Chloride in Lead Chloride-Derived Organo-Metal Halides for Perovskite-Absorber Solar Cells


ABSTRACT: Organo-metal halide perovskites are an intriguing class of materials that have recently been explored for their potential in solar energy conversion. Within a very short period of intensive research, highly efficient solar cell devices have been demonstrated. One of the heavily debated questions in this new field of research concerns the role of chlorine in solution-processed samples utilizing lead chloride and 3 equiv of methylammonium iodide to prepare the perovskite samples. We utilized a combination of X-ray photoelectron spectroscopy, X-ray fluorescence, and X-ray diffraction to probe the amount of chlorine in samples before and during annealing. As-deposited samples, before annealing, consist of a crystalline precursor phase containing excess methylammonium and halide. We used in situ techniques to study the crystallization of MAPbI₃ from this crystalline precursor phase. Excess methylammonium and chloride evaporate during annealing, forming highly crystalline MAPbI₃. However, even after prolonged annealing times, chlorine can be detected in the films in X-ray fluorescence measurements.

1. INTRODUCTION

Perovskite-absorber solar cells have become a research area with high expectations for their potential in revolutionizing solar energy conversion technology. Seminal work utilizing hybrid organic–inorganic absorber materials as light harvesters in liquid electrolyte dye-sensitized solar cells demonstrated promising efficiency metrics but low stability due to the rapid dissolution of the perovskite absorber in the liquid electrolyte environment. After replacing the liquid electrolyte with a solid hole transporting material, efficiencies of solar cell devices incorporating the perovskite-absorber methylammonium lead iodide (MAPbI₃) have undergone an unprecedented climb in the past 2 years. High solar energy conversion efficiencies have been achieved for device architectures derived from solid-state dye-sensitized solar cells as well as for devices utilizing an inert metal oxide as a scaffold and thin-film devices.

In the first reports, the organo-metal halide was deposited in one step from a solution containing lead iodide (PbI₂) and methylammonium iodide (MAI) in equimolar ratio dissolved in gamma-butyrolactone. Lee et al. reported a different deposition approach using lead chloride (PbCl₂) as the source for lead and a 3-fold excess of methylammonium iodide. Compared to the equimolar deposition route, this deposition method requires annealing at 100 °C for 45 min until the perovskite absorber is fully formed. While early reports suggested a composition of MAPbClₓI₃₋ₓ, the exact amount and role of chlorine in PbClₓ-derived organo-metal-halide perovskites has been debated, and the stoichiometry of this material is frequently stated as MAPbClₓI₃₋ₓ en lieu of a more defined stoichiometry. While the bandgap of MAPbClₓI₃₋ₓ is nearly identical to MAPbI₃, the chlorine-derived compounds have been shown to exhibit superior charge carrier diffusion lengths. Infiltrated into mesoporous titania, MAPbClₓI₃₋ₓ had a considerably lower series resistance compared to that of pure MAPbI₃. The differences in the optoelectronic properties could thus be due to chlorine doping, passivation of trap states, or differences in sample crystallinity. Unlike the mixed bromide–iodide methylammonium lead halides, the chloride–iodide mixed halide perovskites exhibit low miscibility. Thin-film samples are often found to be highly oriented with the (110) direction perpendicular to the substrate. In this case, no scattering information is collected from other crystallographic directions in conventional θ–2θ X-ray diffraction (XRD) measurements, preventing the full determination of the crystal
structure. Early work speculated, therefore, that chloride is incorporated into the perovskite structure along the (001) direction.12,13 Powder-XRD analysis of scraped-off PbCl2-derived thin films exhibited lattice parameters suggesting a stoichiometry close to that of pure MAPbI3 with a maximum atomic ratio of 3 to 4% chlorine to iodine in MAPbClI3-x.12 From X-ray photoelectron spectroscopy (XPS) analysis, the chlorine content of fully annealed films was found to be on the order of 1% (Cl to I).2,13 It was therefore suggested that pure MAPbI3 forms even in the preparation route using PbCl2 and 3 MAI as precursors, with excess MACl subliming during annealing.21,23 In this article, we studied the formation kinetics and analyzed the chlorine content of perovskite-absorber thin films deposited from PbCl2 and 3 equiv of MAI in DMF before, after, and during annealing. Chlorine was detected in the nonannealed films using X-ray photoelectron spectroscopy (XPS), energy-dispersive X-ray spectroscopy (EDX) during annealing at 100 °C for various time spans. For annealing experiments performed outside of the glovebox, exposure of samples to ambient environment was minimized, as this causes rapid sample degradation (see Figures S1 and S2 and brief discussion in Supporting Information). For samples used for X-ray fluorescence measurements, samples were annealed at 95 °C, as temperatures lower than 100 °C have been reported to give better substrate coverage.30

