Influence of Temperature, Pressure and Humidity on the Stabilities and Transitions Kinetics of the Various Polymorphs of FAPbI$_3$

Francesco Cordero,∗,† Floriana Craciun,† Francesco Trequattrini,‡,† Amanda Generosi,† Barbara Paci,† Anna Maria Paoletti,¶ and Gloria Zanotti¶

†Istituto di Struttura della Materia-CNR (ISM-CNR), Area della Ricerca di Roma - Tor Vergata, Via del Fosso del Cavaliere 100, I-00133 Roma, Italy
‡Dipartimento di Fisica, Università di Roma "La Sapienza", p.le A. Moro 2, I-00185 Roma, Italy
¶Istituto di Struttura della Materia-CNR (ISM-CNR), Area della Ricerca di Roma 1, Via Salaria, Km 29.300, I-00015 Monterotondo Scalo, Roma, Italy

E-mail: francesco.cordero@ism.cnr.it

Abstract

The phase transitions between the various polymorphs of FAPbI$_3$ (FAPI, FA = formamidinium CH(NH$_2$)$_2$+) are studied by anelastic, dielectric and X-ray diffraction measurements on samples pressed from δ−FAPI (2H phase) yellow powder. The samples become orange after application of as little as 0.2 GPa, which has been explained in terms of partial transformations to the other hexagonal polymorphs 4H and 6H. The phenomenon is discussed in the light of what is known about the stability of the various polymorphs of hybrid and inorganic perovskites ABX$_3$ with large A cations and hence large tolerance factor $t$. Remarkably, FAPI at room and higher temperature behaves like a perovskite with large $t$, while just below room temperature it behaves like a perovskite with small $t$. The kinetics of the transformations between the polymorphs is enhanced by small amounts of intercalated water. It seems therefore worthy to try improving the atomic diffusion and crystallization during synthesis, and hence the final photovoltaic performance, through controlled small amounts of water that should be thoroughly removed after a sufficiently homogeneous and smooth microstructure is achieved.

Introduction

The hybrid metalorganic and the inorganic halide perovskites, ABX$_3$ with A = organic cation or Cs$^+$, B = Pb$^{2+}$, Sn$^{2+}$, X = I$^-$, Br$^-$, Cl$^-$, have been the object of extensive investigations since it was demonstrated that they exhibit excellent photovoltaic performance and may enable the creation of solar cells and optoelectronic devices with low costs and high performance. What prevents the commercialization of devices based on these materials is their poor stability, especially in the presence of humidity, light and heat, all factors that are especially crucial in photovoltaic applications.

The main directions for improving the phase stabilities and power conversion efficiencies are compositional engineering or use of additives or surface protecting layers, but the effect of pressure is also explored since effects similar to the application of pressure may be obtained by shrinking the lattice of the perovskite film through the choice of the substrate. In some cases it has been reported that the application of pressure and even of humidity during prepa-
ration have positive roles in improving the stability or morphology and photovoltaic efficiency of films of these perovskites.

The main effect of pressure in perovskites with rigid B–X bonds is promoting tilting of the BX$_6$ octahedra. This occurs in order to relieve the mismatch between the shrinking A–X framework and the rigid BX$_6$ octahedra, which is usually quantified by how much the Goldschmidt's tolerance factor, $t$, defined in terms of the equilibrium ionic radii as

$$t = \frac{r_A + r_X}{\sqrt{2} (r_B + r_X)} ,$$

is less than 1. In fact, $t = 1$ for radii that perfectly fit the cubic perovskite; when $t < 1$ the BX$_6$ octahedra are too large to fit the A–X bonds and therefore, if they are also more rigid than the A–X bonds, they tilt without shrinking. In the hybrid perovskites, however, the H bonds between the A organic molecule and the X anions also play a role.$^{12}$ Much less clear is the role of pressure in promoting the transitions between the various polymorphs of the halide perovskites with different octahedral coordinations. This is particularly true for the case of FAPbI$_3$ (FAPI), for which the literature on the effects of pressure is contradictory.$^6$ The topic is of particular relevance, since the other polymorphs of these perovskites are also the phases into which they generally transform during degradation, being more stable in ambient conditions. These phases have yellow or orange colors and definitely lower photovoltaic performance. The various phases are often labeled as $\alpha$ for the black cubic perovskite, which at lower temperature transforms into $\beta$ and $\gamma$ with tilted BX$_6$ octahedra and $\delta$ for the yellow non-perovskite,$^{13,14}$ though recently it has been shown that a series of intermediate polymorphs of FAPI exist.$^{15}$ They are recognizable by diffraction and from the color, or more quantitatively from the absorption bands in the UV-visible region.$^{15,19}$ In this context Ramsdell’s notation$^{19}$ is useful, according to which the cubic perovskite phase is labeled 3C and the $\delta$–FAPI phase is 2H, while the intermediate phases are 4H and 6H. All first-principle calculations indicate that the lowest energy and therefore stable polymorph of FAPI is the $\delta$ phase, and indeed this is the phase obtained at room temperature with chemical methods. Yet, dry grinding or ball milling the starting FAI and PbI$_2$ powders may produce the perovskite phase,$^{13,20,21}$ and similarly for MAPbI$_3$,$^{22}$ (MAPI, MA = methylammonium (CH$_3$NH$_3$)$^+$). Although a relationship between the application of high pressure and mechanosynthesis is not recognized, it can be estimated that in ball milling the impacting balls generate pressures of several GPa in the contact region.$^{23}$

