Understanding the Methylammonium Chloride-Assisted Crystallization for Improved Performance of Lead-Free Tin Perovskite Solar Cells

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In the quest for perovskite materials with reduced toxicity, Sn perovskites are emerging. However, they suffer from material instability and rapid crystallization, leading to high defect densities in the films. In this work, the methylammonium chloride (MACl)-assisted crystallization as a route to improve stability and optoelectronic quality of quasi 2D/3D PEA$_{0.08}$FA$_{0.92}$SnI$_3$ perovskite is demonstrated. For an optimal additive amount (10 mol%), a 37% increase in power conversion efficiency is found. Notably, MACl enhances the films’ stability, evidenced by temporal PL tracking. Understanding the effect of MACl addition in this system is interesting for the pursuit of efficient and stable tin-based devices. The investigations show that MACl addition causes a shift in the optical bandgap and improves morphology, indicating effects in the bulk crystal structure. X-ray photoelectron spectroscopy confirms the presence of Cl on the surface, but no indication of MA$^+$ is found. Intriguingly, UV photoelectron spectroscopy shows pronounced changes in the density of states. For the first time, it is shown that MACI promotes the formation of a two-dimensional layer via the surface accumulation of PEA$^-$. The MACI additive lowers the absorber’s ionization energy, possibly facilitating hole extraction. Overall, this work highlights a facile route to control the crystallization of Sn perovskites.

1. Introduction

Perovskite solar cells (PSCs) have reported a certified power conversion efficiency (PCE) of 26.1%, which is achieved by controlling composition and crystallization kinetics of the perovskite absorber layer and optimizing the device heterojunctions to ensure minimal losses during charge extraction.[1–5] Perovskite materials offer strong absorption, tunable bandgaps from violet to the near-infrared part of the electromagnetic spectrum, high defect tolerance and a low defect density, and solution-based low-temperature compatible fabrication.[6–8] The development of PSCs has so far been focused mainly on lead-based perovskites, which raise toxicity concerns and might hinder their commercial deployment.[9–11] Although strategies for the leakage prevention of toxic Pb additives have been explored,[12,13] Pb-free alternatives are highly desirable due to environmental and regulatory concerns.[14,15]

Various alternatives have been explored to replace toxic Pb such as germanium (Ge),[16] antimony (Sb),[17] bismuth (Bi),[18] copper (Cu),[19] and tin (Sn). Among these, Sn-perovskites are, to date, the most promising choice as they offer a narrow bandgap of 1.2–1.4 eV[20] that renders them suitable as top cells in tandem cell configurations, low exciton binding energy, and a high electron mobility.[21–26] Nonetheless, Sn-based PSCs have inherent critical issues that currently hamper their performance compared to their Pb counterparts. First, the strong tendency of Sn$^{2+}$ to oxidize to Sn$^{4+}$ results in p-type doping, which contributes to a high defect density and instability for this class of perovskites. Second, the fast and difficult-to-control crystallization of Sn perovskite thin films that leads to pinholes in the film. Third, prompt material degradation is induced by atmospheric oxygen and water.[25–27] Several strategies are currently being investigated to improve device performance and stability of Sn perovskites. These include the addition of reducing agents into the precursor solution or in...
the fabrication atmosphere, surface passivation treatments, solvent engineering, and the introduction of large organic cations to yield hybrid 2D/3D perovskite structures.\textsuperscript{[28–31]} A PCE of 11.75% is reported for mixed formamidinium (FA\(^+/\))/ethylammonium (EA\(^+\)) (FA\(_1\),EA\(_{0.99}\))ED\(_{0.05}\)Sn\(_{0.95}\)I\(_3\) perovskite, which was further improved to 13.24% upon surface passivation via a Lewis base. Inclusion of EAI resulted in improved energy level alignment of the perovskite layer with the charge transport layers as well as a reduced defect density.\textsuperscript{[32]} Similarly, the use of reducing agent phenylhydrazine (PhNHN\(_2\)) and its halide containing counterparts resulted in a PCE of 13.4%.\textsuperscript{[33]} Certified PCEs exceeding 14% have been reported in Sn-based PSCs by controlling in situ the oxidation from Sn\(^{2+}\) to Sn\(^{4+}\) via: 1) coordinating metallic Sn and I\(_2\) in DMSO solution to form an SnI\(_2\)–(DMSO)\(_x\) adduct that results in a preferred crystal orientation, and 2) by employing the 2D cation 4-fluoro-phenethylammonium bromide to promote highly oriented crystal growth in 3D FASnI\(_3\).\textsuperscript{[34,35]}

