Supplementary Information

Direct Observation of Phase Transitions between delta- and alpha-Phase FAPbI3 via Defocused Raman Spectroscopy

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1. Temperature dependent PL of $FAPbI_3$

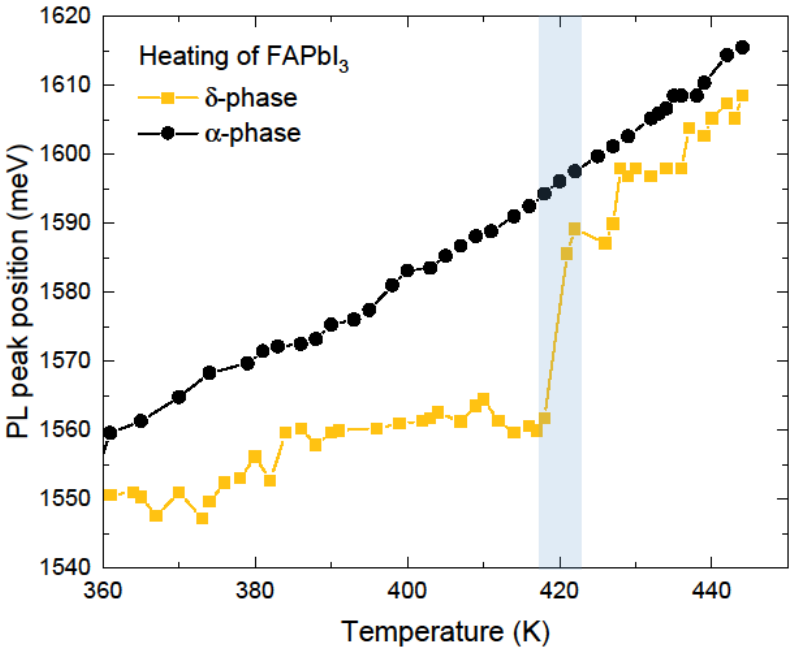

Fig. S1: Temperature dependent Photoluminescence of FAPbI3 single crystals. Delta phase crystals can be converted back into the alpha phase by heating to temperatures above 420K at a heating rate of 3K/min, as can be seen by the change in PL peak position (highlighted in blue). Samples were excited with a 532nm laser.

2. Single Crystal X-ray Diffraction

Single crystal diffraction data were collected using an Oxford Diffraction (Agilent) SuperNova instrument with a molybdenum (0.71973 Å) microfocus X-ray tube. Unit cell indexation, detwinning, data integration, and reduction were performed using Rigaku CrysAlisPro software. The structures were solved and refined using SHELX-2013, implemented through Olex2 software. Structural and refinement parameters can be found in Tables S1 and S2. Images of the crystal structures are shown in Figure S2. $FAPbI_3$ crystals were found to be a two-component twin. The second twin component had a twin matrix of (0.6703 0.6620 -0.3384, -0.6677 0.3351 -0.6660, -0.3275 0.6716 0.6666) with respect to the first component. Twin components 1 and 2 contributed to 62(1)% and 38(1)% of the observed reflections, respectively. The structural solution was refined against the full data set (hklf5 file). No twinning was observed for the $FAPbI_3$-M crystals.

CIF files of the two crystal types investigated in this work have been submitted to the CCDC. The deposition numbers are 2299142 for FAPbI3 and 2299143 for FAPbI3-M.

Images of model (Figure S2)

