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Supporting Information

Perovskite crystallization dynamics during spin casting: an in situ wide angle X-ray scattering study.

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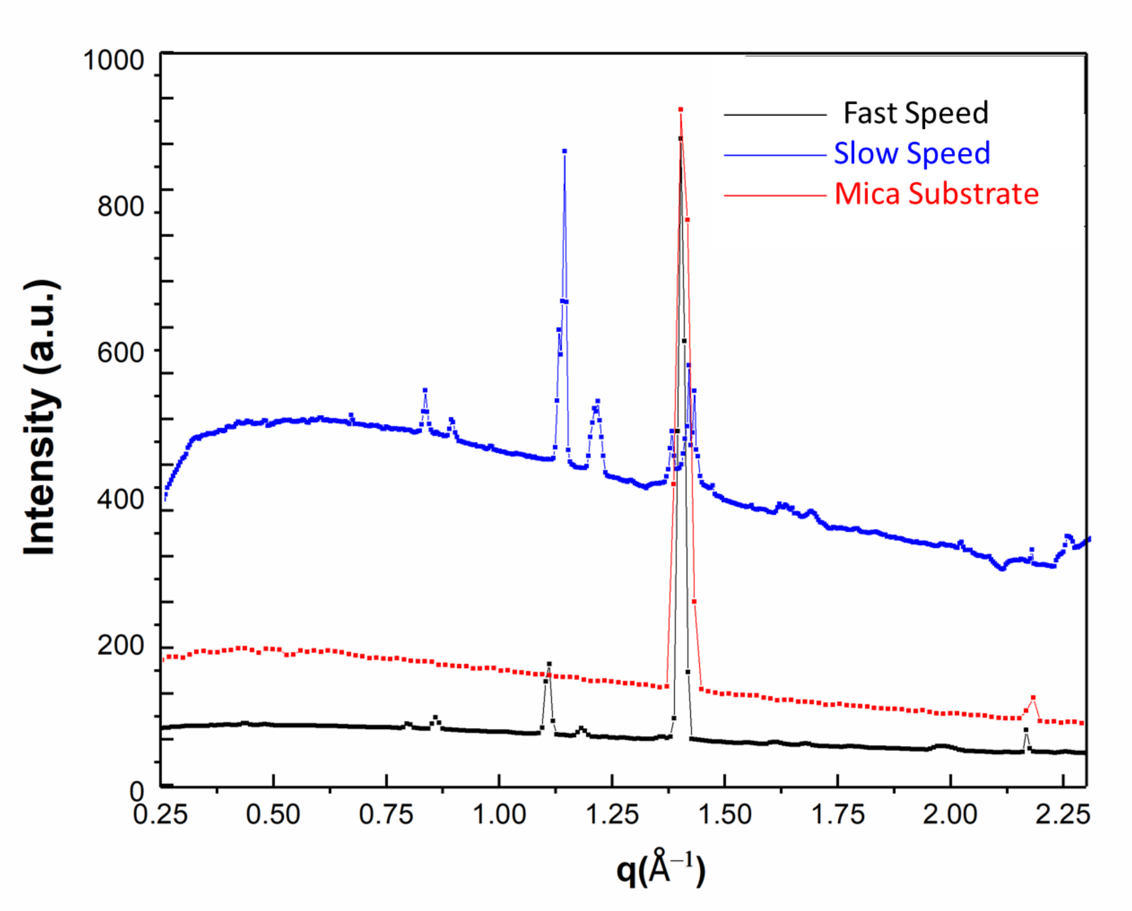

Figure S1: 1D integrated radial profile of the WAXS of generated during the spin casting of $MAPbI_{3-x}Cl_x$ solution using slow and fast speed with the WAXS of mica substrate without any solution. The mica has strong scattering peaks at 1.4 $Å^{-1}$and 2.16 $Å^{-1}$. The sample spun at high speed shows less scattering which is attributed to the film formed being thinner.

