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PCCP

SUPPLEMENTARY INFORMATION

Hidden polymorphism of $FAPbI_3$ discovered by Raman Spectroscopy

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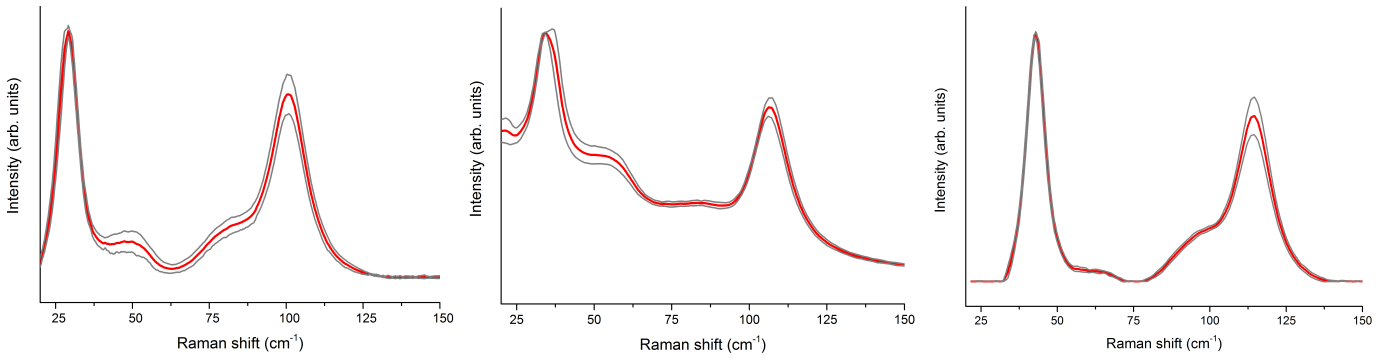
Raman spectroscopy and Photoluminescence

Raman spectroscopy and photoluminescence (PL) were performed on single crystals (SC).



(a) α_i (b) α_δ (c) α_{rec}

Fig. 1 Average Raman spectra of different samples and standard deviation. The average value ($\bar{x}$) are presented by the red lines, while the standard deviation of each point (σ) are presented by the grey line ($\bar{x}+\sigma, \bar{x}-\sigma$).

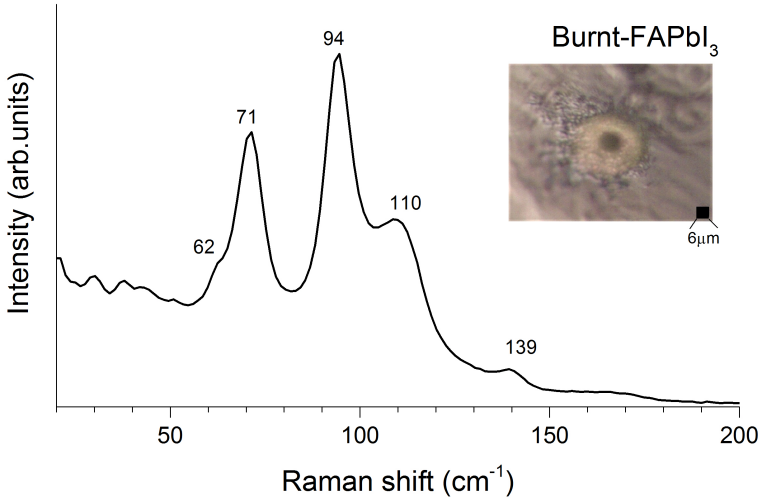


Fig. 2 Raman spectrum of PbI_2 resulting of placing $FAPbI_3$ under an excitation power higher than 1 mW (λ=633 nm).

