

Influence of the Substrate on the Bulk Properties of Hybrid Lead Halide Perovskite Films

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Keywords: hybrid halide perovskites, Raman analysis, photoluminescence, synchrotron X-Ray diffraction

Abstract

In addition to the known effect of substrate on interfacial properties of perovskite films, here we show that bulk properties of Hybrid Lead Halide Perovskite films depend on the type of substrate used for film growth. Despite the relative large film thickness, ~600 nm, the roughness and nature of the substrate layer (glass, FTO, TiO₂ and PEDOT:PSS) affect not just the degree of preferential orientation and crystal grain size

but also the lattice parameters of $\text{CH}_3\text{NH}_3\text{PbI}_3$ films synthesized from PbCl_2 precursor. The obtained changes in lattice parameters indicate that Pb-Pb distance varies around 0.7%. We suggest that substrate roughness and chemical nature determine the concentration of defects mainly by varying chlorine content and probably by the incorporation of oxygen and iodine vacancies during film nucleation and growth. These differences have also consequences in the observed light induced transformations. Upon laser illumination, the formation of additional defects, most probably related to oxygen, is revealed by 110 and 165 cm^{-1} Raman peaks. For increasing laser power the chemical transformation into PbO_x is clearly identified by the 140 and 275 cm^{-1} Raman peaks. The irreversible photoluminescence enhancement observed at low power with illumination time, also dependent on the substrate nature, is proposed to be due to the localization of the electron-hole excitons created in the vicinity of the light generated defects. The results shed light into the performance of the perovskite layer and help understanding how bulk processes, where ion migration is a conspicuous example, are severely affected by interfacial properties as those imposed by the substrate.

1. Introduction

The structure and physical properties of hybrid perovskite organometallic halides $\text{CH}_3\text{NH}_3\text{MX}_3$ ($\text{M} = \text{Pb}$ or Sn , $\text{X} = \text{Cl}$, Br or I) were first reported by Weber in 1978.^{1,2} The first attempt to use $\text{CH}_3\text{NH}_3\text{MX}_3$ ($\text{X} = \text{Br}$ and I) as semiconductor sensitizer in dye-sensitized liquid junction-type solar cells was in 2009, leading to a power conversion efficiency (PCE) of 3–4%.³ But research in photovoltaic devices based on these materials was triggered in 2012 by the reported 10-11% PCE of a solid-state perovskite solar cell based on $\text{CH}_3\text{NH}_3\text{PbI}_3$ ^{4,5} (in short MAPbI_3) with a 500 h confirmed stability. Few materials have generated so much research production in recent years, allowing solar cells based on them to reach a top PCE up to 22.1% (KRICT, South Korea).⁶ Also, MAPbI_3 crystallizes easily from solution phase, enabling cost-effective processing such as spin-coating and printing. This development has been boosted by the band gap tailoring ability through chemical substitution, superior charge-transfer properties and, specially, advances in controlling the morphology and composition of these materials.^{7,8,9,10,11,12,13}

However, despite its outstanding performance, there is still much about their working principles that remains poorly understood as their photophysical properties and their relationship with structure and morphology. One clear example is the influence of contacts which affect charge separation and interfacial properties of perovskite devices but there are many results that point to a deeper influence. For example, the hysteresis observed in operation conditions is tightly related to ion migration, which is a bulk property, and is also strongly dependent on the choice of contacts. Different explanations have been provided in order to understand hysteresis observed for Perovskite Solar Cells (PSCs).¹⁴ The most accepted hypothesis attributes part of this hysteresis to bulk ion migration along the perovskite layer^{15,16,17} although this hysteresis

is also strongly affected by the kind of substrate employed.¹⁸ In this work we have investigated to what extent the substrate is influencing not just interfacial properties but also bulk properties of perovskite films by the use of different oxide and non-oxide substrates.

In the case of iodine perovskites, used for photovoltaic devices, it is worth to highlight the role of Pb precursors in the properties of the MAPbI₃ layer.¹⁹ Specifically, in this work, MAPbI₃ layers have been prepared using PbCl₂ precursor (in short MAPbI₃:Cl) with a reported Cl content lower than 0.2 % wt.^{20,21} MAPbI₃:Cl has demonstrated improved properties over MAPbI₃. While the bandgap is nearly identical to that of MAPbI₃, in MAPbI₃:Cl the carrier diffusion length is one order of magnitude larger than that of the MAPbI₃ (exceeding 1 μm) and exhibits improved charge carrier properties due to higher crystallinity.^{7,22,23,24} It has been shown that the perovskite film is intrinsically heterogeneous in crystal size, and that Cl plays an important role in improving the crystallization process.²⁰ However, the influence of the underneath layer on the stability, lattice parameters, orientation and the structure-properties relationship needs further understanding.

Halide perovskites exhibit a complex structural behavior with not clearly stated room temperature (RT) structure, having been proposed several tetragonal space groups: *I4cm*, *I4/mcm*, and *I4/m*.^{25,26,27} Lattice dynamics calculations reveal a significant coupling between low-frequency vibrational modes associated with the inorganic (PbX₃)_n framework and those of the organic CH₃NH₃⁺ cation, which emphasizes the interplay between molecular orientation and the corner-sharing octahedral framework in the structural transformations.^{28,29} These particularities together with the high sensitivity to ambient conditions and the instability under laser irradiation lead to a difficulty in the determination of the Raman modes, which are, in general, very useful

tools to track structural, compositional or electronic changes in solids. The low frequency part of the Raman spectrum is still unclear and there is a great diversity in the phonon identification, as well as in the reported evolution of the Raman peaks in different atmospheres and upon illumination.^{30,31,32} Also large variability of the photoluminescence (PL) wavelength for MAPbI₃ films has been reported remarking that mechanisms leading to these changes are not well understood yet.³³ Shifts of the PL peak up to 20 nm have been observed and related to grain size, either controlled by the substrate morphology^{20,34,35} or by the synthesis for aggregated perovskite dots.³⁶ On the other hand, theoretical studies correlate the optical band gap, and therefore PL wavelength, mainly with Pb-I-Pb bond angle and Pb-I bond length which could be controlled through the steric size of the molecular cation without altering the metal-halide chemistry.^{37,38} Grain size or defects located at the surface of the grains are invoked to explain the large emission wavelength variation observed both in bulk and films, though for different crystal size ranges, while theory points to modifications of the inorganic framework.