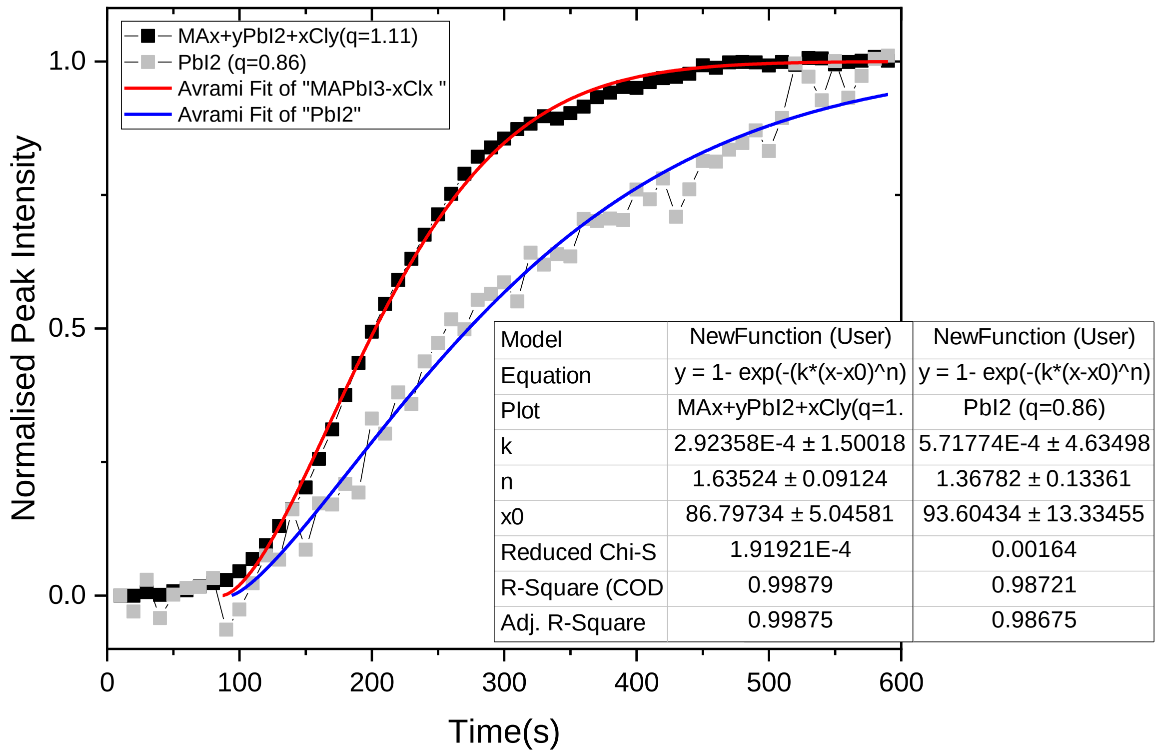

Figure S2 Details of the Avrami fitting for the casting solution for $MAPbI_{3-x}Cl_x$

Fig S3(a) is the 2D WAXS image from the $MAPbI_{3-x}Cl_x$ film that was taken once the spinning had stopped. In this image it is clear that the scattering rings observed when the sample was rotating are made up of some discrete X-ray scattering spots arranged around a ring. The spots are caused by X-ray scatting from discrete crystallites. If enough individual crystallites were present a continuous ring would be observed as occurs in a powder diffraction experiment. These speckled rings are observed in the area between q = 0.8 $Å^{-1}$ and q = 1.33 $Å^{-1}$. In the as cast samples the strongest feature is noted at 1.1$Å^{-1}$ and is attributed to scattering from (100) planes of a cubic crystal structure after solvent evaporation

Fig S3(b) is the 2D WAXS image from the $MAPbI_{3-x}Cl_x$ film that was taken after annealing. A fuller scattering ring at q=1 $Å^{-1}$ is observed. The fuller ring of the X-ray scattering indicates that the X-ray beam is probing crystals with more random orientations resulting a more uniform distribution in orientation. Similar scattering patterns have been reported in the literature [20]. The annealed $MAPbI_{3-x}Cl_x$ film can therefore be described as consisting of a randomly orientated collection of crystals with d spacing resulting in scattering at q=1 $Å^{-1}$. In contrast, the speckled ring in the as cast samples **Fig S3(a)** is much less continuous implying a smaller number of crystals at a small number of fixed random orientations around a ring corresponding to q= 1.1 $Å^{-1}$ The observation of random orientations of the $MAPbI_{3-x}Cl_x$ annealed film is similar to what was highlighted previously [4, 18, 21].

