Crystal structure features of CH₂NH₃PbI₃₋ₓBrₓ hybrid perovskites prepared by ball milling: a route to more stable materials

Carlos Alberto López,*a,b María Consuelo Alvarez-Galván,c María Victoria Martínez-Huerta,c François Fauth,d and José Antonio Alonso*a

The hybrid organic-inorganic perovskites, MAPbX₃ (MA: methyl-ammonium CH₃−NH₃⁺; X= halogen), are the active absorption materials in the new generation of solar cells. The triiodide specimen (MAPbI₃) remains the most widely studied perovskite due to its ability to absorb broadband light below its bandgap of 1.6 eV, but the degradation in a humid atmosphere has remained a major obstacle for commercialization. Here we found that CH₃NH₂PbI₃−ₓBrₓ (x = 0.0, 1.0) perovskites, prepared by ball milling, exhibit a superior stability, showing no signs of degradation after several months exposed to humid air. A synchrotron X-ray diffraction (SXRD) investigation was useful to determine some peculiar structural features that may account for the improved stability. The crystal structure was analysed in I4/mcm and acentric I4cm space groups, yielding similar agreement factors. In both, the inorganic framework presents a conspicuously lower tilting effect than that observed in samples prepared by wet methods; an additional difference arises since the tetragonal phase at 140 K shows that the MA⁺ units lie along c axis with 25% probability. The structure at 140 K shows that the MA⁺ contribution along the c axis vanishes at this temperature. By contrast, MAPbI₃Br crystallizes in the cubic phase with space group Pm₃m, also with a larger unit-cell volume than that previously described. The absence of phase transitions down to 120 K suggests that the anion disorder prevents the localization of MA units upon cooling.

Introduction

Organic-inorganic hybrid lead trihalide perovskites are highly promising semiconductors for both multi-junction photovoltaic and light emitting applications due to their tunable band gaps.³ MMA lead triiodide perovskites (MAPbI₃) have received much attention due to its ability to absorb broadband light below its bandgap of 1.6 eV. However, MAPbI₃ still faces several complex challenges that need to be addressed, where the thermal and moisture instability has remained the major obstacle for commercialization.⁴ In this regard, tuning the halide anions of hybrid perovskites are the most common methods reported to seek a better system for photovoltaic applications, since they are also capable of band gap tuning by changing the composition of perovskites.⁵–⁹ Incorporation of bromine to produce mixed halide hybrid perovskite (MAPbI₃ₓBr₃−ₓ) changes the physical properties, enhancing the stability of the material, but also increasing the band gap⁶,⁸–¹⁰. The morphology as well as the properties of mixed halide hybrid perovskites are highly sensitive to the adopted synthetic strategy and could be varied by carefully manipulating the solvent(s) and surface capping ligands. Several methods have been developed for producing hybrid perovskites including precipitation from solution and gas-phase deposition.¹¹ In the solution-based method, stoichiometric mixtures of metal halides and organic ammonium halide precursors are normally dissolved in dimethylformamide (DMF) or dimethysulfoxide (DMSO). In the gas-phase method, the precursors are generally co-evaporated in a vacuum deposition chamber onto a substrate by the use of two separate sources to form uniform and controlled-thickness films. Mechanochemical synthesis has emerged as an attractive alternative, solvent-free method, featuring remarkable simplicity, low cost, swiftness and reproducibility in line with exceptional green credentials (e.g. solvent-less solid-state synthesis) for the design of a wide range of perovskites.¹²–¹⁶ The combination of the mechanical energy generated under ball-milling conditions and the inherent chemical modification of structures/surfaces make this methodology extremely promising for alternative greener perovskite synthesis. Moreover, ball-milling procedures allow the formation of more stable perovskites, which are not degraded, forming

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* Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049 Madrid, Spain. † I.A. Alonso: ja.alonso@icmm.csic.es
b Instituto de Investigaciones en Tecnología Química (INTEQUI), UNSL, CONICET and Facultad de Química, Bioquímica y Farmacia, UNSL, Ej. De los Andes 950, San Luis, 5700, Argentina. ‡ C.A. Lopez: calclopez@gmail.com
c Instituto de Catálisis y Petroleoquímica, CSIC, Cantoblanco 28049 Madrid, Spain.
d CELLS–ALBA synchrotron, Cerdanyola del Vallès, Barcelona, E-08290, Spain.