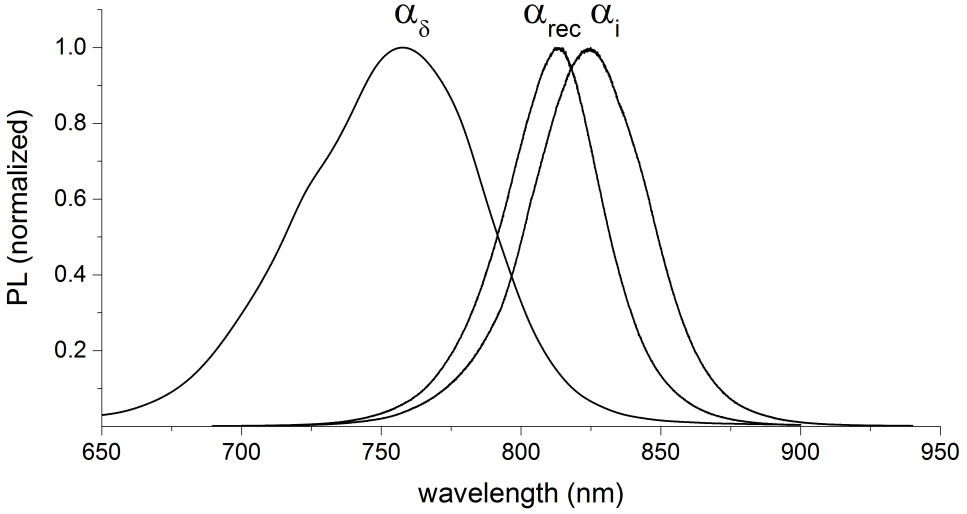


Fig. 3 PL signal of the $FAPbI_3$ polymorphs at RT: α_i (824 nm), α_δ (765 nm) and α_{rec} (814 nm).

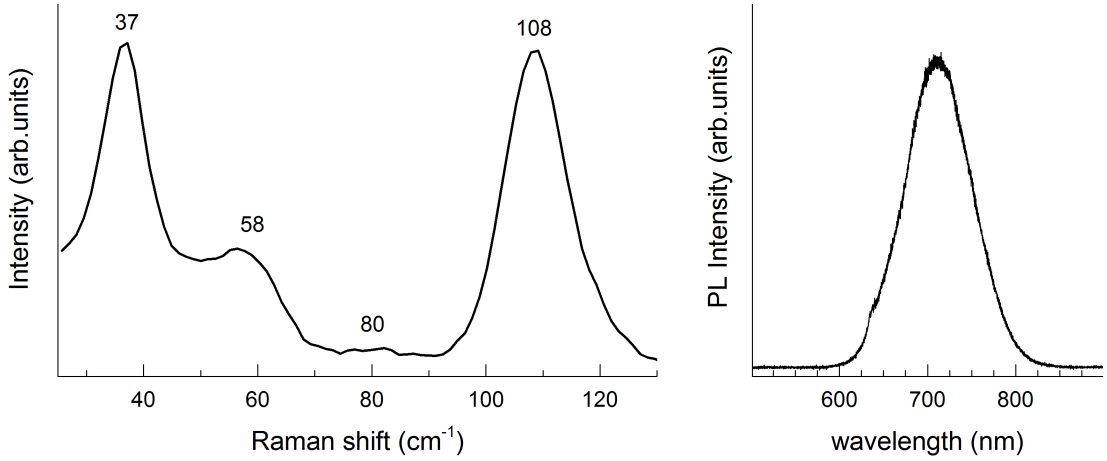


Fig. 4 Raman spectrum and PL signal of $\alpha_\delta * -FAPbI_3$. This corresponds to the α_δ-phase that appears in yellow needle-like $FAPbI_3$ crystals. These are directly synthesized via heating the 1M $FAPbI_3$+GBL solution at 70℃ overnight.

