The Impact of the Crystallization Processes on the Structural and Optical Properties of Hybrid Perovskite Films for Photovoltaics

Giulia Grancini,† Sergio Marras,‡ Mirko Prato,*,‡ Cinzia Giannini,§ Claudio Quartì,‖ Filippo De Angelis,‖ Michele De Bastiani,‖ Giles E. Eperon,⊥ Henry J. Snaith,⊥ Liberato Manna,‡ and Annamaria Petrozza*†

†Center for Nano Science and Technology @ Polimi, Istituto Italiano di Tecnologia, via Giovanni Pascoli 70/3, 20133, Milan, Italy
‡Department of Nanochemistry, Istituto Italiano di Tecnologia, via Morego, 30, 16163 Genova, Italy
§Institute of Crystallography, National Research Council, via Amendola 122/O, Bari 70126, Italy
‖Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, I-06123, Perugia, Italy
⊥Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford, OX1 3PU, United Kingdom

Supporting Information

ABSTRACT: We investigate the relationship between structural and optical properties of organo-lead mixed halide perovskite films as a function of the crystallization mechanism. For methylammonium lead tri-iodide, the organic cations rearrange within the inorganic cage, moving from crystals grown in a mesoporous scaffold to larger, oriented crystals grown on a flat substrate. This reduces the strain felt by the bonds forming the cage and affects the motion of the organic cation in it, influencing the electronic transition at the onset of the optical absorption spectrum of the semiconductor. Moreover, we demonstrate that in mixed-halide perovskite, though Cl\textsuperscript{−} ions are not present in a detectable concentration in the unit cell, they drive the crystallization dynamics. This induces a preferential order during crystallization, from a molecular, i.e., organic—inorganic moiety arrangement, to a nano-mesoscopic level, i.e., larger crystals with anisotropic shape. Finally, we show that while Cl is mainly expelled from flat films made of large crystals, in the presence of an oxide mesoporous scaffold they are partially retained in the composite.

SECTION: Physical Processes in Nanomaterials and Nanostructures

Since methylammonium lead halide perovskites were identified as promising absorbers for solar cells\textsuperscript{1–6} the performance of perovskite-based devices has tremendously boosted, reaching power conversion efficiencies as high as 19.3%.\textsuperscript{7–9} They consist of a MAX\textsubscript{3} structure, where MA accommodates the organic cation (CH\textsubscript{3}NH\textsubscript{3})\textsuperscript{+} and X is the lead halide based on lead cation (Pb\textsuperscript{2+}) and iodine or chlorine (Cl\textsuperscript{−}, Cl\textsuperscript{2−}) halide anions. The most developed perovskite materials for photovoltaics (PV)\textsuperscript{3–4,10} consist of methylammonium lead-iodide perovskite (CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}, here on MAPbI\textsubscript{3}), fabricated from a solution of methylammonium iodide (CH\textsubscript{3}NH\textsubscript{3}I) and lead iodide (PbI\textsubscript{2}), along with its analogous mixed-halide perovskite, (CH\textsubscript{3}NH\textsubscript{3}Pb\textsubscript{1−x}I\textsubscript{x}Cl\textsubscript{x}), obtained by substituting the PbI\textsubscript{2} precursor with lead chloride (PbCl\textsubscript{2}). Despite the well-defined structure based on a tetragonal unit cell made of interconnected Pb\textsubscript{X\textsubscript{3}} octahedra,\textsuperscript{11} the film structural organization from a molecular to a mesoscopic level is still obscure, thus preventing a full control of the device optimization protocol.\textsuperscript{11–16} X-ray diffraction (XRD),\textsuperscript{11,13,17,18} scanning electron microscopy (SEM)\textsuperscript{14} and UV–vis spectroscopy,\textsuperscript{19–21} along with electronic structure calculations\textsuperscript{22–26} have shown how the perovskite film is intrinsically heterogeneous,\textsuperscript{22,27,28} especially in terms of a huge variability in crystal size and aggregation. This is particularly affected by the substrate used for film deposition.\textsuperscript{12,14,16,27} In the case of MAPb\textsubscript{1−x}Cl\textsubscript{x} deposited on a flat glass substrate, a polycrystalline film with grain sizes larger than 500 nm is formed, while if the same perovskite is infiltrated into a mesoporous oxide scaffold, the perovskite grains are smaller, with an inhomogeneous size distribution ranging from a few nm up to 100 nm.\textsuperscript{27} This directly impacts the PV parameters, thus the overall solar cell efficiency.\textsuperscript{12,27} Reports on distribution function analysis of XRD patterns\textsuperscript{28} on MAPbI\textsubscript{3} have recently shown that when integrated into an oxide mesoporous network (either titania\textsuperscript{1} or alumina\textsuperscript{2}), two phases are formed, composed of 30% relatively crystalline and ordered component, responsible for the crystalline tetragonal structure observed in the XRD patterns,\textsuperscript{11,13,17,18} immersed in a mainly disordered nanoscopic-structured matrix characterized by short-range (<2 nm) order.\textsuperscript{28} For MAPbI\textsubscript{1−x}Cl\textsubscript{x}, the hot debate regards the role of chlorine on the crystallization process and its influence on the optoelectronic properties of the film.\textsuperscript{28,29} It has been observed that MAPbI\textsubscript{1−x}Cl\textsubscript{x} thin films, for instance, present improved carrier transport properties with respect to MAPbI\textsubscript{3},\textsuperscript{18,29} and