In this work perovskite films are grown on commonly used electron and hole injection layers: compact TiO₂, poly(3,4-polyethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS), commercial fluorine doped SnO₂(FTO) and bare glass for comparison. MAPbI₃:Cl films are compared with MAPbI₃ polycrystalline powder. Synchrotron X-Ray diffraction is used for an accurate structural characterization of films and bulk samples. Micro-photoluminescence (PL) and micro-Raman are used for in-situ monitoring the optical properties variations with irradiation power and time. First, we have identified the Raman and PL characteristics of unperturbed MAPbI₃ bulk powder and films at very low laser power and studied their evolution and transformation in room ambient conditions at increasing laser power. We find that the nature of the

underneath substrate influences the properties of the MAPbI₃:Cl films not only at the substrate-film interface as it is commonly believed but also the structure, morphology and composition of the whole film, so the bulk properties of the film. The different behavior for MAPbI₃:Cl on oxide and polymeric PEDOT:PSS layers is indicative of the influence of the nature of the substrate on the reactivity of the MAPbI₃:Cl film and on the role of oxygen in the radiative recombination.

2. Experimental details

2.1 Sample preparation

Glass and glass/FTO substrates were cleaned with soap and deionized water, followed by sonication in a mixture acetone/ethanol (1:1v/v) during 15 min. The cleaned substrates were further treated with UV (ultraviolet) – O₃ lamp during 15 min. The TiO₂ compact layer was deposited on glass/FTO by spray pyrolysis at 450°C using a solution of titanium diisopropoxidebis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) diluted in ethanol (1:39 v/v) and compressed oxygen as carrier gas. After spraying the precursor solution, the substrates were sintered on a hot plate during 5 min at 450 °C. Then, the hot plate was turned off, and the samples were left to cool down to room temperature. The PEDOT:PSS (Clevios P VP. Al 4083) layer was deposited by spin coating (3000 r.p.m. during 60 s). Then, the films were annealed on a hot plate at 150 °C during 30 min.

To obtain the hybrid halide perovskite MAPbI₃:Cl films, 100 μL precursor solution was prepared by mixing PbCl₂ and CH₃NH₃I (1:3 molar ratio) (Aldrich, used as received) in anhydrous dimethylformamide (DMF, 40% w/w) and spin coated in air by onto the substrates, previously heated at 70 °C during 10 min, and cured at 100 °C in an oven under air flow during 90 min. The films thickness of the MAPbI₃:Cl films is around

550-700 nm as evaluated by profilometry (Figure S2). Also, for comparison, bulk MAPbI₃ powder has been prepared by mixing 461 mg of PbI₂ and 158,9 mg of MAI and grinding in an agatha mortar. The color changed immediately obtaining MAPbI₃ as a brown-black powder.

2.2 Characterization techniques

The room temperature micro-photoluminescence (PL) and micro-Raman spectra were measured using 488 nm excitation wavelength of an Ar⁺ laser in backscattering geometry with an Olympus microscope, a “super-notch-plus” filter from Kaiser and a Jobin–Yvon HR-460 monochromator coupled to a Peltier cooled Synapse CCD. The light was collected from 0.8 μm or 4.5 μm diameter spots (corresponding to x100 and x20 objectives). Different neutral optical filters were used to avoid damaging the samples. The used laser power values were then: 6 μW, 50 μW, 100 μW or 4 mW. In situ PL measurements associated to Raman spectra were taken using the minimum output power density (6 μW, 12 W/cm²).

Synchrotron X-ray diffraction data were collected on a six-circle diffractometer (15 KeV; 0.826 Å) at the BM25B (SpLine) beamline at the European Synchrotron facility (ESRF), for the films deposited on the different substrates and for a powder sample at RT. A constant dry nitrogen flux was maintained on the samples to avoid possible degradation of the samples under the X-ray radiation in air. The six-circle diffractometer allowed different measurement configurations: i) the standard θ - 2θ configuration with the transferred momentum perpendicular to the substrate and ii) in a geometry which reveals the in-plane order. In this later case, the incident angle is fixed to 2° and the detector is scanned in the horizontal plane so that the transferred momentum has its larger component in the substrate plane. Diffraction maxima were fitted using a Voigt function starting from the instrumental resolution values for the

profile parameters. These starting values were obtained by fitting data obtained for a powder Si standard reference supplied by NIST. The background was modeled by use of a twelve coefficient polynomial function. Lattice parameters were refined by the profile matching (Le Bail fit) procedure using the FullProf program integrated in the WinPLOTR software.³⁹ The average crystallite size was calculated using the Scherrer formula. The width (in transferred momentum) of the diffraction maxima of the same family was constant for each film for the whole measured range so strain effects are discarded.

Even though MAPbI₃ is a highly reacting material at room conditions that may lead to its degradation that derives in the quenching of the PL emission, upon the suitable conditions (very low incident laser power), the qualitative evolution of the emission and Raman spectra upon illumination or in dark are reproducible for the films prepared on the same substrate and over different places for each films. AFM and diffraction experiments are totally reproducible.

3. Results and discussion

3.1. Morphology and crystal structure

To establish the correlation between the characteristics of the underneath layer substrate and those of MAPbI₃:Cl film (as grain size, crystal size and optical properties) a morphological and structural study is required. The morphology of the four substrates (glass, glass/FTO, glass/FTO/PEDOT:PSS and glass/FTO/TiO₂) has been analyzed by atomic force microscopy (AFM) (**Figure S1**) and that of MAPbI₃:Cl films by optical microscopy and contact profilometry (**Figure S2**). The average roughness measured by AFM in the substrates was: 3.2, 15.3, 0.8 and 6.8 nm for bare glass, FTO, PEDOT:PSS and TiO₂ respectively. The thicknesses of the MAPbI₃:Cl films were 650, 650, 550, and

750 nm for the films growth on glass, glass/FTO, glass/FTO/PEDOT:PSS, and glass/FTO/TiO₂, with roughness of 156, 143, 116 and 126 nm respectively.

The lattice parameters, preferential orientation and domain size were obtained for the MAPbI₃:Cl films on the four substrates and compared to the MAPbI₃ powder (bulk) sample. The MAPbI₃ powder pattern was fit within the non-centrosymmetric *I4cm* space group (in Supp. Info. **Figure S3** and **Table S1**) and the same group was used for the films (in Supp. Info. **Figure S4** and **S5**). The films show a very strong preferential orientation in the <110> direction as evidenced by comparing the relative intensities of the different reflections with those of the powder sample (**Figure 1a**), and in particular of (004) and (220) maxima (Figure S5). The tetragonal symmetry of MAPbI₃ perovskite can be approximated to a pseudocubic one where the correlation of the lattice parameters with the tetragonal description is as follows: $a_{pc} = b_{pc} = a_t/\sqrt{2} = b_t/\sqrt{2}$ and $c_{pc} = c_t/2$, inset of Figure 1. Note that the tetragonal (004) and (220) reflections result from the splitting of the (200) reflection in the pseudocubic perovskite representation.