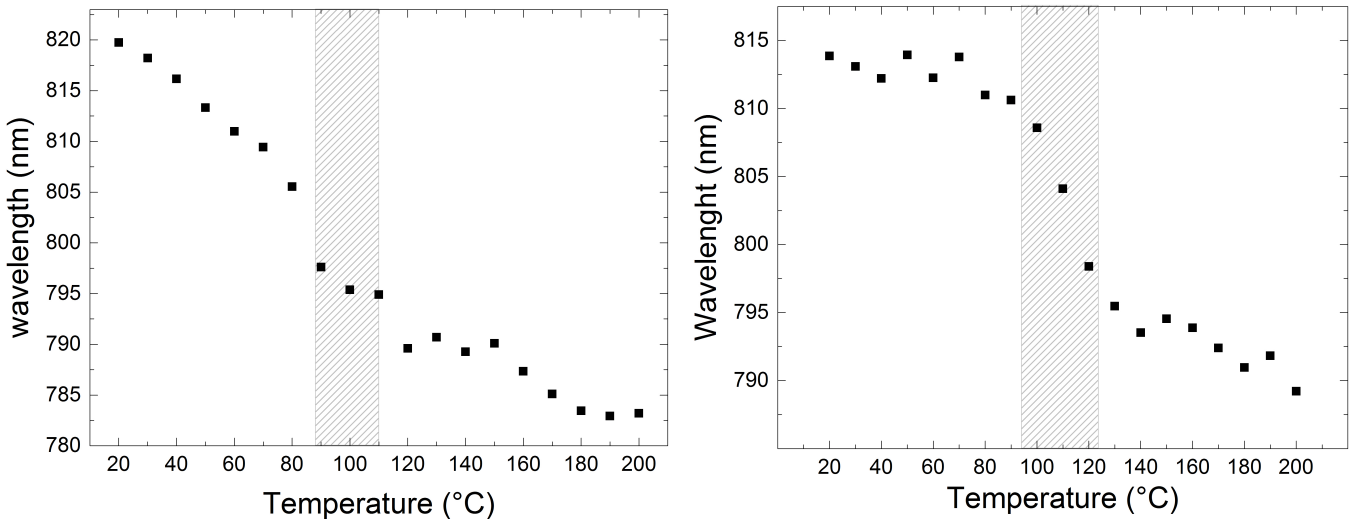


Fig. 5 Temperature dependence of PL signal position of the transitions of $FAPbI_3$: (a) $\alpha_i \rightarrow \alpha$ and (b) $\alpha_{rec} \rightarrow \alpha$.

XRD patterns

Single Crystals

$FAPbI_3$ powder obtained by crumpling SCs transforms in a matter of seconds into the yellow state. To avoid this visible $\alpha_i \rightarrow \delta$ transition during measurement we employed relatively large sub-millimeter size of crystallites (ca. 0.5mm), even though this stipulated poorer statistics (Fig. 1). The SCs were prepared by heating the 1M $FAPbI_3 + GBL$ solution at 120°C for 3 h and dried in filter paper using N_2 flux.