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carrier diffusion length exceeding 1 μm, one order of magnitude larger than that of the MAPbI3.30,31 Moreover, it has been shown that increasing the amount of chlorine in the precursor solution of MAPbI3−xClx films leads to an unexpected enhancement of the photoluminescence lifetime.30−32 It is therefore straightforward that the intrinsically complex nature of these materials, including various types of interactions and structural disorder, plays a fundamental role in governing the overall device function. Unfortunately, the currently poor understanding of the relationship between structural and optoelectronic properties still prevents the PV community from defining a clear roadmap for a rational improvement in perovskite-based PV technological exploitation.28,33

In this work we shine light on the optical and structural properties of both MAPbI3 and MAPbI3−xClx (here on Cl-doped MAPbI3) perovskite polycrystalline films which have been previously characterized in the full device configuration by some of us.14,27,30 We show that the nature of the substrate and the presence of chlorinated species (PbCl2) in the precursor solution can affect the interplay between the organic and inorganic moieties and tune the optical band gap. Moreover, we find that the presence of PbCl2 precursor affects the crystal growth process favoring a higher degree of order, with larger crystals growing with a preferential orientation. Importantly, we demonstrate that chloride ions are released during the growth of large perovskite crystals and such ions are not detected in the final large crystals, while in the presence of a mesoporous metal-oxide scaffold the chloride ions are retained.

As said before, MAPbI3 and Cl-doped MAPbI3 perovskites are the two most successfully materials exploited as active layer in PV cells either into a mesoporous metal-oxide network or deposited on a flat compact layer.3,6,27,30 First, we investigate the structure of MAPbI3 by means of vibrational Raman spectroscopy both on a mesoporous scaffold (named “meso” in the following) and on a flat glass surface (named “flat” substrate). Notably, for the “meso” sample, crystal growth is constrained, which on average reduces the grain size.27 The vibrational Raman spectrum of the “meso” MAPbI3 (shown in Figure 1) has been previously reported by some of us,34 and the main fingerprint related to both the inorganic (Pb−I stretching and bending modes) and organic cations vibrational modes have been identified.34

Briefly, the two peaks at lower frequencies, at around 62 and 94 cm−1, represent the diagnostic modes of the inorganic phase.34 The peak at 119 cm−1 is associated with the organic liberation modes along with the unstructured feature in the frequency range of 150−160 cm−1. Moreover, the broad, intense band at about 250 cm−1 is assigned to the organic torsional mode.34,35 The latest, being sensitive to the specific organic−inorganic interactions (mainly occurring through Coulomb and hydrogen-bonds interactions between the NH3 groups of MA and the electronegative iodine atoms) represents an important marker of the orientational disorder of the material.34,35 In particular, in the more disordered phase of MAPbI3 (whose extreme is represented by the cubic phase for T > 327 K11) the MA cations are arranged in a random orientation within the inorganic cage due to their large orientational mobility.35 This leads to a broadening and a red-shifting of the band at around 250 cm−1.35 On the contrary, in the more ordered “head to tail” arrangement34 of the MA cations (whose extreme is represented by the orthorhombic phase for T ≤ 160 K11), this band looses intensity (by symmetry selection rules) and it considerably blue-shifts.34 Finally, the broad shoulder peaking at ~160 cm−1 is assigned to liberation of the MA cations, calculated at 156 cm−1. From the simulation it is additionally expected to become sharper and more intense, in the more ordered “head to tail” arrangement.35