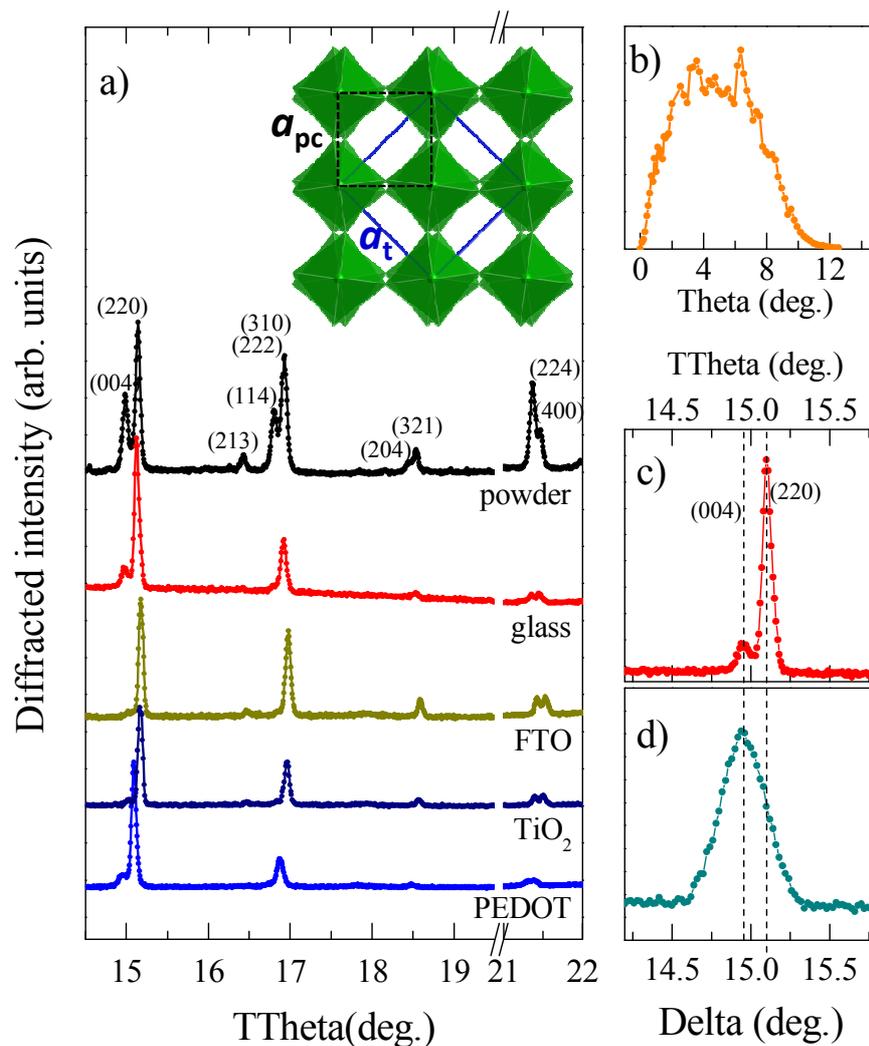


Figure 1. (a) Synchrotron X-Ray (15 keV = 0.826 Å) patterns of MAPbI₃:Cl films on glass (red), glass/FTO (FTO; olive), glass/FTO/TiO₂ (TiO₂; dark blue), glass/FTO/PEDOT:PSS (PEDOT; blue) and MAPbI₃ powder (black) for comparison. The allowed Bragg reflections in *I4cm* space group are indicated, (b) (220) rocking curve of MAPbI₃ on glass, (c) zoom of the θ - 2θ scan of MAPbI₃ on glass and, (d) of the δ scan of MAPbI₃ on glass. Inset: Crystal structure of MAPbI₃ on the *ab*-projection showing tetragonal and pseudocubic cells.

It can be seen that the intensity of all diffraction peaks with high *l* index (as 004, 213, 114, 204 or 224) are depleted indicating not only the prevalence of the $\langle 110 \rangle$ orientation but also that *c*-axis tends to be contained in the substrate plane for any of the other orientations. The width of the rocking curve of the (220) reflection (Figure 1b) indicates that the angular variation of the (220) grains around the surface normal is

around 4° . To test the in-plane orientation of the film on glass we recorded the diffracted intensity in a configuration with the transferred momentum almost parallel to the surface with a fixed incident angle (2°) and scanning the detector angle (δ) in the sample plane (Figure 1d). The comparison of this scan to the standard θ - 2θ scan (Figure 1c) clearly shows that (004) grains, and therefore c axis, are parallel to the substrate.

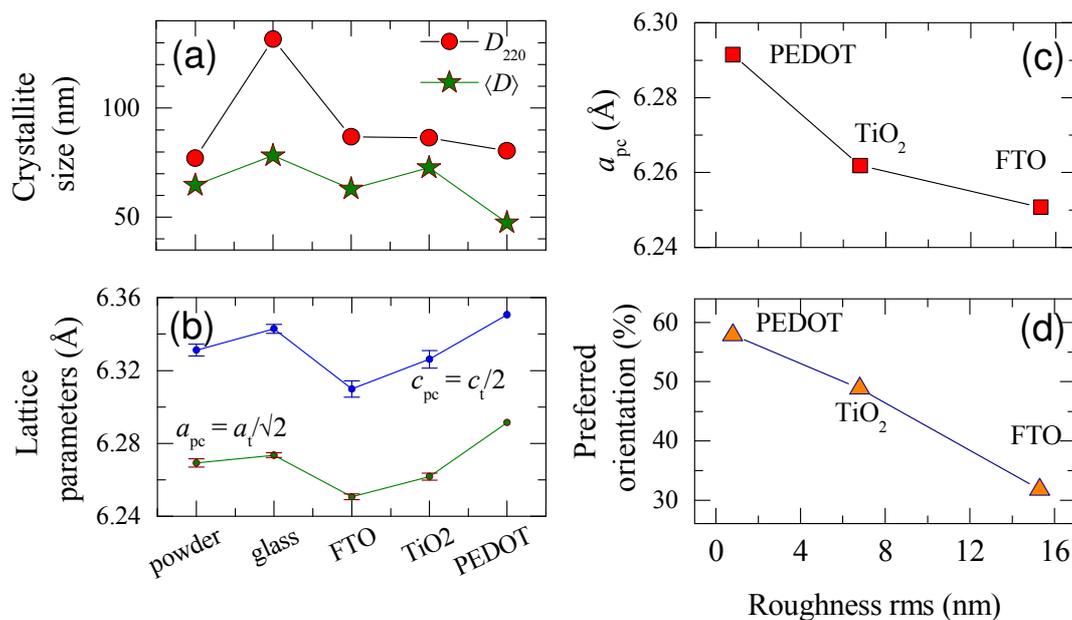


Figure 2.(a) Variation of the crystallite size for MAPbI₃:Cl on glass, glass/FTO, glass/FTO/TiO₂, glass/FTO/PEDOT:PSS and MAPbI₃ powder, for crystals in the $\langle 110 \rangle$ direction (red circles) and average value for the other directions (green stars) (b) Pseudocubic lattice parameters (a_{pc} and c_{pc}) of MAPbI₃:Cl for this series, (c) Substrate roughness dependence of the pseudocubic lattice parameter a_{pc} and (d) preferred orientation.