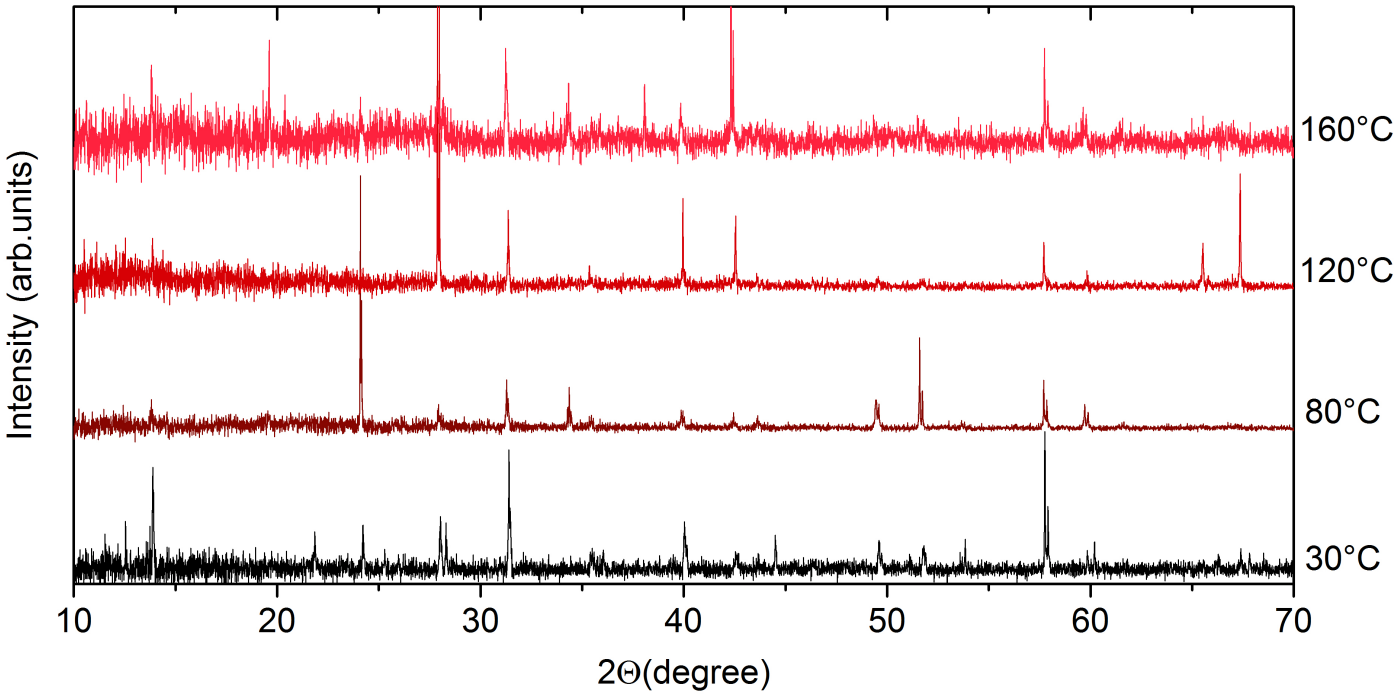


Fig. 6 Temperature dependent XRD measurements of α_i-$FAPbI_3$ SCs.

Table 1 Results of the Pawley refinement using cubic $Pm\bar{3}m$ space group for the patterns presented in Fig.6.

T° (°C)	Lattice parameter a ($Pm\bar{3}m$)
30	6.364
80	6.385
120	6.375
160	6.397

Thin films

Raman spectroscopy requires additional information for a better understanding. On one hand, we analyse the multiple phases of the degraded and recovered samples. On the other, the Raman spectra of α_δ, δ and α_{rec} are red-shifted compared to the case of α_i. This last can be explained by lattice expansion or change of direction of the Pb-I bond of each state. To identify the most likely cause, we compare the lattice constants of the different polymorphs. Since we could not reach very good XRD statistics for the sub-millimeter SCs, $FAPbI_3$ films were also considered.

Thin films were prepared by a modified method of the two-step spin-coating deposition proposed by Han et al.[1]. 450 mg of PbI_2 was dissolved in 1 mL dimethylformamide and the solution was placed over a preheated hot plate at 60°C for at least 1 h. FAI was dissolved in 2-propanol and left at RT for the same time. The PbI_2 solution was spin-coated over glass substrates at 2500 rpm for 30 s and left at 70°C for 10 min. Then, FAI was spin-coated on top at 3000 rpm for 30 s in the dry air. Samples were annealed at different temperatures: 80°C, 100°C and 120°C for 45 min. All operations were performed inside the glovebox. These temperatures were chosen to disclose a difference, if exists, to the single crystals which form and grow in a temperature range 90°C-115°C (see Methods).

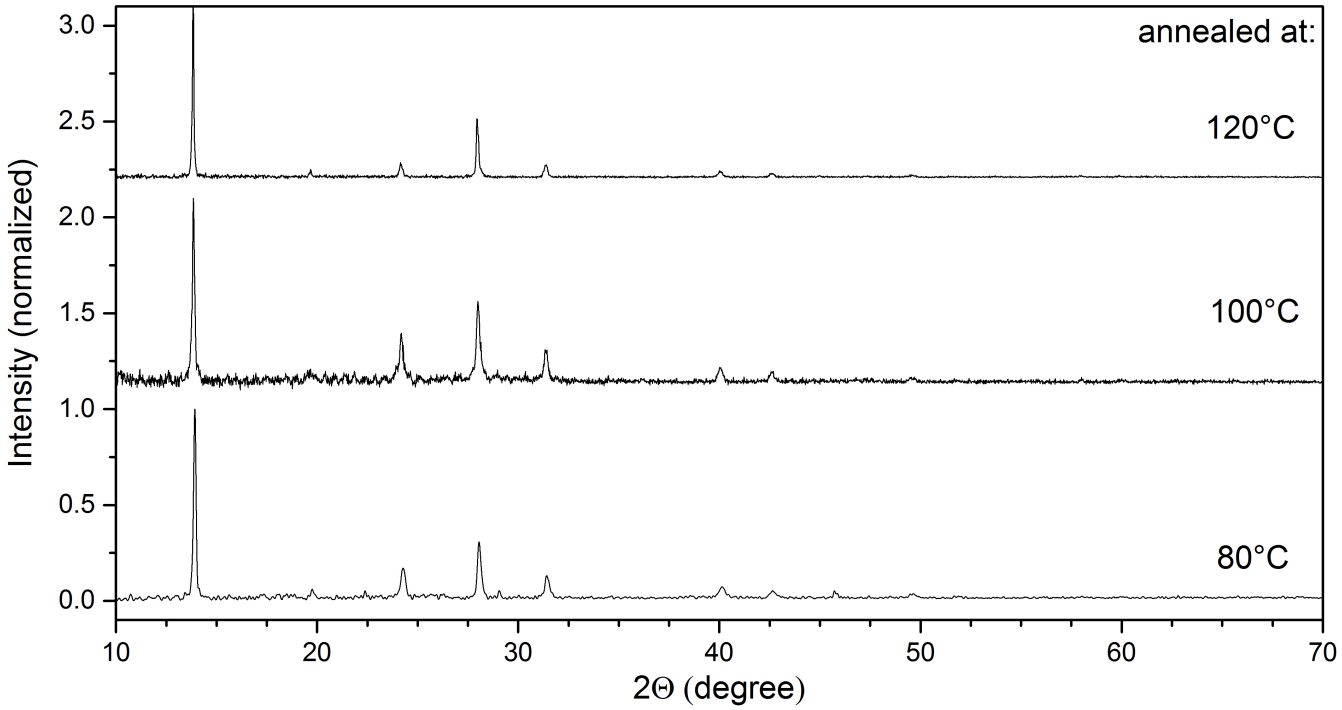
All the films were degraded and recovered in air and the corresponding polymorphs were analysed by XRD and fitted using the Pawley refinement.