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Electronic Supplementary Information (ESI) available: [Tables with crystallographic parameters at low temperature; EDX and chemical analysis]. See DOI: 10.1039/x0xx00000x
MA$_2$PbI$_6$·2H$_2$O or MA$_2$Pb$_2$Br$_7$·2H$_2$O, within a short time, by reaction with ambient humidity$^{15}$. Herein, two different polycrystalline hybrid perovskites, MAPb$_4$I$_8$ and MAPb$_3$Br$_7$ have been successfully prepared by mechanochemical synthesis. The resultant polycrystalline powders were characterized by diffraction methods with synchrotron x-ray radiation, in complement with UV-Vis spectroscopic measurements. Remarkably, these specimens resulted stable in laboratory air atmosphere for several months, which is ascribed to conspicuous structural features induced during the ball milling process.

Experimental

MAPb$_3$I and MAPb$_3$Br$_2$ were obtained as microcrystalline powders from mechanochemical synthesis of stoichiometric amounts of PbI$_2$ (or PbBr$_2$) and MAI (or MABr). A total of 1.5 g of the reactants were milled using 30 zirconia balls of 5 mm diameter, with a final 8:6:1 mass ratio, for 4 h at 400 rpm in a Retsch PM100 mill in Ar atmosphere. For comparison purposes, MAPb$_3$I was also synthesized from a solution of stoichiometric amounts of PbI$_2$ and MAI in dimethylformamide$^{16}$. Laboratory XRD patterns were collected on a Brucker D5 diffractometer with KaCu ($\lambda = 1.5418$ Å) radiation; the 2θ range was 4° up to 90° with increments of 0.03°. The absorption capacity of each perovskite powder was investigated by diffuse reflectance UV/Vis spectroscopy. The UV-Vis spectra of the materials were recorded with a UV-Vis spectrometer equipped with a Varian Cary 3 UV-Vis spectrometer equipped with an integration sphere. The synchrotron X-ray powder diffraction SXRD patterns were collected in the MSPD high-resolution diffractometer at the ALBA facility, Barcelona (Spain), selecting an incident beam with 38 keV energy, $\lambda = 0.3252$ Å. The high angular resolution mode (MAD set-up) on the MSPD-diffractometer was utilized.$^{17}$ The polycrystalline powder was contained in quartz capillaries of 0.3 mm diameter, which were rotating during the acquisition time. SXRD patterns were collected at 140, 180, 298 and 393 K for MAPb$_3$I, and at 120, 298 K for MAPb$_3$Br$_2$. The refinement of the structure was performed by the Rietveld method using the Fullprof software$^{18,19}$. The following parameters were refined: zero-point error; scale factor; occupancy of the elements; atomic coordinates; and anisotropic displacements for all the atoms. The profile shape was modeled using the Thompson-Cox-Hastings pseudo-Voigt function$^{20}$ and the instrumental resolution parameters were considered in the refinements in order to obtain the microstructural parameters. Thus, the u, v and w Caglioti parameters are fixed and correspond to the instrumental broadening, hence only the Lorentzian isotropic strain (X) and size (Y) parameters were refined. From these parameters the apparent size and strain were calculated from Scherrer and Stokes-Wilson formula, respectively.

The Scanning Electron Microscope images were obtained on a Hitachi instrument, model TM-1000, coupled to an energy-dispersive X-ray spectrometer (EDX), working with an acceleration voltage of 15 kV and 60 sec. of acquisition time.

Results and discussion

Structural characterization

Chemical analysis (EDX, CNHS and TXRF) confirmed the expected stoichiometries (See ESI). The initial crystallographic identification was made from laboratory XRD. Figure 1 illustrates Le-Bail fits of the XRD patterns. Both correspond to pure perovskites with tetragonal symmetry for MAPb$_3$I and cubic for MAPb$_3$Br$_2$ at RT.