The crystallite sizes for the differently oriented grains (D_{hkl}) shown in **Figure 2a** are obtained from the full width at half maximum (FWHM) of the corresponding reflections. The results show that the sizes of the $\langle 110 \rangle$ oriented grains (D_{220}) are significantly larger than the average of the other orientations ($\langle D \rangle$) indicating a growth habit along $[110]$ tetragonal direction which correspond to $[100]_{pc}$ pseudocubic axis,

and this behavior is enhanced in the films especially when deposited on bare glass. The ratio between the integrated intensity of the 220 reflection and the total integrated intensity between 14.5° and 19.5° in two-theta (the definition is detailed in SI) provides an estimation about the $\langle 110 \rangle$ preferred orientation degree which is also indicating the random-oriented grain fraction of MAPbI₃:Cl films. The $\langle 110 \rangle$ preferred orientation fraction reaches its maximum for PEDOT:PSS substrate (**Figure 2d**).

A very important conclusion of this study is that the lattice parameters of the MAPbI₃:Cl films are found to be sensitive to the substrate, see **Figure 2b**. The obtained changes in lattice parameters indicate that the Pb-Pb distance varies around 0.7% for the film on PEDOT:PSS compared to that on FTO. The use of synchrotron radiation has allowed an accurate determination of the lattice parameters, see **Figure 2b**. Note that the variations reported from among different substrates are larger than the error bars. The substrate dependence of the pseudocubic lattice parameters is depicted in **Figure 2c**. The presence of an oxide substrate (FTO or TiO₂) produces a shrinking of both parameters (a_{pc} and c_{pc}) compared to those in bulk, while that of PEDOT:PSS layer below, with a quite different chemical nature, an increase. A physical origin of this dependence (strain imposed by the substrate) is not especially expected for these quite large MAPbI₃:Cl crystalline domains (from 80 to 140 nm) since no epitaxial growth is occurring. We therefore propose that the chemical nature and reactivity (related to the roughness and density of the underneath layer) of the substrate is modifying the lattice parameters more probably by varying chloride content as well as by the incorporation of oxygen and iodine vacancies in the MAPbI₃:Cl films during the synthesis.

Within each film, the crystallite size measured by diffraction is different depending on its crystallographic orientation relative to the substrate being larger for those grains [110] oriented (or [100] and [010] in the pseudocubic representation as shown in the

inset of **Figure 2**) for all substrates. The average crystal sizes vary in a range from 40 to 140 nm and the prevalence of (110) grains increases on smoother substrates. The (110) preferential orientation growth of MAPbI₃:Cl on TiO₂ (anatase) has been reported to be related to a higher binding energy between MAPbI₃:Cl (110) and TiO₂ (101) surfaces compared to that of the other orientations. The higher binding energy is calculated to be due to the better structural matching between rows of adjacent perovskite halides and TiO₂ under-coordinated titanium atoms due to the octahedral tilting in MAPbI₃.⁴⁰ However the present results indicate that this preferential orientation occurs for any of the evaluated substrates which are polycrystalline or even amorphous and thus do not present a defined orientation. When no epitaxy can occur between the film and the substrate, as it is the case, the denser planes usually grow parallel to the substrate. In fcc structures this corresponds to (111) planes or in hcp to (001), but here, using the pseudocubic representation, the grains are (100) oriented which is not the denser. This is therefore an intrinsic and specific characteristic of MAPbI₃. In a cubic perovskite the [100], [010] and [001] directions are totally equivalent and, in the distorted pseudocubic MAPbI₃ perovskite, these are also very similar directions. To explain the prevalence of (100)_{pc} grains we propose that, since the film grows directly from a solution onto the substrate, the driving force for the grain alignment may be the only strongly non isotropic component which is the axial the MA⁺ molecule. . The CN-methylammonium bond axis, in the non-centrosymmetric *I4cm* space group, is along the [001] direction which, for the (110) grains, lies in the perovskite-substrate interface. In this case we can understand that the substrate roughness is an important factor for the fraction of the grains (110) oriented, as evidenced in our results. The key point may rather be related to the orientation of MA cations on the surface. Moreover, the preferential (110) fraction is found to increase as the roughness of the underneath layer is reduced (**Figure 2d**)

indicating also that the interface morphology and chemical nature are playing a role in the nucleation and growth of the MAPbI₃:Cl grains. Previously we have reported that preferential orientation of perovskite layer is also influenced by the presence of scaffold.⁴¹

3.2. Photoluminescence and Raman analysis.

The measured steady state PL band maximum lies within in a close range, 775.5-779 nm, for MAPbI₃:Cl films on the different substrates exciting at 488 nm laser wavelength with very low power (6 μW, 12 W/cm²) (left panel of **Figure S6**) which corresponds well to the reported MAPbI₃ emission.⁴² We did not observed a large difference in the PL wavelength for the films contrary to the large variations reported before.^{20,36,34} The measured PL wavelengths do not correlate to the observed lattice parameters, which are directly related to the Pb-Pb interatomic distances. The homogeneity of the PL intensity for the different samples has been checked by micro-PL images within 20x20 μm size areas (right panel Figure S6). The most uniform emission is for the films on PEDOT:PSS and TiO₂ even if their roughness is very different (0.8 and 6.8nm).The structural and morphologic diversity of the films does not have important impact on the PL thus we find that the small changes in the emission peaks are not related to crystal size, within the 40 – 140 nm range, to substrate roughness up to around 16 nm or to obtained small variations of lattice parameters. Theoretical studies predict a variation of around 0.02 eV/degree for band gap energy with Pb-I-Pb angle.^{37,38} Assuming that the mayor effect derived from the observed lattice parameter variation (around 0.7%) is due to the change in Pb-I-Pb angles maintaining Pb-I bond lengths, a change in the band gap of 0.02 eV (10 nm), larger than that observed (3 nm), is expected. However experimental data for hybrid SnI³⁷

perovskites show variations in the 0 to 2 nm range for equivalent angle change. Therefore the observed wavelength shifts are more probably influenced by the presence of defects since substitutional Cl and oxygen and I vacancies may induce local modifications of the exciton binding energies.