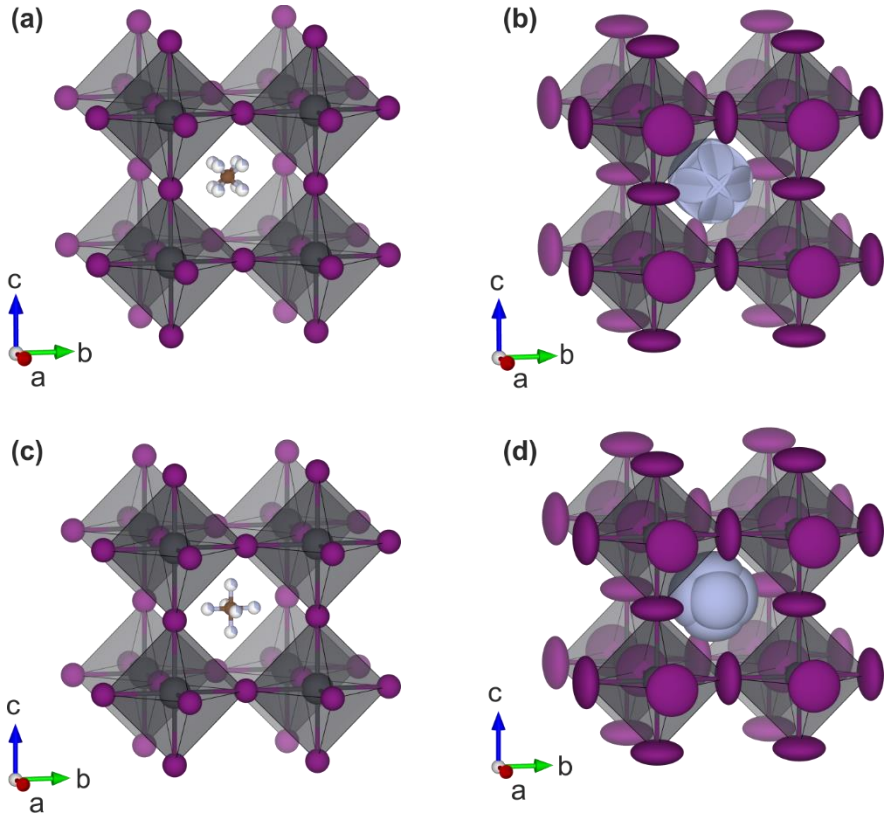

Fig. S2. The crystal structures solved from single crystal X-ray diffraction measured on $FAPbI_3$ crystals**,** showing without (a) and with (b) the 100% thermal ellipsoids. Similarly, the crystal structures of $FAPbI_3$-M crystals**,** are shown without (c) and with (d) the 100% thermal ellipsoids. Both crystals are in the cubic α-phase, and the electronic distribution of the organic cation can be considered quasi-spherical due to rotational disorder. Structural and refinement parameters can be found in Tables S1 and S2, respectively.

Table S1. Structural models for $FAPbI_3$ and $FAPbI_3$-M crystals, refined against the single crystal X-ray diffraction data.

	Atom	x	y	z	Occupancy	Multiplicity	Equivalent Isotropic Displacement Parameters ($Å^2×10^3$)
$FAPbI_3$	Pb	0	0	0	1	1	30.1(10)
	I	0.5	0	0	1	3	84.1(17)
	C	0.5	0.5	0.5	1	1	110(60)
	N	0.58(1)	0.58(1)	0.58(1)	0.25	8	150(100)
$FAPbI_3$-M	Pb	0	0	0	1	1	36.6(4)
	I	0.5	0	0	1	3	89.4(6)
	C	0.5	0.5	0.5	1	1	170(40)
	N	0.5	0.5	0.337(6)	0.33	6	131(19)

Table S2. Parameters of the crystal structure models refined against the single crystal X-ray diffraction data.

Identification code	exp_001_twin1_hklf5 (**$FAPbI_3$**)	exp_246 (**$FAPbI_3$-M**)
Empirical formula	C I_3 N_2 Pb	C I_3 N_2 Pb
Formula weight	627.92	627.92
Temperature/K	293(2)	293(2)
Crystal system	cubic	cubic
Space group	*Pm*-$\bar{3}$*m*	*Pm*-$\bar{3}$*m*
a/Å	6.36382(16)	6.35293(19)
b/Å	6.36382(16)	6.35293(19)
c/Å	6.36382(16)	6.35293(19)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/$Å^3$	257.724(19)	256.40(2)
Z	1	1
ρ_{calc}g/cm^3	4.046	4.067
μ/mm^{-1}	25.275	25.406
F(000)	261.0	261.0
Crystal size/mm^3	0.2 × 0.15 × 0.1	0.1 × 0.15 × 0.25
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.402 to 59.1	9.074 to 57.526
Index ranges	-8 ≤ h ≤ 7, -8 ≤ k ≤ 8, -8 ≤ l ≤ 7	-8 ≤ h ≤ 5, -6 ≤ k ≤ 5, -3 ≤ l ≤ 8
Reflections collected	274	352
Independent reflections	274 [R_{sigma} = 0.0173]	91 [R_{int} = 0.0346, R_{sigma} = 0.0296]
Data/restraints/parameters	274/0/9	91/0/9
Goodness-of-fit on F^2	1.136	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0636, wR_2 = 0.1659	R_1 = 0.0224, wR_2 = 0.0388
Final R indexes [all data]	R_1 = 0.0656, wR_2 = 0.1695	R_1 = 0.0265, wR_2 = 0.0400
Largest diff. peak/hole / e $Å^{-3}$	1.29/-1.26	0.42/-0.65