First, we show that XRD patterns of as-prepared thin films do not reveal principal differences for the used annealing temperatures (Fig. 7 a). There are also no diffraction maxima that are characteristic for the suggested $Im\bar{3}$ symmetry. For instance, the expected peaks at 22.5° and 26.5° are absent, as shown in the red area in Fig.7 b. For this reason, we proceed to fit the cubic patterns with the $Pm\bar{3}m$ space group.

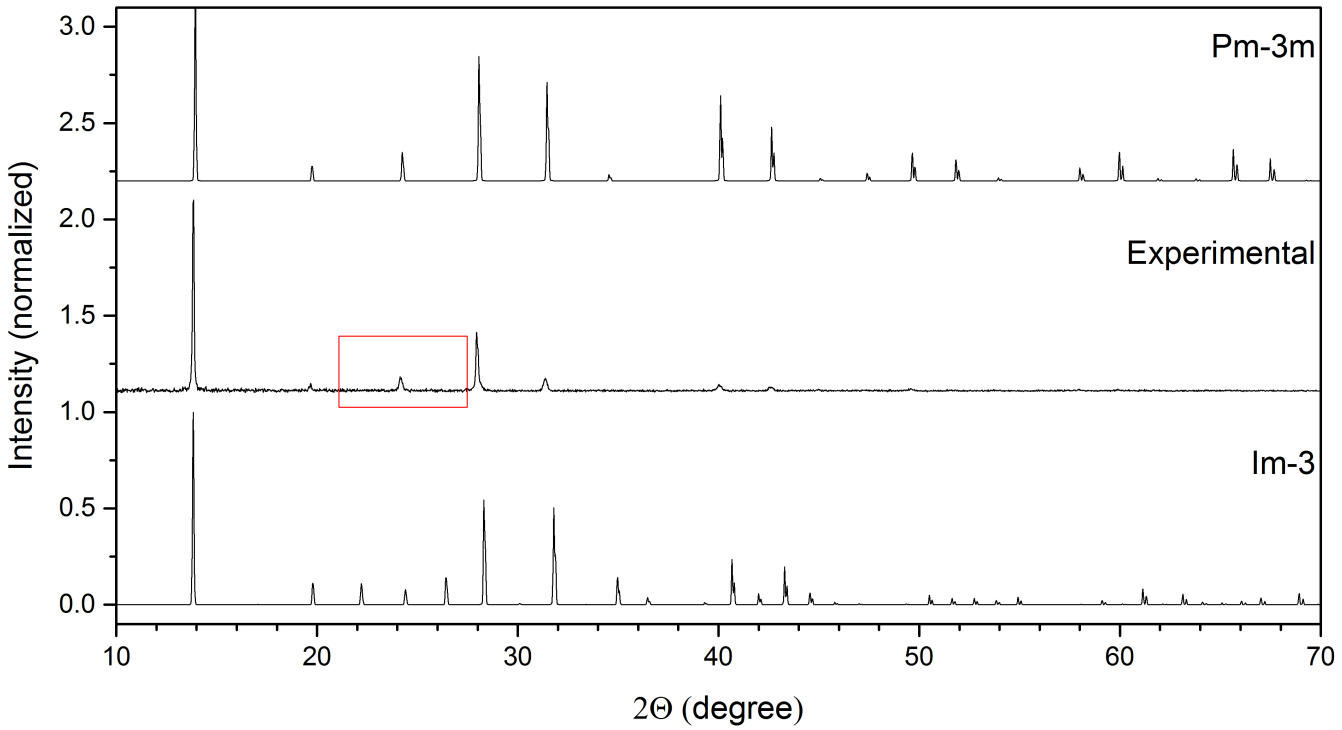
As an example, the XRD patterns for the different states of a film crystallized at 120°C are compared in Fig.8. All the states show characteristic $Pm\bar{3}m$ patterns. The mean value of the lattice constants were 6.372 Å , 6.361 Å and 6.353Å for the as-prepared, degraded and recovered states, respectively. In the degraded state, the δ-phase (hexagonal $P6_3mc$) presents lattice constants a=8.682 Å and c=7.929Å . In the recovered state, PbI_2 (hexagonal $P\bar{3}m1$) is presented as a secondary phase with lattice constants a=4.809Å and c= 6.983 Å.

