Supporting Information

Compositional Variation in Hybrid Organic-Inorganic Lead Halide Perovskites: Kinetically- versus Thermodynamically-controlled Synthesis

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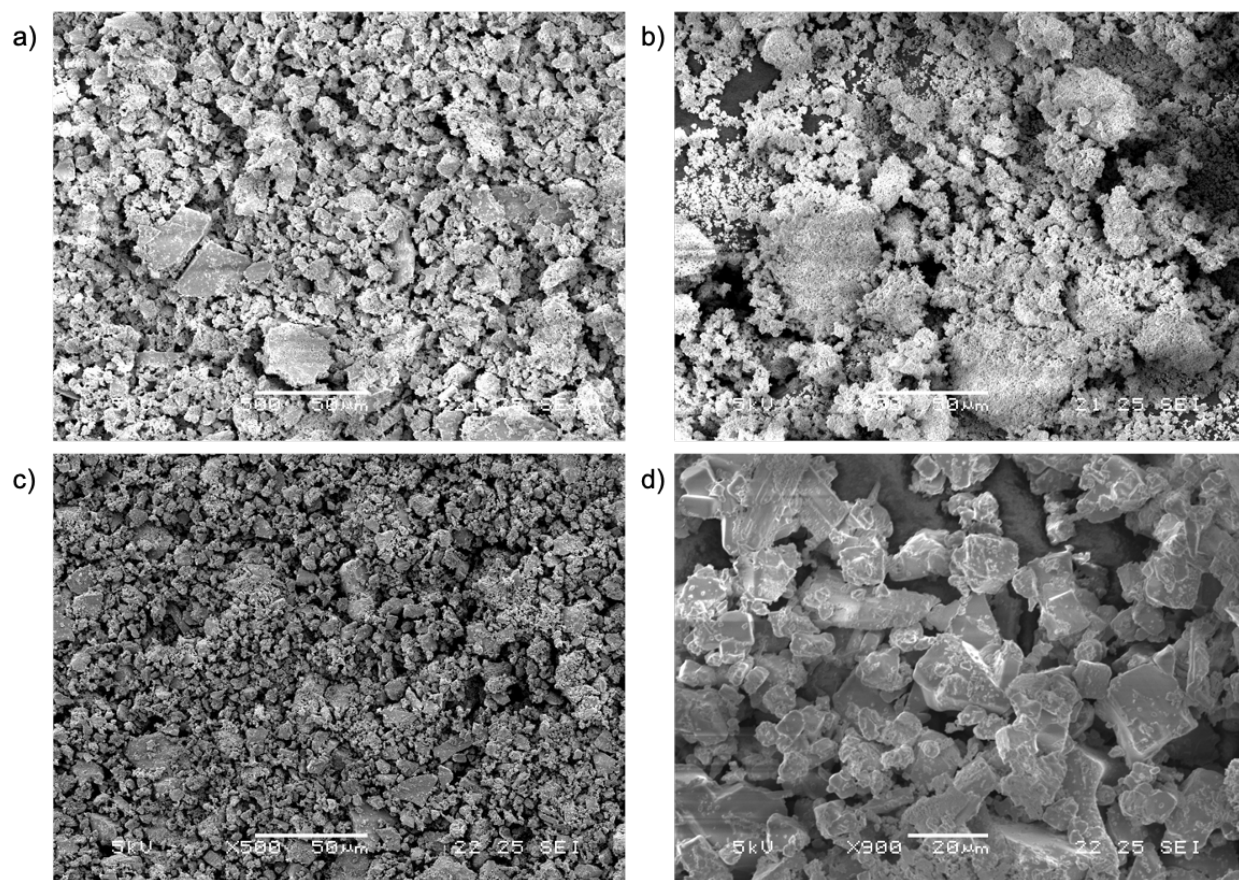
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Figure **S1**. SEM images of $AzPbBr_3$ from a) mechano- b) precipitation synthesis and $FAPbBr_3$ from c) mechano- d) precipitation synthesis. The white scale bar is 20 μm for image d) while scale bar in other images is 50 μm.