Recently, methyl ammonium chloride (MACl)-assisted crystallization of formamidinium lead iodide (FA\(_0.08\)FA\(_{0.92}\))Sn\(_{0.95}\)I\(_3\) perovskite has shown to induce intermediate phases of α-FAPbI\(_3\), even before annealing of the perovskite films. The addition of MACl resulted in larger grains, enhanced film crystallinity, and enhanced carrier lifetime—all contributing to an improvement in the PCE reaching a certified value of 23.3%.\textsuperscript{[36]} Chloride doping has also been shown to passivate the bulk and surface defects in Pb-based perovskites. Park et al. used a combination of alkylammonium chlorides to enhance the crystallization of α-FAPbI\(_3\), achieving a record certified PCE of 25.73%.\textsuperscript{[37]} Recently, the use of Cl-based additives has also been extended to lead-free perovskites. It has been reported that the use of a Cl-based bifunctional additive, namely 1,3-diaminoguanidine monohydrochloride (DAGCl), improved the crystallinity of Sn perovskites, reduced defect density and demonstrated \(\approx\)32% increase in the PCE compared to a pristine counterpart.\textsuperscript{[38]} However, a comprehensive understanding of Cl-additives in the Sn-based perovskites toward crystallization dynamics, surface properties, energetics, carrier lifetime, and stability remains elusive. Central questions remain regarding how the Cl anion interacts with the Sn\(^{2+}\) in the lattice, and how and where it is included in the perovskite crystal.

In this work, we provide a thorough investigation on the role of MACl on the crystallinity, film composition, surface density of states (DOS), and optoelectronic properties of PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) perovskites. We demonstrate that the addition of MACl into a PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) precursor solution PE\(^+\) = phenethylammonium promotes the formation of a PE-rich (2D) surface that correlates linearly with the MACl concentration and is evident from the induced changes in the DOS measured using ultraviolet photoelectron spectroscopy (UPS). MACl inclusion also improves the morphology and crystallinity of the PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) films. An optimized MACl concentration of 10 mol\% enhanced the carrier lifetime threefold and resulted in an improved photoelectricity of perovskite films in air. Importantly, we find a 37% increase in the PCE compared to a MACl-free counterpart. Combining the MACl additive with a surface passivation strategy, we achieve a champion PCE of 8.25% in n-i-p PSCs. Remarkably, the devices were processed in a multipurpose glovebox with a relative high level of O\(_2\) (3–7 ppm) and H\(_2\)O (5–8 ppm), differently from the sub-ppm values conditions reported by other groups.\textsuperscript{[29,34,38]}

2. Results and Discussion

We first discuss the effect of MACl inclusion on the morphology of the PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) thin films. The films were prepared from a precursor solution (containing also 10 mol\% of SnF\(_2\)) with a hot antisolvent method first introduced by Liu et al.\textsuperscript{[29]} The use of hot antisolvent has been shown to overcome the inhomogeneous film coverage issues arising from rapid crystallization of Sn perovskites.\textsuperscript{[39]} Nonetheless, our pristine PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) thin films still feature pinholes and large voids (Figure 1a). The addition of MACl into the precursor solution progressively improves the surface coverage (Figure 1a–c). For an additive amount of 35 mol\%, the perovskite grains tend to coalesce in larger domains (Figure 1d) and grains of a few microns in size are evident, which can be beneficial to charge transport. The effect of grain boundary suppression upon the addition of alkylammonium chlorides has been recently reported by Park et al. and is attributed to the decrease in the crystallization rate of the thin film during antisolvent-assisted spin coating.\textsuperscript{[3]} We attribute the improvement of the morphology upon addition of MACl also to another effect, specific to Sn-based perovskite. In such a system, the interaction between Sn\(^{2+}\) and Cl is significant owing to their hard acid and base characters, respectively, in terms of the hard and soft acids and bases (HSAB) theory. We suggest that during the crystallization process, a single Cl can connect two distinct Sn\(^{2+}\) centers (Figure 2c). When these centers are located on separates crystallites in formation, the resulting bridging effect mediated by chloride will join those crystallites, promoting the formation of large grains, as particularly evident in the 35% samples. Obviously, this same effect will prevent the formation of voids and pinholes.