There are also reports of new phases, also with improved photovoltaic properties and stabilities, obtained after the application of high pressure. These phases generally have shorter bonds, higher orbital overlap and reduced bandgap, resulting in enhanced photocurrents. They are proposed to be accessible after pressure–induced amorphization and subsequent recrystallization, as in the case of tetragonal MA$_3$SnI$_5$, which becomes cubic$^{23}$ or the 2D perovskite (BA)$_2$ (MA)$_3$Pb$_4$I$_9$ (BA$^+$ = butylammonium (CH$_3$(CH$_2$)$_3$NH$_3$)$^+$).$^{25}$ In FAPI a similar improvement of the bond configuration accompanied by bandgap decrease has been reported to persist after removal of a pressure of 2.1 GPa, rather surprisingly, even in the absence of any intermediate pressure–induced phase transition or amorphization.$^{29}$ However, there are contrasting results on the effect of pressure on $\alpha$–FAPI.$^{22}$ It has also been found that as little as 0.1 GPa would promote the $\alpha \rightarrow \delta$ transformation,$^{29}$ while a single crystal has been found to undergo at 0.49 GPa a transition to the tetragonal $P4/mmb$ structure, due to octahedral tilting,$^{29}$ presumably the same $\beta$ phase that is obtained upon cooling below 285 K. Finally, pressures of 4–6 GPa have been found to reversibly turn the black and yellow phases into red,$^{20}$ and piezochromism has been found also in nanocrystalline FAPI$^{31}$ and in FAPbBr$_3$,$^{32}$ interpreted in terms of the dependence of the bandgap on the Pb–I–Pb bond lengths and angles in the variously tilted perovskite phases.$^{31}$

Also humidity affects FAPI and generally
metal–organic perovskites in different manners. Besides the well established role as catalyst of the degradation of the perovskite $\alpha$ phases into non-perovskite $\delta$ and final decomposition, a relative humidity (RH) of 30% has been found to generally improve the quality of films compared to the dry process and particularly to improve the crystallization and enlarge the grain size of MAPI and FAPI films. Also in the mechanosynthesis of MAPI a RH of 40% accelerates the reaction between MAI and PbI$_2$.

Here we present dielectric, anelastic and x–ray diffraction measurements on samples compacted from $\delta$–FAPI powder. The dielectric and elastic properties are particularly sensitive to the level of hydration and volume fractions of $\alpha$ and $\delta$ phases, since dry $\alpha$–FAPI has elastic modulus and dielectric constant at least twice as large as the $\delta$ and hydrated phases. These experiments shed light and allow some rationalization to be made on the behavior of the several polytypes of FAPI under pressure and humidity.

**Methods**

We performed dielectric, anelastic and X-ray diffraction (XRD) measurements on samples compacted from the yellow $\delta$–FAPI powder. The powder was obtained following a procedure already reported with slight modifications, precipitating with toluene the $\delta$–FAPI phase from a solution of HCN$\text{H}_2$I and PbI$_2$ in GBL. The yellow powder was recovered by centrifugation and dried at room temperature in vacuum overnight as described in the Supporting Information (SI). The powder for one of the bars (FAPI #7) was prepared in water following the procedure reported in Ref. with slight modifications, as detailed in the SI, obtaining pure $\delta$–FAPI according to the XRD analysis.

The bars for the anelastic and discs for the dielectric measurements were obtained by pressing the FAPI powder for few minutes at maximum pressures of 0.2 and 0.62 GPa respectively in dies with section $40 \times 6$ mm$^2$ or 13 mm diameter and their thicknesses were between 0.5 and 1 mm.

The complex Young’s modulus $E = E' + iE''$ versus temperature was measured in a high vacuum (HV) insert with base pressure $< 10^{-6}$ mbar, with the introduction of $< 0.2$ mbar He below room temperature for thermal exchange or in controlled H$_2$O pressure. The FAPI thin bars were suspended on thermocouple wires and electrostatically excited on their flexural modes as described in Ref. The real part of the complex Young’s modulus is proportional to the square of the fundamental resonance frequency $f$ of the first flexural mode as

$$f = 1.028 \frac{h}{l^2} \sqrt{\frac{E}{\rho}} ,$$

where $l$, $h$, $\rho$ are the sample’s length, thickness and density. The elastic energy loss $Q^{-1} = E''/E'$ was measured from the width of the resonance peaks or the free decay.

The dielectric permittivity $\varepsilon$ versus temperature was measured in a small closed volume, a modified Linkam cell, that does not allow HV tight conditions. Previous experience taught us that the standard purging procedure of few minutes with dry N$_2$ flux at 40 °C is totally ineffective in removing the water absorbed by FAPI. In addition, at low temperature some humidity may leak into the cell and condense on the sample, giving rise to a broad peak of $\varepsilon$ during heating back to room temperature. Therefore, in order to remove water as efficiently as possible from the sample, purging was made at the highest temperature possible under the given conditions at the beginning and at the end of each temperature run.

The XRD spectra were acquired in air at various stages of the anelastic and dielectric experiments and on freshly prepared discs, as described in more detail in the SI.