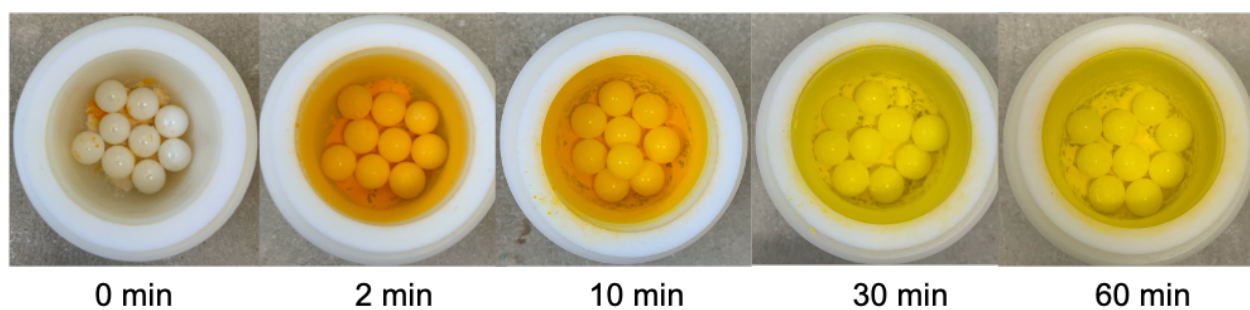

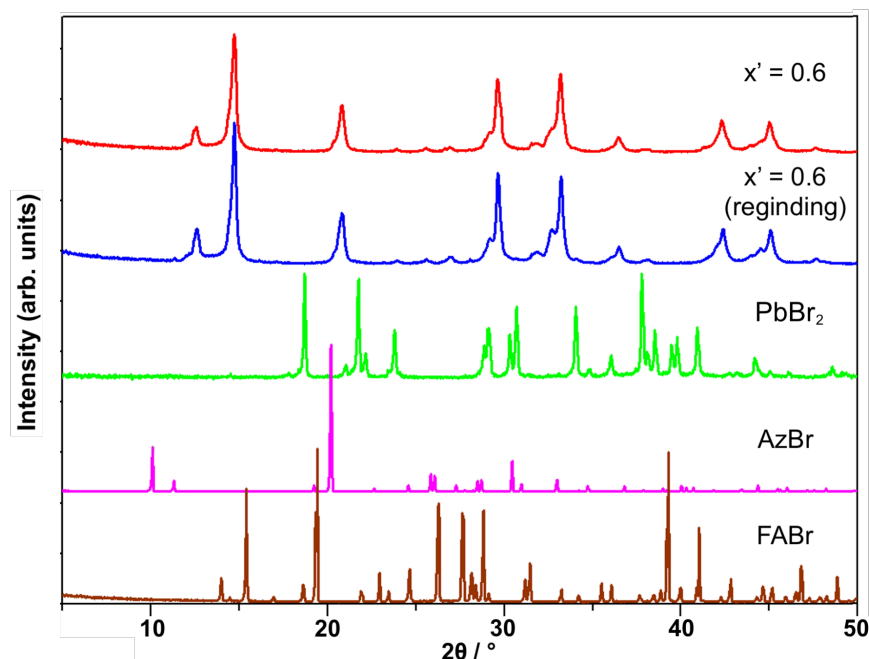Figure **S2**. Photos of color progression of $Az_{0.5}FA_{0.5}PbBr_3$ during mechanosynthesis.

Figure **S3**. PXRD of mechanosynthesised $Az_{0.4}FA_{0.6}PbBr_3$ before and after regrinding for an additional hour and PXRD of starting materials $PbBr_2$, AzBr and FABr.

No trace of starting materials is observed in samples before and after regrinding. Reground samples showed no visual change in appearance and Rietveld refinement indicated an insignificant change (within error) in both phase fraction (cubic phase ratio from 0.436 to 0.453) and lattice parameters of 6H (~1% change) and 3C (~2% change) phase. These analyses suggest all starting materials were consumed during mechanosynthesis.

Crystallite size estimation using the Scherrer equation

Analysis of PXRD data using the Scherrer equation was used to estimate the particle/crystallite size of $Az_{1-x}FA_xPbBr_3$ powders according to:[1]

$$p = \frac{K\lambda}{b\cos\theta} \quad \text{(Eq. 1)}$$

where p is the mean crystallite size, K is Scherrer (shape) constant, λ is the X-ray wavelength (1.5406 Å), b is the breadth at full-width at half maximum intensity (FWHM), in radians, θ is Bragg angle. The Scherrer equation analysis on 6H phase is shown in Table **S1**. The FWHM of the high intensity (011) peak was chosen for the analysis. The shape constant was set to 0.9 as the symmetry of the corresponding crystallite is hexagonal (non-cubic).[1]

Table **S1.** Calculation of crystallite size of 6H phase in the mix-cation $Az_{1-x}FA_xPbBr_3$ ($x \leq 0.8$) perovskite and $FAPbBr_3$ ($x = 1$) in both mechano- and precipitation synthesis using the Scherrer equation.

	Grinding				Precipitation		
x	Peak position(2θ)/ °	FWHM / °	L / nm	x	Peak position(2θ)/ °	FWHM / °	L / nm
0	12.398	0.185	43.2	0	12.417	0.107	74.7
0.1	12.367	0.332	24.1	0.1	12.376	0.091	87.8
0.2	12.452	0.264	30.3	0.2	12.423	0.092	86.9
0.3	12.504	0.224	35.7	0.3	12.385	0.101	79.1
0.4	12.520	0.382	20.9	0.4	12.442	0.098	81.5
0.5	12.544	0.316	25.3	0.5	12.401	0.115	69.5
0.6	12.595	0.357	22.4	0.6	12.416	0.114	70.1
0.7	12.376	0.236	33.9	0.7	12.390	0.102	78.3
				0.8	12.456	0.121	66.0
Average			28.8 ± 7.7	Average			77.1 ± 7.7
1	14.736	0.080	100	1	14.760	0.072	111

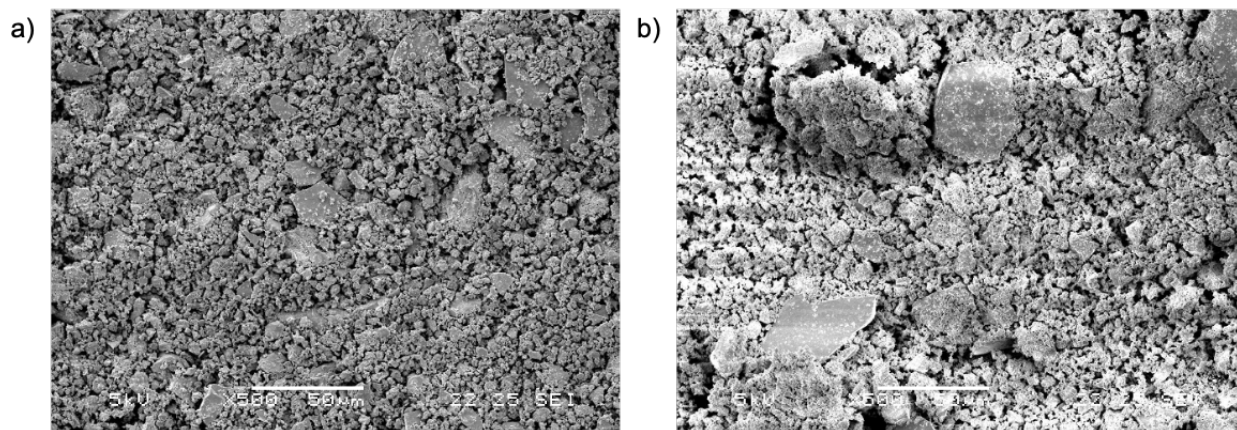**Figure S4**. Examples of SEM images of $Az_{0.6}FA_{0.4}PbBr_3$ from a) mechano- b) precipitation synthesis. The white scale bar is 50 µm in both images.