MAPb$_3$I

The tetragonal symmetry for MAPb$_3$I at RT is confirmed from synchrotron data; Figure 2 shows the thermal evolution of the SXRD patterns. At 393 K it becomes cubic, but between 140 K and 298 K it remains tetragonal. However, there are some differences regarding the previously informed tetragonal space group.
The oldest structural report is authored by Poglitsch et al. in 1987 and described this phase in the I4/mcm space group at room temperature.\(^2\) Fifteen years later, Kawamura et al. confirmed this model from single crystal X-ray diffraction.\(^2\) Then, in 2013, two new works analyzed the crystal structure: Baikie et al. confirmed this space group, but, they failed to model the location of the MA group.\(^1\) On the other hand, Stoumpos et al., also from single crystal X-ray diffraction, proposed the I4mcm space group.\(^2\) In both cases the unit-cell parameters are related to primitive cubic perovskite as: \(a_0 = b_0 = 2a_\text{c}\) and \(c_0 = 2a_\text{c}\); but the main difference lies in that I4/mcm is a centrosymmetric space group, in contrast to I4cm, with an off-centering ferroelectric component along the c-axis. Then, in 2015, Weller et al. from neutron powder diffraction reported this phase again in the I4/mcm space group.\(^2\) Regarding the MA \(^{+}\) orientation, Kawamura et al. found that MA units are aligned along the \([101]_\text{c}\), \([001]_\text{c}\), \([0\overline{1}1]_\text{c}\) and \([0\overline{1}0]_\text{c}\) directions of the cubic structure.\(^2\) This MA configuration is like \([110]\) orientation, but, without the alignments on the \((001)\) plane (\([1\overline{1}0]_\text{c}\) and \([110]_\text{c}\)). Stoumpos et al., who proposed the I4cm space group, did not consider the MA \(^{+}\) disorder, refining a unique MA unit along the c-axis.\(^2\) Finally, the MA \(^{+}\) orientation reported by Weller et al.\(^2\) is similar to that informed by Kawamura et al.\(^2\).

To analyze this dichotomy, we tested both models, I4/mcm and I4cm on our SXRPD pattern at RT, placing first the lead and iodine atoms and then building difference Fourier maps (DFM). The PbI\(_2\) lattice in the I4/mcm space group was assembled by placing Pb at 4\(c\) \((0,0,0)\) and I at 4a \((0,0.1/4)\) and 8b \((x,x+y/2,0)\) sites. For I4cm, Pb was placed in 4a \((0,0,z)\) (with \(z\) fixed to 0) and I allocated in 4a \((0,0,z)\) and 8c \((x,x+y/2,z)\) positions. As can be noted, the atomic coordinates are the same except by the \(z\) component, which is the polarizing direction in this non-centrosymmetric space group. At this point, the difference Fourier synthesis maps built for both symmetries reveal the missing electron density, which indicates that the MA units are clearly delocalized. Figure 3 illustrates the PbI\(_2\) network in comparison with the electron density at 9e\(^-\) for both space groups. From the shape and the intensity of these 3D plots it is possible to infer the C/N positions. Six density maxima corresponding to C/N are observed, and these are well modeled with the following two sites for I4/mcm: \((1,1/2,0)\) and \((1,1/2,0)\).

\[\begin{array}{c}
T = 393 K \\
\text{Cubic} \\
Pm\overline{3}m
\end{array}\]

\[\begin{array}{c}
T = 298 K \\
\text{Tetragonal} \\
I4/mcm
\end{array}\]

\[\begin{array}{c}
T = 180 K \\
\text{Tetragonal} \\
I4/mcm
\end{array}\]

\[\begin{array}{c}
T = 140 K \\
\text{Tetragonal} \\
I4/mcm
\end{array}\]

\[\Delta \theta (°)\]

\[\begin{array}{c}
2.8 \\
3.0 \\
3.2 \\
3.4 \\
3.6 \\
3.8 \\
4.0 \\
4.2 \\
4.4 \\
4.6 \\
4.8 \\
5.0 \\
5.2 \\
5.4 \\
5.6 \\
5.8 \\
6.0 \\
6.2 \\
6.4 \\
6.6
\end{array}\]

\[\begin{array}{c}
6.8
\end{array}\]

Figure 2: Thermal evolution of selected regions of the SXRD patterns of MAPbI\(_3\), in which a cubic-tetragonal phase transition is evidenced.