3. Spot size Measurements

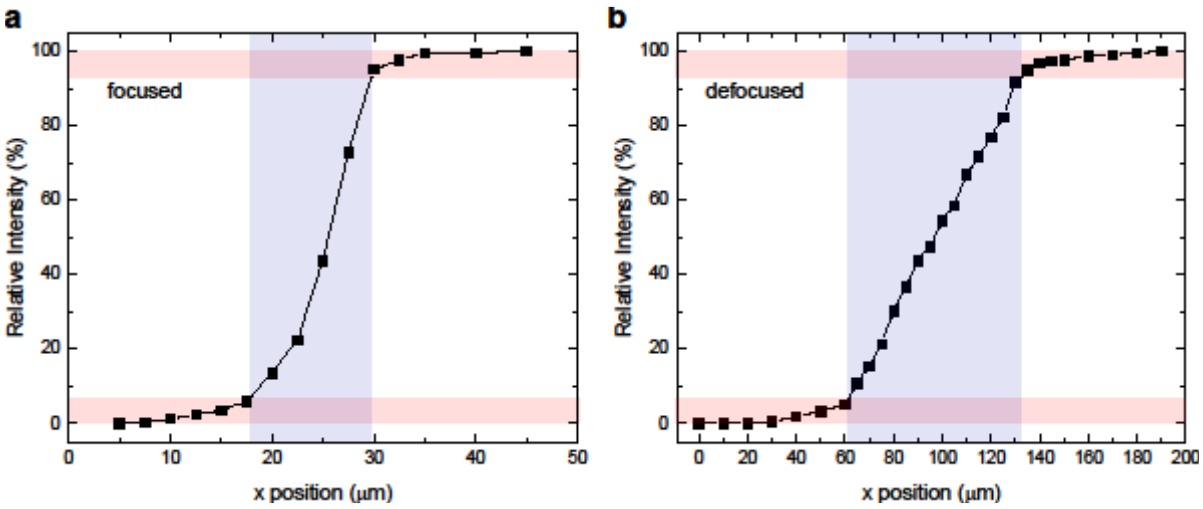

Fig. S3: Laser spot size measurements for the two Raman configurations. The laser spot was moved across the edge of a Silicon wafer with a micrometre stage. The limits of the $1/e^2$ intensity profile are highlighted in red and the diameter of the spot is highlighted in blue. **a)** Data for the focused and **b)** defocused Raman setup.

4. Molecular modes of FA+ in FAPbI3 crystals

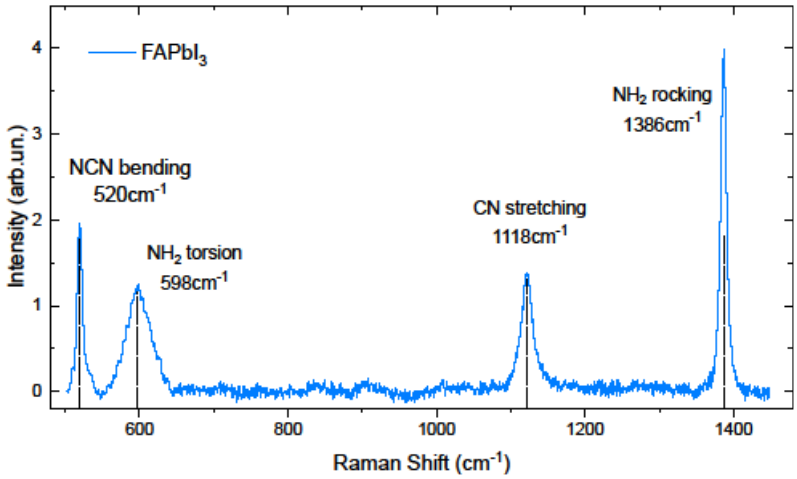

Fig. S4: Molecular Raman modes of FA+ in FAPbI3 single crystals. The spectra were acquired with the defocused setup with a 50x600s acquisition time and combined at 1000cm^{-1} after background subtraction. The four molecular vibrations and their theoretically expected positions are indicated in black.