# Supporting Information for:

# Direct Laser Writing of $\delta$ - to $\alpha$ -phase Transformation in Formamidinium Lead Iodide

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#### δ-FAPbI3 UV-VIS optical absorption spectrum:



**Fig. S1:** Absorption spectra recorded in reflection mode from the surface of a  $\delta$ -FAPbI<sub>3</sub> single crystals, along with the relative wavelength of the 458 nm laser line for comparison.

#### Raman spectral fitting procedure:

Figure S2 shows an overview of the region of interest for the Raman spectral fitting, with an example fit provided in the inset. For the wavenumber range 60 to 190 cm<sup>-1</sup>, Raman spectra fits are made using the Multipeak Fitting 2 procedure in the IgorPro software program, implementing three Lorentzian oscillators (I<sub>δ</sub>, I<sub>α</sub> and I<sub>Pb-O</sub>) and one Gaussian-like Voigt lineshape (I<sub>δ'</sub>; broad low-energy shoulder of the δ-phase). Given the energy of vibrations I<sub>δ</sub> and I<sub>Pb-O</sub> were not observed to vary drastically between measurements (in dynamics or kinetics experiments), the frequency of these vibrations were held constant with respect to other variables, which were free to fit the data. The low energy shoulder of the fit region is seen to rise rapidly as it approaches the Rayleigh scattering line and defines the rising background on the data. For background (BG) handling, a linear function is seen to be a reasonably approximation over the narrow fitting range, as well as facilitating a robust method of accurately comparing the fits of differing spectra, compared to BG fits made with higher order "curved" functions (*i.e.* polynomials).



**Fig. S2:** Raman spectrum of FAPbI<sub>3</sub> after exposure to 0.63 kW.cm<sup>-2</sup> laser power density (same trace as presented in Fig. 2(a) of the article), with the inset showing the fit made from the sum of the identified vibrations and the background (BG) within the energy range 60 to 190 cm<sup>-1</sup>.

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### Comparison to lead monoxide (PbO) Raman spectrum:



**Fig. S3:** Comparison of Raman spectra recorded following exposure of  $\delta$ -FAPbI<sub>3</sub> surface to extremely high laser power densities (2 kW.cm<sup>-2</sup>; producing PbO deposit on crystal surface) with that measured from pure room-temperature table PbO crystal powder. Both Raman spectra were recorded using low excitation power (<50 W.cm<sup>-2</sup>). The arrows here highlight the mode softening seen in each of the vibrations compared.



#### Thermal $\delta$ - to $\alpha$ -phase transformation:

**Fig. S4:** (a) Raman scattering spectra recorded *ex situ* from the FAPbI<sub>3</sub> surface using a low excitation intensity (<0.01 kW.cm<sup>-2</sup>) for sample receiving 10 minute thermal annealing treatments up to 150° C, with mode assignment indicated. (b) Powdered XRD of annealed FAPbI<sub>3</sub> samples showing the onset of the  $\alpha$ -phase-related peak measured at 14° for an annealing temperature of 130° C. The asterisks in (b)u (\*) identify the weak presence of the  $\alpha$ -phase peaks.

#### Johnson-Mehl-Avrami-Kolmogorov (JMAK) theory:

The JMAK theory presumes that the transformed volume fraction X(t) will follow an exponential dependency on time:

$$X(t) = 1 - \exp[-k(t-t_0)^n]$$
(S1)

Here *t* is time,  $t_0$  starting time of the transformation, *k* is the reaction rate constant and *n* is a constant variable dependent on the character of nucleation and growth. By theoretical considerations, the Avrami exponent *n* acquires an integer or half integer value in the range 0.5 to 4, depending on the dimensionality of the transformation and is defined as the local slope in a double-logarithmic Avrami plot:  $\ln[-\ln(1-X(t))]$  vs  $\ln(t)$ . A constant Avrami exponent as a function of  $\ln(t)$  can be considered an adherence to normal JMAK crystallisation theory and indicates that the transformation dynamics of the system possess temporal stability. In relation to our data, we assume that the integrated Raman intensity of the  $\alpha$ -FAPbl<sub>3</sub> mode at 137 cm<sup>-1</sup> – selected for its relatively strong Raman signal – is proportional to the volume of transformed  $\alpha$ -phase material synthesised within the Raman micro-probe, *i.e.* represented by *X* in the equation above.

#### Comparison to lead monoxide (PbO) PL spectrum:



**Fig. S5:** Comparison between the normalised PL peak measured at roughly 660 nm near the DLW tracks on the  $\delta$ -FAPbI<sub>3</sub> surface and that recorded from pure PbO powder (purchased from Sigma-Aldrich). To highlight the relatively large variability in the emission peak wavelengths measured from both of these materials, relatively high and low emission wavelengths are presented together (*i.e.* two spectra each).

# Morphology of lead monoxide (PbO) PL emission:



**Fig. S6:** Micro-PL mapping data recorded from DLW areas atop  $\delta$ -FAPbl<sub>3</sub> single crystals, showing the variations in final morphology of luminescent species. The mapping analysis here receives the same treatment as in Fig. 5 of the article; top (red) images represent intensity map of the NIR peak ( $\alpha$ -FAPbl<sub>3</sub>-like) and the bottom (green) maps show the morphology of the peak recorded at 660 nm (PbO-like emission). The parameters for the DLW patterning are as follows (NA / laser power intensity in 2 kW.cm<sup>-2</sup>): (a) 0.75 / 0.8, (b) (a) 0.4 / 1.3, (c) 0.75 / 1.5, and (d) 0.4 / 1.7,. Here we see (from left to right) the progression of the more intense coverage of 660 nm emission, paralleled by the formation of less distinct 780 nm emissions.

# Temporal phase stability of DLW $\alpha$ -phase PL emission:



**Fig. S7:** Normalised emission spectra recorded from the DLW pattern investigated in Fig. 5 (d) and (e) of the main article several weeks following DLW, along with the full spectrum measured on day 0 using the PL microscope ( $\lambda_{exc}$  = 532 nm), for comparison. The significant difference between the labelled temporal spectra scans recorded using the fluorescence microscope and the complete emission lineshape (bottom grey trace) is attributed to measuring the former near its detection limits, where a strong spectral response exists which alters the lineshape.

# **Exposure to ozone:**

Three pairs of black FAPbI<sub>3</sub> single crystals were studied (as-grown materials, and two others receiving 5 minute thermal treatments of 150  $^{\circ}$ C and 160  $^{\circ}$ C) and one sample from each pair of FAPbI<sub>3</sub> single crystals received a 10 minute ozone treatment. The color of the crystals were then observed and compared over the proceeding hours (see photographs below).



**Fig. S8:** Photographs comparing the temporal response of fresh as-grown and thermally treated FAPbI<sub>3</sub> ~2mm single crystals following 10 minutes in an ozone reactor. For scale, the top grids indicate 1 mm units.

# Morphology of $\delta$ -FAPbI<sub>3</sub> single crystals and thin films:



**Fig. S9:** SEM micrographs of (a) typical single crystal surface morphology, showing the nature of the smooth angulating surface described in the main text, and (b) the DLW patterning drawn on the thin film shown in Fig. 6(e) of the main article.