Fourier synthesis maps built for both symmetries reveal the missing electron density, which indicates that the MA units are clearly delocalized. Figure 3 illustrates the PbI\(_2\) network in comparison with the electron density at 9e\(^-\) for both space groups. From the shape and the intensity of these 3D plots it is possible to infer the C/N positions. Six density maxima corresponding to C/N are observed, and these are well modeled with the following two sites for I4/mcm: \((1,1/2,0)\) and \((1,1/2,0)\).

\[\begin{array}{c}
20 (°)
\end{array}\]

Figure 4: a) SXRD profile after Rietveld refinement and b) schematic view for MAPbI\(_3\) at RT in I4/mcm space group. Only the C/N (undistinguishable) atoms of the MA units are shown.
it is possible to assume the possible alignments of MA structure is shown in Figure 4b. From the refined C/N position, with respect to the mcm 4/3 space group was selected as the more adequate model to describe MAPbI$_3$ at RT. This is in agreement with recent works from Second Harmonic Generation (SHG),\textsuperscript{26,27} revealing that there is no evidence of non-centrosymmetric symmetry, thus confirming the I4/mcm space group in MAPbI$_3$.

The Rietveld plot from the SXRD pattern at RT is plotted in Figure 4a, and the results of the crystallographic refinements are listed in Table 1. A schematic view of the tetragonal crystal structure is shown in Figure 4b. From the refined C/N position, it is possible to assume the possible alignments of MA units with respect to the c axis; hence, the MA could be parallel or perpendicular (up or down to (1,1/2,1/4) position) as is highlighted in Figure 4b. Considering the occupancy factors, it is possible to infer that MA$^+$ is along c axis with 25% probability. In order to study the crystal structure at lower temperatures, synchrotron patterns were collected at 180 K and 140 K and the same analytical procedures were developed.

The structures at 180 and 140 K can also be defined at the I4/mcm space group, although some distinct features concerning the orientation of the MA$^+$ units were identified. The DFM at 140 K (Figure 3.d) only reveal the electron density compatible with (x,x-1/2,z) and (x,x-1/2,-z) sites, showing that the MA$^+$ contribution along c axis vanishes at this temperature. The Rietveld refinements of the C/N positions and occupation factors confirm the nonexistence of MA$^+$ orientation along the c axis at 140 and 180 K. Figures 5.a and 5.b show the Rietveld refinement and a schematic view of crystal structure at 140 K, respectively. Table S1 (Supplementary Information) lists the main crystal data after the refinements at 180 and 140 K. The obtained C/N sites at 140 and 180 K show that the MA$^+$ units can be found either up or down the (1,1/2,1/4) position. Besides, it is possible to observe that this MA$^+$ displacement is concomitant with the PbI$_6$ octahedral tilt. This fact is deduced from the analysis of the C/N–I distances. Figures 5.c and 5.d show three non-equivalent distances: C–I$_1$, C–I$_2$ and C–I$_2$' with the following values: 3.89(3), 4.07(4) and 3.92(5) Å, respectively. These values can be considered equal within the experimental errors. A similar situation is found at 180 K, (<C–I$_1$>: 3.99(3) Å, <C–I$_2$>: 4.14(4) Å and <C–I$_2$'>: 4.03(5) Å). Despite ignoring the H positions and the H-bond interactions, it is possible to observe a reduction in the degree of freedom of MA$^+$ units with respect to the RT structure. The tilting angles of PbI$_6$ octahedra framework also evidence this reduction; these values (estimated as $\phi = (180^\circ - \beta)/2$, where $\beta = \langle$Pb–I–Pb$\rangle$) are: 8.06°, 11.18° and 11.50° at 298, 180 and 140 K, respectively. There is an increase in the tilting angle as temperature decreases; however, this is not a linear increase as is usually observed purely inorganic perovskites, supporting the reduction in the freedom degree of MA$^+$ at lower temperatures. Additionally, the tilt at RT is lower than that reported previously by Kawamura et al. (in I4/mcm)\textsuperscript{22} and Stoumpos et al. (in I4/mcm)\textsuperscript{23} whose tilts are 9.79° and 8.21°, respectively. In both cases, MAPbI$_3$ was synthesized from wet methods. This difference allows inferring that the milling method yields a crystal structure closer to the ideal cubic symmetry, or in other words, with a tolerance factor$^{28}$ closer to 1. This also would explain the fact that down to 140 K the structure still remains tetragonal, in contrast to the informed phase transition temperatures to orthorhombic symmetry, at around 165 K\textsuperscript{21,24}. These behaviours can be related to an enhancement in the crystal structure stability.