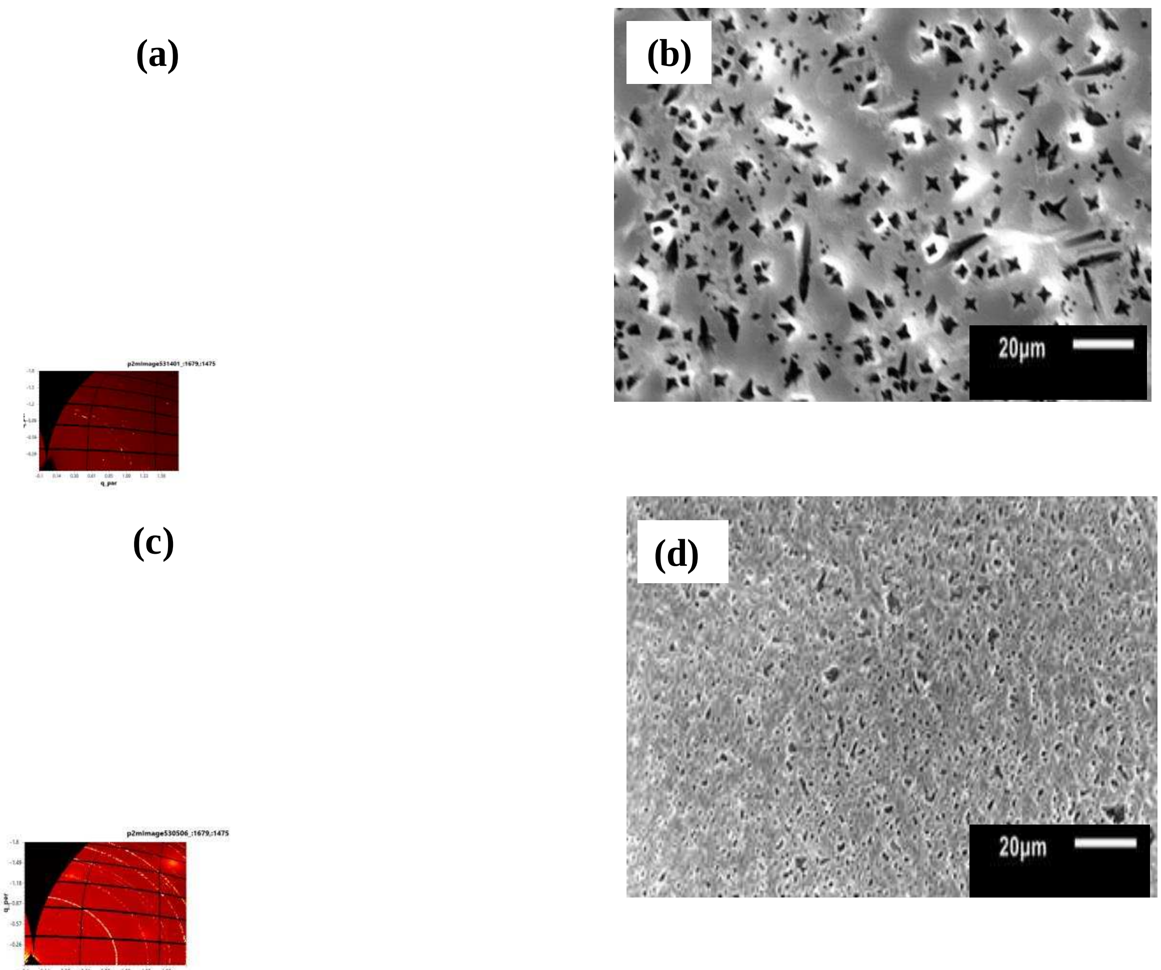

Figure S3. The WAXS image of the film after the spin coating (a), and the surface morphology of a precursors preceding intermediate perovskite of $MAPbI_{3-x}Cl_x$ film observed by SEM directly after spin coating (b), the WAXS image of an annealed $MAPbI_{3-x}Cl_x$ film, (c) and SEM images after thermal annealing (d).

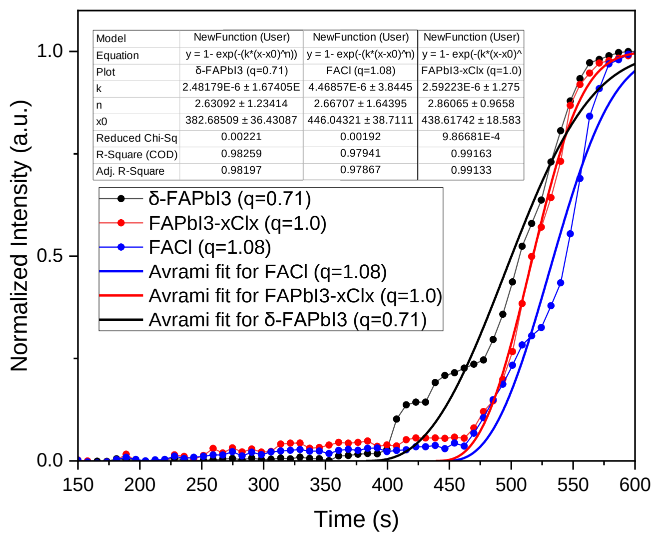

Figure S4 Details of the Avrami fitting for the casting solution for $FAPbI_{3-x}Cl_x$