Analyzing the evolution of the Raman spectrum from the “meso” to the “flat” MAPbI3 sample (see Figure 1 and fitted single peaks as dot lines along with fitted parameters collected in Table S1, Supporting Information) a clear trend is visible at first glance: (i) the band at around 250 cm−1 blue-shifts and its intensity strongly decreases; (ii) the peak at 119 cm−1 decreases in intensity and red shifts to 115 cm−1; (iii) the band at around 160 cm−1 becomes sharper and more resolved; (iv) the peak at around 94 cm−1 gains strength.

According to the rationalization above, these observations highlight the different organic−inorganic interactions affecting the orientational order of the organic cation in the unit cell when the perovskite film is grown on the two different substrates. The experimental findings point to a clear trend, that is, an ordered (“head-to-tail” like) arrangement34,35 of the MA cations in “flat” samples versus a more disordered cation arrangement in the “meso” sample, similar to the effect...
observed in the IR spectrum of MAPbI$_3$-Cl when decreasing the temperature.\cite{35} It is important to notice that, as a consequence of increasing structural order, the peak at 94 cm$^{-1}$ increases in intensity and gets sharper along with the reduction of the close peak at 119 cm$^{-1}$. This appears in the spectrum as an inversion of their relative amplitude. A similar effect has been already observed in the literature when comparing pure ordered PbI$_2$ crystals (for which the mode at 96 cm$^{-1}$\cite{37} represents the main peak\cite{38}) with ammonia-intercalated PbI$_2$ compounds, which present distorted Pb-I bond. Overall, our analysis suggests an ordered arrangement of the organic cation in MAPbI$_3$ crystallites grown on “flat” substrates, while it results in fully random orientation the crystallites grown in the “meso” scaffold. Although the MA cations do not directly participate to the frontier orbitals of the semiconductor,\cite{36} their interaction with the inorganic cage and the displacement of the organic cation affect the electronic properties of the compound.\cite{37,38} Here, we clearly observe a red shift of the UV–vis absorption onset and photoluminescence (PL) peak when moving from “meso” to “flat” MAPbI$_3$ film (see Figure 1b). It must be also noted that some of us have experimentally observed a clear excitonic transition—already evident just below room temperature—at the onset of the “flat” MAPbI$_3$ absorption spectrum only.\cite{19} No excitonic transition has been observed, even at 4K, for the “meso” film. Notably, Even et al.\cite{22} have recently predicted an excitonic transition with an exciton binding energy of only 5 meV due to exciton screening by collective motions of the MA cations. This suggests that the preferential order of the organic cation in the “flat” film may possibly slow down the rotational motion of the MA cations, which in turn affect the screening of the excitonic transition at the onset of the absorption spectrum.

In Figure 2a we compare the normalized Raman spectra of the flat MAPbI$_3$ film with the one from the Cl-doped MAPbI$_3$ on a mesoporous Al$_2$O$_3$ scaffold.