**Results**

The samples pressed from the yellow $\delta$–FAPI were orange. The discs, with smaller surface and subjected to higher pressure, were of more uniform and intense color, while the bars presented lighter zones corresponding to regions where the initial thickness of the powder and
therefore local pressure and final density were smaller (see Figs. 6 and 7(a) in SI). We understand this phenomenon as a pressure-induced transformation from the yellow 2H phase to the orange and red 4H and 6H phases more complete in the case of the discs subjected to higher pressure. The presence of these phases is evident from the color but does not give clear signatures in the XRD spectra, as shown in the SI.

Figure 1 shows the dielectric permittivity of an initially orange disc pressed from yellow δ-FAPI.

![Figure 1: Dielectric permittivity of the disc FAPI #4 pressed from powder of δ-FAPI measured at 100 kHz during several temperature runs (only few are shown). The colors are indicative of the state of the sample; the yellow color of the sample in curve 2 after three days at room temperature in the measurement cell corresponds to the δ phase but has not been checked.](image)

We started the first heating (curve 1) with the intention of stopping temperature immediately after the dielectric permittivity started to rise, indicating the onset of the nH→3C transition, where nH indicates some mixture of 2H, 4H and 6H phases. Such a transition, however, was so fast that we were not able to prevent the formation of 3C phase, as indicated by the α → β and β → γ transitions measured during the subsequent cooling. The final purging at 380 K was apparently insufficient to remove water from the sample, which after three days (curve 2) was back in the δ (presumably 2H) phase with low permittivity, no trace of the α → β and β → γ transitions, and instead the transition to the LT-δ phase known to occur at 173 K upon heating (167 K in the cooling curve 2) after thermal expansion and neutron diffraction. A new temperature run (curve 3) was extended to 450 K, but this time the 2H→3C transition was slower than in curve 1, and, even though a 12 min purging was done at 430 K, the subsequent cooling did not show signs of a more complete transition to the α phase with respect to curve 1. On the contrary, the permittivity was slightly lower and the transitions less marked. After the series of dielectric measurements the sample had a shiny black surface, with some dark violet reflections, but no signs of cracks, indicating that the transitions between the nH and 3C phases occur in a nearly congruent manner without excessive internal strains. The XRD spectra (pattern 1 of Fig. 2) contained only the peaks of the 3C and 2H phases; the latter was evidently induced by humidity and its presence is in agreement with the lower permittivity during the last dielectric run.

After further dielectric runs including a prolonged aging of 110 min at 430–440 K (not shown) the XRD reflections of the α phase were found more intense, but also some reflections of PbI₂ started being detected (pattern 2).

Even if taken within one day after a dielectric or anelastic experiment, the XRD spectra do not capture the status of the sample at the end of that experiment, as is clear from the near total transformation of these compacted samples from the α to the δ phase in only three days in presence of humidity (Fig. 1). Yet, we noted several times an overemphasized appearance of the XRD peaks of the hexagonal δ and PbI₂ phases over the α phase with respect to the last anelastic or dielectric experiment and the sample appearance. We speculate that this...
Figure 2: XRD pattern collected on sample FAPI #4 after the dielectric measurements in Fig. 1 (curve 1) and after further temperature runs including longer annealing at 430–440 K. Black, red and green lines are the expected reflections of the $\alpha$, $\delta$ and PbI$_2$ phases respectively.

is due to a superior crystallinity of the hexagonal phases over cubic $\alpha$-FAPI, as explained later on.

We pass to the description of the results of the anelastic spectra obtained during several temperature runs in HV conditions ($10^{-6} - 10^{-5}$ mbar or $\sim 10^{-2} - 10^{-1}$ mbar He below room temperature).