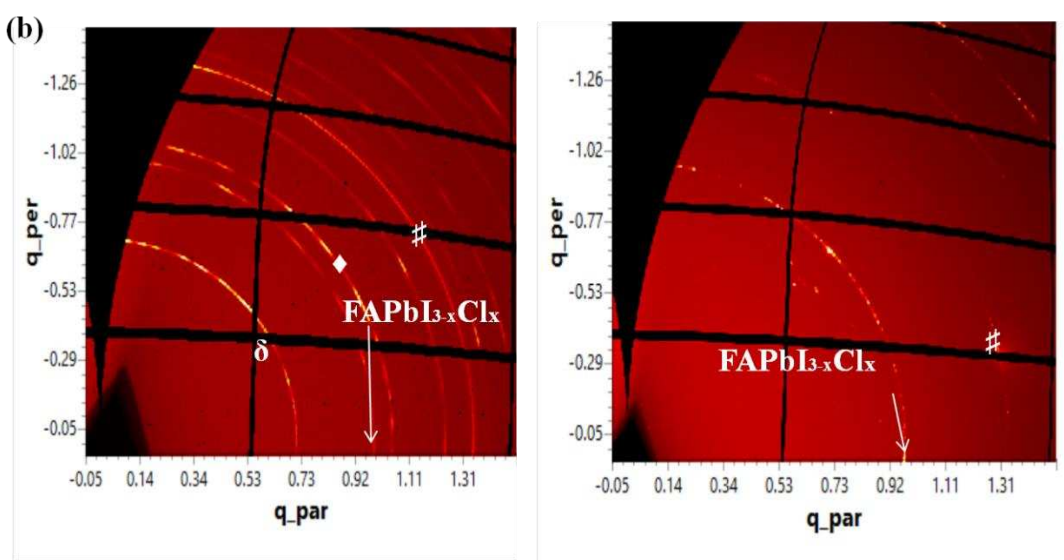

Figure S5 The 2D data WAXS images demonstrate the orientation of the crystalline structures in (b) $FAPbI_{3-x}Cl_x$ films before (left) and after annealing (right).

Fig S4 illustrates the difference in the 2D WAXS images collected before and after the thermal annealing of $FAPbI_{3-x}Cl_x$ film. Before annealing, several X-ray scattering rings with different intensities can be seen, that indicate the presence of δ-$FAPI_3$ at q = 0.7 $Å^{-1}$ and 1.3 $Å^{-1}$, $FAPbI_{3-}$

$_x Cl_x$ at q = 1.0 $Å^{-1}$ and FACl at q = 1.1 $Å^{-1}$. Before annealing a weak scattering ring with irregular distribution of intensity around the ring of the perovskite phase that is observed at q=1.0$Å^{-1}$. This confirms that some individual crystals of the perovskite have already formed during the spin coating stage. The bright spots within the ring are caused by larger single crystals of fixed orientation. The high intensity continuous X-ray scattering ring of δ-$FAPI_3$ at q=0.7 $Å^{-1}$ indicates the δ-$FAPI_3$ crystals are more randomly oriented. In contrast, after annealing there is no scattering at 0.7 $Å^{-1}$ indicating the thermal instability of the δ-$FAPI_3$. This intensity is replaced by a uniform distribution of intensity around the $FAPbI_{3-x}Cl_x$ ring at q=1.0 $Å^{-1}$ after annealing which indicates that after annealing the crystal orientations are more random.

The uniform distribution of intensity around the scattering ring associated with the FACl crystallites observed at q=1.1$Å^{-1}$ before annealing also indicates that they are randomly orientated and there are many crystallites present due to the high intensity of the WAXS. The FACl features disappear upon annealing as shown in the 2D-WAXS image on the right in **Fig 8 (b)** at q=1.4 $Å^{-1}$ is remarkably reduced, showing only a few bright spots in the WAXS image after annealing that most likely refer to an un-reacted large crystal of $PbCl_2$ as was report previously [23].