We observe that the Raman spectrum of the “meso” Cl-doped MAPbI$_3$ resembles very much that of the “flat” MAPbI$_3$, keeping the same Raman peaks and relative intensity. This result demonstrates that the presence of chloride ions in the starting composition does not change the chemical nature of the inorganic cage, but it affects the local structure, inducing a preferential order of the MA cation organization in the inorganic cage, even in the mesostructured samples. To gather more information on the crystallization process of the Cl-doped MAPbI$_3$, we monitored the chemical species formation during the film crystallization combining Raman spectroscopy with steady state photoluminescence spectroscopy. In particular, we have identified three critical steps: (step 1) deposition by spin coating of the precursors’ solution with no further annealing; (step 2) film annealed for 4 min at 100 °C; (step 3) film annealed for 45 min at 100 °C. Their Raman spectra are shown in Figure 2b. The film fabricated up to step 1 exhibits a Raman spectrum showing a main broad peak at around 104 cm$^{-1}$, related to the Pb—I modes.\cite{36} The spectrum loses the characteristic Pb—Cl features (see PbCl$_3$ spectrum in Figure 2b), in line with the predicted thermodynamic stability of the MAPbI$_3$ perovskite upon Cl to I substitution\cite{25} and suggests that, despite the use of PbCl$_2$ precursor, Pb—I bonds are quickly formed. In accordance, the PL spectrum registered at step 1 peaks at 500 nm, confirming the presence of PbI$_2$\cite{39,40} as primary species in the crystallization process before annealing (see Figure 1c). Upon 4 min annealing, the Raman spectrum dramatically changes. Notably, it essentially resembles the
Raman spectrum of the “meso” MAPbI₃ (see Figure 1a for comparison). This similarity indicates that this structure is an intermediate phase in the Cl-doped perovskite film formation. In accordance, at step 2 the PbI₂ PL is not totally quenched, indicating that the perovskite conversion is not fully completed yet (Figure 2c). Finally, we measure the Cl-doped MAPbI₃ “meso” sample upon full conversion into the perovskite structure in step 3. We find that the longer annealing time in the presence of the PbCl₂ precursor allows for a reorganization of the organic−inorganic moieties within the crystal. As expected, the PbI₂ PL is completely quenched, and we only observe the emissive band peaking at 770 nm (Figure 2c), typical of the Cl-doped MAPbI₃.30 Our results indicate that the chloride ions in the Cl-doped MAPbI₃ do not form a clearly detectable chemical bond with Iodine within the unit cell, neither any PbCl₂ residual is left over, but Cl has an important role in governing the crystallization process and the arrangement of the organic moieties.

To gain further insight into the local crystalline arrangement, we performed XRD analysis of both MAPbI₃ and Cl-doped MAPbI₃ in “flat” and “meso” samples. Figure 3 shows the XRD experimental data (dotted curves) along with the Rietveld fitted profiles41 (continuous curves) and the markers of the MAPbI₃ reference structure for all the investigated thin films.

A summary of the refined parameters are reported in Table 1. Figure 3a–d indicate that the XRD patterns were correctly indexed as the MAPbI₃ crystal structure majority phase. The retrieved parameters clearly show that the presence of Cl in the precursors does not significantly affect the unit cell parameters, for whatever substrate, as it would have been expected for Cl ions entering as substitutional impurities in the lattice according to Vegard’s law42,43 (see “XRD data analysis” section of the Supporting Information for details on XRD spectra analysis). We have also performed an analysis of the preferred orientations (POs) along the[004] and[220] crystallographic directions. In Table 1 we report the fitted March parameter (G1), 0 < G1 <1, which is an indicator of the strength of the preferred orientation along a selected preferential crystallographic direction: at G1 = 1 (random powder) there is no orientation; at G1 = 0 (perfect uniaxial preferred orientation), there is total preferred orientation. First of all, we can highlight a trend which depends on the nature of the substrate, i.e., crystals grown on the “flat” substrate present grains that are much more oriented with respect to the mesoporous substrates. In addition, there is an evident effect related to the presence of Cl. For the “flat” substrate, Cl doping induces slightly more pronounced and strongly unbalanced orientation of the grains in the [220] crystallographic direction, i.e., 88% of the grains...
present \( G_{220} = 0.2200 \), 12\% of the grains \( G_{004} = 0.600 \). Notably these grains also reach the largest extension (about 1000 Å). In the case of the “meso” samples, the Cl doping increases the (220) PO degree: \( G_1 \) reduces from 0.4815 to 0.2542 going from MAPbI3 to Cl-doped MAPbI3. In this case, it must be noted that a preferential interaction of chloride with the metal-oxide surface has been computationally predicted.24 In conclusion, no signature of Cl in the unit cell is present, in accordance with the Raman analysis, but its presence in the precursor solution strongly affects the mesoscopic structure of film.