The enhancement in phase uniformity and crystal quality is further confirmed by the XRD patterns of the thin films. The 10 mol\% and 35 mol\% MACl films display a significant increase in the intensity of the (100) and (200) crystal planes at 14.0° and 28.3°, respectively (Figure 1f).

The increased crystallinity, which is also confirmed by a decrease in the full width at half maximum (FWHM) of the (100) signal (0.165°, 0.152°, and 0.141° for 0, 10, and 35 mol\% MACl samples, respectively), could be attributed to the larger size of the crystalline domains as well as a preferred crystal orientation upon addition of MACl. The absorbance spectra of the thin films show the typical absorption profile of halide perovskites, with a slight blue shift of the absorption onset that increases with the MACl amount (Figure 1g).

Furthermore, with the addition of MACl, a new exciton absorption feature appears at 600 nm. This could be due to the formation of small amounts of PE\(_{2}\)SnI\(_4\), as will be discussed later.\textsuperscript{[40]} In addition, we observe a drop in absorption intensity for the 35 mol\% MACl containing sample, which we attribute to the prompt degradation of this sample during the measurement and to the highly defective crystal quality obtained by adding an excessive MACl amount. Both of these aspects will be discussed in detail in the following. The shift in absorption is well-matched by the corresponding blue shift in the steady-state photoluminescence (PL) peaks (Figure 3a). The PL peak shifts from 893 nm for the pristine films to 873 and 863 nm for the 10 and 35 mol\% MACl containing films, respectively. We attribute this blue shift to the increasing Cl ion concentration in the PE\(_{0.08}\)FA\(_{0.92}\)Sn\(_{0.95}\)I\(_3\) films.
perovskite, the presence of which broadens the bandgap of Pb- and Sn-based perovskites, as has been reported in literature.[20,41–43] The presence of Cl is also confirmed by the X-ray photoelectron spectroscopy (XPS) investigation discussed below. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion. An increase in the PL intensity is also noted upon MACl inclusion.

Figure 1. Top-view SEM images of the Sn perovskite thin films containing a) 0 mol%, b) 5 mol%, c) 10 mol%, and d) 35 mol% of MACl additive. Scale bar: 1 μm. e) Photographs of the as-prepared thin films on ITO substrates. f) XRD patterns of the pristine and modified Sn perovskite films. g) UV-vis-NIR spectra of the pristine and modified Sn perovskite films.