Finally, the cubic symmetry defined in the space group Pm$^{-3}m$, observed above room temperature (393 K) was also previously reported by Weller et al.\textsuperscript{24}. They informed a phase transition to the cubic system at 327 K, describing a crystal structure at 352 K where the MA molecule was aligned along the (100) direction. However, our DFM at 393 K shows that the MA units are clearly aligned along (110) directions; therefore the C/N atoms are placed and could be refined at the Wyckoff site 12j.

Table 1: Crystallographic data for MAPbI$_3$ phase in tetragonal system (I4/mcm) from SXRPD at RT. $a = 8.85728(6)$ Å, $c = 12.651049(9)$ Å and $V = 992.49(1)$ Å$^3$.

|        | x    | y    | z    | Uiso*/Ueq | Occ |
|--------|------|------|------|-----------|-----|
| Pb1    | 0    | 0    | 0    | 0.031(2)  | 1   |
| I1     | 0    | 0    | 0.25 | 0.081(3)  | 1   |
| I2     | 0.2854(3) | 0.7854(3) | 0 | 0.082(3) | 1   |
| C/N1   | 0.933(5) | 0.433(5) | 0.231(5) | 0.013* | 0.13(3)/0.13(3) |
| C/N2   | 0.933(5) | 0.433(5) | 0.231(5) | 0.013* | 0.18(2)/0.18(2) |

$R_h = 10.2\%$, $R_{wp} = 13.4\%$, $\chi^2 = 1.28$, $R_{bragg} = 4.67\%$

Atomic displacement parameters (Å$^2$)

$u^{11}$ $u^{22}$ $u^{33}$ $u^{12}$ $u^{13}$ $u^{23}$

Figure 5: a) SXRD profile after Rietveld refinement and b) schematic view of MAPbI$_3$ at 140 K in I4/mcm space group. c) and d) Detailed views of main C/N–I distances of a MA unit in the PbI$_6$ framework.
(1/2, y, y). Figure 6 plots the Rietveld refinement and a view of the cubic crystal structure at 393 K. Table S2 lists the main crystallographic data at this temperature.

MAPbI₂Br

In contrast with MAPbI₃, MAPbI₂Br crystallizes at RT in the cubic phase with space group Pnma, in the same way as described in previous work for MAPbBr₃ perovskites. Inspired in the behavior of this tribromide perovskite, which experiences two consecutive phase transitions from cubic Pnma to tetragonal I4/mcm (∼235 K) and then to orthorhombic Pnma (150 K), we additionally collected a SXRD pattern at 120 K for MAPbI₂Br, observing that it also exhibits a cubic symmetry. In fact, the absence of transitions at low temperatures was also observed recently in mixed halide MAPb(BrₓCl₃₋ₓ)₃ perovskites where the anion disorder prevents the occurrence of phase transitions.