Corresponding developed results are presented in Fig.9. According to the Fig. 9b, the smallest crystallites transformed into the δ-phase that was expressed in an overall decrease of FWHM values. The following recovery at 140°C was possibly accompanied with grain growth, however, the optics used had not allowed detecting it for the 002-maxima. Changes of the lattice constant (Fig. 9a) look more complicated. In the case of films, the larger lattice constant may result from the compressive stress acting in a lateral direction and increasing with annealing temperature. As-prepared crumbled SC sample may be considered then as a stress-free state. In a degraded state, cubic $FAPbI_3$ appear to become stress-free in all samples. High temperature recovery possibly imposes isotropic compressive stresses in the SC-powder, whereas in the films rather lateral tensile strain appears.

[1] Q. Han, S.-H. Bae, P. Sun, Y.-T. Hsieh, Y. Yang, Y. S. Rim, H. Zhao, Q. Chen, W. Shi, G. Li et al., Advanced Materials, 2016, 28, 2253–2258.



(a)



(b)

Fig. 7 Comparison of experimental XRD patterns of as-prepared$FAPbI_3$ thin film annealed at 120℃ with: a) annealed at 80℃ and 100℃ and with b) simulated cubic $Pm\bar{3}m$ and $Im\bar{3}$ patterns via Le Bail fitting.