Figure 2. Illustration of the effects of: a) MACl addition in Pb-based perovskites. The Pb$^{2+}$–Cl$^{-}$ interaction is weak, an intermediate phase is formed and both MA$^{+}$ and Cl$^{-}$ are removed following a deprotonation step and the resulting α phase is stabilized; b) No MACl addition in Sn-based perovskites. The crystallization is fast and uncontrolled and results in defective crystals and smaller domains. c) MACl addition in Sn-based perovskites: the Sn$^{2+}$–Cl$^{-}$ interaction is strong, chloride slows crystallization and can serve as a bridge, resulting in larger crystalline grains in which Cl$^{-}$ ions are incorporated. The single dash line symbolizes a weak interaction, the double dash line a strong interaction.
intermediate additive amounts and fitting parameters). The 10 mol% MACl films resulted in a longer PL lifetime ($\tau_n$) of 8.13 ns, representing a 3.3-fold increase with respect to the reference film ($\tau_n$ of 2.43 ns). The longer lifetimes are beneficial for an improved charge carrier transport to the selective layers. The $\tau_n$ of the 35 mol% sample drops below 1 ns, which is surprising given the enhanced crystallinity and suppression of grain boundaries in this sample. We propose that the high amount of MACl additive results in the coexistence of multiple phases (probably Cl-rich or I-rich) in a disordered arrangement, thus creating non-radiative recombination pathways. This is confirmed via Kelvin probe force microscopy (KPFM) measurements, as will be discussed later. Photoluminescence quantum yield (PLQY) measurements also affirm the improved quality of the optimal 10% MACl films and the $\tau_n$ trend (the PLQY for 0%, 10%, and 35% samples are 0.36%, 0.99%, and 0.33%, respectively). In Figure 3c, we show the calculated quasi-Fermi level splitting (QFLS) in these films using a method developed by Stolterfoht et al.\cite{44,45} The QFLS quantitatively represents the density of free charge carriers in the conduction and the valence bands of the perovskite films, and it is generally correlated with the open-circuit voltage ($V_{OC}$) in the corresponding devices. The 10% MACl samples showed the highest QFLS, followed by the reference and the 35% sample, affirming the trend observed in the $\tau_n$ measurements. A similar trend (improvement from 0% to 10% and decrease again for 35%) was observed when considering the champion $V_{OC}$ of the solar cells, as can be seen by the corresponding points in the plot. The device performance will be discussed in detail in a following part.

The reduced defect density in the optimal 10 mol% MACl samples is further confirmed by space-charge limited current (SCLC) curves measured in hole-only devices (Figure 3d–e). The voltage intersection corresponding to trap filling level ($V_{TFL}$) manifests a four times reduction upon MACl inclusion. This corresponds to a nearly four times reduced trap density, as the $V_{TFL}$ and trap density are linearly correlated. The Urbach energy $E_U$ values extracted from the analysis of several hole-only devices are available (Figure S4, Supporting Information). The Urbach energy $E_U$ obtained from photothermal deflection spectroscopy (PDS) measurements (Figure 3f) also confirms a reduction in the trap density in the optimal 10 MACl sample and an increase upon further increasing the MACl concentration to 35 mol%. The $E_U$ decreases from $\approx$45 meV in the reference sample to $\approx$30 meV in the 10% MACl counterpart and rises to 50 meV for 35% MACl sample. The $E_U$ value correlates with the degree of order within the crystal, suggesting an optimum crystal quality for 10% MACl samples while higher MACl concentration adversely affect the crystallinity, thereby increasing disorder in the film, as also evidenced by the PL and TRPL measurements.
Several studies employing alkylammonium chlorides (RACl) in Pb-based perovskites show that both RA+ and Cl− ions are removed from the thin films upon fabrication and annealing, through a deprotonation of the ammonium ion, followed by the coordination to the Pb2+ center, and subsequent removal of HCl, as illustrated in Figure 2a.[16,47,48] While Sn counterparts might follow a similar pattern, the stronger Lewis acidity of Sn2+ compared to Pb2+ could result in a stronger interaction with Cl−, as this is a harder base than Br− or I−; this could result in the persistence of Cl− in the thin films (Figure 2c), including at the surface. This would explain the spectral shift observed upon MACl inclusion, whereas in Pb perovskites the addition of RACl does not generally cause a spectral shift.[3,47]

In order to understand the increased recombination in 35% MACl samples in spite of their improved crystallinity and larger grain size, atomic force microscopy (AFM) and KPFM were carried out. The root mean square roughness of the perovskite films in agreement with the SEM results shown in Figure 1. Although the 35%-MACl sample features a significant improvement in the grain size, it also shows larger pinholes in the film that can facilitate recombination in the device.