For solar cell devices, chlorine-containing conducting glass substrates (FTO, Pilkington TEC15) were partially etched using 2 M HCl and Zn powder, cleaned following the procedure described above, and covered with a ca. 50 nm dense TiO2 layer via spray-pyrolysis at 450 °C using a commercial airbrush and compressed air as a carrier gas. After annealing, the perovskite layers were contacted with a hole transporting layer consisting of spiro-OMeTAD (2,2′,7,7′-tetrakis[N,N-diphenylamino]-9,9′-Spirobifluorene, Lumtec) containing 12 mol % of a pre-oxidized spiro-OMeTAD (TFSi2)2 compound synthesized as described elsewhere,31,32 3 mM of LiTFSi (bis(trifluoromethane)sulfonimide lithium salt, Aldrich) predissolved in dry acetonitrile (Acros), and 0.2 M t-BP (4-tert-butylpyridine, Aldrich). Gold contacts (50 nm) were evaporated to form the back contact of the devices. Current density–voltage (J–V) measurements on solar cell devices were performed with a software-controlled potentiostat (2400 Series SourceMeter, Keithley Instruments) under 100 mW cm−2 AM 1.5 irradiance (Abet Class AAB sun 2000 simulator). Current–voltage measurements were carried out with 50 mV steps and a delay time of 5 s after each step from open circuit to short circuit to avoid artifacts from hysteretic phenomena.32 The light source was calibrated with an NREL-calibrated KG5 filtered Si reference cell. During testing, the solar cells were masked with a metal aperture of 0.12 cm2, whereas the area of the evaporated counter electrode was 0.2 cm2.

Grazing incidence wide-angle X-ray scattering was measured at beamline 11-3 at the Stanford Synchrotron Radiation Lightsource (SSRL). Silicon substrates were treated with a 40 mM TICl3 solution and annealed at 450 °C for 30 min to deposit a thin layer of TiO2. Data was collected at an X-ray energy of 12.7 keV and an incident angle of 1.5° to ensure that scattering occurred from the bulk of the thin film. Exsitu scattering was collected using a Mar 345 image plate as the detector. Two-dimensional data was reduced using the WxDiff software developed by Dr. Stefan Mannsfeld. Fitting of the collected diffraction pattern to extract the lattice parameters and space group was accomplished using the GSASII software.53 The sample-to-detector distance was 250 mm and calibrated using a LaB6 standard. In situ X-ray-diffraction (XRD) experiments were carried out using a lab-scale Panalytical X’Pert Pro X-ray diffractometer equipped with a temperature control stage. In situ absorption experiments were carried out using an Ocean Optics UV–vis fiberoptics spectrometer equipped with a reflectance probe placed closely above the sample on a hot plate during annealing at 100 °C. X-ray photoelectron spectra (XPS) were recorded on a SSI S-Probe XPS spectrometer. X-ray fluorescence measurements (XRF) on samples annealed for different amounts of time at 95 °C were taken at a fixed X-ray energy above the absorption edge using a Vortex Detector (Cl: K-edge = 2822 eV, Pb: M3-edge = 2484 eV and M4-edge = 2586 eV). Samples were excited at an energy of 3000 eV to study fluorescence from both Cl and Pb as well as 2800 eV, which causes only Pb to fluoresce. The elemental composition was also analyzed using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray (EDX) analyzer.

2. EXPERIMENTAL SECTION

Methylammonium iodide (MAI) was prepared as described elsewhere using a 2-fold molar amount of methylamine (Sigma-Aldrich) with respect to hydroiodic acid (HI, 57% in water, Aldrich).3,5 Methylammonium iodide (0.42 g, 2.64 M, 3 equiv) and lead(II) chloride (0.24 g, 0.88 M, 1 equiv, Sigma-Aldrich) were dissolved in anhydrous N,N-dimethylformamide (Sigma-Aldrich). For optical and structural characterization, samples were prepared on microscope glass slides. All substrates were cleaned by the following procedure: sonication in Extran (15 min), rinsing with deionized water (3 times), sonication in acetone (15 min), sonication in isopropanol (15 min), and a UV–ozone treatment (15 min). The perovskite layer was deposited by spin-casting ca. 50 µL of the precursor solution onto the substrates at 4000 rpm for 30 s in a glovebox environment followed by annealing at 100 °C for various time spans. For annealing experiments performed outside of the glovebox, exposure of samples to ambient environment was minimized, as this causes rapid sample degradation (see Figures S1 and S2 and brief discussion in Supporting Information). For samples used for X-ray fluorescence measurements, samples were annealed at 95 °C, as temperatures lower than 100 °C have been reported to give better substrate coverage.30
3. RESULTS AND DISCUSSION