As a final point we aim to understand whether the Cl ions, even if not detectable in the unit cell, are still retained in the perovskite film. Thus, to visualize the presence of Cl atoms, we performed energy dispersive X-ray spectroscopy (EDS) analysis on Cl-doped perovskite films deposited on mesoporous \( \text{Al}_2\text{O}_3 \) scaffold and on flat glass. In Figure 4a (left panel) we compare the EDS compositional spectra from each sample in the [2, 3] keV energy region, typical for the main Pb and Cl lines, after normalization to the intensity of the Pb M\( \alpha \) line.

A zoom into the range of Cl K\( \alpha \) lines (energies between 2.5 and 2.9 keV) is also reported (right panel) to emphasize the relevant differences we observed. It has to be noted that Cl K\( \alpha \) lines (usually centered at approximately 2.62 keV) slightly overlap with a minor Pb line (Pb M\( \gamma \), at 2.65 keV). In Figure 4b,c we show representative BSE-SEM images of the investigated samples (“flat” and “meso”, respectively). For the “flat” sample, though obtained from Cl-containing precursors, the observed chlorine content is always below the detection limit of the technique (0.1 wt % in the analyzed volume), in agreement with what was recently reported by Docampo et al.32 on similar samples. Interestingly, a different scenario is found for the “meso” sample, where a Cl signal (approximately 0.2 wt %, just above the detection limit) is detected. In order to gain a better insight, for the “meso” sample, we repeated the compositional analysis on different detection spots on a pure “meso” area (see green ellipse in Figure 4c), inside which nanocrystals of the hybrid perovskite have grown, on a large crystalline aggregate that constitutes the capping layer over the “meso” scaffold (red square in Figure 4c). We find that the Cl signature is only detected from the pure “meso” areas where the capping layer is missing. In fact, the large crystallites grown on top of the scaffold do not show any detectable Cl signal (preliminary studies where the gas phase species evolution is monitored by means of a quadrupole mass spectrometer show evaporation of Cl during the annealing—data not shown). This suggests that the metal-oxide scaffold plays a significant role in retaining the Cl ions.

In conclusion, our investigations on MAPbI3 and Cl-doped MAPbI3 films highlight the complexity of these compounds and their extreme sensitivity to environmental stimuli. First of all, we have demonstrated that the simple choice of the substrate strongly affects the structural properties of the thin film from a molecular to a mesoscopic level. In particular, we have clarified how the crystallization process influences the inorganic—organic moieties interplay and how this plays a role in determining the optical response of the thin film. Leaving MAPbI3 free to crystallize in larger crystals allows the organic cation to arrange itself in a head-to-tail-like configuration, with oriented grains. This results in a reduced strain on the Pb—I cage induced by the cation motion, thus affecting the electronic structure at the optical absorption onset of the semiconductor. This can in part contribute to the tuning of the open circuit voltage and short circuit current in operational devices as already observed when comparing meso and flat film based devices.27,45 Meanwhile, how this influences polarization effects in the different films’ morphology will deserve further investigation. Moreover, it is important to consider that when meso structures coexist with a capping layer in the same device architecture an energetical disomogeneity will be present.27,45 Raman and XRD analysis points out the predominant absence of Cl in the unit cell, even in the presence of Cl source in the crystallization process. However, the presence of Cl influences the crystallization dynamics, favoring a higher order of the organic moieties in the inorganic cage and inducing a preferred orientation of the crystalline grains even in small crystals, in contrast to MAPbI3. Thus, the presence of Cl helps to minimize the morphological and energetic disorder of the film, one of the
main issues in the field of thin film solar cells. Importantly, the film made of small crystals grown within the mesoporous metal-oxide scaffold is found to retain a small amount of Cl. Whether such ions passivate the crystallites surface or are adsorbed by the oxide is still unclear; however, it will definitely play a role in determining the energetics of the interfaces, critical in device operation.

## ASSOCIATED CONTENT

### Supporting Information

Experimental Methods, tables including all the parameters and fit procedure for the Raman analysis, and fitting details on XRD measurements are included in the Supporting Information. This material is available free of charge via the Internet This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

### Corresponding Authors

*E-mail: mirko.prato@iit.it.*

*E-mail: annamaria.petrozza@iit.it.*

### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. G.G. performed Raman Measurements; G.E. and M.D.B. prepared the samples; S.M. and M.P. performed XRD and EDS measurements; C.G. performed the XRD fitting analysis; C.Q. and F.D.A. calculated Raman modes; all the authors analyzed the data.