We further recorded contact potential difference (CPD) maps of the perovskite films at a relative humidity level below 2%. The CPD values are related to the local work function (WF) at nanoscale and are thus important in understanding spatial electronic heterogeneity and charge transport behavior in the films. A few important considerations can be drawn from the CPD maps as follows. First, the difference in the potential distribution across the different films. Both the MACl treated films show a more uniform CPD distribution over the entire scan area than the reference 0% MACl counterpart (Figure 4h–i), which can reduce nonradiative recombination and improve charge extraction in general.[49] Second, we observe the presence of dark spots (suggesting different CPD value or WF) arising from local compositional changes in the different films. These would lead to a variation in the ΔCPD (the variation in the CPD value of each sample from an average baseline), the highest being in the 0% MACl reference sample, followed by the 35% and the least in the 10% MACl samples. A detailed analysis of local surface features (Figure 4k and S6–S8, Supporting Information) suggests that the local ΔCPD can exceed 150 mV for 0% and 35% samples, whereas the 10% MACl sample shows a smaller ΔCPD of 100 mV or even lower. Important is the presence of negative WF regions (higher CPD values) in the 0% MACl sample, as high as 100 mV, which suggests that the inhomogeneity in this sample has more than one origin. Although at this point the origin of the local inhomogeneities cannot be concluded, these

![Figure 4. a–c) AFM images of the three perovskite films deposited on ITO/PEDOT:PSS. d) Roughness comparison of different perovskite films deposited over baser ITO and ITO/PEDOT:PSS. For each type at least 2 samples were measured. e,f) CPD maps of perovskite films measured at relative humidity below 2%. Scale bar is 2 μm. h–j) CPD distribution over entire scan area of 0%, 10% and 35% MACl samples, respectively. k) Line profiles showing ΔCPD across the different regions in all three perovskite samples.](image-url)
can probably be the different species of Sn ($\text{Sn}^{2+}$, $\text{Sn}^{4+}$) or segregated ions (MA or FA-rich or I, Cl-rich in the case of MACl treated samples). Similar heterogeneity in Pb-based perovskites is attributed to the presence of Pb-rich clusters\cite{50,51} which will lead to region of higher WF in the film. Such a scenario can also hold true for our samples, but this would require confirmation with a locally resolved complementary chemical mapping. These local variations can also explain why the 35% MACl samples, in spite of their larger grain sizes and a higher crystallinity, leads to a higher defect density and thus a higher recombination in the devices.

The UV-vis-NIR and PL spectra discussed earlier, along with the local heterogeneity demonstrated by CPD maps, hint toward incorporation of chloride into the perovskite lattice. To corroborate this finding, the surface compositions of these perovskites were studied using XPS. In Figure 5a, survey scans of perovskites containing different amounts of MACl additive are shown with their characteristic core level peaks highlighted in gray. For reasons that will be explained in the subsequent discussion, a 2D PEA$_2$SnI$_4$ perovskite was also measured and is included in this graph. Despite 10 mol% SnF$_2$ being added to all precursor solution, no evidence of F can be detected on the film surfaces in the survey scans. This is in line with previous reports on FASnI$_3$-based perovskites, suggesting that SnF$_2$ might accumulate close to the PEDOT:PSS interface.\cite{52,53} In Figure 5b-d, the detailed scans of the core level signals belonging to Sn 3d$^{3/2}$, C 1s, and Cl 2p can be seen, respectively. Here, only the 0%, 10%, and 35% scans are shown, and additional measurements of 3%, 5%, and 50% are included in the Supporting Information (Figure S8).