3.1. Solar Cell Devices. Solar cell devices were prepared in a glovebox environment. The annealing time following spin-coating deposition of the PbCl$_2$/3 MAI precursor was varied, 0, 20, 40 to 60 min at 100 °C. Nonannealed samples (0 min) turned brown in color after drying, and XRD peaks were consistent with the 110 and 220 reflections of MAPbI$_3$ (Figure S1). However, nonannealed samples and those annealed only for 20 min were found to rapidly degrade when exposed to ambient environment changing in color and morphology to yellowish, needle-shaped crystals (Figure S2).

The device performance analysis of thin-film perovskite devices by current–voltage measurements is strongly affected by hysteresis as we discuss elsewhere. For the investigation of methylammonium halide. After 20 min of annealing, the degradation due to the hygroscopic nature of the excess e could be achieved. The average device e remains low. After 40 min of annealing, device efficiencies of up to 8% could be achieved. The average device efficiency for samples annealed for 60 min is comparable. Annealing for more than 40 min at 100 °C is thus crucial to attain perovskite–absorber films with high solar-to-electrical power conversion efficiencies.

3.2. XRD of Annealed Samples. Samples of MAPbCl$_{1-x}$I$_x$ thin films deposited on planar substrates and annealed for 45 min at 100 °C were found to be very crystalline and highly oriented, apparent in the dominance of the 110, 220, and 330 reflections of the tetragonal perovskite phase (Figure S4), in agreement with other reports. To analyze other crystallographic reflections, we performed grazing-incidence wide-angle X-ray scattering (GIWAXS) on a sample of MAPbCl$_{1-x}$I$_x$ deposited onto a silicon wafer substrate covered with a thin TiO$_2$ layer to minimize scattering from the background, shown in Figure 2. The sample was annealed for 45 min at 100 °C.

The intensity variation as a function of polar angle (ϑ) within the observed diffraction rings is typical for crystalline films with an orientation that is partly isotropic and partly oriented, giving rise to the more intense arcs and the strong (110) family of peaks observed in the θ–2θ XRD spectra (see Figure 5a or Figure S4). Similar GIWAXS patterns have been reported by others. Figure 2 (bottom) shows the integrated peak intensity over all polar angles as a function of the 2θ angle equivalent to the Cu Kα X-ray source.

The intensity variation as a function of 2θ angle was converted to match other data reported herein that was measured using Cu Kα radiation for XRD experiments (e.g., Figure 5a or Figure S4). This sample was found to be a tetragonal crystal structure with lattice parameters of a = 8.84 Å and c = 12.64 Å. For comparison, we also measured the θ–2θ XRD spectra of MAPbCl$_{1-x}$I$_x$ deposited onto a mesoporous alumina substrate (Figure S4). The mesoporous scaffold randomizes the crystal orientation sufficiently to detect crystallographic reflections from other lattice planes. From this sample, the lattice parameters of the tetragonal MAPbCl$_{1-x}$I$_x$ were determined to be a = 8.87 Å and c = 12.65 Å.

Due to a larger difference in ionic radii, the miscibility of the Cl/I mixed halide perovskite absorbers is lower, unlike for mixed Br/I methylammonium lead halides where a homologous series of the mixed halides could be obtained. To determine the Cl content from the small variation in lattice parameter, we utilized the dependence of the unit cell volume (V$_{cell}$) on the effective halide ion radius for the tetragonal mixed...
bromide–iodide MAPbBr\(_{3-x}\)–MAPbI\(_x\) perovskites, accounting for the difference in atomic radii between chloride and bromide (Figure S5).\(^7\) From this relation, the maximum amount of Cl incorporated into the crystal lattice of the mixed halide MAPbCl\(_{3-x}\) is \(x = 0.15\), or 5% of the total halide concentration. This agrees with results presented elsewhere.\(^{12}\)

For the sample on Al\(_2\)O\(_3\) (Figure S3), the estimated chloride concentration is only \(x = 0.05\), or 1.7%, with respect to the total halide concentration. These values indicate that there may be residual chlorine present in perovskite-absorber samples derived from PbCl\(_2\). However, comparison with literature values for pure iodide MAPbI\(_3\) single crystals,\(^{34–36}\) PbCl\(_2\)- and PbI\(_2\)-derived thin films,\(^{12}\) as well as PbCl\(_2\)-derived samples on mesoporous scaffolds\(^{25,26}\) (Table S1) shows that there is a huge variance in reported values. The values for MAPbCl\(_{3-x}\) determined herein are slightly smaller than those reported for other MAPbCl\(_{3-x}\) samples\(^{12,25,26}\) but are comparable to pure MAPbI\(_3\) single crystals. This illustrates that it is not trivial to determine the Cl content from lattice parameters determined from XRD measurements, as thin films or samples deposited onto scaffolds can be inherently strained compared to bulk crystals. Thus, caution must be used when inferring Cl concentration from XRD lattice parameters.

