Electronic Supplementary Material (ESI) for Chemical Science.

SUPPORTING INFORMATION FOR: Chemical Tuning of Dynamic Cation Off-Centering in the Cubic Phases of Hybrid Tin and Lead Halide Perovskites

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Synthesis Details

$CH_3NH_3PbI_3$: 4.46 g (20 mmol) of PbO were initially dissolved in 15 ml of concentrated aqueous HI (57 % w/w) and the solution temperature was raised and held to boiling (ca. 130 °C) to afford a clear yellow solution. Addition of 1.35 g (20 mmol) of solid CH_3NH_3Cl in the solution resulted in the immediate precipitation of a fine black precipitate. The solution was stirred for 1 min and filtered hot under vacuum. The dry black solid produced 7 g (65 % yield based on Pb) of crystallographically pure material which was used for the scattering experiments.

$HC(NH_2)_2PbI_3$: 4.46 g (20 mmol) of PbO were initially dissolved in 15 ml of concentrated aqueous HI (57 % w/w) and the solution temperature was raised and held to boiling (ca. 130 °C) to afford a clear yellow solution. Addition of 1.61 g (20 mmol) of solid $HC(NH_2)_2Cl$ in the solution resulted in the immediate precipitation of a fine black precipitate. The solution was stirred for 1 min and filtered hot under vacuum. During filtration the black solid turned to yellow completely converting over a period of 5 min to 10 min. The dry yellow solid produced 9 g (71 % yield based on Pb) of crystallographically pure material which was used for the diffraction experiments.

$CH_3NH_3SnI_3$: 2.69 g (20 mmol) of SnO were charged in 15 ml of concentrated aqueous HI (57 % w/w) and 5.1 mL of H_3PO_2 (50 % w/w) were added before the mixture temperature was raised and held to boiling (ca. 130 °C), leading to a clear yellow solution. Addition of 1.35 g (20 mmol) of solid CH_3NH_3Cl in the solution resulted in the immediate precipitation of a fine black precipitate. The solution was stirred for 1 min and filtered hot under vacuum. The dry black solid produced 8 g (75 % yield based on Sn) of crystallographically pure material which was used for the scattering experiments.

$HC(NH_2)_2SnI_3$: 2.69 g (20 mmol) of SnO were charged in 15 ml of concentrated aqueous HI (57 % w/w) and 5.1 mL of H_3PO_2 (50 % w/w) were added before the mixture temperature was raised and held to boiling (ca. 130 °C), leading to a clear yellow solution. Addition of 1.61 g (20 mmol) of solid $HC(NH_2)_2Cl$ in the solution resulted in the immedi-

ate precipitation of a fine black precipitate. The solution was stirred for 1 min and filtered hot under vacuum. The dry black solid produced 9 g (83 % yield based on Sn) of crystallographically pure material which were used for the scattering experiments.

$CH_3NH_3PbBr_3$: 4.46 g (20 mmol) of PbO were initially dissolved in 20 ml of concentrated aqueous HI (48 % w/w) and the solution temperature was raised and held to boiling (ca. 130 °C) to afford a clear yellow solution. Addition of 1.35 g (20 mmol) of solid CH_3NH_3Cl in the solution resulted in the immediate precipitation of a fine orange precipitate. The solution was stirred for 1 min and filtered hot under vacuum. The dry orange solid produced 7.5 g (78 % yield based on Pb) of crystallographically pure material which was used for the scattering experiments.

$HC(NH_2)_2PbBr_3$: 4.46 g (20 mmol) of PbO were initially dissolved in 20 ml of concentrated aqueous HBr (48 % w/w) and the solution temperature was raised and held to boiling (ca. 130 °C) to afford a clear yellow solution. Addition of 1.61 g (20 mmol) of solid $HC(NH_2)_2Cl$ in the solution resulted in the immediate precipitation of a fine orange precipitate. The solution was stirred for 1 min and filtered hot under vacuum. The dry orange solid produced 8.5 g (86 % yield based on Pb) of crystallographically pure material which was used for the scattering experiments.

