figure S9 – Integrated X-ray diffraction data roughly 5 minutes after full conversion to the perovskite phase at 100°C from 3MAI + $PbCl_2$ precursor solution. Data is shown in blue with the Rietveld refinement fit in red, difference is shown on expanded sale at bottom with tick marks indicating allowed peak positions.

Crystal Data:	
Space Group	Pm-3m
a (Å)	6.3496(2)
V (Å^3)	256.00(3)
X-ray Wavelength	0.9744Å
R_{wp}	3.297
Atomic Parameters:	
Pb Position	(0,0,0)
Thermal Parameters	U_{iso} = 0.166(3)
I Position	(1/2, 0, 0)
Thermal Parameters	U_{11} = 0.117(4) $U_{22} = U_{33}$ = 0.302(6) $U_{12} = U_{13} = U_{23}$ = 0
C Position	(0.526, 0.611, 0.526)
Thermal Parameters	U_{iso} = 0.2304(9)
N Position	(0.474, 0.389, 0.474)
Thermal Parameters	U_{iso} = 0.2304(9)



Refinement of perovskite annealed from 2.5MAI + 0.75$PbCl_2$ + 0.25PbI_2 precursor solution

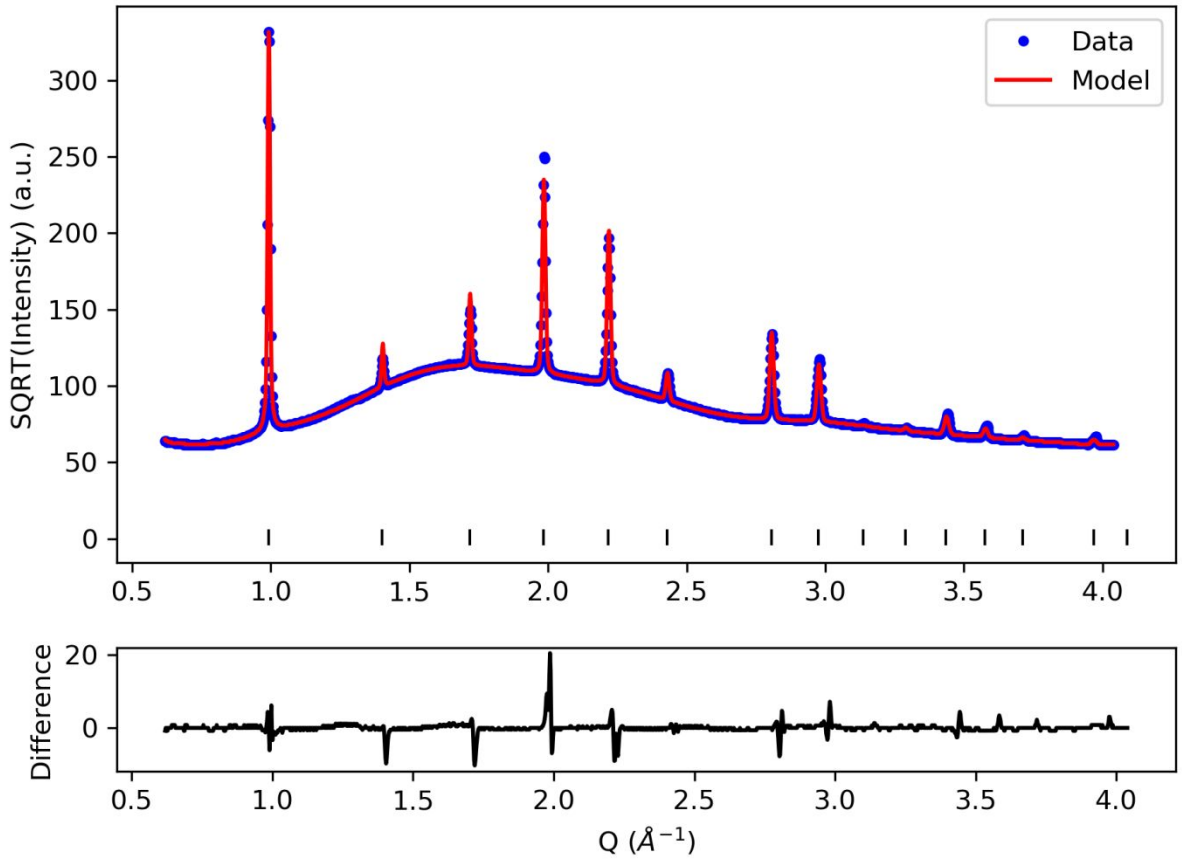
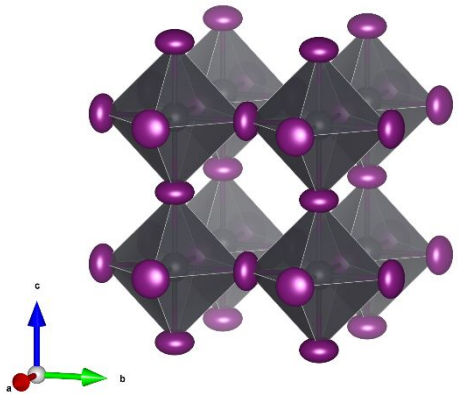


Figure S10 – Integrated X-ray diffraction data roughly 5 minutes after full conversion to the perovskite phase at 100°C from 2.5MAI + 0.75$PbCl_2$ + 0.25PbI_2 precursor solution. Data is shown in blue with the Rietveld refinement fit in red, difference is shown on expanded sale at bottom with tick marks indicating allowed peak positions.