Figure 3 shows few temperature runs on sample FAPI #5, an initially orange bar (fig. 7(a)) obtained by pressing yellow powder of freshly prepared $\delta$-FAPI. The initial state is therefore a mixture of 2H, 4H and possibly 6H and similar phases. The upper panel is the relative change of the Young’s modulus $E$, deduced from the resonance frequency. The reference $E_0$ corresponds to $f = 2.0$ kHz in the $\alpha$ phase. Its absolute value can be estimated as 8.5 GPa but with a large error, of the order of 20%, due to the non uniform thickness and density of the bar. The lower panel is the elastic energy loss coefficient $Q^{-1} = E''/E'$. Below 380 K the major feature of the anelastic spectrum of $\delta$-FAPI is the phase transformation at $T_{LT} = 170$ K, also visible in the dielectric spectrum (curve 2 of Fig. 1). We label $\delta$–LT the phase below 170 K, which has been shown to cause a lattice expansion and the appearance of new Bragg peaks and has a reduced number of possible orientations of the FA molecules. The Young’s modulus softens almost linearly at both sides of the minimum at $T_{LT}$, with higher slope on the low temperature side, suggesting a proper or at least pseudoproper ferroelastic transition, where a strain component is the order parameter or has its symmetry and the corresponding compliance has a maximum of the Curie-Weiss type. Notice that the minimum in the softened elastic constant is more marked than it appears in the polycrystalline Young’s modulus $E$, which contains the contribution of the other elastic constants of the 2H phase not involved in the transition and of the other $n$H phases, which presumably do not undergo the same transition. A similar elastic anomaly has been observed in the metal–organic framework perovskite [(CH$_2$)$_3$NH$_2$]Mn(HCOO)$_3$ in correspondence with a phase transition where the azetidinium molecules undergo orientational or-
dering\textsuperscript{15} which probably is similar to what occurs to the formamidinium molecules in the $\delta$–LT phase of FAPI. In that case, in order to maintain that the coupling between strain and order parameter is linear-quadratic, the linear increase of the elastic constant above the transition temperature has been interpreted as due to coupling between strain and strong fluctuations of the order parameter, while the stiffening below the transition was explained supposing that the transition is close to tricritical.\textsuperscript{15} Indeed, there is little hysteresis, $\leq 2$ K, in $T_{LT}$ between heating and cooling, but regarding possible fluctuations above $T_{LT}$, they do not seem to appear in the dielectric permittivity, which just has a sharp step below $T_{LT}$. In addition, there is a marked hysteresis in the value of the minimum of $E$, since the material is softer during heating and partially recovers at room temperature (not shown). This accounts for the fact that curve 2, measured after a few cycles at low temperature, does not coincide with curve 1. Curve 2 was measured after the sample had been 6 days in the insert for anelasticity measurements in HV or static He atmosphere and therefore the sample was completely dehydrated (at 340 K the vacuum was $7 \times 10^{-7}$ mbar). Therefore curve 2 represents the transition from the $\delta$ phase, actually a mixture of 2H, 4H and possibly other hexagonal phases, to the 3C cubic $\alpha$ phase during heating at 1.5 K/min in totally anhydrous condition. The transition occurs between 400 and 420 K. Heating was stopped at 443 K since no further stiffening was observed, indicating that the transformation was completed, and in order to avoid the sample decomposition. In this condition the Young’s modulus and losses were perfectly stable and the cooling curves were identical to those previously measured on FAPI\textsuperscript{19} with the $\alpha \rightarrow \beta$ transition accompanied by a negative step in the modulus and rise of dissipation, and the $\beta \rightarrow \gamma$ transition accompanied by a seemingly critical softening followed by marked stiffening well above the value in the $\alpha$ phase.

The dielectric experiments suggested that the transition to the cubic black 3C phase was faster for the orange $n$H ($n > 2$) phases induced by pressure than for the yellow 2H phase, but the above anelastic experiments on an orange sample did not show the sudden transition to 3C at $\leq 400$ K. In order to check whether also the content of water has a role in the kinetics of these structural transitions, we prepared a new bar (FAPI #7) from yellow powder and heated it at 1.5 K/min in 7 mbar H$_2$O (up to 445 K and then HV as usual; 7 mbar correspond to a relative humidity of 30% at room temperature). The comparison with the previous measurement on FAPI #5, completely dehydrated and heated in a vacuum of $10^{-6}$ mbar at the same temperature rate, is presented in Fig. 4. The rise of the modulus indicating the transition to the 3C $\alpha$ phase, the transitions to the $\beta$ and $\gamma$ structures are observed during cooling. In both cases the heating rate was 1.5 K/min.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{Young’s modulus and elastic energy loss of two bars $\delta$–FAPI (mixture of $n$H phases) heated in completely anhydrous condition (FAPI #5, same as Fig. 3) and under 7 mbar H$_2$O (FAPI #7). After the transformation to the 3C $\alpha$ phase, the transitions to the $\beta$ and $\gamma$ structures are observed during cooling. In both cases the heating rate was 1.5 K/min.}
\end{figure}
hydrated sample. There is also a sudden rise of dissipation when heating through 334 K, which disappears at the $\delta \rightarrow \alpha$ transition.

**Discussion**

**Relative volumes of the FAPI polymorphs**

We will base our discussion of the present experimental results on the hexagonal phases that are intermediate between the well known $\delta$ phase and the cubic $\alpha$ phase and that have been observed in FAPI partially substituted with MA, Cs and Br.\textsuperscript{15,16} The structures of these ABX$_3$ polymorphs can be described in terms of stacking of AX$_3$ close-packed layers between which the B ions are octahedrally coordinated with the X ions.\textsuperscript{15,16,17} Adjacent AX$_3$ layers are horizontally shifted with respect to each other so that the A cations are never first neighbors and this gives rise to two types of stacking. If a layer is sandwiched between identical layers, the BX$_6$ octahedra do not touch with each other in the planar directions but share faces perpendicular to it and form a hexagonal lattice; instead, in a stack of three different layers the octahedra share corners in all directions and form the cubic perovskite. Many combinations of cubic and hexagonal stacking are possible and may be labeled according to Ramsdell’s notation,\textsuperscript{19} as $nY$, where $n$ is the number of layers forming the unit cell and $Y = C, H, R$ denotes the cubic, hexagonal, rhombohedral symmetry of the resulting lattice. The polytypes found in the FA–based halide perovskites are shown in Fig. 5 and are: cubic (3C = $\alpha$ phase); pure hexagonal ($h$) stacking (2H = $\delta$ phase), where columns of face-sharing octahedra are separated by FA cations; mixed $hc$ ($4H$) and $chehc$ (6H) stacking.