LeBail fits of the X-ray diffraction data against cubic $Pm\bar{3}m$ at 360 K

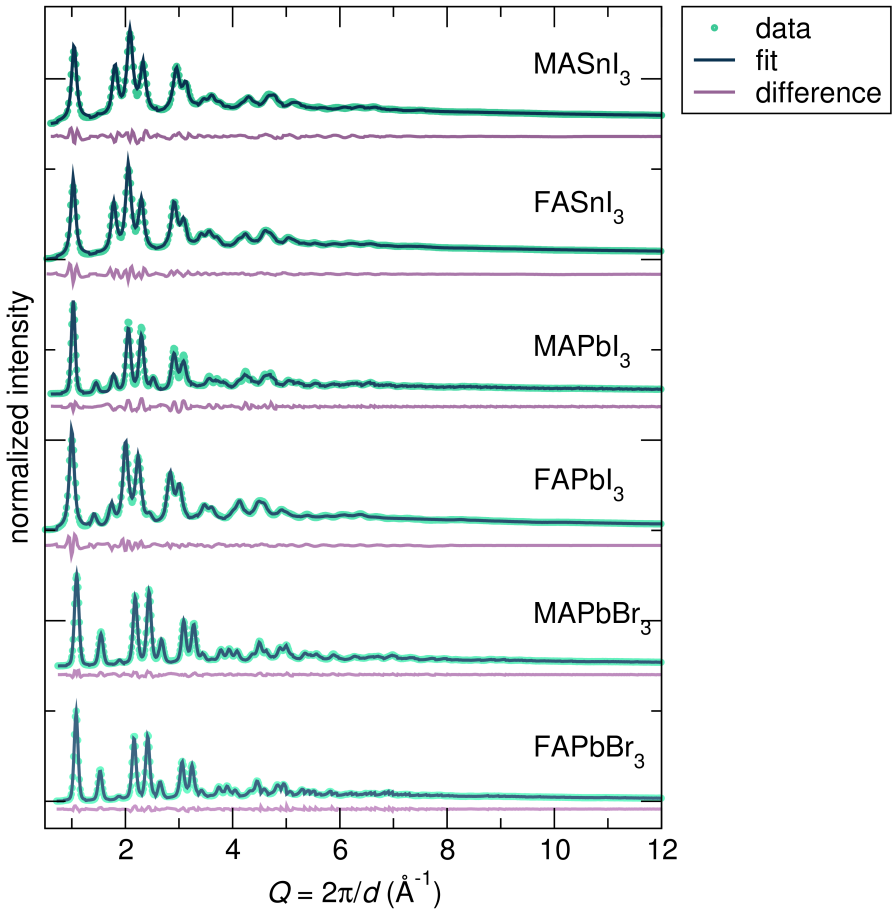

Figure 1: LeBail profile fits of the reciprocal space data at 360 K indicates phase purity. Data for all samples can be indexed to the $Pm\bar{3}m$ space group, indicating all samples are crystallographically cubic at this temperature.