### Notes

The authors declare no competing financial interest.

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## REFERENCES


Supplementary Information

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Giulia Grancini1, Sergio Marras2, Mirko Prato2*, Cinzia Giannini3, Claudio Quartí4, Filippo De Angelis4, Michele De Bastiani1, Giles E. Eperon5, Henry J. Snaith5, Liberato Manna2, Annamaria Petrozza1*

1Center for Nano Science and Technology @Polimi, Istituto Italiano di Tecnologia, via Giovanni Pascoli 70/3, 20133, Milan, Italy
2Department of Nanochemistry, Istituto Italiano di Tecnologia, via Morego, 30, 16163 Genova, Italy
3Institute of Crystallography, National Research Council, via Amendola 122/O, Bari 70126 Italy
4Computational Laboratory for Hybrid/Organic Photovoltaics (CLHYO), CNR-ISTM, I-06123, Perugia, Italy
5Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, United Kingdom
Methods

Sample Preparation. Perovskite samples were prepared either on glass microscope slides that were cleaned sequentially in water, acetone, isopropanol and O₂ plasma or on mesoporous alumina. In the last case a commercial (Sigma Aldrich) alumina nanoparticle dispersion (20%wt in IPA) was diluted down in a 1:2 ratio with IPA, and spin-coated at 2500 rpm to form a ~400 nm thick mesoporous layer. This was then dried at 150°C for 10 minutes.

Methylammonium lead triiodide MAPbI₃ precursor was prepared by dissolving at a 3:1 molar ratio methylammonium iodide (synthesized according to a literature procedure) and PbI₂ in anhydrous DMF at 0.88M. Films were spin-coated in air at 2000 rpm and annealed at 100°C for 45 minutes for the meso and 170° for 10 minutes for the flat. For the “two step deposition” PbI₂ was dissolved in DMF (460 mg/ml) and spin coated on glass substrates at 2000 rpm in order to obtain a 300 nm thick layer. Samples were annealed on an hot plate for 30 min at 70 °C. Subsequently the substrates were dipped in a solution of CH₃NH₃I in anhydrous IPA (10 mg/ml) for 5 min and rinsed with fresh anhydrous IPA. Methylammonium lead mixed halide To form the Cl-doped MAPbI₃ precursor solution, methylammonium iodide and lead (II) chloride were dissolved in anhydrous DMF at a 3:1 molar ratio of MAI to PbCl₂, with final concentrations 0.88M lead chloride and 2.64M methylammonium iodide. Films were spin-coated in air at 2000 rpm and annealed at 100°C for 45 minutes. All samples were incapsulated by depositing a 500 nm thick PMMA layer on top. PMMA was dissolved in anhydrous chlorobenzene at 80mg/ml and spin-coated at 1800 rpm.

Raman measurements. The micro Raman system is based on an optical microscope (Renishaw microscope, equipped with 5x, 20x, 50x and 100x short and long working distance microscope
objectives) used to focus the excitation light and collect it in a back scattering configuration, a monochromator, notch filters system and a charge coupled detector. The sample is mounted on a translation stage of a Leica microscope. The excitation used consists of a diode laser at 532 nm. The system has been calibrated against the 520.5 cm\(^{-1}\) line of an internal silicon wafer. The spectra have been registered in the 60-300 cm\(^{-1}\) range, particularly sensitive the \(Pb-I\) modes. The final data have been averaged over ten accumulations in order to maximize the signal to noise ratio. The measurements were conducted at room temperature and in air. The laser power intensity has been kept of the order of 300 \(\mu W\) in order to avoid any sample degradation effects.

**X-ray diffraction (XRD).** XRD patterns were recorded with a Rigaku SmartLab X-Ray diffractometer equipped with a 9 kW CuK\(\alpha\) rotating anode, operating at 40 kV and 150 mA. A Göbel mirror was used to convert the divergent X-ray beam into a parallel beam and to suppress the Cu K\(\beta\) radiation (1.392 Å). The diffraction patterns were collected at room temperature over an angular range \(2\theta=10^\circ\)-80\(^\circ\), with a step size of 0.02\(^\circ\) in a symmetric \(2\theta/\omega\) scan reflection mode.