In the perovskite based polytypes, the reason why the 2H phase is more stable than 3C is that in the latter the A cation is too large for its cavity surrounded by eight BX$_6$ octahedra.\textsuperscript{15} In the 2H structure the problem of the mismatch between B–X and A–X bonds is completely eliminated by the fact that the B–X bonds are confined within the columns of octahedra, whose spacing is determined by the A–X bonds. In the columns of face-sharing octahedra, however, the B–B distances are much reduced with respect to corner-sharing (red arrows in Fig. 5), with consequent increase of the electrostatic repulsion. The balance between B–B repulsion and B–X and A–X mismatch makes competitive the intermediate structures with both corner– and face–sharing octahedra, and these trends are confirmed by the distortions of the octahedra and displacements of Pb from their centers in the structures of (FA$_{0.85}$MA$_{0.15}$PbI$_3$),\textsuperscript{15} from the Crystallographic Information Files (CIF) supplied in Ref. 15 it can be found that in the 4H and 6H structures Pb$^{2+}$ is displaced.

Figure 5: Structures of the 3C, 6H, 4H and 2H phases of FAPI, based on the data of Gratia et al.\textsuperscript{15,16} for FA$_{0.85}$MA$_{0.15}$PbI$_3$. The red arrows indicate the short Pb–Pb distances across the shared faces of the octahedra; $c$ and $h$ indicate cubic and hexagonal stacking of the FAI$_3$ layers.
away from the shared face in order to increase the separation from the nearest neighbor Pb\(^{2+}\) atom and the face is shrunk in order to enhance the electrostatic screening of the three I\(^-\) anions. Identical observations can be made in 6H–AzPbBr\(_3\).\(^{19}\)

The fact that pressing the yellow powder of 2H phase induces a change of color to orange already at 0.2 GPa and the color becomes more intense and dark with increasing pressure, should be explained in terms of pressure-induced transformations from the 2H to the 4H and 6H phases. Indeed, the latter are respectively orange and red in FAPI partially substituted with MA, Cs and Br,\(^{18,19}\) and this may be explained in terms of an increase of the band gap when increasing the octahedral connectivity from corner– to edge– and face–sharing.\(^{20}\) To our knowledge, a sequence of pressure-induced transformations of the purely hexagonal 2H structure into the more corner–sharing 4H and 6H structures has not been reported so far for hybrid halide perovskites. Yet, this is what happens in other inorganic perovskites, notably fluorides and chlorides,\(^{15,20}\) but also oxides such as BaRuO\(_3\),\(^{20}\) though at pressures well above 1 GPa and the sequence of phases is not general.

The fact that pressure induces transitions to other polymorphs may be put in direct relationship with their smaller volumes per unit formula but a trend of the relative volumes of the hexagonal and cubic polymorphs of ABX\(_3\) compounds cannot be deduced simply from geometrical considerations, since there are strong variations depending on the ion types. For example, among the inorganic lead halides it was found that CsCdBr\(_3\) remains in the 2H phase up to 23 GPa, almost isotropically squeezed down to 65% of its original volume.\(^{17}\) On the other hand, CsPbI\(_3\) undergoes the \(\delta \rightarrow \alpha\) transition at 560 – 600 K, but the cubic perovskite phase has a volume 6.9% larger than that of the \(\delta\) phase, in spite of a 9% reduction of the volume of the octahedra.\(^{21}\) and CsSnI\(_3\) behaves similarly.\(^{22}\) It must be noted, however, that those \(\delta\) phases are not 2H but orthorhombic with double chains of edge–sharing octahedra and among the hybrid halides there is a variety of non–perovskite structures.\(^{23,24}\)

Unfortunately, based on our diffraction data and the literature it is not trivial to find solid information on the volumes per formula unit of the various polymorphs of FAPI. Most of our diffraction data were acquired during fast scans in order to minimize possible effects from degradation of the compacted powders during the scans in air, and were unsuitable for Rietveld refinement. Therefore we do not deduce cell volumes of the various phases from our data but we refer to the studies of Gratia \(et\ \al.\)\(^{15,16}\) on (FAPbI\(_3\))\(_{1-x}\)(MAPbBr\(_3\))\(_x\) with \(x \lesssim 0.2\), which should be indicative also for pure FAPI. Table 1 is based on their cell volumes \(V\) with multiplicity \(Z\) with respect to the formula unit. The first row reports the type of layer stacking, according to Ramsdell’s notation,\(^{19}\) and the table is sorted in order of increasing molecular volume \(V_m = V/Z\) (volume per formula unit). It results that indeed the molecular volume decreases with increase of the cubic coordination, following the sequence 2H, 4H, 6H nd 3C. There is another hybrid halide where the compactness of the 3C phase with respect to the hexagonal ones is even more marked: a stable 6H phase has been found in Az\(_{1-x}\)MA\(_x\)PbBr\(_3\) (Az = azetidinium = C\(_3\)H\(_6\)NH\(_2\))^+ with a coexistence region 0.4 < \(x\) < 0.7 of the 3C and 6H phases where \(V_{3C}\) is a remarkable 9.7% smaller than \(V_{6H}\).\(^{19}\)