Determination of the molar ratio of A-cation in as-synthesised perovskite

^{1}H NMR was used to determine the molar ratio of the mixed-cation perovskite. The as-synthesised perovskite powder (ca. 60 mg) was dissolved in ca. 0.6 mL d_6-DMSO. The solutions were stirred at room temperature until the powder was dissolved. The solutions from precipitation synthesis were transferred into an NMR tubes while the solutions from mechano-synthesis were filtered to clear non-perovskite particles, such as polymer fibbers or micro-particles from the ball mill before the transfer. A dichlorobenzene internal standard (20 µL) was added by micropipette. The solution was mixed before the analysis. Before integration, the baseline was corrected using Whittaker Smoother method and the phase was corrected using the whitening algorithm. The peaks of standard reagent – dichlorobenzene was integrated first and normalized to 4.00 (4 × [1]H). Then, the peaks of FA^+, Az^+ were integrated as I_{FA^+}, I_{Az^+}, respectively. One example of this procedure is shown in Figure **S5b**. The molar ratios of FA^+ cation was calculated by the equation:

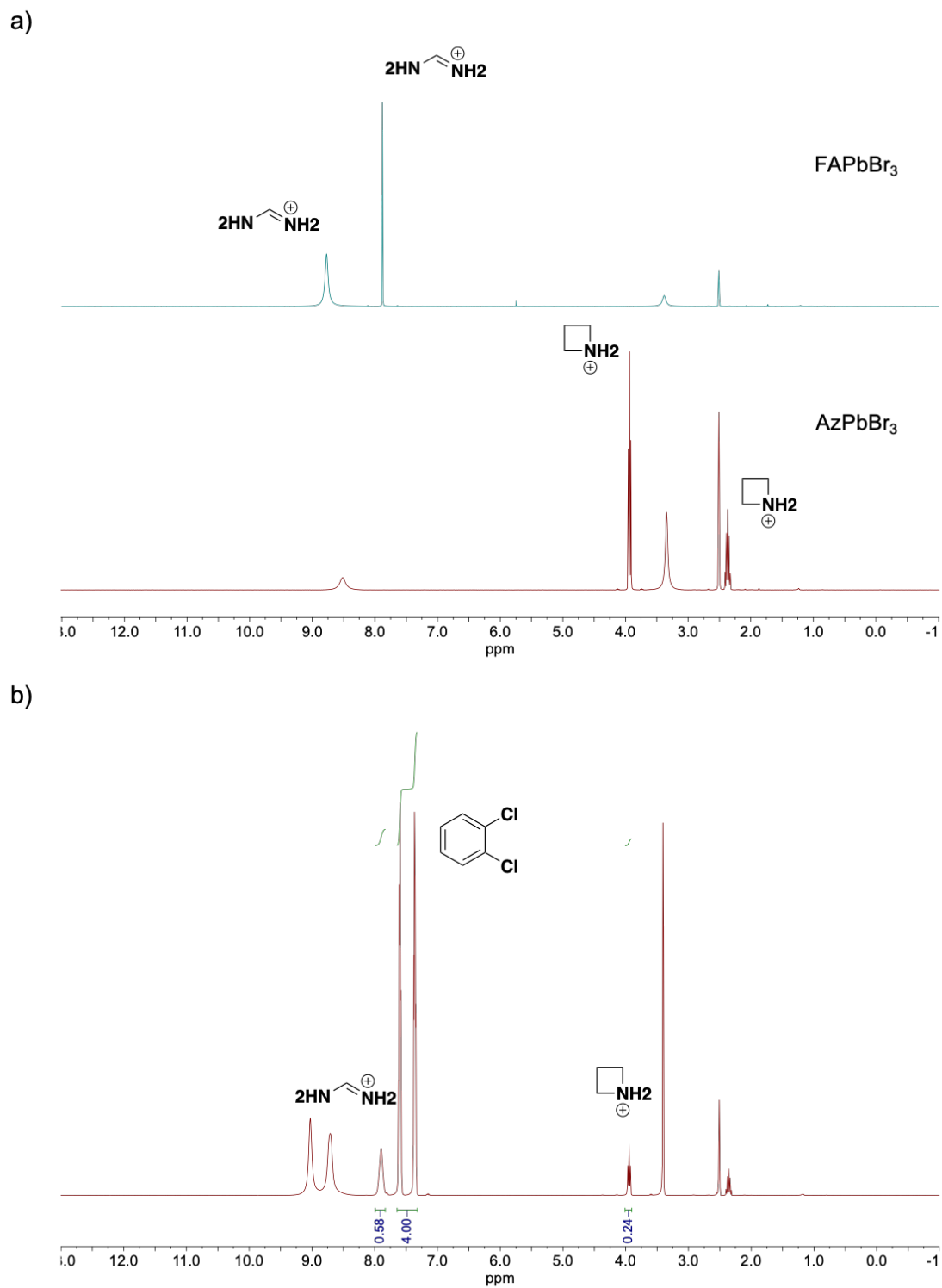$$\alpha_{FA^+} = \frac{I_{FA^+}}{I_{FA^+} + I_{Az^+}/4} \qquad \text{(Eq. 2)}$$

a)

b)

Figure **S5.** Example of the analysis by ^{1}H NMR on a) AzPbBr$_3$ and FAPbBr$_3$ b) a mixed A-cation perovskite Az$_{0.1}$FA$_{0.9}$PbBr$_3$ in d_6-DMSO. Dichlorobenzene (20 µL) was used as the internal standard.