Crystal Data:	
Space Group	Pm-3m
a (Å)	6.3358(2)
V (Å^3)	254.33(3)
X-ray Wavelength	0.9744Å
R_{wp}	3.224
Atomic Parameters:	
Pb Position	(0,0,0)
Thermal Parameters	U_{iso} = 0.161(3)
I Position	(1/2, 0, 0)
Thermal Parameters	U_{11} = 0.1223(4) $U_{22} = U_{33}$ = 0.291(5) $U_{12} = U_{13} = U_{23}$ = 0
C Position	(0.587, 0.578, 0.498)
Thermal Parameters	U_{iso} = 0.214(3)
N Position	(0.413, 0.422, 0.502)
Thermal Parameters	U_{iso} = 0.214(3)



Refinement of perovskite annealed from 2MAI + 0.5$PbCl_2$ + 0.5PbI_2 precursor solution

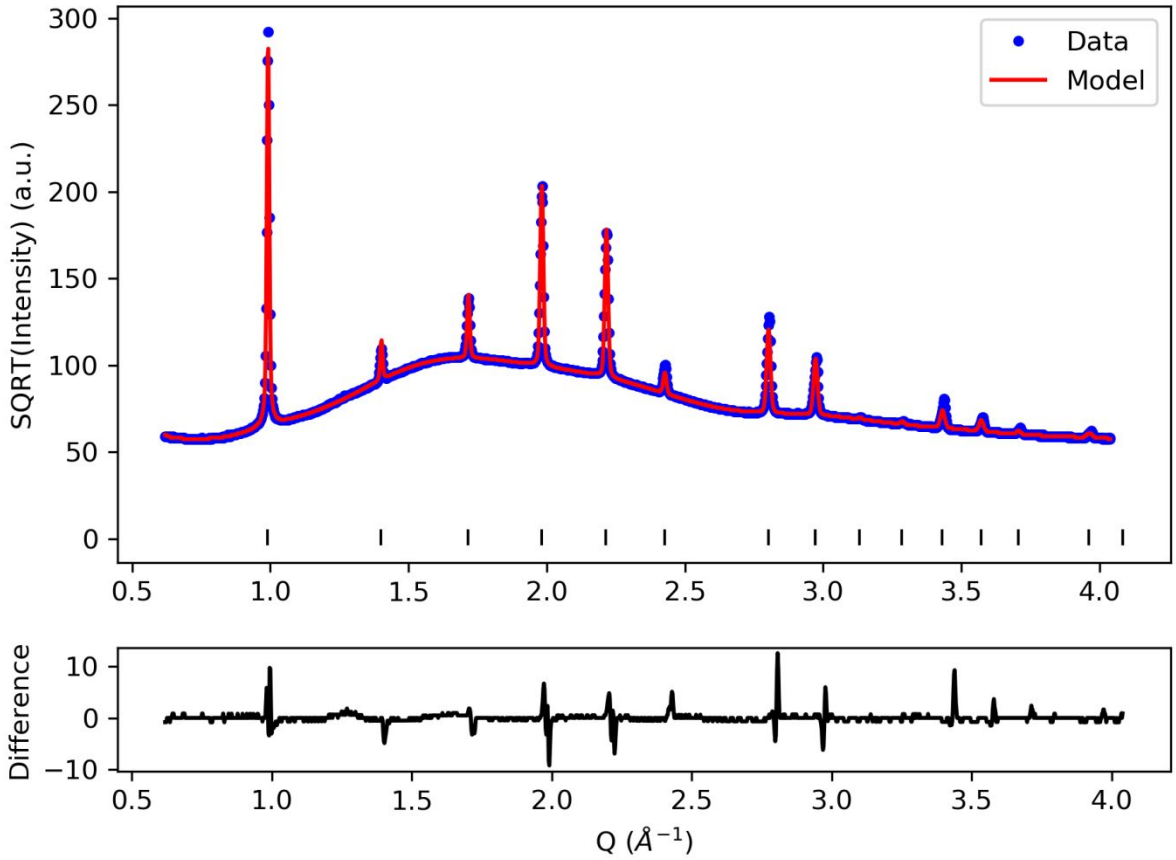


Figure S11 – Integrated X-ray diffraction data roughly 5 minutes after full conversion to the perovskite phase at 100°C from 2MAI + 0.5$PbCl_2$ + 0.5PbI_2 precursor solution. Data is shown in blue with the Rietveld refinement fit in red, difference is shown on expanded sale at bottom with tick marks indicating allowed peak positions.

Crystal Data:	
Space Group	Pm-3m
a (Å)	6.3445(2)
V (Å^3)	255.39(3)
X-ray Wavelength	0.9744Å
R_{wp}	2.831
Atomic Parameters:	
Pb Position	(0,0,0)
Thermal Parameters	U_{iso} = 0.152(3)
I Position	(1/2, 0, 0)
Thermal Parameters	U_{11} = 0.147(4)
	$U_{22} = U_{33}$ = 0.268(5)
	$U_{12} = U_{13} = U_{23}$ = 0
C Position	(0.550, 0.602, 0.525)
Thermal Parameters	U_{iso} = 0.253(3)
N Position	(0.450, 0.398, 0.475)
Thermal Parameters	U_{iso} = 0.253(3)