Fourier transform optimization of X-ray total scattering data

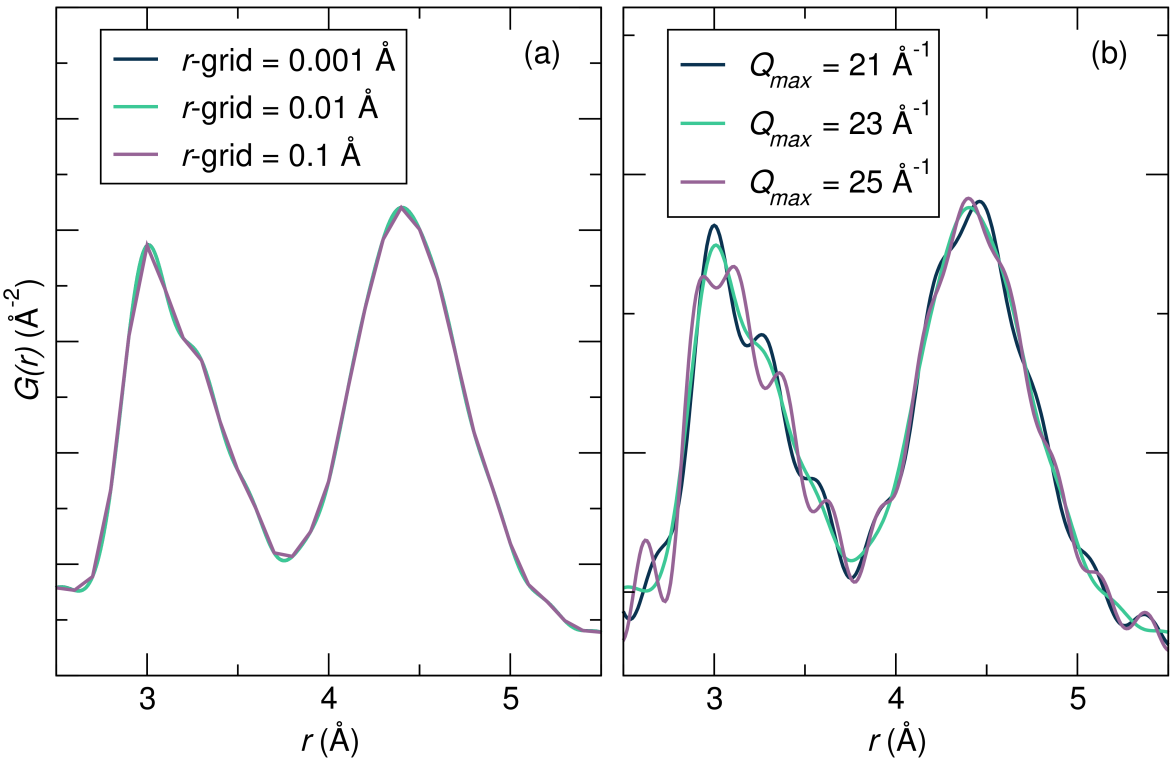

Figure 2: (a) r-grid and (b) Q_{max} series used to determine the optimized Fourier transform parameters of r-grid = 0.01 Å and $Q_{max} = 23\,\text{Å}^{-1}$ for representative sample $FASnI_3$ at 360 K.