Table **S2.** Comparison of actual x in mechano-synthesis of $Az_{1-x}FA_xPbBr_3$ between the powder removed from ball mill (actual x) and powder left in ball mill (actual x - residue).

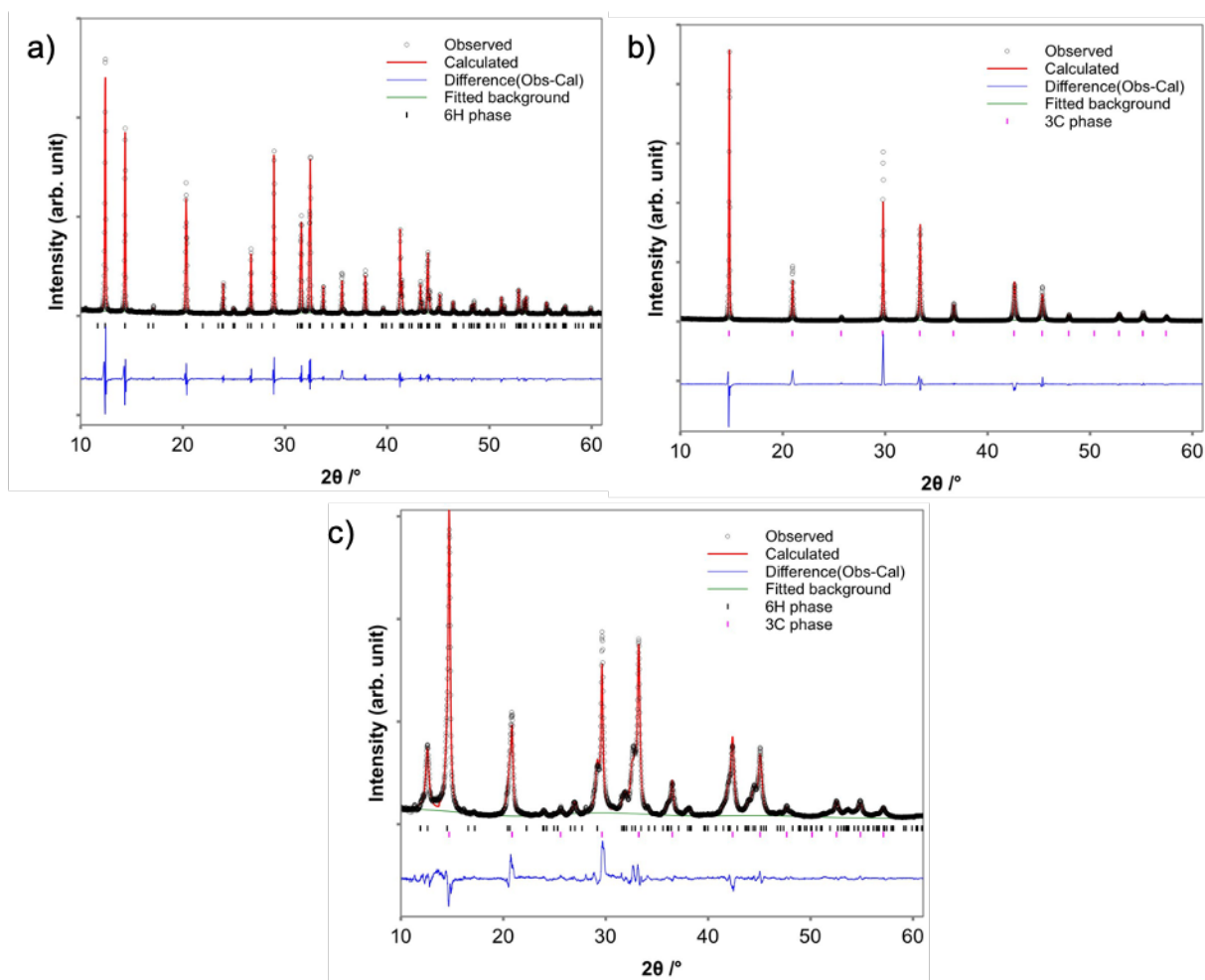| Nominal x'	Actual x	Actual x - residue	Nominal x'	Actual x	Actual x - residue
0.1	0.142	0.158	0.8	0.799	0.800
0.2	0.268	0.265	0.9	0.906	0.900
0.6	0.634	0.597			

Figure **S6.** Examples of Rietveld refinement profile of PXRD data for a) $AzPbBr_3$, b) $FAPbBr_3$ and c) $Az_{0.4}FA_{0.6}PbBr_3$ with observed intensity (open circles), calculated intensity (red line), background (green line), reflection position (black bar for 6H phase and magenta bar for 3C phase) and difference curve (blue line).

Step antisolvent precipitation synthesis

Set 1: AzBr, FABr and $PbBr_2$ were dissolved in DMF/DMSO (4:1) – 0.4 M where the nominal composition was $Az_{0.5}FA_{0.5}PbBr_3$. The solution was divided evenly into 5 sample vials after stirring. The volume of antisolvent (MeCN) added into the solution ranged from 1 mL, 2 mL, 5 mL, 10 mL to 20 mL (excess), The precipitates were dried in vacuum for 24 h before analysis.

Set 2: AzBr, FABr and $PbBr_2$ were dissolved in DMF/DMSO (4:1) – 0.4 M where the nominal composition was $Az_{0.5}FA_{0.5}PbBr_3$. The total amount, including rinsing and washing, of antisolvent

(MeCN) added into the solution was recorded. To obtain enough powder for the analysis, the total amount of antisolvent ranged from 1 mL, 7 mL, 16 mL to ca. 30 mL (excess). The extra volume of antisolvent was to compensate for the loss during vacuum filtration. The precipitates were dried in vacuum for 24 h before analysis.