In the case of Sn 3d$^{3/2}$, the fit of the data with two Voigt profiles shows two different oxidation states due to different chemical environments; these likely correspond to the intact perovskite ($\text{Sn}^{2+}$ at 494.5 eV) and a degraded phase ($\text{Sn}^{4+}$), which is marked as a light gray peak at a higher binding energy (495.5 eV).\cite{34} The Sn$^{4+}$ signal is present on all the surfaces in a comparable amount, possibly due to the presence of oxygen during film fabrication. Surprisingly, this indicates that the Sn$^{4+}$ formation does not correlate with the MACl additive. In Figure 5c, the carbon 1s core levels are shown. The signal belonging to FA$^+$ can be found around 288 eV\cite{20} and is color coded for the respective samples. The area of this peak is not affected with increasing MACl content. The pure 2D PEA$_2$SnI$_4$ film shown at the top is used to fit the carbon signal belonging to the bulky cation, which is also present in all the other Sn perovskite precursor solutions (8 mol%). The asymmetric shape of this dark shaded signal comes from the C—C as well as C—N bonds present in the molecule. The PEA$^+$ C signal is centered at 284.7 eV and can be clearly seen in all samples. Intriguingly, with increasing MACl concentration, this feature becomes stronger, suggesting that PEA$^+$ preferably accumulates at the surface. Surprisingly, no clear evidence of a signal belonging to MA$^+$ can be detected. The corresponding C 1s signal is expected to be located around 286 eV, a region where the PEA$^+$ signal is also noted. However, the complete C spectrum for all samples can be well fitted assuming FA$^+$ and PEA$^+$ only. This means, as far as XPS is concerned, no MA$^+$ is present on the surface of perovskite films. In contrast, the presence of Cl$^-$ can be clearly observed on the surface, as shown in Figure 5d, and the intensity of this Cl 2p signal correlates well with the amount of MACl used in the solution. The ratios of FA$^+$: PEA$^+$: Cl for 0% MACl, 10% MACl, and 35% MACl are 1:0.1:0, 1:0.2:0.3, and 1:0.3:0.5, respectively. The ratios of the complete sample set as well as the XPS core level fits can be found in the Supporting Information (Figure S8 and Table ST2, Supporting Information).

In addition to the XPS analysis, the surfaces were also analyzed using UPS, to investigate the changes in the electronic

![Figure 5.](image-url)

**Figure 5.** a) XPS survey scans of PEA$_{0.08}$FA$_{0.92}$SnI$_3$ perovskite with various molar percentages of MACl additive. In addition, a measurement of PEA$_2$SnI$_4$ is shown. XPS core level spectra of b) Sn 3d$^{3/2}$, c) C 1s, and d) Cl 2p. e) Corresponding UPS spectra of the various perovskite film. For better comparability, spectra are shifted vertically. The characteristic features in the DOS are indicated with dashed lines; gray line belonging to PEA$_2$SnI$_4$ and red line belonging to reference perovskite film without added MACl. The extracted positions of VBM are given by black vertical markers.
properties due to the MACl additive. On the right-hand side of Figure 5e, the valence band (VB) regions are displayed for the complete sample set, here the spectra are shifted vertically for clarity. The bottom curve represents the PEA$_{0.08}$FA$_{0.92}$SnI$_3$ reference, and the shape of the DOS is in good agreement with previously published data of pure FASnI$_3$ films.\[20\] Upon MACl addition, the shape of the DOS clearly changes, and the new features are reminiscent of the ones observed for pure PEA$^+$-based 2D perovskite, as can be seen by comparing to the measurement of PEA$_2$SnI$_4$ shown on the top of the graph. Characteristic features are indicated by the black dashed-dotted lines at 3.4, 6.25, and 11 eV. The red dashed-dotted line is used to assign a feature at 5 eV associated with the FA$^+$ cation.\[20\] In both these features, the effect of MACl addition can be well distinguished when changing from 0% to 50% of the additive. As the MACl percentage increases, the PEA$^+$ containing 2D feature on the surface becomes more pronounced while the intensity of the FA$^+$ feature decreases. The measurement therefore indicates that the additive leads to an increase in the formation of a lower dimensional, likely PEA-rich layer on top of the perovskite film. The underlying mechanism of this accumulation is beyond the scope of this study. The 2D top layer can cause changes in the energy level offsets at the interface. Therefore, we also extracted the values for the valence band maximum (VBM), marked by black vertical lines. The value is 0.47 ± 0.02 eV relative to the Fermi energy and does not change significantly between the different MACl samples. Similarly, the work function and ionization energy are barely affected, though there is a small difference for samples with and without additive. Upon MACl addition, both, the Wf and IE decrease by approximately 100–200 meV. Figures S11–S12 and Table ST3, Supporting Information display all the measured spectra and relative extracted values. These results show that the addition of MACl and the related increase in 2D surface layer, only have a small effect on the IE. However, we can assume an even more pronounced effect on the conduction band (CB) position, since the 2D layer should produce a wide bandgap surface layer.