### 3.3. MACl Evaporation

We noticed deposition of a white residue on the Petri dish used to cover samples during annealing. The recorded X-ray diffraction spectrum of this precipitate is shown in Figure 3 in comparison with data recorded for a film made by evaporation of pure MACl at similar conditions and the literature XRD spectra for MACl.\(^{37}\) All peaks but the one at a 2θ angle of about 32° correspond to the tetragonal (P4/\(nmn\)) MACl phase with \(a = b = 6.04\) Å and \(c = 5.05\) Å, reported previously.\(^{37}\) The peak at 32° remains unidentifiable; it matches a peak from crystalline HCl\(_3\) but no additional peaks were observed that allow definite identification of this phase.

This is direct evidence for the sublimation of MACl during sample annealing at 100 °C hypothesized elsewhere.\(^{3,21}\) The temperature of MACl sublimation is predicted to be above 250 °C from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).\(^{21}\) In DSC experiments, we observed a small exothermic peak at 224 °C for a pure MACl sample (Figure S7). From DSC measurements of dried and scraped-off precursor samples, no strong evidence of MACl sublimation at 100 °C or lower was observed. The weak exothermic peak at 50 °C was obscured by a strong endothermic peak at 76 °C, which may indicate the onset of perovskite crystallization. A high surface-to-volume ratio in thin films and ground MACl samples can explain sublimation at a temperature below the value for pure MACl. Possibly, the heat dissipating in the sample during the formation of methylammonium lead iodide further promotes evaporation of excess MACl. In addition, the excess methylammonium and halide do not necessarily exist as MACl but likely as dissociated ions in the precursor phase. It is possible that excess halide and methylammonium leave the sample as methylamine and hydrochloric acid rather than MACl.

Perovskite-absorber samples can also be prepared from PbI\(_2\) and 3 equiv of MAI as precursors.\(^{37,18}\) We utilized this approach to see whether slow growth from a precursor phase containing excess methylammonium halide is sufficient to form highly crystalline perovskite-absorber thin films. In this case, annealing temperatures on the order of 150 °C were necessary to form MAPbI\(_3\), which is consistent with temperatures reported for the evaporation of MAI.\(^{39}\) In DSC measurements of pure MAI, we observed a small exothermic peak at 144 °C (Figure S7). The PbI\(_2\)-derived samples consisted of smaller, disoriented crystallites, and the photoluminescence lifetime of these samples was 2 orders of magnitude lower compared to that of PbCl\(_2\)-derived samples (Figure S8), in agreement with results reported elsewhere.\(^{17,40}\) This indicates that excess methylammonium halide alone is not the reason for the formation of highly crystalline and oriented thin films but that sublimation of MACl at a lower temperature compared to that for MAI is beneficial, as overannealing can be avoided.

### 3.4. In Situ Analysis of Film Formation

We investigated the formation of MAPbCl\(_{3-x}\) during annealing at 100 °C inside the glovebox environment by monitoring the evolution of the absorption spectra with a fiber optic UV–vis spectrometer equipped with a reflectance probe. The evolution of the sample absorption during the annealing processes is shown in Figure 4a. After 10 min of annealing at 100 °C, the absorption below 740 nm starts to increase, indicating the formation of MAPbCl\(_{3-x}\). During the consecutive 30 min, the increase in absorbance indicates growth of MAPbCl\(_{3-x}\). No further changes in the absorption spectra were observed after 40 min of annealing, suggesting that the formation of MAPbCl\(_{3-x}\) is complete. This agrees with reported annealing times of 45 min at 100 °C necessary to prepare photovoltaic devices discussed in Section 3.1. The time evolution of the absorption spectra also reveals an increased absorption around 570 nm. This could be indicative of the formation of an intermediate phase preceding the formation of MAPbCl\(_{3-x}\).
We also performed in situ XRD measurements on an X-ray diffractometer equipped with a temperature control stage. As we could perform these experiments only in an ambient environment, as-deposited samples were transferred as rapidly as possible from an inert atmosphere container to the heat stage at 100 °C. At room temperatures, rapid degradation of the as-deposited precursor was observed when exposed to ambient humidity, as discussed in Figures S1 and S2. Methylammonium lead iodide crystals are known to degrade rapidly in the presence of water at temperatures below 45 °C. 35,41