Actual x was determined by ^{1}H NMR and unit cell volume of the 6H phase is determined by Rietveld refinement.

Table **S3.** Actual x and 6H phase unit cell volume of set 1 and set 2 step antisolvent precipitation synthesis of $Az_{0.5}FA_{0.5}PbBr_3$.

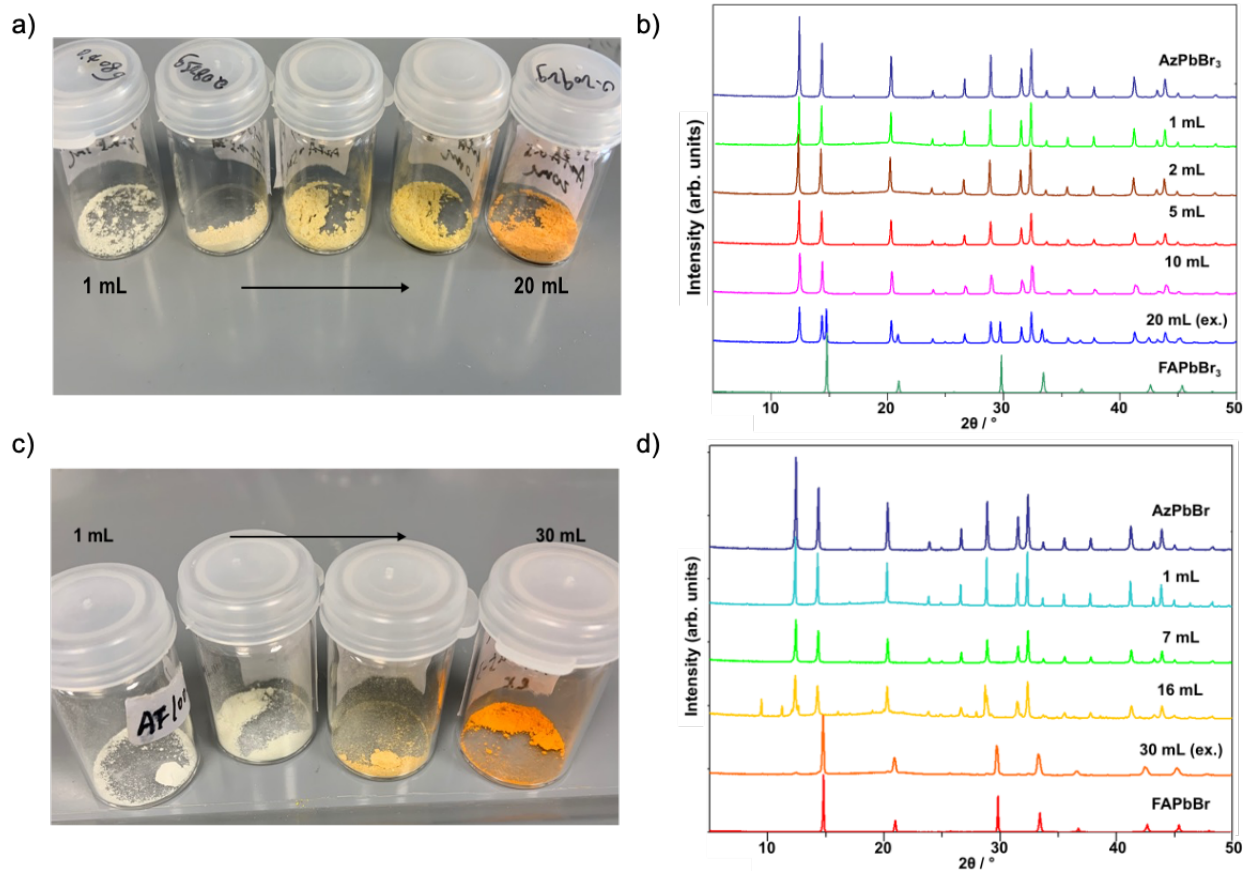| Set 1			Set 2		
Volume of MeCN / mL	Actual x	Unit cell Volume / $Å^3$	Volume of MeCN / mL	Actual x	Unit cell Volume / $Å^3$
1	0.025	1420.308	1	0.024	
2	0.044	1419.838	7	0.060	
5	0.063	1418.322	16	0.294	
10	0.171	1410.823	30 (ex.)	0.803	/
20 (ex.)	0.298	1419.055			

Figure **S7**. Step antisolvent precipitation synthesis of $Az_{0.5}FA_{0.5}PbBr_3$ analysed by (a, c) PXRD; (b, d) visualisation of the color of the powder. (a, b) are from set 1 and (c, d) are from set 2.