In the present case, the DFM also was calculated to unveil the MA delocalization. As illustrated in Figure 7, the isosurface density at 3e⁻ reveals that the MA unit is aligned along the [111] direction at both RT and low temperature (120 K). Also, the electron density presents a particular triangular shape that is magnified at RT. This fact can be understood considering the H-bond interactions existing in these compounds. In the [111] delocalization the three hydrogen atoms of MA units interact alike with the three halides that are in the face of a single PbX₆ octahedron. However, taking into account the intrinsic halide disorder present in MAPbI₂Br, it is expected that the face of the octahedron will not be symmetric, in average, inducing deviations towards some corner of the triangle. This is not unlikely, considering that the 44.4% of the triangular faces are composed by two I and one Br, where the N-H···Br bonds will be shorter than N-H···I distances. Figure 8 displays the final refinements from the 298 and 120 K SXRD patterns, and Tables 2 and S3 list the main crystallographic data. The inset in Figure 8b shows schematic views of the obtained crystal structure. Considering the used synthesis method, the microstructural behavior is another important aspect, which was considered in the Rietveld refinements. From this analysis, the average particle size is 176.3(3) nm and 84.4(1) nm for MAPbI₃ and MAPbI₂Br, respectively.

Optical gap by UV-Vis spectra

Figure 9 depicts the optical absorption coefficient related to the Kubelka–Munk function (F(R)=a=(1-R)²/2R, being R the reflectance of each sample) versus wavelength in eV, for both MAPbI₃ (red line) and MAPbI₂Br (blue line). The band gap for

Table 2: Crystallographic data for MAPbI₂Br phase in cubic system (Pm-Tm) from SXRD at RT. a = 6.17605(9) Å and V = 235.577(6) Å³.

| Oct. | x | y | z | Uliso*/Ueq | Occ. |
|------|---|---|---|------------|------|
| Pb1  | 0 | 0 | 0 | 0.050(1)   | 1    |
| Br1  | 0.5 | 0 | 0 | 0.122(3) | 0.37(3) |
| I1   | 0.5 | 0 | 0 | 0.122(3) | 0.63(3) |
| C1   | 0.569(3) | 0.569(3) | 0.569(3) | 0.03(2) | 0.12 |
| N1   | 0.569(3) | 0.569(3) | 0.569(3) | 0.03(2) | 0.12 |

R_m = 11.1%, R_m = 14.2%, χ² = 1.02 R_min = 10.7%
each perovskite has been calculated by extrapolating the linear region to the abscissa. The value obtained for MAPbI₃ (~1.6 eV) is typical for this material. The blue shift observed for the perovskite MAPbI₂.Br (~1.75 eV) is also in accordance with data reported in literature 31–33.

Microstructure by scanning microscopy (SEM)

SEM images were obtained to understand the effect of the morphology of the crystals on the stability of the perovskites obtained by ball milling. Figure 10 illustrates some typical views of the as-prepared MAPbI₃ and MAPbI₂.Br. From a mechano-synthesis process, involving the collision of high energy ZrO₂ balls against the specimens, one would expect a highly disaggregated product, formed by amorphous particles. However, surprisingly we can observe a heterogeneous picture where quite large particles with sharp edges and large surfaces are mixed with smaller fragments with undefined shapes. This scenario illustrates that the growth of large microcrystals (as large as 20 microns in some edges) is not perturbed by the dynamical motion of the reactants and ZrO₂ balls; the obtained images, after 4 hours of reaction, would suggest that the large particles grow at the expense of the remaining fine powder. The reasonable size of the obtained crystals account for the good crystallinity observed in the diffraction diagrams, endorsing this procedure as complementary to the standard solution chemistry, with the added advantage of dispensing with organic solvents that, as we will see, are probably at the origin of the observed chemical instability of those perovskites.

The results from EDX analysis are shown in figures S1 and S2 and in Table S4 (Supplementary Information). For both samples, the EDX spectra show well defined peaks corresponding to lead, bromine and iodine. The obtained weight % of these elements (Table S3) are in agreement with the nominal values.

Chemical stability

Figure 11.a shows two XRD patterns of MAPbI₃ prepared after 6 months, either by ball milling or crystallization from DMF, stored at ambient conditions in laboratory air (typically 40% humidity). The sample obtained by mechanosynthesis is unaltered, with respect to the pristine pattern collected immediately after preparation (Figure 1.a); differences in peak intensities arise from preferred orientation effects. By contrast, in the XRD pattern of a sample of the same composition prepared by the standard procedure from a solution in DMF starting from MAI and PbI₂, the peaks of the perovskite are accompanied by important amounts of impurities, mainly MAI and PbI₂. Even visually, after some weeks since it was synthesized, it is observed that the
characteristic black color is decorated by grey particles, looking inhomogeneous even at macroscopic scale.