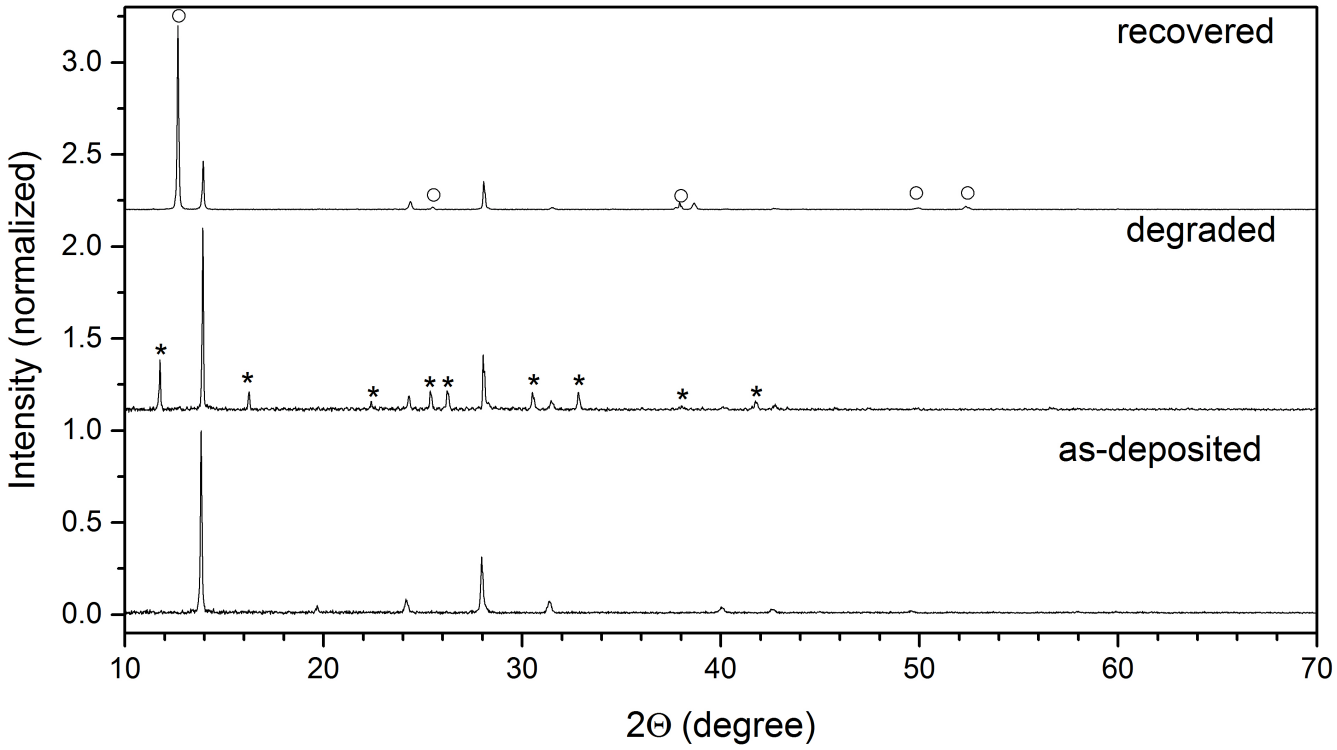


Fig. 8 Comparison of the experimental XRD patterns for as-prepared, degraded and recovered $FAPbI_3$ thin films. Peaks corresponding to the patterns of the δ-phase and PbI_2 are denoted by $*$ and $\circ$, respectively.

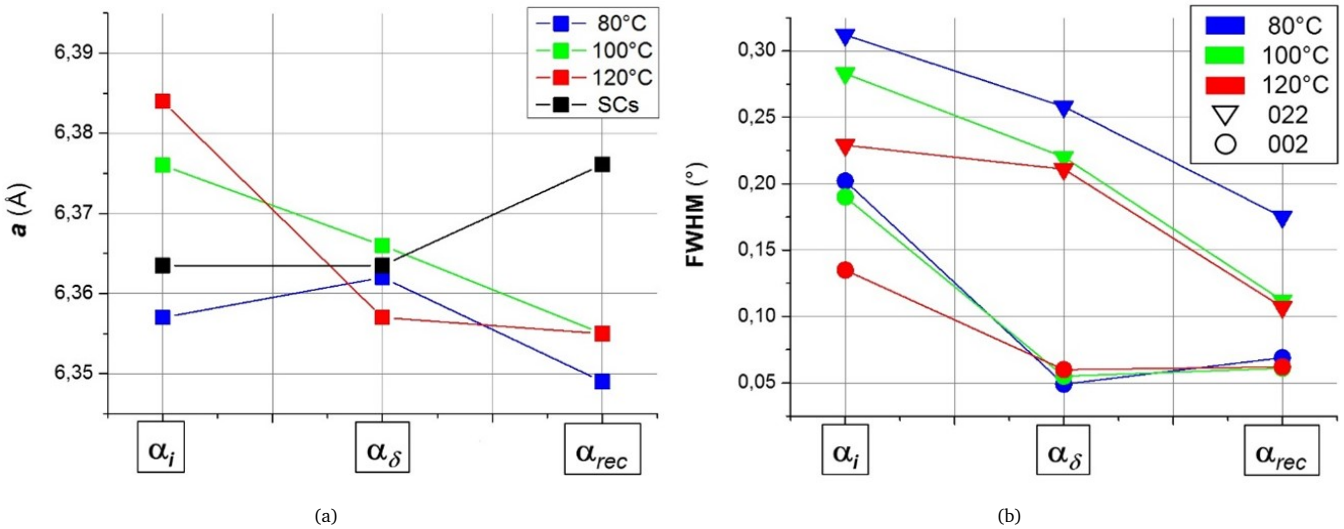


Fig. 9 Graphical representation of the results obtained from Pawley refinement of the XRD patterns obtained at RT: (a) lattice constants of cubic ($Pm\bar{3}m$) phase and (b) full-width-at-half-maximum (FWHM) values for the corresponding 002- and 022-diffraction maxima. Coloured points correspond to thin films prepared at noticed temperatures. On the abscissa, three polymorphs of the samples are given: as-prepared (α_i, cubic - 100%), degraded (α_δ, cubic – 19-24%, the rest is δ-phase) and recovered (α_{rec} , cubic – 77-93%, the rest is PbI_2).