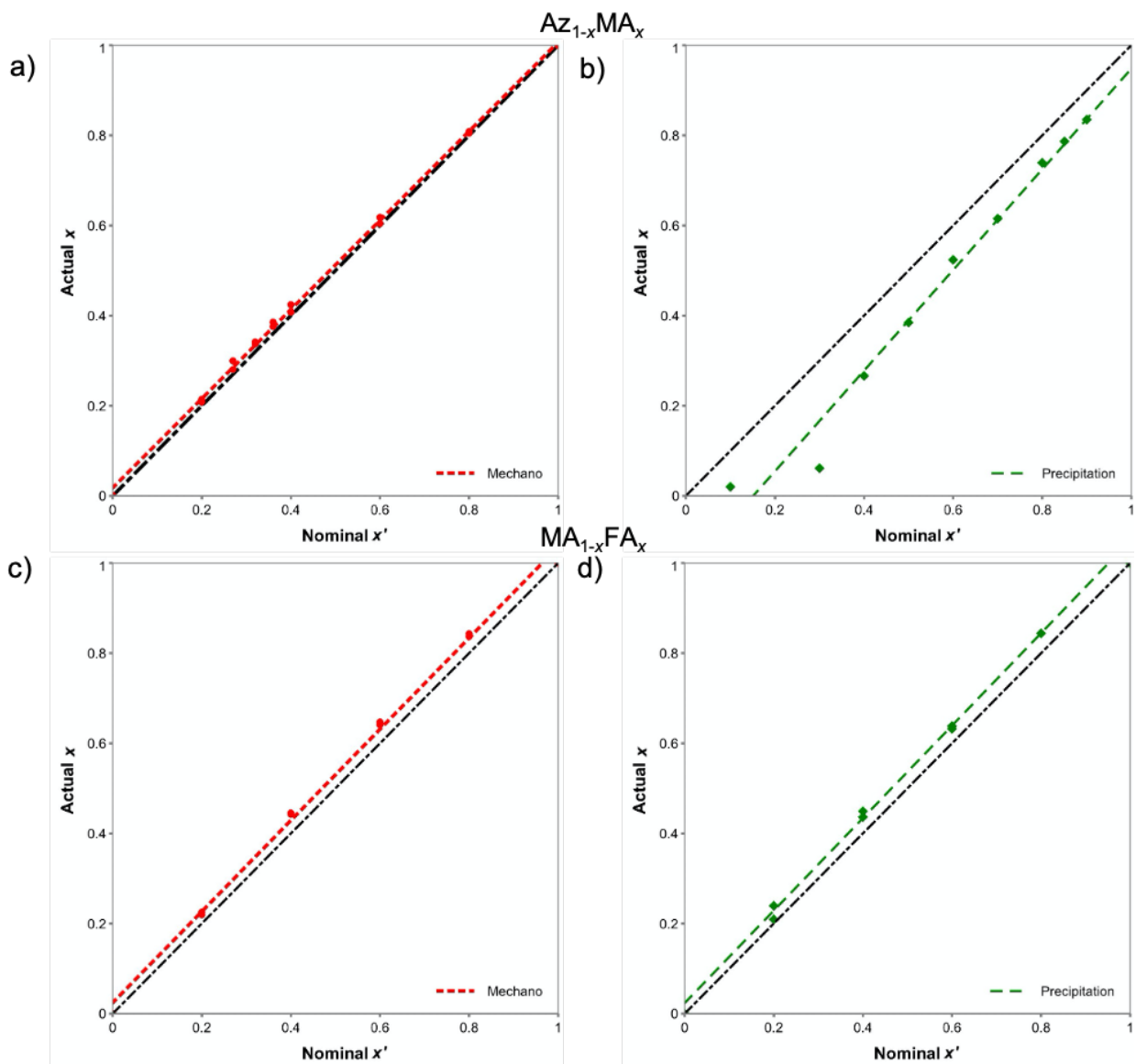Figure **S8**. The comparison of nominal (x') and actual (x) MA^+/FA^+ cation content determined by ^1H NMR analysis in $Az_{1-x}MA_xPbBr_3/MA_{1-x}FA_xPbBr_3$ ($0 \leq x \leq 1$), respectively, prepared by (a, c) mechano-synthesis, and (b, d) precipitation synthesis. Dash lines are linear fit to the actual values and black dot-dash lines indicate the instance for $x' = x$ composition for comparison.
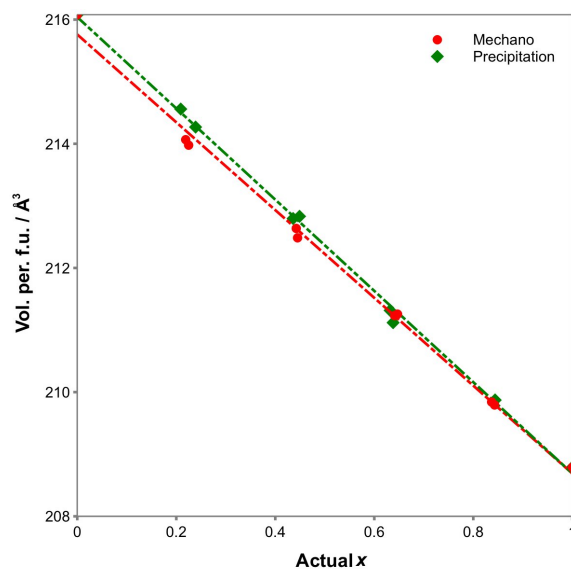
Figure **S9**. Unit cell volume of cubic (3C) perovskite phases as determined by Rietveld refinement of PXRD data for $MA_{1-x}FA_xPbBr_3$ samples prepared by mechano- (circles) and precipitation synthesis (diamonds). Values are shown as a function of overall, actual x as determined by NMR. The dash-dot lines and dash-dot-dot lines are fit of UCV with actual x of mechano- and precipitation samples, respectively.
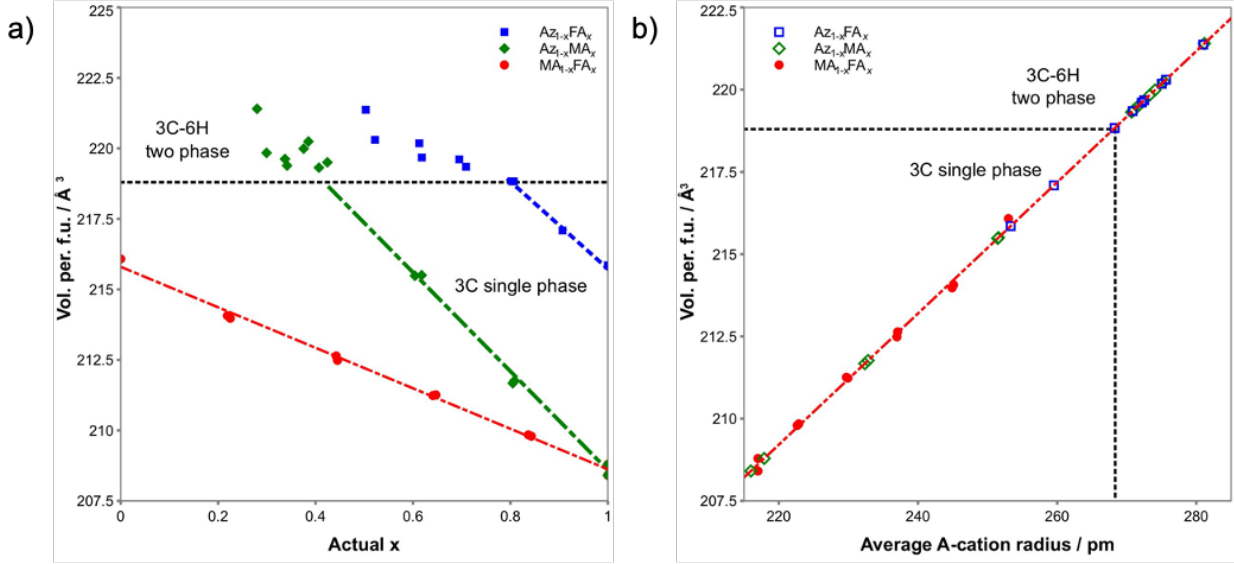
Figure **S10**. a) Unit cell volume of cubic (3C) perovskite phases as determined by Rietveld refinement of PXRD data for $MA_{1-x}FA_xPbBr_3$, $Az_{1-x}FA_xPbBr_3$ and $Az_{1-x}MA_xPbBr_3$ samples prepared