It seems logical to explain the trend of increasing volume when passing from the 3C to 2H, 4H, 6H structures of the metal–organic halides in terms of an overall loss of connectivity of the octahedra, whose strong Pb–X bonds restrain the lattice expansion due to the large A molecular cations. When the connectivity is purely one-dimensional along the chains of the octahedra in the 2H phase, the distance between the chains can more freely accommodate the molecular cations, in the absence of strong A–A and A–X bonds. Increasing \(n\) in the \(nH\) series progressively redistributes the octahedral connectivity from face sharing along \(c\) to edge sharing in all directions and is indeed accompanied by a decrease of the molecular volume. Only based on this concept one would expect that within the \(nH\) series shrinking is larger
within the $ab$ plane than along $c$ (it is not possible to extend the comparison to $a$ of the 3C cubic structure due to the drastic structural rearrangements, also including rotations of the octahedra by $45^\circ$ with respect to the principal axes). Contrary to the naive expectation, the volume shrinking from 2H to 6H is totally due a contraction along $c$, while there is even a small expansion within the $ab$ plane. This can be understood in terms of the strong electrostatic repulsion between the Pb$^{2+}$ atoms on either sides of the $3I^{-}$ faces shared by adjacent octahedra, as explained above.\textsuperscript{48,49,55,56} It seems therefore that the large size of the FA molecules drives the volume expansion along the 3C to 2H series, but the distortion of the cell is driven by the electrostatic repulsion of the Pb atoms along the columns of face sharing octahedra.

In this context it is usual to introduce the concept of tolerance factor defined in Eq. \textsuperscript{(1)}.

When \( t < 1 \) the BX$_6$ octahedra are too large to fit the A–X bonds and therefore, if the B–X bonds are more rigid than the A–X ones, they tilt if an external pressure is applied or when the temperature is lowered and the thermal shrinking of the more anharmonic A–X bonds exerts enough pressure.\textsuperscript{57} On the opposite instance of \( t > 1 \) the polymorphs with octahedra sharing faces or edges become favored over cubic perovskite, as explained above. A particularity of FAPI is that at room temperature it exhibits both the phenomena typical of perovskites with large $t$, namely the formation of the hexagonal phases of face–sharing octahedra, and small $t$, namely tilting of the octahedra just below room temperature. This is probably due to an important role of the H bonds between FA and PbI$_6$ octahedra,\textsuperscript{58} which adds to the usual steric constraint of fitting cations into the spaces between the octahedra, and to an exceptionally large thermal expansion,\textsuperscript{59} which accelerates the shrinking of the FA–I network with respect to the Pb–I one during cooling and causes tilting.

### Intercalated water as catalyst of the structural transitions

The comparison between the dielectric measurement of the initially humid sample in a small closed volume (curve 1 of Fig. \textsuperscript{1}) and the anelastic measurements in HV reveals that interstitial water molecules promote the transformations from the hexagonal $n$H phases to the perovskite 3C. This is further confirmed by the anelastic experiment with heating in humid atmosphere (Fig. \textsuperscript{4}).

The interstitial water molecules certainly interfere with the H bonds between formamidinium molecules and $I^{-}$ anions, which contribute keeping the $n$H structures, and likely form H bonds with the $I^{-}$ ions, so weakening the Pb–I bonds and helping the rearrangement process of the PbI$_6$ octahedra. The role of interstitial water as catalyst has been demonstrated in MAPI and FAPI for the degradation transformations but may well exist for the reverse transformations at higher temperature. In addition, humidity promotes the crystallization of large grains of MAPI and FAPI films,\textsuperscript{34} and accelerates the reaction between MAI and PbI$_2$ in the

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### Table 1: Volumes per formula unit of the polymorphs of (FAPI)$_{0.85}$(MAPBr)$_{0.15}$, according to Ref. \textsuperscript{15}

| Ramsdell | 3C | 6H | 4H | 2H |
|----------|----|----|----|----|
| $Z$      | 1  | 6  | 4  | 2  |
| $V/Z$ [Å$^3$] | 251| 253.5| 255.75| 256.5|
| $V/(Z V_{3C})$ | 1  | 1.009| 1.019| 1.022|
| $a$ [Å]  | 6.31| 8.84| 8.814| 8.667|
| $2c/Z$ [Å] | 6.31| 7.48| 7.604| 7.908|
| space group | $Pm\bar{3}m$ | $P6_3/mmc$ | $P6_3/mmc$ | $P6_3/mmc$ |
| color     | black | dark red | orange | yellow |
mechanisms act in other metal-organic frameworks or coordination polymers. Remaining with the halide perovskites, it has been demonstrated by DSC under dry and humid conditions that water catalyzes the $\alpha \rightarrow \delta$ transition in CsPbI$_3$; here we see that, at least for FAPI, also the reverse transition is accelerated. As suggested for CsPbI$_3$, intercalated water lowers the enthalpy of small uncontrolled amounts of water and the resulting XRD spectra contain no trace of PbI$_2$ after the first set of measurements (pattern 1 of Fig. 2). The proof that water was present in the measuring cell is the complete transformation back to the $\delta$ phase after three days, while samples of FAPI can be maintained in the $\alpha$ phase for months in the HV insert. On the other hand, beyond some threshold water induces decomposition, and indeed traces of PbI$_2$ were detected in sample #4 after additional temperature runs (curve 2 of Fig. 2). Also for FAPI #7 heated in 7 mbar H$_2$O up to 450 K in two hours the subsequent XRD analysis indicated decomposition, though the amount of PbI$_2$ is difficult to assess. The anelastic spectra measured in HV after the transformation to the $\alpha$ phase showed a perfect perovskite with full transitions to the $\beta$ and $\gamma$ phases. Yet, the presence of PbI$_2$ phase probably does not cause any major elastic anomalies and simply results in a slightly lower elastic modulus (and dielectric constant). Once extracted from the HV insert, the sample was black with non uniform yellow shades (Fig. 7(b)), and was cut into pieces to check that also the interior was black. Against the expectation from the anelastic and visual evaluation, the XRD spectrum measured in reflection from the sample surface presented a prevalence of the PbI$_2$ peaks over the $\alpha$–FAPI ones. As already noted in reference to Fig. 2 we attribute this fact to a superior crystallinity of the hexagonal phases over cubic $\alpha$–FAPI. Indeed, the transformation of $\alpha$–FAPI into $\delta$ phase or its decomposition into PbI$_2$ catalyzed or induced by water at room temperature occurs relatively slowly, presumably from few nuclei with larger concentration of H$_2$O molecules, so allowing large hexagonal crystallites to grow. On the contrary, the transformation from the $\delta$ to the cubic phase occurs at high temperature with a faster kinetics, especially if catalyzed by intercalated water. As explained above, the transitions from the
nH phases to 3C do not require long range ion diffusion but only rearrangements in the stacking of the PbI₃ planes. If this occurs simultaneously at closely spaced intervals, nanometric domain configurations may arise, which indeed have been observed in α−FAPI and mimic a trigonal or hexagonal symmetry rather than cubic. It is then possible that the X-ray reflections from the so nanotwinned cubic phase are much less sharp than those from nearly perfect crystallites of PbI₂ and δ phase.