Cubic fits of the XPDF data over 10 Å to 20 Å

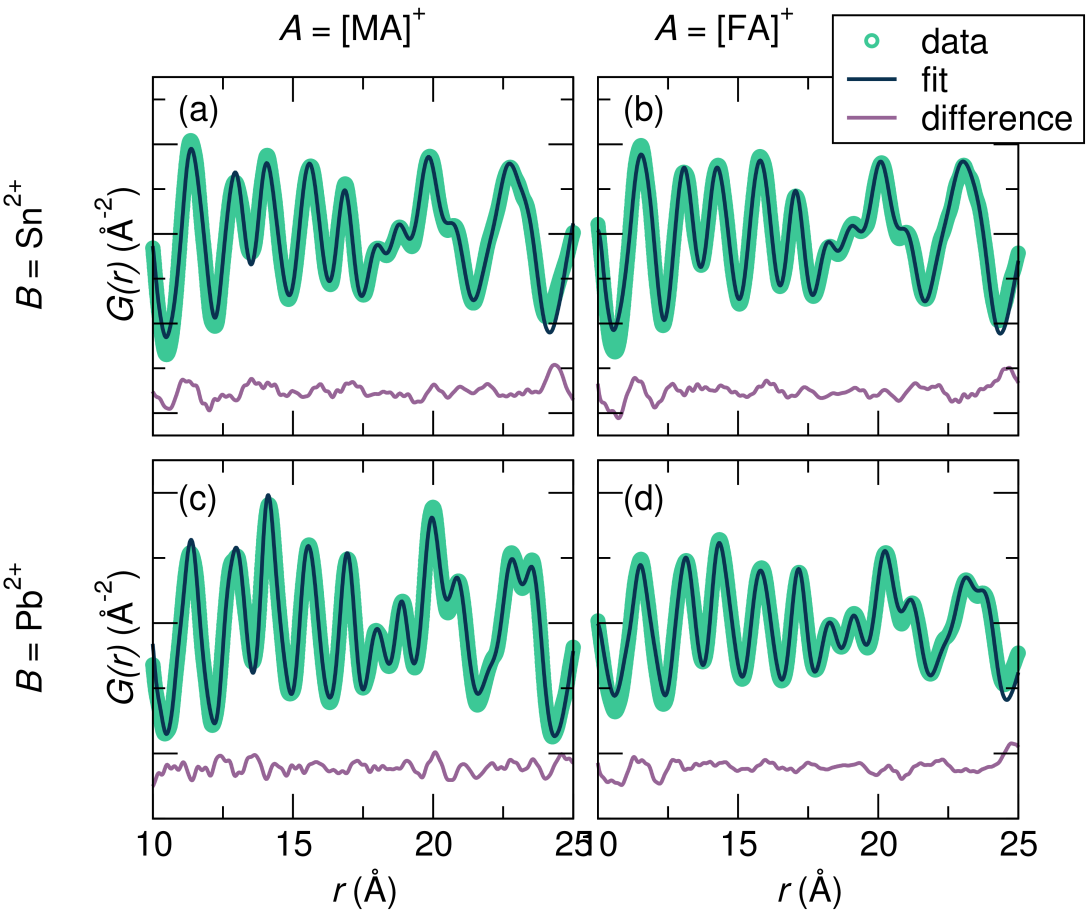

Figure 3: Fits of the synchrotron X-ray PDF data over an r-range of 10 Å to 20 Å against the cubic model with space group $Pm\bar{3}m$ for (a) $MASnI_3$, (b) $FASnI_3$, (c) $MAPbI_3$, and (d) $FAPbI_3$. Fits indicate the data is reasonably described by the cubic model as fit range approaches a crystallographic length scale.