by mechanosynthesis. b) Unit cell volume of cubic (3C) FA/MA perovskite samples plotted with average A-cation radius under the assumption of Vegard's law with $r_{FA} = 253$ pm and $r_{MA} = 217$ pm[2]. The line is fitted with the results from $MA_{1-x}FA_xPbBr_3$ and the hollow points from $Az_{1-x}FA_xPbBr_3$ and $Az_{1-x}MA_xPbBr_3$ samples are added in the figure according to their unit cell volume. Black dotted lines indicate the upper limit cell volume (approx. 219 $Å^3$ per formula unit) of cubic single-phase solid solution and corresponding average A-cation radius, which separates the 3C single phase region and 3C-6H two-phase region.
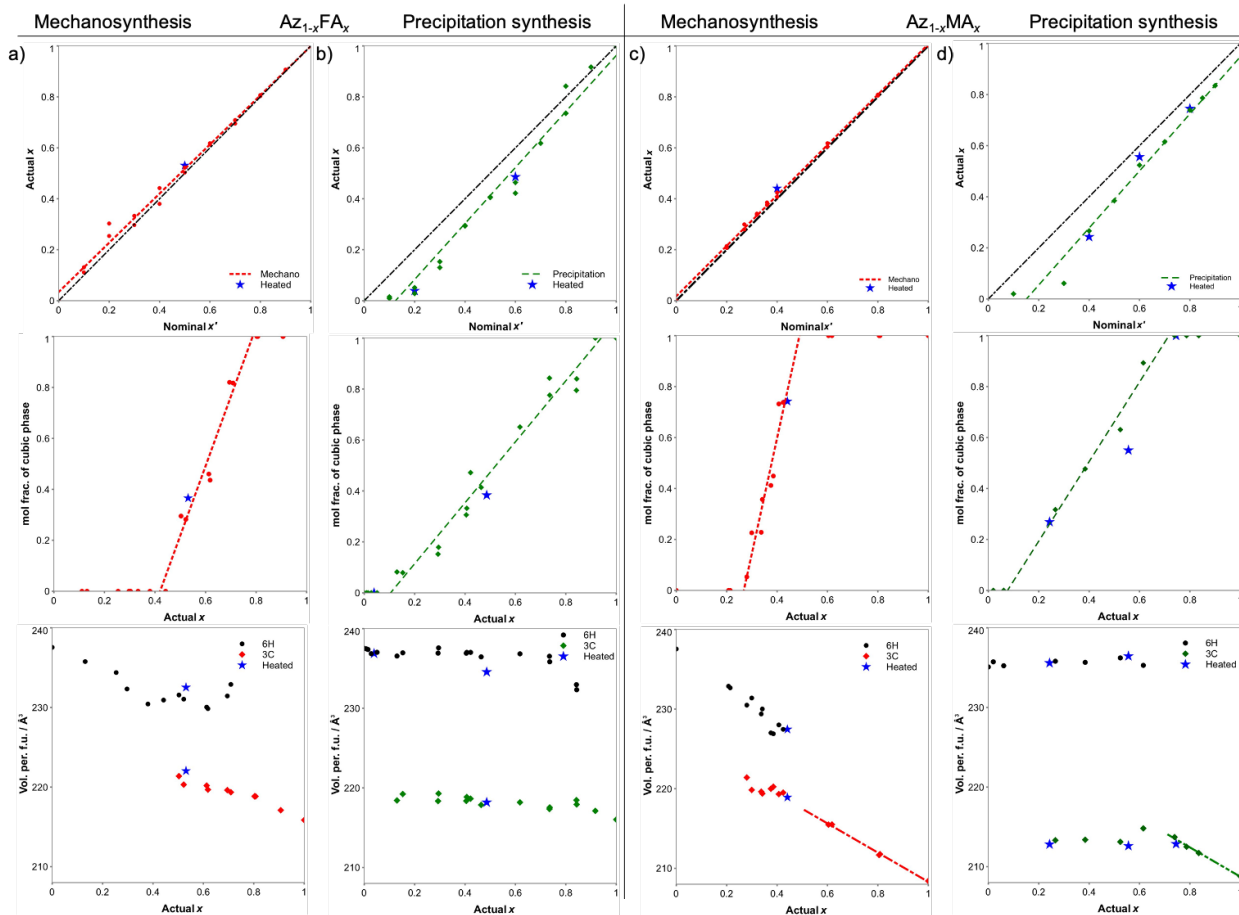
Figure **S11**. Nominal (x') and actual (x) MA^+/FA^+ cation content determined by ^1H NMR analysis, and mole fraction and cell volume (per formula unit) of hexagonal (6H) and cubic (3C) perovskite phases as determined by Rietveld refinement of PXRD data for heated $Az_{1-x}FA_xPbBr_3$ (a, b) and $Az_{1-x}MA_xPbBr_3$ (c, d) samples, prepared by mechano- (a, c) and precipitation synthesis (b, d). The results from heated samples are marked with star.