3.2.1. Bulk perovskite

To study the influence in the emission properties of different parameters on MAPbI₃:Cl films, as their morphology or environmental and substrate effects in devices, it is important to undoubtedly identify possible degradation residues. These halide perovskites present low energy formation and therefore also require low energy to separate the perovskite solid into ions during operation.⁹ The laser itself and ambient conditions can induce degradation that may lead to misinterpretation because Raman signal from the perovskite can be much lower than those of precursor compounds and/or degradation products. In addition the kind of degradation observed depending on the substrate can provide important information on the influence of substrate in the film bulk properties. Raman spectra at different laser power were collected and compared with the spectra of possible residues generated upon light irradiation.

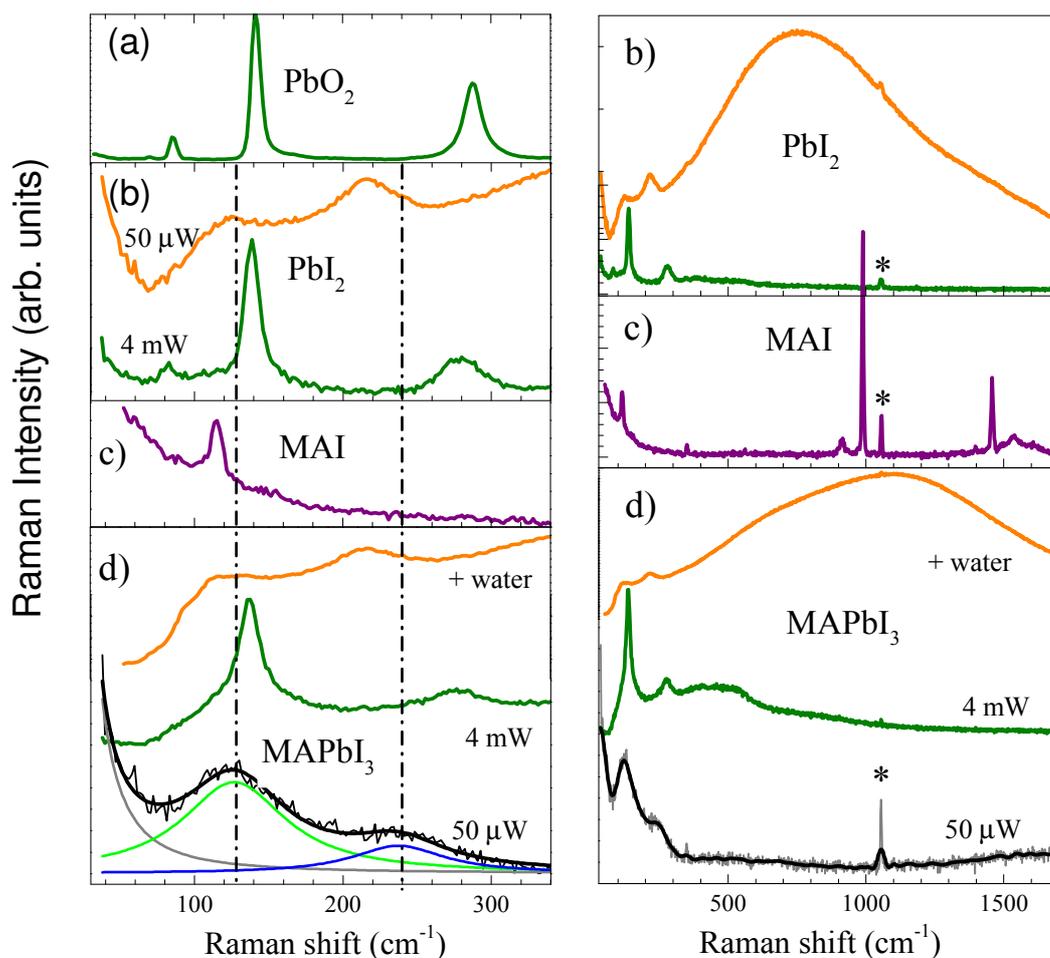


Figure 3. Raman spectra obtained with 488 nm excitation at RT for low (left) and high (right) frequency ranges of (a) PbO₂ (green line) and (b) PbI₂ polycrystalline samples. Resonant Raman spectra obtained at low laser power (orange lines) showing the typical Raman modes (left panel) and emission of PbI₂ (right panel) and, at high power (olive lines) show its transformation into PbO_x. (c) MAI (purple lines), (d) bulk MAPbI₃ spectra at low laser power (black lines with their fit), high power (olive lines) showing the transformation into PbO_x and low power with water droplet (orange lines) showing the transformation into PbI₂. The vertical dash-dot lines signal the MAPbI₃ Raman peaks. (* indicate laser plasma line).

The Raman spectra, obtained with 488 nm excitation wavelength, for bulk MAPbI₃ and for relevant related compounds (PbO₂, PbI₂ and MAI) are shown in **Figure 3** in the low frequency range up to 350 cm⁻¹, left panels, and in an extended range, right panels. In

Figure 3a, the olive line corresponds to PbO_2 spectrum. In Figure 3b, orange lines are the spectra of PbI_2 pressed pellet and small crystals present on the surface at low laser power ($50\mu\text{W}$, $2.5\text{kW}/\text{cm}^2$) while olive ones are measured with high power (4mW , $200\text{kW}/\text{cm}^2$). PbI_2 has an energy gap typically of 2.5 eV ⁴³ and is therefore Raman resonant under 488 nm (2.54 eV) excitation. In this situation the intensity of the peak around 210 cm^{-1} (assigned to a two-phonon mode) is enhanced compared to the first order Raman modes around $110\text{-}120\text{ cm}^{-1}$, this peak being not observable out of resonance. The broad band detected at 770 cm^{-1} in Raman shift (right panel) is more probably due to the exciton emission (2.45 eV) close to the bandgap of PbI_2 . The spectra are totally modified when increasing the laser power, from $50\mu\text{W}$ to 4mW . In this case the observed spectra correspond to lead oxide similar to that shown in Figure 3a. Different lead oxides can be formed (PbO , PbO_2 , Pb_3O_4) but all show a characteristic peak in the range $135\text{-}140\text{ cm}^{-1}$.^{44,45} In the present case the peak at 138 cm^{-1} and the presence of the two-phonon peak around 278 cm^{-1} indicate the transformation of PbI_2 into PbO_2 . This transformation is observed also for the films, as we will see below. Figures 3c collects the spectra of MAI, which is a precursor of the synthesis. Beside the internal modes of MA detected at frequencies above 900 cm^{-1} , a narrow Raman peak at 115 cm^{-1} is more probably due to a MA mode. MAI is totally stable with laser power.