The absence of crystalline impurities and high yield of the mechanochemical synthesis of MAPbI₃ in comparison to other methods (such as reaction in solution) has been also reported in literature, even for the samples that are recently prepared.

In fact, the water degradation mechanism of MAPbI₃ was previously studied by different authors. Niu et al. reported that the MAPbI₃ degrades into PbI₂ and MAI in presence of H₂O, where MAI further decomposes into CH₃NH₃I (aq) and H₂I(aq). Frost et al. proposed two reversible reactions, where the combination of H₂O and MAPbI₃ leads to the formation of CH₃NH₂ and [(CH₃NH₃⁺)(n−1)CH₃NH₂)n⁺PbI₃][H₂O], and the latter further degrades into [(CH₃NH₃⁺)PbI₃]n⁻, HI, PbI₃ and H₂O. On the other hand, Habiserutiger et al. speculated that the weak hydrogen bonds allow that MAI escapes from the crystal lattice, which eventually leads to the formation of PbI₂.

Another possible reason mentioned for the instability of MAPbI₃ could be related to the interaction of residual traces of DMF. Thus, the hydrolysis of DMF traces could form dimethylammonium formate, compromising the ability of Pb²⁺ and MA⁺ to stabilize the perovskite structure.

Regardless of the mechanism, it seems that the degradation is developed when the MA units are in touch with the environment. Moreover, it is well known that, during the mechanical milling, a lot of high-energy impacts are produced, which generate high temperatures locally and for short periods of time. This process drives the reaction; however, this also generates a high disorder in the crystal surface and probably defects of MA⁺. Considering these facts, it is possible to infer that the dry mechanochemical synthesis produces a surface deficient in MA⁺, which slows down the MAPbI₃ decomposition similarly to a “passivation layer”. Moreover, it seems it is not only a surface behaviour, but the mechanochemical synthesis could also affect the bulk crystal features. As stated previously, the inorganic framework presents a conspicuously lower tilting effect than observed in samples prepared by wet methods; an additional difference arises since the tetragonal structure is stable down to 140 K. The smaller octahedral rotation suggests an increased tolerance factor of the perovskite, which is a known consequence of the partial deficiency of MA at the A positions of the ABX₃ perovskite, and therefore an improved structural stability, also accounting for the absence of structural transitions down to 140 K. Both effects and, finally, the chemical stability increase, can be attributed to both surface and bulk crystal features or a combination of them.

Conclusions

Two hybrid perovskites of the family MAPbX₃ have been successfully prepared by mechano-chemical synthesis in inert atmosphere. They have demonstrated to exhibit a superior chemical stability towards humidity than specimens prepared by solution chemistry. Despite the dynamical process inherent to the ball-milling process, well-crystallized specimens have been obtained, which allowed a high resolution SXRD study to be carried out. MAPbI₃ is better defined in the tetragonal I4/mcm space group between RT and 140 K; difference Fourier synthesis allowed us to determine the orientation of MA⁺ units, which evolves with temperature even if the symmetry does not change. At 393 K, this triiodide perovskite becomes cubic, space group Pm₃m. Several conspicuous structural features of MAPbI₃ may be related to a better stability, probably originated by the elimination of MA⁺ during the ball milling process; these include the absence of an additional phase transition to orthorhombic symmetry at 140 K, distinct tilting angles and MA conformation at different temperatures.

Regarding MAPbI₃Br, it is cubic in the 120 K-298 K range, suggesting that the anion disorder prevents the occurrence of phase transitions. In this case, the MA unit is aligned along the [111] direction in all the temperature range.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Authors acknowledge financial support given by the Spanish Ministry of Economy and Competitiveness (MAT2017-84496-R), as well as by KIC RAW MATERIALS from European Union (OPTNEWOPT project). C.A.L. acknowledges ANPCyT and UNSL for financial support (projects PICT2017-1842 and PROICO 2-2016), Argentine.

Notes and references

Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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