Conclusions

We studied the phase transitions between the various polymorphs of FAPI by anelastic, dielectric and X-ray diffraction measurements on samples pressed from δ−FAPI (2H phase) yellow powder. The application of a pressure as low as 0.2 GPa changes the color to orange, which has been explained in terms of transformations to the other hexagonal polymorphs 4H and 6H, having smaller volumes. The stability of these intermediate hexagonal phases has been put in the broader perspective of the hybrid and inorganic perovskites ABX₃ with large A cations, or large tolerance factor. It appears that the several polymorphs of FAPI are rather close in free energy at room temperature and, remarkably, FAPI is susceptible to both the phenomena due to a large tolerance factor, namely the formation of the hexagonal phases of face–sharing octahedra, and small tolerance factor, with octahedral tilting just below room temperature. This structural susceptibility is certainly enhanced by the extremely large thermal expansion and is probably a cause for the contrasting observations on the effects of pressure, temperature and aging on the FAPI structure.

In addition, it is observed that a small amount of water may enhance the kinetics of the transformations from the various polytypes to the cubic phase. Rather than to a surface effect of adsorbed H₂O, as often assumed for the improved grain growth in films in moderately humid atmosphere, this effect is attributed to H₂O intercalated in the bulk. The catalytic effect of water presents a similarity with the accomplishment of fast formation of α−FAPI with large grains from δ−FAPI films in presence of DMSO and other solvents, but the highly polar H₂O should be an even more effective solvent. This fact acquires particular interest in the light of the recent observation that the trapping of photocarriers, a major cause of reduction of the photovoltaic performance, occurs at specific types of grain boundaries, so that "managing structure and composition on the nanoscale will be essential for optimal performance of halide perovskite devices." It seems therefore promising to explore strategies where controlled small amounts of water are introduced during the synthesis in order to improve the atomic diffusion and crystallization, and thoroughly removed after a sufficiently homogeneous and smooth microstructure is achieved.

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Synthesis

Formamidine acetate (99%), HI (57 wt% in water), γ-butyrolactone (GBL 99%), PbI$_2$ (99%), and other solvents were purchased from Sigma-Aldrich and were used as received without further purification.

We first describe the synthesis of the powders for samples FAPI #4 and 5. The preliminary synthesis of CH(NH$_2$)$_2$I (FAI) was accomplished by reacting 50 mL hydroiodic acid (0.38 mol) and 25 g formamidine acetate (0.24 mol) in a 250 mL round bottomed flask at 0 °C for 6 h under N$_2$ atmosphere with stirring. The precipitates were recovered by reduced pressure evaporating the solutions at 65 °C for about 3 h. The product was washed with absolute ethyl alcohol and diethyl ether until the washings were colorless and finally dried at 60 °C in a vacuum oven for 24 h. (E.A. FAI calculated: C 6.98, H 2.93, N 16.29, found: C 6.98, H 2.96, N 16.05).

Synthesis of FAPI δ phase: equimolar mixture (1.2 M) of prepared FAI and PbI$_2$ were dissolved under vigorous stirring in GBL at ∼ 50 °C until a clear solution was obtained; then a small amount of toluene was added to the solution at room temperature, the yellow precipitates were recovered by centrifugation, washed with toluene and dried under vacuum.

For the synthesis of the powder for sample FAPI #7 a method in water was followed: 0.32 g of formamidine acetate (Aldrich) (3 mmol) were added to 2 mL of HI (aq solution 57% ACROS) (9 mmol), then 1.14 g of Pb(CH$_3$CO$_2$)$_2$·3H$_2$O (CarloErbaReagents RP, 3 mmol) were added under stirring; the yellow suspension was put in a ultrasonic bath at room temperature for 10 min, then was filtered and washed with ethyl acetate and dried under vacuum first for 4 h at 50 °C and then at room temperature overnight, obtaining pure δ−FAPI according to the XRD analysis.