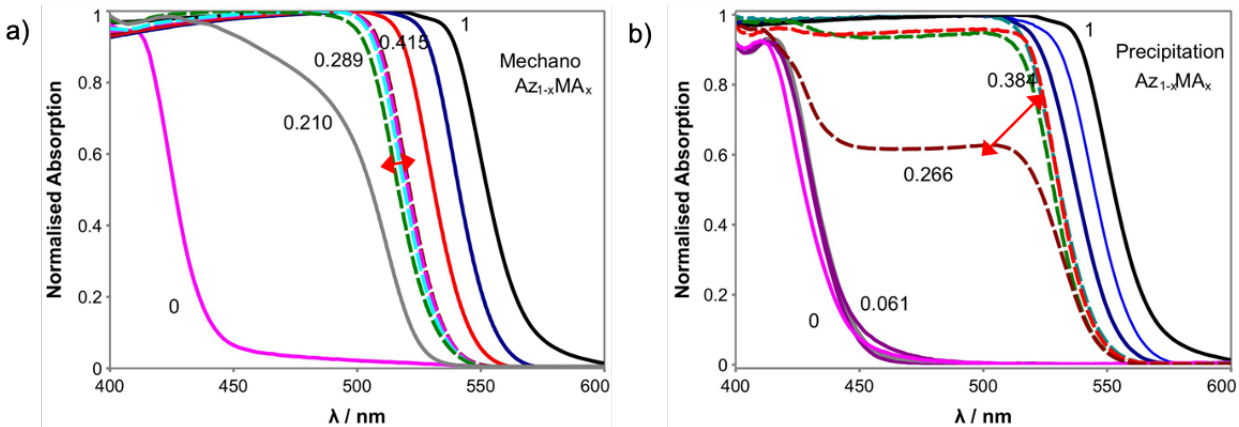Figure **S12**. Absorption spectra of $Az_{1-x}MA_xPbBr_3$ samples prepared by a) mechanosynthesis b) precipitation synthesis. Spectra from single phase (solid solution) compositions as determined by PXRD are plotted with solid lines and multi-phase samples with dashed lines.
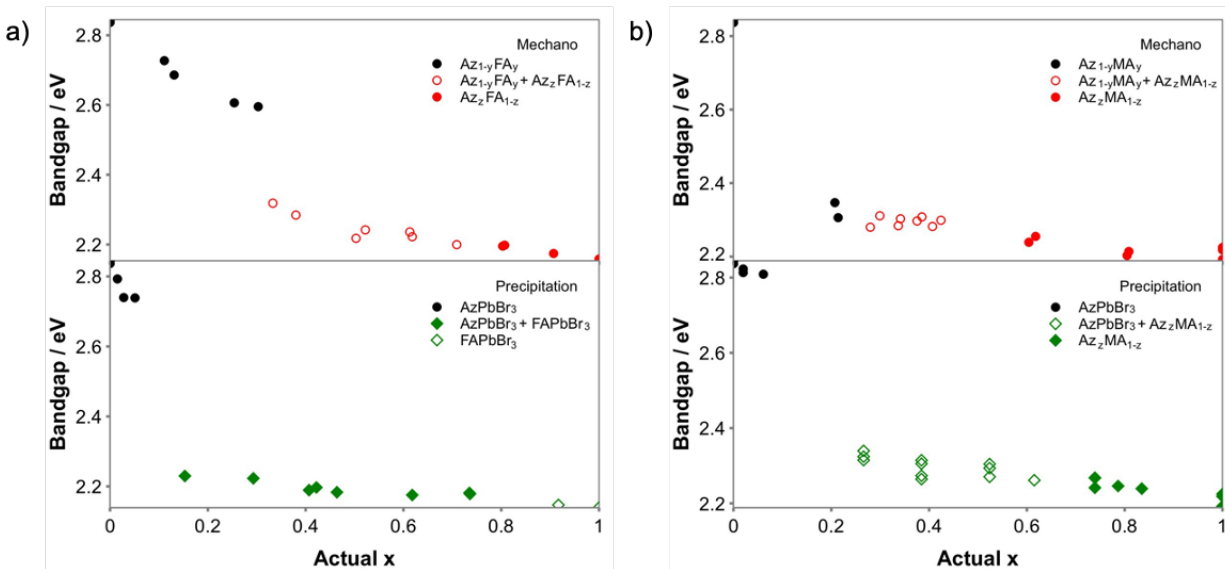

Figure **S13**. Bandgap determined from the absorption onset in the absorption spectra of a) $Az_{1-x}FA_xPbBr_3$; b) $Az_{1-x}MA_xPbBr_3$ synthesized from both mechano- and precipitation synthesis.

References

(1) Langford, J. I.; Wilson, A. J. C. Scherrer after Sixty Years: A Survey and Some New Results in the Determination of Crystallite Size. *J. Appl. Crystallogr.* **1978**, *11* (2), 102–113.

(2) Kieslich, G.; Sun, S.; Cheetham, A. K.; Cheetham, T.; Gregor, K.; Shijing, S.; Anthony, K. C. Solid-State Principles Applied to Organic-Inorganic Perovskites: New Tricks for an Old Dog. *Chem. Sci.* **2014**, *5* (12), 4712–4715.