3. Photovoltaic Performance of PSCs

The 0, 10, and 35 mol% MACl-doped films were used to fabricate PSCs in an architecture ITO/PEDOT:PSS/KSCN/perovskite/ICBA/BCP/Ag. Statistical analysis of the PV parameters including various batches of PSCs fabricated (Figure 6a–d) shows an increased PCE for the optimal MACl concentration of 10 mol%, followed by a decrease for the 35 mol% case. Figure S11, Supporting Information shows the distribution of PV parameters for the intermediate MACl amount addition of 5 and 20 mol%. The increase in the PCE is mainly due to the improved $J_{SC}$ from a median (champion) value of 16.4 (19.4) mA cm$^{-2}$ for the reference PSCs to 19.1 (21.6) mA cm$^{-2}$ for the 10 mol% MACl containing devices. The $J_{SC}$ drops massively for the 35 mol% samples to merely 7.5 mA cm$^{-2}$, probably due to the inefficient charge extraction caused by the presence of 2D-rich PEA perovskite on the surface. The $V_{OC}$ also increases from a median (champion) value of 0.43 (0.53) V of the 0% MACl perovskite to the 0.49 (0.63) V of the 10 mol% MACl perovskite. This increase in the $V_{OC}$ affirms the trends of the QFLS shown in the current–voltage (J–V) curves of the best-performing Sn PSC containing 10% MACl and no surface passivation, EDA or PEAI passivation.

![Figure 6. a–d) Statistical analysis of photovoltaic parameters of Sn PSCs with 0, 10, 35 mol% MACl additive. The horizontal bar represents the median value. e) J–V curves of the best-performing Sn PSC containing 0, 10, and 35 mol% MACl additive. f) J–V curves of the best performing Sn PSC containing 10% MACl and no surface passivation, EDA or PEAI passivation.](image-url)
earlier and follows the trend of the varying defect density in the investigated perovskite films. The increase in the $V_{OC}$ can be attributed to the more favorable ionization energy in the 10% MACl sample. The $V_{OC}$-QFLS correlation also suggests a reduced recombination for 10% MACl samples, which is evident from a higher fill factor (FF). The median (champion) FF increases from 46 (53)% of the reference devices to 51 (60)% of the 10 mol% MACl-containing samples. The $V_{OC}$ and FF values show a spread, which is most pronounced for the 35 mol% MACl devices followed by the reference samples. These trends confirm a higher degree of disorder and heterogeneity in these films arising from uncontrolled crystallization (reference samples) and probably inhomogeneous distribution of halide ions (35 mol% samples). We point out that all the devices exhibited $J$–$V$ hysteresis as commonly reported for many perovskite compositions and cell architectures (Figure S12 and S13, Supporting Information). Furthermore, the trends in the PCE of the devices following 10 or 35 mol% MACl additions compared to the pristine counterpart were confirmed, even under different fabrication conditions (Figure S12 and S13, Supporting Information).

The addition of MACl has thus far manifested several beneficial effects in the perovskite films. Since the MA$^+$ is not incorporated on the surface, as shown by XPS (although its presence in the bulk cannot be ruled out), we suggest that Cl plays a crucial role in determining several important properties of the resultant perovskite films. These include the crystallization kinetics leading to changes in the morphology of films, variations in the band structure and energetics of the Sn perovskite, and notably, the formation of PEA-rich 2D perovskite on the surface with increasing MACl concentration.

The devices are not fully optimized and for example surface treatments can help to further increase the device performance. Two types of surface treatments were performed on the 10 mol% MACl devices, using either ethylenediamine (EDA) or PEAI. Specifically, a diluted solution of these small molecules was spin coated during fabrication between the absorber and the electron-selective layer. While the EDA devices had a significantly lower $J_{SC}$ than the unpassivated counterparts, a higher $V_{OC}$ up to 0.78 V and a higher FF up to 63.0% could be achieved. Remarkably, the additional PEAI passivation resulted in a minor decrease of $J_{SC}$ but in turn the $V_{OC}$ and, crucially, the FF could be improved up to 0.73 V and 64.4%, respectively, resulting in a champion PCE of 8.25%. Details about the PV parameter distribution are available in Figure S14 and Table ST4, Supporting Information. We assume that the beneficial effect is due to the passivation of surface point defects and subsequent improvement of the perovskite/ETL interface. It shows that further improvement by optimizing interfaces is possible.