MAPbI_3 is well known to be very susceptible to the laser power and to atmosphere, in particular to humidity. At very low laser power the obtained spectrum, plotted in black lines in Figures 3d, is very well fitted to two Lorentz functions peaking at 127 and 237 cm^{-1} . As the incident power is increased in low humidity atmosphere ($<40\%$) the spectrum is progressively modified reaching the situation plotted in olive lines which clearly corresponds to PbO_2 , as in the case of PbI_2 , measured at high power as previously described. In these conditions only the addition of a water droplet produces

the transformation to PbI_2 (orange spectra) showing both Raman modes and luminescence band. In any of these situations, transformation of MAPbI_3 into PbI_2 or PbO_x , the intense characteristic PL emission band of MAPbI_3 perovskite around 775 nm vanishes. Raman peaks in the range 135-140 cm^{-1} are undoubtedly indicating the formation of PbO_x . The experimental frequencies obtained here for the different compounds are summarized in **Table SI** together with some reported experimental and calculated ones. The observed MAPbI_3 band around 127 and 237 cm^{-1} are associated to MA^+ libration and torsional modes respectively. The assignment discussion is detailed in the Supp. Info.

This extreme susceptibility of MAPI_3 and the large width of the bands make difficult extracting information from the Raman spectra for these compounds. A key question is why Raman peaks are so poorly defined. On one hand the bandgap of MAPbI_3 (around 1.6 eV) is smaller than most of the laser excitation energies used for Raman spectroscopy therefore the high absorption and the use of highly focused beams produce important local heating of the samples. In our case we monitored the stability of the 775 nm characteristic PL emission and associated Raman spectra to elucidate if any transformation of the sample was occurring. Nevertheless, the actual temperature of the sample at the laser spot may be increased and, since MAPbI_3 suffers a structural transition at only around 30°C above RT, the sample can transit to the high temperature phase. In this case, the Raman modes may differ from those of the RT tetragonal $I4cm$ phase. Nevertheless a small temperature increase does not justify the observed large peak width. Above 160 K the MA^+ ions are tumbling within the inorganic cage.⁴⁶ This movements induces a dynamical disorder in the Pb-I octahedra which, through the coupling between MA and Pb-I octahedra, will influence the MA libration and torsional modes. This situation can be paralleled to the effect of polaron hopping in doped

manganese perovskites (as $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) in the paramagnetic phase. We reported that the hopping electron induces a dynamical Jahn Teller distortion of the perovskite structure so that wide poorly defined Raman peaks are detected.⁴⁷ We therefore propose that the Raman peak width is related to the dynamical deformations induced by the MA tumbling in the tetragonal and cubic or pseudocubic phases.

3.2.3 Films on different substrates

Similar formation of PbO_x lead oxide is observed also for the films on glass (**Figure 4**), FTO and FTO/ TiO_2 substrates (**Figure S7**). The identification of these peaks to PbO_x is crucial since some authors reported the 140 and 270 cm^{-1} peaks as MAPbI_3 phonons.³² Recently Kong et al.⁴⁸ reported that oxygen intercalation into the frameworks of MAPbI_3 induced by photocatalysis on the surface induces this 140 cm^{-1} peak. But in fact this peak is more probably related to the partial transformation of MAPbI_3 into PbO_x as the PL emission is quenched. Also, some authors associate the 140 cm^{-1} peak to the TiO_2 buffer layer.⁴⁹ But the usually small thickness of TiO_2 layers in devices, the nanosize of the particles, their uncertain ordering and the strongly absorbing MAPbI_3 overlayer make improbable the detection of Raman TiO_2 modes. Therefore, in this case also, these bands are indicating the formation of PbO_x . As far as we know there is no assignment to PbO_x phases in previous works.

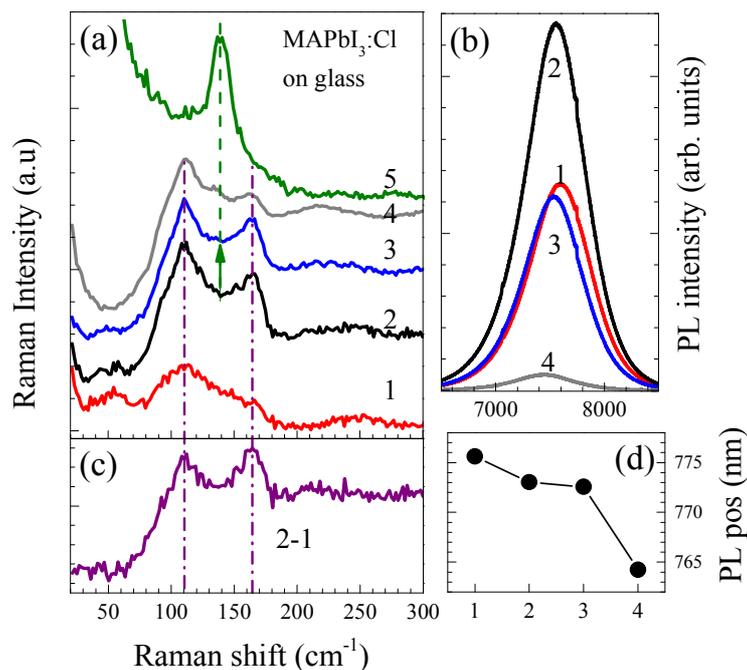


Figure 4. (a) Raman spectra of MAPbI₃:Cl film on glass at low power incident light (1, red line) and increasing laser power: 1= 50 μW (2.5 kW/cm²), 2= 100 μW (5 kW/cm²), 3= 1 mW (44 kW/cm²), 4= 3 mW (130 kW/cm²) and 5= 4 mW (200 kW/cm²) respectively, and (b) corresponding PL emission obtained at a constant low laser power, 6 μW (0.3 kW/cm²), just after recording the Raman spectra (c) difference of Raman spectra 1 and 2 and (d) evolution with irradiation of the PL wavelength for the 4 stages. Purple lines indicate the emerging peaks of the intermediate stage at 110 and 165 cm⁻¹ and green line and arrow the final PbOx stage.

The perovskite film has been intentionally degraded by increasing progressively the laser illumination power to obtain information about defects nature in the different samples analyzed. The Raman spectra obtained at different laser power and the PL recorded at constant very low laser power (6 μW, 0.3 kW/cm²) from the same location in the sample were obtained for the films on the four different substrates (Figures 4 and S7). In Figure 4 we can observe the Raman spectra for the perovskite film on glass with increasing incident power laser and their associated PL emission. At the lowest power (**stage 1**) the spectra are similar to that of bulk MAPbI₃ but in **stage 2** quite sharp peaks

at 110 and 165 cm^{-1} are detected concomitantly to a significant PL intensity increase (Figure 4b). In **stages 3** and **4** the PL decrease coincides with the appearance and increase of a peak at 138 cm^{-1} which we previously demonstrated to be the fingerprint of the formation of PbO_x , see Figure 3. Finally in **stage 5** the PL peak disappears completely (not shown) and major transformation to PbO_x within the laser spot occurs. Intermediate stage 2 is especially interesting since an enhancement of PL intensity is occurring, see **Figure 4b**. Light-induced halide migration has been reported to occur in metal halides such as PbBr_2 and PbI_2 .^{50,51} Also, halide vacancies and halide migration are energetically probable in hybrid halide perovskites.^{52,53} Thus, in this **stage 2**, the Raman modes at 110 and 165 cm^{-1} may be activated by the presence of different type of defects as halide vacancies and the incorporation of oxygen into these vacancies of the MAPbI_3 structure. Nevertheless halide vacancies are required for charge neutrality compensation of O^{2-} , therefore a certain concentration of vacancies will be present. The evolution of Raman spectra is similar for the films in all substrates except that for PEDOT:PSS where PbO_x phase cannot be identified, see Figure S7. Also the transformation degree for a given laser power is not identical for the four films.

It is important to highlight that Raman spectra are originated from the top part of the perovskite film as absorption depth for the employed excitation wavelength (488 nm) is around 85 nm, (much smaller than the film thicknesses) calculated from reported absorption coefficient.⁵⁴ Consequently the light induced observed changes are not originated in the perovskite/substrate interface but in the bulk of the film. Nevertheless, the different behavior observed for samples grown on oxide or on PEDOT:PSS substrates, see **Figure S7**, are explained by the influence of the substrate in the nucleation and growth of the film, not only in terms of structure and morphology but also regarding the type and relative content of point defects. So that the chemical nature

of bulk MAPbI_3 is indeed affected by the substrate which plays an important role in light induced modifications.

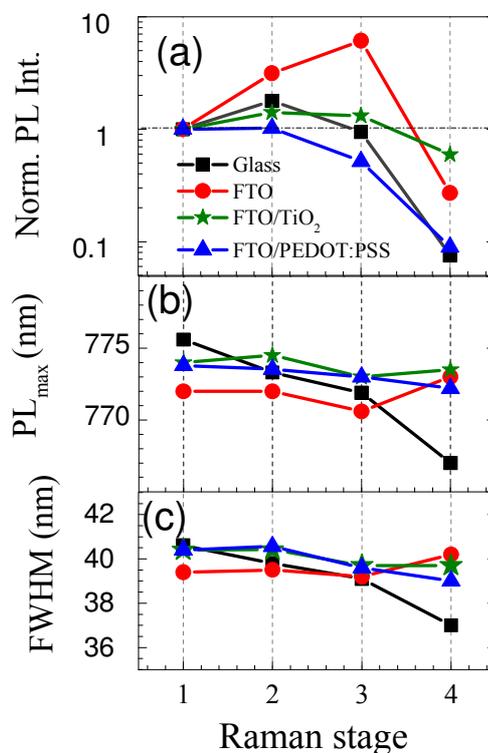


Figure 5. Evolution of the PL corresponding at each Raman stage induced by increasing incident laser power. (a) Evolution of the PL intensity normalizing at initial state, (b) wavelength and (c) FWHM.

Figure 5 summarizes the evolution of the corresponding PL band at each Raman stage (obtained after recording the Raman spectra at the same position with very low laser power) for the four films. Only small changes are detected in the PL wavelength and FWHM but the intensity does significantly vary. Associated to the appearance of Raman peaks related to the incorporation of oxygen, and possibly also of vacancies as mentioned above, (stages 2 and 3), the PL intensity increases and reaches its maximum value either in stage 2 or 3 depending on the substrate. In stage 4, when the transformation to PbO_x is evidenced in Raman spectra, the PL intensity decreases. We

propose that the intensity increase in stages 2 - 3 can be related to e-h exciton localization by the photo-induced defects. The localization of the excitons would enhance the radiative recombination probability by hindering charge mobility. The different behavior for MAPbI₃:Cl on polymeric PEDOT:PSS layer, where increasing the incident power does not produce an increase in PL intensity, is indicative again of the influence of the nature of the substrate in the final properties of the perovskite film.

At the lowest incident laser power the Raman spectra of the samples do not evolve apparently but, maintaining sufficient time the laser beam illuminating the samples can induce stage 2 and PL shows changes over time. Upon illumination, PL emission of MAPbI₃:Cl films again exhibits different effects for the different substrates, despite excitation light is absorbed on top perovskite layer far from the substrate. **Figure 6** shows the evolution of the PL wavelength, full width and intensity normalized to the initial state different times under illumination of 6 μW (12 W/cm²) 488 nm laser light (solid symbols) and dark condition (open symbols) up to 4 hours for the films on the four substrates. The PL intensity experiences an irreversible enhancement of different degree depending on the substrate, being more pronounced for oxide substrates. The intensity continuously increases upon illumination and, after the laser light is turned off and the sample is kept in the dark, the PL remains almost constant for hours. The observed effect is therefore not reversible, contrary to ref ⁵⁵ for MAPbI₃ in N₂ atmosphere, and we conclude that the creation of defects is permanent.

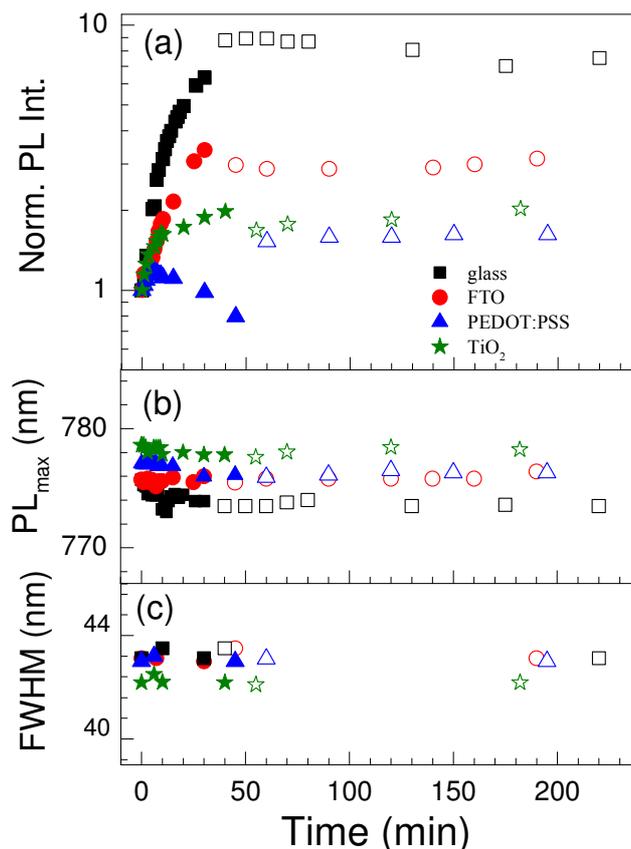


Figure 6. (a) Evolution of the PL intensity normalized to initial state measured at very low incident laser power ($6 \mu\text{W}$, 12 W/cm^2) (b) PL wavelength, and (c) full width at half maximum (FWHM) over time up to 4 hours for the films on the four substrates, under illumination of 488 nm laser light (solid symbols) and dark (open symbols). Black square for glass, red circles for FTO, green stars for TiO₂ and blue triangles for PEDOT:PSS.