Fits of the XPDF data over 2 Å to 5 Å against all models

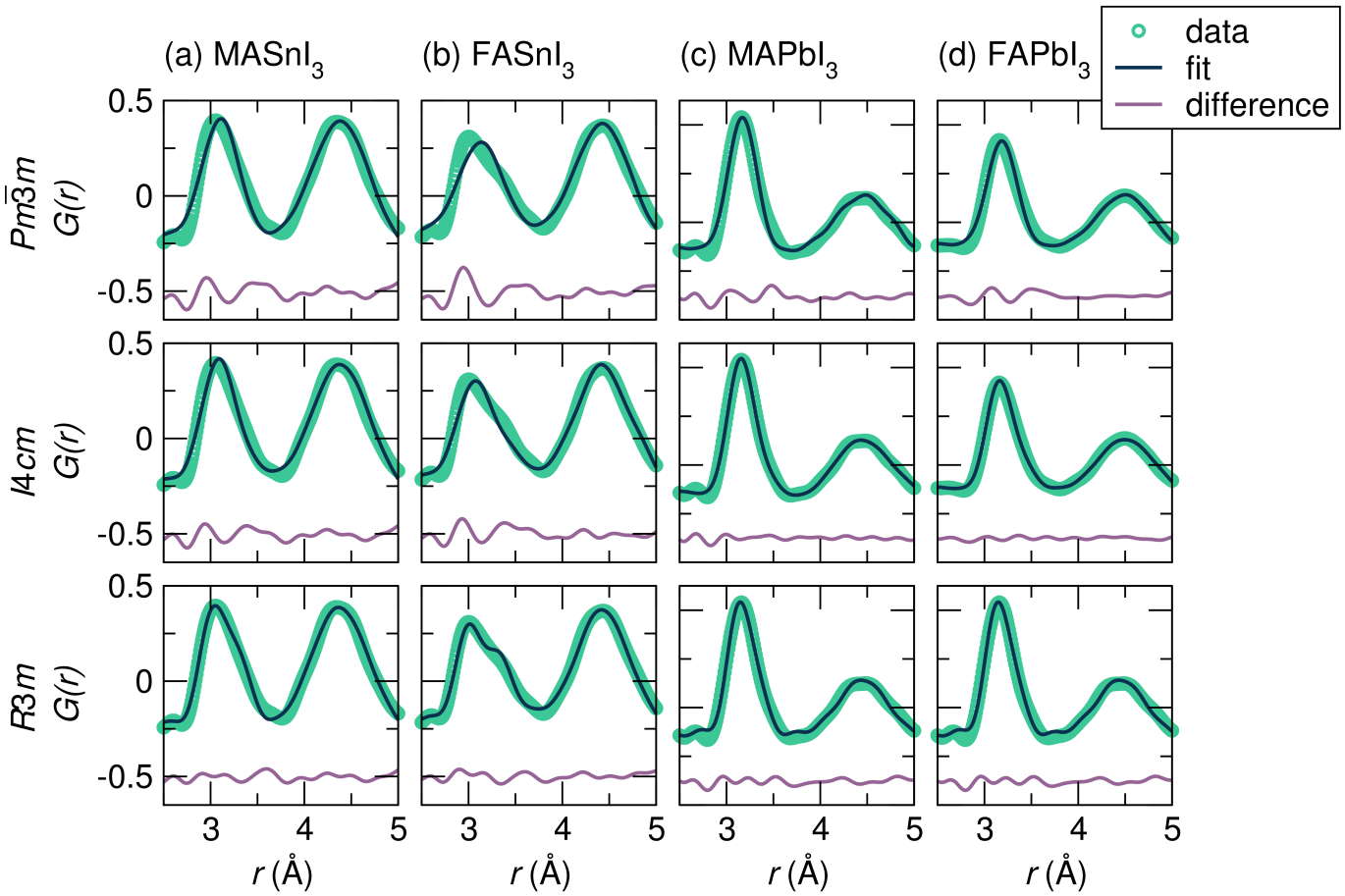

Figure 4: Fits of the synchrotron X-ray PDF data over an r-range of 2 Å to 5 Å against the various space group models $Pm\bar{3}m$ (top row), $I4cm$ (middle row), and $R3m$ (bottom row) for (a) $MASnI_3$, (b) $FASnI_3$, (c) $MAPbI_3$, and (d) $FAPbI_3$. For both Sn^{2+} samples, the local structure is best described by the $R3m$ model, while similar fits are obtained in the Pb^{2+} samples with both the $I4cm$ and $R3m$ models.

Cubic fits of APbBr$_3$ at 300 K and 360 K

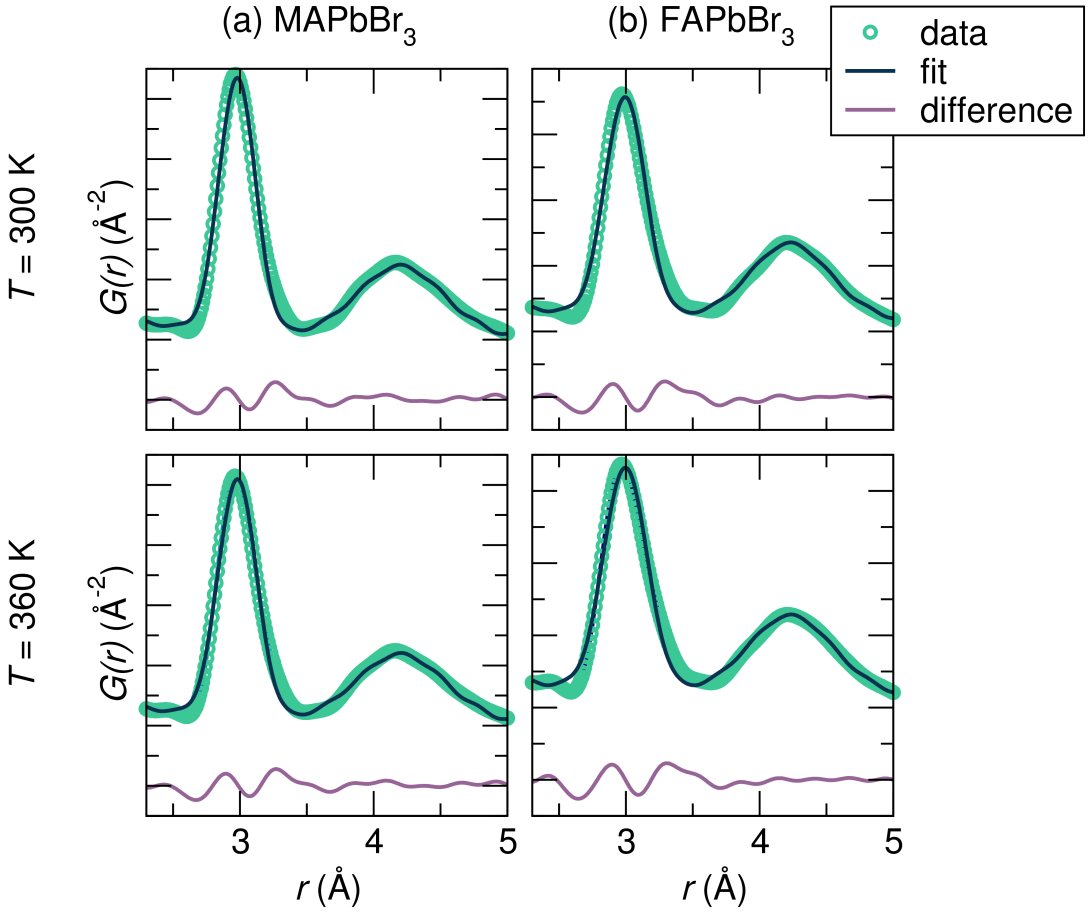

Figure 5: Fits of the synchrotron X-ray PDF data for (a)MAPbBr$_3$ and (b) FAPbBr$_3$ over an r-range of 2 Å to 5 Å against the cubic $Pm\bar{3}m$ models at 300 K (top row) and 360 K (bottom row). The difference curves for all fits indicate the cubic model does not accurately describe the shape of the first Pb–Br correlation at approximately 3 Å.