After 50 min of annealing at a temperature of 100 °C, the XRD spectra were consistent with the cubic MAPbI3 perovskite phase and are labeled P1 (100), P2 (110), P3 (111), P4 (200), and P5 (210). At the beginning of the experiment, reflections P1 and P5 are observed but with a higher peak ratio of the 200 to 100 peak than is expected for the ideal cubic perovskite. This peak ratio changes during the course of annealing (Figure 5b). This observation is consistent with changes in sample texture during annealing. Alternatively, one of the reflections may stem from one of the precursor phases. The final diffraction patterns recorded at 100 °C exhibit the correct ratio of peak intensities expected for the randomly oriented cubic perovskite structure. As observed in the in situ UV–vis measurements (Figure 4), there is a time lag of about 10 min before the perovskite phase, represented by reflection P1, starts to grow. During the consecutive 30 min of annealing (Figure 5b), the peak intensity of P1 increases in a similar manner as that observed in the in situ UV–vis absorption measurements for the absorption at 740 nm (Figure 4b).

Additional peaks from intermediate phases are observed in the beginning and during annealing. By analyzing the changes in peak intensities with respect to annealing time, we were able to group these reflections into subsets assigned as A and B in Figure 5a. In Figure 5b, we plotted the normalized peak intensities of phases A (represented by A2) and B (represented by B2) in comparison with P1 and P2. This illustrates that subsets A and B are consumed during formation of the perovskite phase P. Figure 5c shows the evolution of the diffraction peaks between 11 and 18.5° with annealing time on a logarithmic contour plot. This plot emphasizes that there are subtle differences between the consumption kinetics of the subsets of peaks labeled A and B in the first 10 min of annealing. The peaks assigned to subset B start out at a high intensity, whereas peaks assigned to subset A increase during the first 10 min of annealing. The increase in peak intensities of subset A observed during the first 10 min of annealing correlates with the increase in the absorption feature at 570 nm observed by in situ UV–vis (Figure 4). The peak position of A1 suggests that this phase might be related to PbI3, but the UV–vis absorption signal and other peaks attributed to subset A are not consistent with those of pure PbI2.

The reflections labeled B1 and B2 at 15.3 and 31.0°, respectively, are comparable with reflections expected for methylammonium lead chloride, MAPbCl3, with a cubic lattice parameter of a = 5.67 Å, which is indicated in Figure 5c for comparison. The observed peaks initially start out at lower angles, suggesting a slightly enlarged d-spacing compared to that of MAPbCl3 but the peak maximum shifts during annealing, converging to the d-spacing expected for pure MAPbCl3 and decreases in peak intensity during annealing (Figure 5c). Reflections in this range have been interpreted to stem from PbCl2 seed crystals during crystallization. 20 While these reflections are most probably related to Pb–Cl bonding distances, this data did not allow us to distinguish whether MAPbCl3 grows from one single crystalline precursor phase21 or two precursor phases, and more detailed studies are needed to elucidate this further. The data discussed herein is consistent with other recent reports that highlighted the presence of crystalline lead halide precursor phases 20,21,25,26 in the formation of highly crystalline perovskite-absorber thin films. The presence of an intermediate chloride-rich mixed halide phase during annealing is also consistent with the detection of a MAPbCl3 phase in aged samples. 42 Furthermore, in perovskite samples not derived from PbCl2, the presence of lead halide complexes MAPbCl3 has been observed. 27 Preassociated complexes and crystallite precursors phases likely play an important role in the formation of perovskite-absorber samples and will influence the sample morphology and optoelectronic properties.

3.5. XPS and XRF Measurements. Because XRD is sensitive to crystalline domains, we performed X-ray photoelectron spectroscopy (XPS) measurements for samples annealed for different amounts of time (Figure 6). Before annealing, chlorine can be found in these samples, evidenced by the Cl(2s) and Cl(2p) peaks at 269 and 198 eV, respectively. In samples annealed at 100 °C for 5, 15, and 25 min (Figure 6, inset), the Cl(2p) peak decreases with annealing time. From quantitative XPS analysis, the surface composition of the nonannealed samples was found to be, on average, (MA)2.3PbCl2.I3.5. The amount of MA+ was estimated from the N(1s) signal to be 2 atomic equivalents and reduces to...
The samples were excited at 3000 eV. Longer than annealing times utilized for optimized devices (Figure 7) ranging from nonannealed to 120 min, which is 120 min annealing. Inset: Higher resolution scan of the Cl(2p) peak after 5, 15, and 25 min sublimation during annealing reported herein and postulated findings agree with MACl sublimation during annealing reported herein and postulated elsewhere. After 45 min of annealing, the chlorine content was below the detection limit of XPS. Qualitatively, we were also able to detect chlorine in nonannealed PbCl2-derived samples by energy-dispersive X-ray analysis (EDX) recorded during scanning electron microscopy imaging of samples, but we did not detect a signal from Cl in annealed samples (Figure S6). Quantification of the Cl content using EDX is hampered because the Cl peak overlaps with the Pb signal and the detection limit is on the order of 1%. In addition, the intense electron beam may alter the local Cl content by causing Cl to migrate out of the electron beam.