Pressing

The yellow powders of δ−FAPI were pressed at 5 tons in discs of 13 mm of diameter (0.62 GPa) and at 10 tons in bars with flat surface 40 × 6 mm$^2$ (0.2 GPa). The maximum pressure was reached gradually in about 2 min and kept for about 4 min. Figure 6 shows the pristine yellow powder of δ−FAPI and a disc pressed from the same powder.

![Figure 6: Powder of δ−FAPI before and after pressing into a disc at 0.6 GPa for a few minutes.](image)

Figure 6 (a) shows the bar FAPI #7 just after being pressed.

The non uniform color reflects the non uniform distribution of the powder in the die, with the lighter extreme corresponding to smaller initial thickness and hence density and local pressure. After the initial heating in 7 mbar of H$_2$O the sample transformed into the black perovskite α phase, but the non uniform yellow hue and the XRD spectrum indicate that some PbI$_2$ had formed.

X-ray diffraction

X-ray diffraction measurements (XRD) were performed on a Panalytical Empyrean Diffractometer, using the K$_\alpha$ fluorescence line of a Cu-anode emitting tube as X-ray source. Bragg Brentano configuration was used as incident optical pathway (divergent slits) and a solid-state hybrid Pixcel 3D detector, working in 1D linear mode, accomplished the detection.

None of the samples for the dielectric and anelastic experiments was analyzed with X-rays just after pressing, in order to reduce as
Figure 7: Bar FAPI #7 just after being pressed from $\delta$–FAPI powder and after a series of anelastic measurements during which it transformed into $\alpha$ phase. An edge and the center of a face were made conductive with Ag paint. The black signs were made with a permanent marker at the nodal lines of the first flexural mode.

much as possible any decomposition from the humidity that rapidly coalesces at grain boundaries. Therefore, in order to search for XRD evidence of the orange 4H and 6H phases, we pressed other discs (FAPI #9) in conditions identical to those for the dielectric experiments, as shown in Fig. 6.

XRD measurements were performed with fast data scans (0.5 s/point, overall measurement time 1.5 h.) in the $5^\circ - 45^\circ$ angular range except for the slower scan of Fig. 8 (1 s/point with step in $2\theta$ of 0.002°, overall measurement time 5 h 40 min).

In the absence of literature on the 4H and 6H phases of pure FAPI, we compare our spectra with those simulated with VESTA [Momma, K.; Izumi, F. "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data" J. Appl. Cryst. 44, 1272 (2011)] using the Crystallographic Information Files (CIF) of FA$_{0.85}$MA$_{0.15}$PbI$_3$ from Refs. [15,16]. Even though it is expected that the partial substitution of FA with MA reduces the cell volume, the spectra of the 2H phase simulated in this manner are practically identical with those of the $\delta \equiv 2H$, suggesting that also the reflections of the 4H and 6H phases of the MA–substituted material are representative of those of pure FAPI. Figure 8 shows the XRD pattern of FAPI#9. As expected, the $\delta \equiv 2H$ phase is clearly detected (black column bars also reported in Table 1). Most of the expected 4H and 6H reflections with intensities $> 1\%$ are close to each other and to those of the dominant 2H phase, but the inset highlights the $18^\circ < 2\theta < 37^\circ$ region where it is possible to distinguish two peaks that match two isolated reflections of the 4H and 6H phases (red and green arrows).

It is possible that the difficulty of distinguishing clear reflections from additional phases in orange samples arises from their lower crystallinity with respect to the $\delta$ phase, as discussed for the $\alpha$ phase in the main text.
Figure 8: XRD pattern of FAPI #9 with the expected positions of the reflections from the 2H, 4H and 6H phases.

Table 2: Main reflections of δ–FAPI simulated with VESTA using the CIF from Ref. 13 and corresponding to the black bars in Fig. 8.

| 2θ    | Miller indexes (hkl) | Relative Intensities (%) |
|-------|----------------------|--------------------------|
| 11.790| 100                  | 100                      |
| 16.281| 101 / 10-1           | 7.564 / 6.665            |
| 20.494| 2-10                 | 3.544                    |
| 22.484| 002 / 00-2           | 2.381 / 2.663            |
| 25.460| 102                  | 5.898                    |
| 26.284| 201 / 20-1           | 28.890 / 29.340          |
| 30.606| 2-12 / 2-1-2         | 17.100 / 16.620          |
| 31.535| 3-10                 | 20.529                   |
| 32.903| 202 / 20-2           | 18.731 / 18.803          |
| 33.559| 3-11 / 3-1-1         | 2.063 / 2.009            |
| 35.892| 300                  | 1.114                    |
| 36.112| 103 / 10-3           | 1.149 / 1.057            |
| 39.077| 3-1-2 / 3-1-12       | 2.570 / 2.491            |
| 41.683| 4-20                 | 18.138                   |
| 41.877| 203 / 20-3           | 4.947 / 5.052            |
| 42.768| 302 / 30-2           | 4.530 / 4.466            |
| 43.470| 4-10                 | 6.943                    |
Graphical TOC Entry

FAPI $\delta$ (2H) 4H 6H $\alpha$ (3C)

temperature
pressure
intercalated $\text{H}_2\text{O}$
catalyzes