Rhombohedral fits of APbBr$_3$ at 300 K and 360 K

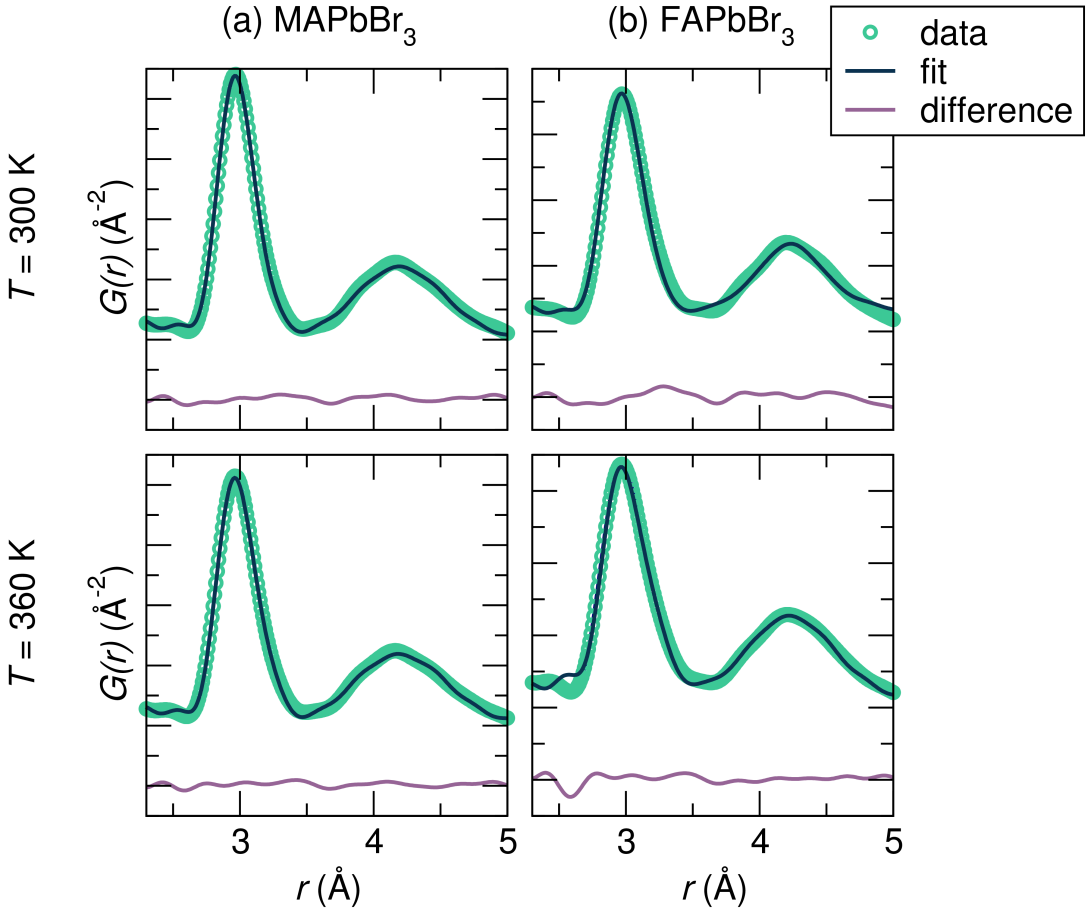

Figure 6: Fits of the synchrotron X-ray PDF data for (a)MAPbBr$_3$ and (b) FAPbBr$_3$ over an r-range of 2 Å to 5 Å against the rhombohedral $R3m$ models at 300 K (top row) and 360 K (bottom row). The difference curves for all fits indicate the rhombohedral model provides a good description of the shape of the first Pb–Br correlation at approximately 3 Å.