XPS is a very surface-sensitive method, and recent reports suggest that most chloride may be situated at the interface with the TiO2 substrate. To analyze the bulk concentration of chloride, we employed X-ray fluorescence spectroscopy (XRF) on samples annealed at 95 °C for different amounts of time (Figure 7) ranging from nonannealed to 120 min, which is longer than annealing times utilized for optimized devices reported elsewhere. The samples were excited at 3000 eV. The signals at 2342 and 2444 eV stem from the M5-N6 and M4-N6 transitions in lead. The chlorine K-L3 transition gives rise to a signal at 2622 eV. For comparison, the spectrum of the nonannealed sample is shown in Figure 7 both for excitation at 3000 and 2800 eV. For the lower excitation energy, no fluorescence from chlorine is observed.

The decrease in XRF intensity at 2622 eV with time is consistent with the large decrease of chlorine in MAPbCl3-xI3-x samples with annealing time observed in the XPS measurements (Figure 6). The amount of Cl remaining in the films is qualitatively found to decrease, but a significant amount of chlorine remains even after 120 min of annealing at 95 °C. A rough estimate of the amount of Cl remaining in annealed samples can be made by comparing integrated peak area at 2622 eV for each spectrum with the integrated peak for the nonannealed film. For the latter, a Cl/Pb ratio of 2:1 was assumed. The chlorine concentration estimated in this way lies in the range 0 < x < 0.3 for a sample annealed at 95 °C for 120 min, where x is the number of chlorine atoms per formula unit. A more accurate quantification cannot be made due to self-absorption effects that are pronounced in films with higher concentrations of chlorine. Comparing the chlorine signals for three different samples annealed under the same conditions (Figure S8), we find the variation among these films to be small, which indicates that the decrease of chlorine content during annealing is fairly similar among different samples and therefore is probably also homogeneous over the whole sample area.

The chlorine content of annealed films analyzed by XRF is an upper limit to the chlorine content in the sample. In XPS measurements, no chlorine signal was detected for fully annealed samples. XPS is a surface-sensitive method, and it is thus plausible that chlorine residues remain in the bulk of the sample or close to the substrate interface. This is in agreement with a recent study using angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and first-principles DFT modeling that suggested that residual chlorine resides near the oxide surface. The presence of chlorine at grain boundaries and at the interface may passivate defects and could be responsible for the much longer photoluminescence lifetimes observed for PbCl2-derived samples (Figures S7).

4. CONCLUSIONS

Highly crystalline and oriented perovskite-absorber thin films can be grown from precursors containing excess chloride and methylammonium as introduced by Snaith and co-workers. From all analytical measurements employed herein, the chloride content was found to decrease during annealing. We provide cogent evidence that most methylammonium chloride evaporates during annealing by analyzing the white deposit collected during annealing above the samples. However, even after prolonged annealing, residual chlorine can be detected in the films using X-ray fluorescence measurements. X-ray diffraction suggests that only a small amount of chlorine is incorporated into the crystal lattice and that most chlorine is likely to reside at grain boundaries or the interface with the substrate. The role of chlorine as a possible dopant, and surface passivant, and its effect on optoelectronic properties needs to be further investigated to understand the superior solar cell device performance achieved for solution-processed MAPbCl3-xI3-x based solar cells.
Sensitivity of nonannealed samples to ambient humidity discussed in terms of observed changes in XRD spectrum (Figure S1) and sample morphology visible in microscope images (Figure S2). Effect of delay time on hysteresis during current–voltage measurements of thin-film solar cell devices (Figure S3). XRD spectra of PbCl_{2}-derived samples on glass and mesoporous alumina substrates (Figure S4) as well as the relation between effective ion radius and lattice parameter $a_{\text{calc}}$ (Figure S5). Differential scanning calorimetry (DSC) measurements of MAI, MACl, and the dried PbCl_{2}/3MAI precursor (Figure S7). SEM images, XRD diffractograms, and PL lifetimes of PbI_{2}-derived samples compared to PbCl_{2}-derived samples (Figure S8). Variation in CI content for XRF measurements on different samples (Figure S9). This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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**ABBREVIATIONS**

XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy; XRF, X-ray fluorescence; UV–vis, UV–visible spectroscopy; EDX, energy-dispersive X-ray analysis; GIWAXS, grazing incidence wide-angle X-ray scattering; spiro-OMeTAD, 2,2′,7,7′-tetrakis[N,N-di(p-methoxyphenylamine)]9,9′-Spirobifi- 

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Supporting Information

Chloride in lead-chloride derived organo-metal halides for perovskite-absorber solar cells

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S1. Air-sensitivity of Nonannealed Samples

After spin-cast deposition, thin film samples derived from PbCl₂ and 3 equivalents of MAI are light yellow in color but turn dark brown upon drying or very brief exposure to ambient environment. The X-ray diffraction pattern of dried precursor samples exhibit peaks, expected for the 110, 220 and 330 reflections of the tetragonal MAPbI₃ phase (Figure S1). When exposing these nonannealed films to ambient atmosphere peaks at 2θ angles of 6, 12 and 18 degrees evolve. After one day of exposure to ambient atmosphere and humidity, only faint reflections from the MAPbI₃ phase are visible. Instead, strong reflections of an unidentified crystalline phase indicate the degradation or reaction of the sample in ambient atmosphere. While we have not yet identified this new crystal phase, we find it important to distinguish these features of the degraded precursor phase from the peaks observed for the crystalline precursor phase, discussed herein. Some of the reflections in the degraded precursor phase have been attributed to the formation of lead chloride oxohydrate.¹ A recent report suggests that brief exposure of PbCl₂-derived perovskite absorber thin films to ambient humidity is beneficial to obtain high solar energy conversion efficiencies.²
Figure S1: Evolution of XRD diffraction of solution-deposited perovskite sample from PbCl$_2$ with 3 equivalents of MAI from dimethylformamide. XRD-reflections indicate the formation of MAPbI$_3$ in the as-deposited precursor phase but samples rapidly degrade in a humid, ambient environment.

When annealing samples that have previously been exposed to ambient humidity for 1 day, the XRD-signature of tetragonal MAPbI$_3$ is found. However, the sample morphology is considerably altered, having formed needle-shaped crystals with low surface coverage (Figure S2, left) during air exposure. This leads to low substrate coverage even in annealed samples (Figure S2, right). High relative humidity or long exposure of nonannealed samples to ambient humidity should thus be avoided in MAPbCl$_x$I$_{3-x}$ preparation.

Figure S2: (left) Microscope image of PbCl$_2$/3MAI samples spin-cast from DMF solution exposed to ambient atmosphere for 1 hour. (right) Air-exposed sample after annealing at 100°C.

S2. **Hysteresis in Current-Density – Voltage Measurements**

In Figure S3, an example of J-V curves for a device annealed for 40 minutes at 100 °C is shown, measured in different scan directions and at different scan rates. At a
delay time of 5 s, current-voltage measurements in the forward and reverse scan direction, indicated by arrows in Figure S3, exhibited little hysteresis while at short delay times of 10 ms, considerable hysteresis is observed. One should note, that the average between the forward and reverse IV-scan measured at short delay times is not equivalent with the device efficiency determined from IV-measurements at long delay times, as discussed elsewhere. For the comparison of device performance as a function of annealing time, the device performance determined at a delay time of 5 s were used (Figure 1).

**Figure S3**: Current-voltage measurement at different scan-rates and directions for selected device, annealed at 100 °C for 40 minutes.

S3. **X-ray diffraction of PbCl₂-derived perovskite on Al₂O₃**

**Figure S4** (top) PbCl₂-derived MAPbI₃ thin film deposited on glass (bottom) PbCl₂-derived MAPbI₃ deposited onto meso-porous Al₂O₃ scaffold (scaffold reflection indicated with asterix).
Figure S4 shows the comparison of MAPbCl$_{3-x}$ samples deposited on glass substrates and on meso-porous alumina substrates. Both samples were annealed for 45 minutes at 100°C. The alumina scaffold randomizes the crystal growth sufficiently to detect reflections from other lattice planes.

In Table S1, literature values for the lattice parameters $a$ and $c$ determined for the tetragonal MAPbI$_3$ and MAPbCl$_{3-x}$ are compared. Our values for PbCl$_2$-derived perovskites determined from GIWAXS are slightly smaller than those reported for MAPbCl$_{3-x}$ by Colella et al.$^4$ However, these values are comparable to lattice parameters determined for pure MAPbI$_3$ single crystals.$^5$ This table illustrates that differences between lattice parameters are also highly affected by sample crystallinity and the point of reference for the estimation of the Cl content from XRD in MAPbCl$_{3-x}$ are difficult to define.