**High Resolution Scanning Electron Microscopy (HRSEM) and Energy Dispersive X-ray spectroscopy (EDS).** The samples were stuck on aluminium stubs with ultra smooth double-sided adhesive tape, made of conductive carbon, specific for UHV systems and then coated with a 15 nm layer of conductive amorphous carbon. HRSEM observation was carried out using a JEOL JSM 7500FA scanning electron microscope, equipped with a cold field emission gun (single crystal tungsten <310> emitter, ultimate resolution of 1 nm) and operating at 10 kV. Images were taken in backscattered electron (BSE) imaging mode using a 2-segment solid state annular detector. EDS analysis was performed using an Oxford X-max LN\(_2\)-free Silicon Drift
Detector (SDD), with 80 mm$^2$ of sensor active area and 129 eV of energy resolution at 5.9 keV (MnK$\alpha$). The Extended Pouchou and Pichoir (XPP) matrix correction algorithm included in the

### Table S1
Parameters (A=Area; $x_c$= Peak Center; w=width) retrieved from the Lorentzian fit function used for fitting the Raman spectra for the sample presented below.

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\[
y = \frac{2A}{\pi} \frac{w}{4(x-x_c)^2 + w^2}
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XRD Data Analysis

The XRD patterns were analyzed by using a whole-profile Rietveld-based fitting program (FULLPROF) \([\text{Refinement of powder (Rietveld) and single-crystal diffraction data; } \text{http://www-llb.cea.fr/fullweb.}]\), as it follows: the instrumental resolution function (IRF) was evaluated by fitting the XRD pattern of a LaB\(_6\) NIST standard \([\text{National Institute of Standards and Technology; } \text{http://www.nist.gov/}]\) recorded under the same experimental conditions of the films; the IRF data file was provided separately to the program in order to allow subsequent refinement of the XRD patterns of the films. In this second step, the crystal structure model of tetragonal CH\(_3\)NH\(_3\)PbI\(_3\) beta-Methylammonium Lead Tri-iodide (space group I\(4\)cm; cell parameters: a=b= 8.849 Å and c = 12.642 Å; \(\alpha=\beta=\gamma=90^\circ\)) was provided to the software. Finally, the peak broadening of XRD pattern reflections was described by a phenomenological model based on a modified Scherrer formula:

\[
\beta_{h,k,l} = \frac{\lambda}{D_{h,k,l} \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{\text{imp}} a_{\text{imp}} y_{\text{imp}}^{\theta_h, \Phi_h},
\]

where \(\beta_{h,k,l}\) was the size contribution to the integral breadth of the \((h,k,l)\) reflection, \(a_{\text{imp}} y_{\text{imp}}^{\theta_h, \Phi_h}\) are the real spherical harmonics that were normalized according to a procedure described in \(^1\). After refinement of the \(a_{\text{imp}}\) coefficients (here only the first spherical harmonic has been refined, as there was no need to add other contributions) the program calculated the mean crystalline domain apparent size (\(D_{\text{mean}}\)). Preferred orientations (POs) were also introduced in the structural model, along the (110) and (002) crystallographic directions, using the March-Dollase function \(^2\):

\[
POD_{h,k,l} \propto G_2 + (1 - G_2) W (\alpha_{h,k,l}) = G_2 + (1 - G_2) \left( G_1 \cos \alpha_{h,k,l} \right)^2 + \frac{\sin^2 \alpha_{h,k,l}}{G_1} \right)^{-3/2}
\]
where $G_1$ and $G_2$ are refinable parameters describing the habit ($G_1$) of the crystallite/grains, and the fraction of not-textured sample ($G_2$). For platy habits ($G_1 < 1$) $\alpha_{h,k,l}$ is the acute angle between the scattering vector and the normal to the crystallites; for fiber habits ($G_1 > 1$), it is the acute angle between the scattering vector and the fiber axis direction. The March parameter, $0 < G_1 < 1$, determines the shape of the function $W(\alpha_{h,k,l})$ and, respectively, the strength of the preferred orientation: at $G_1 = 1$ (random powder), $W(\alpha_{h,k,l}) = 1$ and does not depend on $\alpha_{h,k,l}$; at $G_1 = 0$ (perfect uniaxial preferred orientation), $W(\alpha_{h,k,l})$ transforms to a delta function, and there is total preferred orientation.