An important aspect is whether the MACl addition affects the ambient stability of the perovskite films. To probe this, the Sn perovskite thin films were exposed to ambient air at a relative humidity exceeding 50%. The pristine and modified perovskite films showed different ambient stability, as it is evident from the photographs in Figure 7d. Here, the 10 mol% film still shows a dark shade after 40 h of storage in air (relative humidity 40–50%), whereas the 0% and 35% samples turned completely transparent showing completely degraded films. To learn more about the degradation process, the PL intensity of the films was tracked over time. Figure 7a–c details the PL emission measurement over time of the perovskite films containing 0, 10, and 35 mol% MACl.

Figure 7. a–c) Steady-state PL tracking over time of 0, 10, and 35 mol% MACl-containing Sn perovskites. d) Photographs of Sn perovskites thin films as-prepared and after 40 h in air (RH = 50%). Evolution over time of e) peak center and f) FWHM of the PL peaks of the pristine and modified Sn perovskite films.
The graphs show clearly that while after 60 min the peak of the pristine and the 35 mol% MACl-doped material dropped to below 25% of its initial intensity, the 10 mol% MACl sample exhibited a relatively smaller drop, remaining at 40% of its initial value after exposure to ambient conditions. The temporal PL tracking also shows a shift in the peak position of the PL maximum as well as the peak broadening over time for all samples. These trends were more pronounced for 0 and 35 mol% samples and significantly reduced for the 10 mol% sample (Figure 7e,f). The improved stability of the 10% film can be attributed to the formation of the 2D perovskite layer on the surface, as discussed earlier. The large and hydrophobic PEA$^+$ cation acts as a protective capping layer, slowing down moisture-driven degradation.$^{[55,56]}

However, in the case of exceedingly large concentration of 35% MACl, the resulting films exhibit inhomogeneity and formation of large holes exposing the films to humidity and oxygen.

4. Conclusions

In this work, the role of MACl additive in controlling the crystallization and optoelectronic properties of tin perovskites (a mixed 2D/3D PEA$_{0.08}$FA$_{0.92}$SnI$_3$) is thoroughly explored. Unlike Pb-based perovskite, the MACl addition herein leads to a shift in the optical bandgap suggesting inclusion of Cl in the bulk of the perovskite. X-ray photoelectron spectroscopy measurements confirm that Cl is present on the surface, and its amount scales with the amount of additive in the perovskite solution; however, no traces of MA$^+$ or F were detected. Strikingly, the MACl addition promotes the formation of a PEA (2D)-rich surface in the perovskite films, which impacts the DOS in the perovskite films as demonstrated from the UPS spectra of the different perovskite films. Although an increase in the MACl concentration beyond an optimum of 10 mol% leads to a higher crystallinity and larger grain sizes, this negatively impacts the optoelectronic properties, as confirmed via photoluminescence and PES measurements. This is because the increasing MACl concentration beyond the optimal 10% induces local heterogeneities, as demonstrated by KPFM measurements, which can accelerate nonradiative recombination. This also explains the trends in the devices performance. The photovoltaic parameters first increase as the MACl concentration varies from 0 to 10% and then show a drop for a MACl concentration of 35%. Finally, the impact of Cl inclusion on the intrinsic stability of the films via the generation of a PEA-rich capping layer is also demonstrated by tracking the photoluminescence in air with the highest stability noted for the optimal 10% MACl samples.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

D.T.C., S.D.Ö., and A.F. performed the experimental and analytical research and the original manuscript writing. J.K.L. and E.I. assisted in experiments on devices and thin-film measurements. T.S. performed the PDS measurements and carried out the analysis. A.F., S.O., and L.S.-M. participated in the conceptualization, supervision of the project, and editing of the manuscript. D.T.C., S.D.Ö., A.F., J.K.L., J.R., S.O., and L.S.-M. discussed the results. All authors contributed to the revision of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D perovskites, additive engineering, compositional engineering, crystallization dynamics of perovskites, lead-free perovskites

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