Studies of the PL properties in air, nitrogen, and oxygen/helium environment suggest that oxygen is important for PL enhancement.⁵⁶ In fact, the role of oxygen is supported by the fact that PL intensity decreases upon white illumination in N₂ environment.^{55,55,57} PL intensity enhancement upon illumination in ambient conditions has been reported and tentatively explained by a catalytic reaction induced by oxygen in inorganic SrTiO₃ thin film perovskite.⁵⁸ Other studies reported diverse behaviors of the photoluminescence of MAPbI₃:Cl upon light irradiation and environments. A slow rise of the PL over a time scale of seconds⁵⁹ has been associated with the passivation of gap

states acting as subgap nonradiative pathways. Nevertheless most defects are shallow traps and are therefore not expected to act as non-radiative decay paths.^{60,61} At longer irradiation times, minutes, a PL enhancement, and lifetime increase from nanoseconds to hundred nanoseconds, has been observed⁶² and associated to the de-activation by a photochemical reaction involving oxygen of trapping sites responsible for non-radiative charge recombination. Which are the initial traps and where the oxygen incorporates is not clarified. On the other hand, Shi et al.⁶³ calculated the defect states involving oxygen suggesting that small O^{2-} ions for Γ vacancy replacement is feasible. The calculations are compatible with the here proposed scenario in which laser illumination and oxygen presence induce the incorporation of oxygen and the presence of iodine vacancies and substitutional Cl^- with different concentrations depending on the substrate. The samples with more stable behavior over time, films on TiO_2 and FTO, can obtain oxygen diffused through the surface and from the layer below, contrary to the film on glass. Consequently the substrate induced changes in the $MAPbI_3:Cl$ film structure, more probably originated by different concentrations of defects (likely substitutional Cl , oxygen or vacancies), and the nature of the substrate determine the emission properties and the sensitivity to light. Ambient oxygen is a relevant factor in the observed PL enhancement associated to stage 2 and the peaks at 110 and 165 cm^{-1} observed in Raman spectra could be indicative of its incorporation. Our results provide important insights in the importance of the nature of the substrate on the bulk properties of halide perovskite grown on its top, aimed to provide important clues on working mechanism of PSCs and pointing to optimize the performance of perovskite based optoelectronic devices.

Conclusions

In summary, we have shown that the substrate influences the bulk properties of the MAPbI₃:Cl films by a systematic structural and optical characterization of perovskite films grown on glass, glass/FTO, glass/FTO/PEDOT:PSS and glass/FTO/TiO₂ substrates. The perovskite films present a strong preferential orientation in the <110> direction for any of the evaluated substrates. The preferential (110) fraction is found to increase as the roughness of the substrate is reduced indicating that the interface morphology is playing a role in the nucleation and growth of the MAPbI₃:Cl grains. The key point may be related to the orientation of the CN-methylammonium bond axis at the MAPbI₃:Cl-substrate interface which is parallel to the substrate for the (110) grains in the non-centrosymmetric *I4cm* space group. The average crystal sizes vary in a range from 40 to 140 nm and the prevalence of (110) grains increases on smoother substrates. Besides, the chemical nature and reactivity of the substrate is modifying also the lattice parameters by varying chlorine content as well as by the incorporation of oxygen and probably iodine vacancies in the MAPbI₃:Cl films during the synthesis. The obtained changes in lattice parameter indicate that Pb-Pb distance varies around 0.7%.

Low frequency Raman modes of bulk and films are broad peaks around 127cm⁻¹ (MA libration) and 237 cm⁻¹(MA torsional mode) and their widths are related to dynamical deformations of the Pb-I octahedra induced by the MA tumbling. Light induces the progressive modification of the perovskite up to its transformation into PbO_x revealed by Raman peaks at around 138 and 270 cm⁻¹ besides PL quenching. The addition of water is required for its transformation into PbI₂ (110 and 220 cm⁻¹ Raman peaks). A different behavior for MAPbI₃:Cl films grown on oxide layers (TiO₂ and FTO) is observed compared to that on PEDOT:PSS polymer where PbO_x is not detected. An intermediate stage shows quite sharp peaks at 110 and 165 cm⁻¹ concomitantly to a

significant PL intensity increase in all substrates except on PEDOT:PSS. These Raman peaks may be activated by the presence of defects as oxygen incorporation and halide vacancies.

A non reversible increase of PL with illumination time has been observed for samples on oxide substrates but not for that on the polymer substrate. The intensity increase can be related to localization of a fraction of the electron-hole excitons by the photo-induced defects enhancing the radiative recombination by hindering charge mobility. The different behavior for MAPbI₃:Cl on PEDOT:PSS layer is indicative of the influence of the nature of substrate on the reactivity of MAPbI₃ films and the role of oxygen in the radiative recombination rate.

The mechanism that we propose for the observed changes in the structure, crystal size and preferential orientation of the perovskite films as a function of the substrate are due mainly to the roughness of the surface but also to its chemical nature. The substrate roughness is a key factor in the morphology of the perovskite grains but also in the concentration of defects (substitutional Cl, oxygen and vacancies) by providing different density of nucleation sites and grain growth dynamics. On the other hand, the different behavior with illumination time and power of the films synthesized on polymeric substrate (PEDOT) compared to the inorganic oxide ones (TiO₂, glass and FTO) indicate that the chemical nature of the substrate is playing a role in the relative concentrations of the point defects. These defects are originated within the perovskite film structure during the growth which in turn gives rise to the different degradation and modification with illumination. We also demonstrate the influence of the nature of the substrate on the reactivity of the MAPbI₃ film and the role of oxygen in the radiative recombination rate.

This work highlights how substrate influences not just the interfacial properties of perovskite devices but also bulk perovskite properties, fact with important implications on the PSC working mechanisms. In this sense, major implications on the solar cell performance can be anticipated from the substrate choice and it will have important implications on the device optimization.

Acknowledgments

Funding by the Spanish Ministerio de Economía y Competitividad (MINECO) under Projects MAT2015-65356-C3-1-R and 2-R, MAT2014-54852-R and MAT2015-70611-ERC and Comunidad de Madrid Excellence Network under Project S2013/MIT-2740 (and Associated Lab LABCADIO belonging to CM net labs ref. 351) is acknowledged. We also acknowledge the MINECO for financial support and provision of synchrotron radiation facilities at ESRF and thank María Vila for her assistance in using beamline BM25-SpLine. B.C.H is grateful to the support of the National Council of Technological and Scientific Development (CNPq), Brazil, through the Science without Borders program.

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