Here, the two POs have been described with different $G_1$ refinable parameters.

Other refinable parameters were the unit cell parameters (a, c). The background was linearly interpolated and unrefined. The quality of the obtained fits was checked by means of a goodness-of-fit statistical indicator (GoF). GoF values of $<3-4$ were found, considered to be satisfactory, proving that the initial assumptions were founded.
Figure S1 Zoom of the XRD fitting analysis of the peaks at 28 degrees (experimental patterns and Rietveld fitted profiles). The markers of the reference structure are reported as well.

Ab initio calculation of the Raman spectrum of the pristine and Cl-doped MAPbI₃ perovskite

We calculated the Raman spectrum of the Cl doped (1:12) MAPbI₃ perovskite with the methods and models previously used for the pristine MAPbI₃. The structural model used in the present work is the structure 1 from Ref. 4, proposed for the tetragonal phase of the MAPbI₃ perovskite, see Figure S2. The concentration of Cl atoms in the mixed methylammonium lead halide MAPbI₃₋ₓClₓ is currently not known but an upper limit for the concentration of Cl, if it is present, has been proposed around ~3-4% ⁵. Here, we substituted one iodine atom in the apical position (over the 12 iodine of the tetragonal model) with a chlorine atom, thus introducing a doping of
~8\%, see Figure S2. Such level of doping is probably unrealistic but the present model allows to predict the variation of the Raman spectroscopic response of the MAPbI$_3$ in conditions of high-doping, and to determine the position of the vibrations involving mainly the Cl atoms. We then relaxed both the cell parameters and the atomic positions of the structure at the DFT level of theory and we calculated the Raman spectrum of the Cl-doped MAPbI$_3$ perovskite at the DFT level, with the well known methods reported in the literature $^{6,7}$.

Both structural optimization and vibrational spectroscopic response have been calculated at the DFT level of theory with the used of periodic boundary conditions, in the framework of the plane-wave/pseudopotential approach, as implemented in the quantum-espresso package $^8$. We used LDA, norm conserving, scalar relativistic pseudopotentials for all the atoms, together with a cutoff of 70 Ry for the wavefunction expansion and a 4x4x4 k-point mesh for the sampling of the First Brillouin zone.
**Figure S2.** Optimized structures of the MAPbI$_3$ and of MAPbI$_3$$_x$Cl$_x$ perovskites. The red circles in the latter highlight the position of the chlorine atoms.

In Figure S3 we compare the Raman spectrum computed for the Cl-doped MAPbI$_3$ perovskite with that calculated by some of the authors on the pristine material$^3$, in the 0-500 cm$^{-1}$ frequency region. The spectrum of the Cl-doped material differs from that of the pristine one, especially in the reciprocal intensity. This is likely to be due to the modification of the crystal structure introduced by the substitution of the iodine atom by chlorine. In fact, a substantial variation of the theoretical cell parameters is observed going from the pristine (a=8.85 Å, b=8.84 Å, c=12.93 Å) to the Cl-doped MAPbI$_3$ perovskite (a=8.86 Å, b=8.86 Å, c=12.62 Å). Thus, in presence of a Cl-doping of around the 8% of the MAPbI$_3$ perovskite, a strong decreasing in the crystalline cell
volume and a shrinking of the $c$-axis (about 2% for both the volume and the $c$-axis) is expected. Most notably, a clear vibrational signature of chlorine has been identified. The analysis of the normal modes demonstrates that vibrations involving mainly the Cl atom are present in the 140-180 cm$^{-1}$ frequency region, which largely contributes to the Raman signal in this region.

On the basis of these results, in presence of chlorine doping of the MAPbI$_3$ perovskite, a variation of the Raman response of this material is expected in the 140-180 cm$^{-1}$ frequency region. In particular a more intense signal associated to the vibration of the chlorine should be observed in this region.

Figure S3. Comparison of the theoretical Raman spectrum of the pristine and Cl-doped MAPbI$_3$ perovskite. Calculations at the DFT (LDA) level of theory.
References