<table>
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<th>Report</th>
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<th>$a_{\text{tetr}}$ (Å)</th>
<th>$c_{\text{tetr}}$ (Å)</th>
<th>$V_{\text{tetr}}$ (Å$^3$)</th>
<th>$a_{0,\text{cubic}}$ (Å)</th>
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<td>996.05</td>
<td>6.29</td>
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In Figure S5, the relation between lattice parameter $a_0$ and lattice volume (tetragonal is 4x the cubic perovskite lattice) as a function of effective halide ion radius is plotted. This relation was derived from reported literature values for mixed Br-I methylammonium lead halide perovskites.$^9$ From this relation, the approximate amount of Cl can be estimated. The parameters derived from our GIWAXS analysis yield a relative Cl amount of 5 mol% with respect to the total
halide content. This is comparable to the values for PbCl₂-derived perovskites determined by Colella et al.⁴.

Figure S5 (top) PbCl₂-derived MAPbI₃ thin film deposited on glass (bottom) PbCl₂-derived MAPbI₃ deposited onto meso-porous Al₂O₃ scaffold (scaffold reflection indicated with asterix).

S4. EDX/SEM measurements on samples before and after annealing
From EDX analysis, chlorine was definitely detected in samples prior annealing but the chlorine content after annealing was difficult to determine. The relative amount of chlorine to iodine (Cl:I) was determined to be 0.48:1 before and 0.002:1 after annealing. The absolute signal intensity for chlorine (Cl) is difficult to evaluate as the signal overlaps with the signal for lead (Pb).
Figure S6: (left) Comparison of scanning electron microscopy (SEM) images of perovskite thin films before (b) and after (c) annealing at 100°C for 60 minutes with corresponding energy-dispersive X-ray (EDX) counts.

S4. Differential scanning coulometry (DSC) analysis
Precursor samples were spin-cast from DMF solution in a glovebox environment and dried at temperatures below 50°C. Samples were scratched off the substrates for differential scanning coulometry (DSC) measurements. Methylammonium iodide (prepared as described above) and methylammonium chloride (Aldrich) were analyzed for reference. The compounds were found to be humidity sensitive so air exposure was minimized prior to the analysis. DSC analysis was carried out at a temperature ramp of 10°C/min. The precursor sample exhibits a not very defined slightly endothermic feature at temperatures below 70°C that probably stems from the evaporation of solvent and possibly methylammonium chloride (MACl). A reference measurement on MACl exhibited no defined endothermic peak below 224°C. The latter agrees with reported evaporation tempartures of pure MACl. Methylammonium iodide exhibited an endothermic peak at around 144°C. The precursor exhibited an exothermic peak at 76°C that is indicative of the onset of a crystallization process.

Figure S7: Differential scanning coulometry (DSC) analysis of MAI, MACl and the precursor from PbCl₂/3MAI, dried.

S5. Effect of preparation on thin film morphology and PL lifetime
The preparation procedure of solution-processed perovskite-absorber thin films has a huge impact on thin film morphology. Samples derived from PbCl\textsubscript{2} exhibit a sheet-like appearance in SEM images and are found to be very oriented, apparent in the predominance of the (110), (220) and (330) XRD reflections. In contrast, samples derived from PbI\textsubscript{2} with 3 equivalents of MAI require a higher annealing temperature of ca 150°C, presumably to get rid of excess MAI. The resulting samples exhibited more PbI\textsubscript{2} impurities and were found to consist of smaller and more randomly oriented crystallites from XRD and SEM analysis. In comparison, the PbCl\textsubscript{2}-derived samples exhibit a 2 orders of magnitude longer photoluminescence lifetime. These results agree with the report of Stranks et al.\textsuperscript{10}

![Figure S8: (left) Comparison of X-ray diffraction and Scanning Electron Microscopy images of perovskite thin films derived from PbCl\textsubscript{2} (a) and PbI\textsubscript{2} (b). (right) Photoluminescence lifetimes were found to be much longer for the PbCl\textsubscript{2}-derived thin film.](image)

**S6. Variance in Cl content from XRF analysis**

In Figure S9, XRF spectra of three samples annealed at 95°C for 120 minutes are compared. One sample was annealed in air rather than a N\textsubscript{2} atmosphere for comparison. All three samples exhibit a comparable Cl signal. This shows that there is little sample to sample variation and also that the variation in Cl content is probably also homogeneous within the sample.
Figure S9: XRF-spectra for three different samples annealed at 95°C for 120 minutes.

References: