ABSTRACT: The properties of efficient solar cells fabricated with triple-cation perovskite placed between a mesoporous titania layer and a spiro-OMeTAD layer are studied by using devices either prepared under water-free drybox conditions or fabricated under ambient room humidity. The morphological studies indicate that the content of unreacted PbI2 phase in the perovskite structure is much higher near the interface with titania than near the interface with spiro-OMeTAD. The stationary emission spectra and transient bleach peaks of perovskites show additional long-wavelength features close to the titania side. Time-resolved techniques ranging from femtoseconds to seconds reveal further differences in charge dynamics at both interfaces. The population decay is significantly faster at the titania side than at the spiro-OMeTAD side for the cells prepared under ambient conditions. An increased hole injection rate correlates with higher photocurrent seen in the devices prepared under drybox conditions. The charge recombination loss on the millisecond time scale is found to be slower at the interface with titania than at the interface with spiro-OMeTAD. The ideality factor of the cells is found to increase with increasing DMSO content in the precursor solution, indicating a change in recombination mechanism from bulk to surface recombination. We also found that the charge dynamics are not uniform within the whole perovskite layer. This feature has significant implications for understanding the operation and optimizing the performance of solar devices based on mixed cation perovskites.

KEYWORDS: perovskite solar cells, triple-cation perovskite, perovskite–TiO2 interface, perovskite–HTM interface, ultrafast time-resolved optical spectroscopy, impedance spectroscopy

INTRODUCTION

Perovskite solar cells (PSCs) have undergone a tremendous increase in efficiency from 3.8% in 2009 to an outstanding 25.2% certified only 10 years later in 2019. The initial and the most studied perovskite structure for PSC is methylammonium lead triiodide (MAPbI3). However, the MAPbI3 absorber suffers from instability under ambient conditions; therefore, compositions with substitutions made for MA and I have been investigated. The additions of the larger formamidinium (FA) cation and bromide ion, with the optimized configuration \((\text{FAPbI}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}\), made the structure more thermally stable, increased the band gap, and provided higher tolerance for humidity. Further incorporation of small amounts of cesium atoms brings humidity resistance and less susceptibility for structural impurities. Many other substitutions have been tried, for example, tin or bismuth to reduce toxicity or rubidium to enhance charge mobility. However, the benchmark triple-cation configuration of \(\text{FA}_0.76\text{MA}_{0.15}\text{Cs}_{0.09}\text{Pb}(\text{I}_{0.81}\text{Br}_{0.19})_3\), which we study in the present work, is frequently used when one wants to get both stable and very efficient PSCs. Despite all of that, most fundamental studies of PSCs are still mainly limited to the standard MAPbI3 structure.

Most of the time-resolved studies of PSC, including those implemented in this work, require taking into account the complex response of the perovskite layer to the light excitation. Upon light absorption, pairs of electrons in the conduction band and holes in the valence band are formed, followed by fast processes on the subpicosecond time scale such as charge cooling and exciton dissociation. These processes are accompanied by a band-edge shift due to charge screening or band-gap renormalization effects. After charge thermalization to the valence and conduction band edges, the population of the charges is governed by the interplay of charge recombination and injection of electrons or holes into the electron transporting material (ETM) or hole transporting material.
material (HTM), respectively. In the simplest approximation (i.e., neglecting Auger recombination valid in the low range of excited carriers concentration), the change of the population of the excited carriers \( n \) in the bulk can be described by
\[
-\frac{dn}{dt} = k_1 n + k_2 n^2
\] (1)
The first-order decay with the rate constant \( k_1 \) is related to the trap-assisted recombination (Shockley–Read–Hall recombination). The second-order process described by the rate constant \( k_2 \) is due to free carrier recombination (band-to-band radiative recombination).

The injection of charges into the ETM or HTM contributes to the first-order processes. However, in many cases the apparent charge population decay can be affected by reabsorption and/or diffusion processes, the inclusion of which in eq 1 requires one to numerically solve the kinetic equation. Therefore, the observed kinetics of the charge population can be affected not only by the perovskite, HTM, and ETM materials but also by the excitation wavelength, excitation fluence, or the perovskite layer thickness.

Besides the properties of the perovskite absorber, the crucial parts in the optimized operation of PSC are the perovskite/ETM and perovskite/HTM interfaces. For standard MAPbI\(_3\), time-resolved techniques were employed to study not only the charge injection dynamics but also the influence of interfacial recombination, interface trap states, and band bending.

Therefore, one of the main goals of our work is to investigate the interfaces of the benchmark triple-cation perovskite with ETM and HTM, focusing on the differences in the dynamics (probed by time-resolved techniques) and absorber structure close to both interfaces. The absorption properties of perovskite material allow us to probe the ETM or HTM interfaces in the fully assembled PSC either by illumination from different sides or by tuning the illumination wavelength. Although electronic transport is known to be very fast in perovskites, an effect on the initial spatial distribution of photocarriers is still expected because interfacial charge injection is much faster than transport. Also, with electron/hole diffusion coefficients on the order of 0.5 cm\(^2\)/s, the carriers will travel distances on the order of 200 nm in a time span of nanoseconds. Thus, for typical absorber thicknesses in PSCs of several hundreds of nanometers, the diffusion process can still be observed by using optical time-resolved techniques.

Reducing the fabrication costs is a very important aspect in PSC development. Typically, PSCs are prepared in a highly controlled environment in a glovebox, which makes the procedure expensive and less available. Perovskite crystallization and solar cell preparation can be transferred into an open-air environment; however, a procedure to deal with and control the amount of water content in open air should be considered during preparation of PSCs at ambient conditions.

Therefore, in this work we focus on triple-cation perovskite prepared under highly controlled dry conditions in a drybox (DC) or under ambient conditions (AC) present under a fume hood in the laboratory. It is expected that the performance of AC samples is lower than those of DC ones, but it is also interesting to study devices prepared at ambient conditions for industrial reasons. Thus, another goal is to understand charge dynamics (recombination and charge injection to interfaces) for two state-of-the-art methods of perovskite preparation. For that we take advantage of the information provided by stationary and time-resolved optical spectroscopy techniques as well as impedance spectroscopy measurements in the frequency domain.

## MATERIALS AND METHODS

### Sample Preparation

Two different sample preparation protocols were used. In the first method, the perovskite precursor and spiro-OMeTAD solutions were prepared in an argon-filled glovebox and then transported to drybox where the spin coating of precursors, heating, and spin coating of spiro-OMeTAD took place. These samples are abbreviated as DC. In the second method, the solutions were prepared in a nitrogen-filled glovebox and then transferred to a fume hood under ambient air conditions for further processing; these samples are abbreviated as AC.

Samples were prepared from 2.5 × 2.3 cm\(^2\) (for AC samples) or 2.5 × 1.7 cm\(^2\) (for DC samples) conducting glass (FTO) substrates. The substrates were cleaned with detergent, distilled water, ethanol, and isopropanol for 15 min each. A compact layer of titania (TiO\(_2\)) was applied by using the spray pyrolysis technique from titanium diisopropoxide (6.67% in EtOH v/v). On the top, mesoporous TiO\(_2\) paste (GreatcellSolar, 30NR-D) diluted 1:6 w/w in EtOH was deposited by spin coating (10 s, 2000 rpm). The FA\(_{0.76}\)MA\(_{0.19}\)Cs\(_{0.05}\)Pb(I\(_{0.81}\)Br\(_{0.19}\)) perovskite precursor solution was obtained by mixing 1.5 M formamidinium lead triiodide (FAPbI\(_3\)) with 1.5 M methylammonium lead tribromide (MAPbBr\(_3\)) solutions, both in 4:1 dimethylformamide:dimethyl sulfoxide (DMF:DMSO, with 10% Pb excess), and 1.5 M cesium iodide (CsI) in DMSO with ratio 95:19:6 (v/v/v). The perovskite layer was deposited by two-step spin coating (10 s at 2000 rpm and then 20 s at 4000 rpm) with chlorobenzene (Chb) as antisolvent (10 s before the end). 2,7,7’,-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene (Spiro-OMeTAD, 72.3 mg/mL in Chb) with additives, i.e., 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, 520 mg/mL in acetonitrile) and 29 μL 4-tet-butylpyridine (TBP), was used as hole transporting material, deposited by spin coating (30 s at 4000 rpm). Finally, 80 nm thick gold electrodes were evaporated on top of spiro-OMeTAD layer. For the AC case, different DMSO:DMF ratios were applied in 1.5 M FAPbI\(_3\) solution to create 0.4, 0.32, 0.27, or 0.24 DMSO content (v/v) in final solution. For DC samples only standard 0.24 DMSO content (v/v) was used.

It has been shown recently that the absolute content of water measured in the form of partial water vapor pressure (WVP) is the determining lab parameter that needs to be considered during preparation of PSCs at ambient conditions. This parameter is given by the formula:

\[
WVP = \frac{RH}{100} P_{sat}
\] (2)

where RH is the relative percent humidity and \( P_{sat} \) is saturation vapor pressure (in kPa) for a given temperature. Therefore, the WVP parameter has been also controlled for the cells prepared under ambient conditions.

### Sample Characterization

For spectral characterization of PSC, a steady-state absorption setup (Jasco V-770) and integrating sphere (Jasco ILN-925) was used. In the studies of the solar cells with different absorption values for the active material, it is often helpful to compare the relative corrected photocurrent of the cells, which gives the information about the total efficiency of the
charge separation. Therefore, in our works we introduce the parameter called total APCE (APCE is absorbed photon to current efficiency).\(^2\)\(^2\) It can be calculated based on the measured short-circuit current of the cell, \(J_{SC}\), and the number of absorbed photons, \(N_{ph}\) (obtained from integration of stationary absorption spectrum multiplied by the photon flux spectrum from AM1.5G data):

\[
\text{total APCE} = \frac{J_{SC}}{N_{ph}}
\]

(3)

where \(\epsilon\) is the elementary charge. In the present work we consider the correlation between total APCE and time constants or perovskite layer thickness. We also use the photocurrent to compare to the charge separation efficiency in the cells of different thicknesses.

A femtosecond transient absorption setup (Spectra-Physics laser system and Helios spectrometer, Ultrafast Systems) was used to measure ultrafast dynamics.\(^2\)\(^9\) The excitation wavelength was set at 505 nm (1 kHz repetition rate), and two different pump pulse energy densities (10 or 30 mJ/cm\(^2\)) were used. The instrument response function was 0.4 ps (FWHM). Emission decays as well as stationary fluorescence spectra were obtained by using the time-correlated single photon counting technique (TCSPC) with temporal resolution from picosecond to nanoseconds, detection range from 450 to 820 nm, and excitation wavelength equal to 407 nm (power 400 \(\mu\)W at repetition rate 4 MHz).\(^3\)\(^0\) The kinetics of time-resolved emission and absorption studies were analyzed by determination of half-lifetimes or by fitting with an analytical function. The solution of eq 1 can be given by the function\(^1\)\(^1\)\(^1\)

\[
n(t) = \frac{n_0 k_1}{k_2 (exp(k_2 t) - 1)} + \frac{n_0 k_2}{k_1 (exp(k_1 t) - 1)}
\]

(4)

where \(n_0\) is the initial charge population density. The transient absorption data were also investigated by using global analysis, the band integral, and the stretched exponential function (the details will be given in the Results and Discussion section). The lifetimes are given as averaged values from 5 to 10 samples along with the estimated errors as standard deviation.

For AC samples, current density–voltage (\(J–V\)) curves were measured under a solar simulator (ABET-Sun2000) with an AM1.5 filter by using a scan rate of 100 mV/s and a sweep delay of 20 s. Samples prepared in DC conditions were characterized by an LED solar simulator (VeraSol-2, Newport). A Keithley Model 2400 digital source meter was used to apply external bias and record photocurrent.

Samples prepared in DC conditions were characterized by an LED solar simulator (VeraSol-2, Newport). A Keithley Model 2400 digital source meter was used to apply external bias and record photocurrent. For AC samples, a much higher variety in the perovskite layer thickness was observed (Figure S1B) as compared to the DC samples. For DC samples two batches of cells were prepared (manufactured by two different people), and they differed slightly by the perovskite thickness, as revealed in the absorption spectra. However, within the same batch the absorption spectra were very similar to each other. The DC samples selected for further time-resolved studies varied significantly in photocurrent; therefore, the correlations between dynamic parameters and photovoltaic performances could be explored. For AC samples, a much higher variation in the perovskite layer thickness was observed (Figure S1B) as compared to the DC samples. For DC samples two batches of cells were prepared (manufactured by two different people), and they differed slightly by the perovskite thickness, as revealed in the absorption spectra. However, within the same batch the absorption spectra were very similar to each other. The DC samples selected for further time-resolved studies varied significantly in photocurrent; therefore, the correlations between dynamic parameters and photovoltaic performances could be explored.
allows us to directly relate the absorbance to the width of the active layer. TEM-EELS-SAED experiments (Figure S4) revealed that the distribution of nitrogen and carbon is homogeneous between the top organic layer (spiro-OMeTAD) and the titania layer. Diffraction patterns show a polycrystalline structure of the perovskite layer with interplanar distances comparable to those observed in XRD pattern. TEM-EDX experiments (Figure S5) show a homogeneous distribution of Pb and Cs atoms and their mixing within the TiO2 porous layer. Slightly porous and empty areas resembling bubbles or cavities can also be observed. We have verified that these inhomogeneities do not originate from the way the lamella are cut.

Figure S6 presents the SEM top-view images of the perovskite structure for one batch of AC samples at WVP = 0.9 kPa and different DMSO:DMF ratios. Crystal grains ranging from 100 to 400 nm can be recognized. A smoother and more homogeneous perovskite surface at the HTM contact yields slightly better photovoltaic parameters. In this particular batch, the best performing cells were made with 0.32 DMSO:DMF content. However, for other batches this result was not confirmed, so no general conclusions about this particular DMSO:DMF ratio can be drawn.

The most important findings of this section come from the Gi-XRD studies which give information about the perovskite structure at different penetration depths from the top gold electrode (HTM side) obtained with different angles of the incident beam. Figure 2 presents the maps of X-ray diffraction patterns (2θ angle) as a function of the X-ray beam grazing angle (ω) for the same samples shown in Figure 1. The simulated calibration plots to convert the incident angle into the attenuation depth32 for Au and perovskite are shown in Figure S7. The characteristic diffraction peaks for the perovskite (2θ = 14.1°, 28.5°, and 31.9°, black dots), unreacted PbI2 phase (2θ = 12.7°, red diamonds), and Au (2θ = 38.1°, brown triangles) are indicated in Figure 2. For the thinner sample in Figure 2A, the pattern due to pure perovskite appears just below the HTM surface (∼4 nm, corresponding to ω = 0.12), while the unreacted PbI2 phase occurs around 60 nm (ω = 0.43). It should be noted that the Au (111) peak from the top layer appears at ω = 0.31 (1.5 nm from the top) due to the different density of the materials. Figure S8A shows the XRD patterns for selected penetration depth, and Figure S8B shows the extracted ratio of the PbI2 to perovskite peaks for the same sample. They show that the deeper the X-ray beam reaches, the higher the content of PbI2, with the maximum PbI2 content occurring in the perovskite layer ∼150 nm below the HTM interface. Based on Figure 1A with a perovskite layer thickness of ∼500 nm, unreacted PbI2 is present ∼350 nm from the bottom TiO2 interface. For the second sample with the perovskite layer being thicker by about 250 nm (∼750 nm total perovskite thickness, Figure 1B), the unreacted PbI2 phase does not appear until a penetration depth of 200−300 nm (it becomes present only for ω > 2.5, Figure 2B). These measurements suggest that the presence of PbI2 is found in all samples within a similar distance from the bottom titania interface.

The role of unreacted PbI2 is widely described in the literature.33−35 A small amount of unreacted PbI2 has been reported to improve the efficiency.36−38 It was shown that PbI2-rich grains exhibit a longer lifetime because of the suppression of defect trapping33,39 and PbI2 excess leads to a
more efficient electron injection to TiO₂. However, too large of a contribution of PbI₂ has a detrimental effect on the solar cell performance. Too thick a PbI₂ layer (>20 nm) at the perovskite/HTM interface lowered the photocurrent. An excess of PbI₂ content had undesirable effects on the PSCs stability as well as on device hysteresis. Our results indicate that the content of unreacted PbI₂ phase in the perovskite structure is much higher near the interface with titania (ETM) than near the interface with spiro-OMeTAD (HTM). This means that the perovskite layer is not homogeneous, and the difference observed in spectroscopic experiments described in the next sections could be caused by higher concentration of the unreacted phase in the region closer to the ETM.

Emission. We took advantage of the strong absorption of the perovskite in the short-wavelength range to selectively probe two different interfaces of the cells as the excitation light is absorbed nearest to the illuminated surface. In our samples more than 80% of light is absorbed within the first 100 nm of perovskite layer for the excitation wavelength below 500 nm. In the emission measurements the pump was set at 407 nm, and the laser pulses were directed through either the ETM or HTM side. The stationary emission and fluorescence decay time constants scaling from hundreds of picoseconds to tens of nanoseconds were measured by the time-correlated single photon counting technique. In the case of excitation from the HTM side, the areas of the devices without gold electrodes were used. Figure 3A presents the representative stationary emission results. The spectra were measured up to 800 nm because the second-order diffraction of the pump wavelength obscured the emission signals at longer wavelength. As can be seen, the emission detected from the ETM side results in a red-shifted emission peak with respect to that from HTM side. On average for the AC cells the emission maximum is shifted from 770 ± 3 nm at the HTM side to 784 ± 2 nm at the ETM side. The difference in emission from each side indicates that the perovskite structure and/or composition is different for the layers closest to HTM or ETM, which correlates with the XRD results discussed in the previous section.

Further differences between the excitation from the ETM and HTM side were observed in the kinetics of fluorescence decay measured close to the band maximum (at 785 nm). For AC samples a significantly longer decay at the HTM side was always observed, which is presented in Figure 3B. The kinetics were first analyzed in the simplest way by taking the decay half-lifetime. The first 100 ps was not analyzed as they contained the contribution from the scattering artifact; this contribution was higher on the HTM side, causing the difference in initial intensities in Figure 3B. The emission half-lifetime statistics for cells of similar perovskite thickness (absorbance around 1.0 at 700 nm) show that the average half-lifetime is equal to 1.61 ± 0.12 and 2.37 ± 0.30 ns for ETM and HTM sides, respectively. The other parameters of all samples (15 in total), including those with different thicknesses, were further studied and compared. Table 1 presents the Pearson correlations between half-lifetimes and relative photocurrent, perovskite thickness (absorption), or DMSO:DMF ratio for AC samples. As can be seen, significant correlations can only be found between half-lifetimes and the stationary absorbance at 700 nm (0.55 for ETM-side half-lifetime and 0.82 for HTM-side half-lifetime). The visualization of such correlations is presented in Figure S9A,B. The apparent longer emission decay for thicker samples agrees with recent reports and can be explained by the reabsorption effect. Moreover, the charge population lifetime in thicker samples can also increase due to diffusion effects because there is a longer pathway for electron and holes to reach the contact materials. To exclude the effect of the sample thickness, we performed an analogous analysis limited only to the cells of similar thickness, which confirmed that the DMSO:DMF ratio had no effect on the lifetimes (Table S1). It should be noted that the effect of different probe wavelengths

Table 1. Pearson Correlations between the Parameters of Emission, Corrected Photocurrent (Total APCE), Absorbance (A) (Corresponding to the Sample Thickness), and DMSO Content in Precursor Solution

|                      | ETM half-lifetime | HTM half-lifetime | A(700 nm) | total APCE | DMSO content |
|----------------------|-------------------|-------------------|-----------|------------|--------------|
| ETM half-lifetime    | 1                 | 0.38              | 0.55      | −0.13      | −0.33        |
| HTM half-lifetime    | 0.38              | 1                 | 0.82      | −0.46      | −0.14        |
| A(700 nm)            | 0.55              | 0.82              | 1         | −0.36      | −0.25        |
| total APCE           | −0.13             | −0.46             | −0.36     | 1          | 0.18         |
| DMSO content         | −0.33             | −0.14             | −0.25     | 0.18       | 1            |

**The correlation is statistically significant at the 0.05 level (a 95% confidence interval).**
was also checked (Table S2), and the variation of the emission lifetime within the emission band was not higher than the differences between HTM and ETM.

We have performed a more rigorous analysis by fitting the mixed first- and second-order decay model (eq 4) to the fluorescence kinetics. A good fit quality (correlation $r^2 > 0.99$) was obtained, and an example is presented in Figure 3B. For AC samples of similar thicknesses the average second-order rate constant was higher from the ETM side ($k_{2,ETM} = (13.5 \pm 1.9) \times 10^{-3}$ s$^{-1}$ W$^{-1}$, standard error of the mean for five samples is given) than from the HTM side ($k_{2,HTM} = (10.7 \pm 1.7) \times 10^{-3}$ s$^{-1}$ W$^{-1}$), in agreement with the half-lifetime analysis. The first-order rate constant ($k_1$) was negligible from the HTM side, while from the ETM side a random distribution around the small value of $k_{1,ETM} = 1 \times 10^{-4}$ ps$^{-1}$ was observed. Significant Pearson correlations were found between $k_{2,ETM}$ and absorbance at 700 nm ($-0.57$) and between $k_{2,HTM}$ and the absorbance ($-0.65$), which confirms the findings from half-lifetimes. However, the Pearson coefficients are not any closer to 1 than those obtained from half-lifetime analysis. Therefore, the parameters of eq 4 do not correlate better with the sample thickness than half-lifetimes.

Differences between the dynamics at HTM and ETM sides were also observed for the DC samples; however, the fluorescence decay at the HTM side was not always longer than from the ETM side. Figure 4A presents half-lifetime data for two different batches with different thickness characterized by indicated absorbance value at 700 nm. Clearly, the decay from the HTM side is getting faster with increasing short-circuit current of the measured cell. For the thicker cells (blue triangles) the decays are slightly slower in comparison to the thinner ones (red dots) due to reabsorption processes$^{15}$ and in line with the results for AC samples, but the trend in the correlation with the photocurrent is the same as for thinner cells. The fluorescence decay measured closer to the HTM side is governed more by hole injection into the spiro-OMeTAD layer than electron injection into TiO$_2$. Therefore, for DC cells we can clearly see the correlation between the short-circuit photocurrent and hole injection dynamics: the faster the hole injection, the higher the short-circuit current of the cell. Similar findings have been reported in our recent studies of the mixed MA and FA solar cells.$^{40}$ The ratios of half-lifetimes measured from ETM and HTM side are shown in Figure 4B. A significant asymmetry in the half-lifetimes from both sides is observed. Holes are transported about 3 times faster than electrons in the highest performing cells with photocurrent close to 20 mA/cm$^2$. It indicates that the crucial part responsible for the variation of the solar cell efficiency for our DC cells is the interface between perovskite and spiro-OMeTAD. Moreover, for efficient charge separation, the hole transfer to spiro-OMeTAD needs to be faster than electron transfer to TiO$_2$. It should be noted that we also observed the same trends for the test perovskite cells prepared in planar configuration (only a compact TiO$_2$ layer without the mesoporous layer), but in that case the best photocurrents were significantly smaller.

The lifetimes obtained for AC and DC samples can be compared for samples of similar perovskite layer thickness (absorbance around 1.0 at 700 nm). Lifetimes are always shorter for the cells prepared under ambient conditions. From the HTM side, the DC cells with the best photocurrent show half-lifetimes of about 3 ns (Figure 4A), while for AC cells it is about 2.4 ns. An even larger difference is found for the excitation from ETM side: half-lifetimes are about 6 ns for the best DC cells (Figure 4) and 1.6 ns for AC cells. As the photocurrent for AC cells is about 20% smaller than that for DC cells, it is unlikely that the shorter lifetimes seen in AC samples are due to faster charge injection to the contact materials. The shorter lifetimes are more likely due to the presence of more defects in the AC samples originating from traces of water during fabrication. These defects will decrease the lifetime due to increased trap-assisted recombination. Interestingly, the comparison of the lifetimes suggests that difference in the defect density between AC and DC samples is larger closer to the ETM side where there is a higher concentration of PbI$_2$. An alternative explanation is that the density of defects is similar, but hole injection is significantly slowed due to the humidity-affected spiro-OMeTAD layer in AC cells.$^{26}$

**Transient Absorption.** Femtosecond transient absorption was measured upon excitation at 505 nm (at two intensities 10 or 30 $\mu$J/cm$^2$) in the spectral range from 670 to 830 nm and in the temporal range up to 3 ns. The solar cells were probed in transmission mode in the areas without gold electrodes from either the ETM or HTM side. Similar to the emission measurements, the absorbance at the pump wavelength is so high ($A > 3$) that most of the light absorption in the perovskite...
takes place close to the ETM or HTM interface, allowing these interfaces to be selectively probed.

Figure S10 presents the representative transient absorption spectra of the selected time delays between the pump and probe pulses. The observed features of this triple-cation perovskite look similar to many previous reports on the standard MAPbI₃ perovskite, including those reported by us earlier.⁴³,⁴⁴ After the initial charge carrier relaxation, the signals are dominated by the strong and sharp negative bleach peak at 740–745 nm, close to the absorption edge. This bleach appears due to the band-filling mechanism,⁴⁵ where its amplitude represents the population of the excited carriers¹⁴ and, in the simplest approximation, should follow eq 1. Figure 5A shows the representative comparison between the bleach signal measured at ETM and HTM sides and the clear additional negative feature in the long-wavelength range observed for the ETM side. We have observed these differences for both AC and DC samples. Moreover, Figure 5B presents the statistics of the bleach maximum for the two excitation intensities. The pump fluence was 10 μJ/cm².

The red-shift of the bleach signal for the ETM side agrees with the red-shifted emission from this side reported in the previous section (Figure 3A), which might be explained by differences in the conduction and valence band alignment of perovskite layers closer to titania with respect to those closer to spiro-OMeTAD. In particular, the additional red-shifted features on the ETM side in both the stationary emission and transient absorption bleach bands can originate from the perovskite structure disturbed by the unreacted PbI₂ phase as described earlier (e.g., by introducing additional trap states responsible for the red-shifted absorption and emission). Another possibility is that there is a different ratio of bromide/iodide content at the interfaces, which could modify the bandgap.⁴⁷ However, the latter hypothesis could not be verified in our TEM-EDX analysis because the signals of these elements overlap with copper (from the grid), carbon, nitrogen, and oxygen. Interestingly, ion migration was found to be obstructed in the PbI₂-deficient samples, which both decreased the current voltage hysteresis and increased the photostability.⁴¹ Therefor, it is possible that ion segregation leading to different ratios of bromide/iodide is only possible close to the ETM where we observe an excess of PbI₂ content in our samples.

Our analysis of the transient absorption dynamics started with the simplest approach of global fitting using a two-exponential function.⁴³ The red-shift of the bleach signal for the ETM side agrees with the red-shifted emission from this side reported in the previous section (Figure 3A), which might be explained by differences in the conduction and valence band alignment of perovskite layers closer to titania with respect to those closer to spiro-OMeTAD. In particular, the additional red-shifted features on the ETM side in both the stationary emission and transient absorption bleach bands can originate from the perovskite structure disturbed by the unreacted PbI₂ phase as described earlier (e.g., by introducing additional trap states responsible for the red-shifted absorption and emission). Another possibility is that there is a different ratio of bromide/iodide content at the interfaces, which could modify the bandgap.⁴⁷ However, the latter hypothesis could not be verified in our TEM-EDX analysis because the signals of these elements overlap with copper (from the grid), carbon, nitrogen, and oxygen. Interestingly, ion migration was found to be obstructed in the PbI₂-deficient samples, which both decreased the current voltage hysteresis and increased the photostability.⁴¹ Therefore, it is possible that ion segregation leading to different ratios of bromide/iodide is only possible close to the ETM where we observe an excess of PbI₂ content in our samples.

Our analysis of the transient absorption dynamics started with the simplest approach of global fitting using a two-exponential function.⁴³ Examples of these global fits (pre-
longer time constants of the two-exponential global exponential factor spectra and associated time constants) are shown in Figure 6 and Figure S11. The first subpicosecond component has a shape characteristic of the band-edge shift, which is due to charge cooling and/or exciton dissociation. We have not observed any influence of the excitation side or the solar cell parameters on the time constant of this component. The second, longer component dominated by the bleach band represents the average decay of the charge population. This time constant is always longer on the HTM than on the ETM side for AC samples, which is in agreement with the findings from the emission decays and further endorses the asymmetry in the electron and hole injection dynamics. It is also possible that the presence of PbI₂ affects the recombination and/or charge injection rates, which contributes to the differences in the charge population dynamics between HTM and ETM sides. For AC samples of similar thickness, the average time constants are equal: τ₁(ETM) = 3.50 ± 0.69 ns, τ₁(HTM) = 5.52 ± 0.61 ns for 10 μJ/cm² and τ₂(ETM) = 1.59 ± 0.15 ns, τ₂(HTM) = 2.02 ± 0.18 ns for 30 μJ/cm² pump intensity. The shortening of the time constants at higher pump intensity (and also the differences between the time constant values in transient absorption and emission measurements reported in the previous section) is due to the second-order processes (eq 1) which accelerate the charge population decay for higher charge density.

Table 2 presents the Pearson correlations between the longer time constants of the two-exponential global fit at lower intensity and relative photocurrent, perovskite thickness (absorption), or DMSO:DMF content ratio for AC samples. As can be seen, significant correlations can only be found between the time constants and the stationary absorbance at 700 nm (0.78 for the ETM side) or total APCE (–0.85 for the ETM side). This agrees with the findings presented in the emission section that the apparent lifetime increases for higher perovskite thickness and that the lifetime decreases for better recombination. The visualization of the correlations of the transient absorption lifetime with the absorbance is presented in Figure S9C,D. Similar to the emission study, the Pearson’s correlations limited to the samples of the same thickness are shown in Table S3, again showing no effect of the DMSO content on the lifetimes.

To get further insights into the electron dynamics, a more complex analysis of the transient absorption dynamics was performed. In the multiexponential global analysis, a four-exponential function gives a better fit, especially for a higher pump pulse intensity. As we have previously reported, the additional fit components better describe the initial decay of the charges occupying higher energy levels in the conduction and valence bands. Examples of two- or four-exponential fits are shown in Figure S11. The time constants are always longer for the HTM side, and the additional red-shifted features appear for the pre-exponential factor spectra on the ETM side.

We have recently reported that for MAPbI₃ perovskite the charge population is most properly described by the band integral (BI). The integral calculated over the entire band is insensitive to the spectral shift of the band (e.g., caused by the Burstein–Moss effect in perovskites) and reflects population dynamics if the oscillator strengths of optical transitions do not change. Therefore, such BIs were calculated for the triple-cation perovskite samples studied in this work (Figure S12A), and we have fit them with a stretched exponential function, mixed first- and second-order decay function (eq 4), and its modification. The details of the fits are presented in the Supporting Information (Tables S4 and S5, Figure S13A). In the stretched exponential analysis, the characteristic times (τ) values are smaller on the ETM than on the HTM side, while the values of the stretch parameter (β) are significantly smaller on the ETM side than on the HTM side (Figure S12B), which indicates more stretched kinetics at ETM side. However, the Pearson correlations were not better than those for two-exponential approximation shown in Table 2. Equation 4 was poorly fitted to BI of the transient absorption, especially for the higher pump pulse intensity (30 μJ/cm²). Interestingly, quite a good fit was observed when the mixed first- and second-order function given by eq 4 was “stretched” by raising it to a power lower than 1. We have found the best fits with the power equal to 0.3 (Figure S13B), though its physical meaning is rather hard to explain, and higher k₂ values from ETM than HTM side (Table S5). Overall, the fits of the different analytical functions to BI kinetics confirm the findings from the simple two-exponential global analysis (Table 2), but more physical insights cannot be deduced from the fitted parameters. The true kinetics are most likely described by a more complex model including charge diffusion and reabsorption of the light, which requires the fits to the numerical solutions of the differential charge population equations. A more complex model would result in a more precise determination of the first- and second-order rate constants and their correlations with other solar cell parameters; however, it was beyond the scope of this work.

Electrochemical Impedance Spectroscopy. AC samples prepared under different DMSO:DMF ratios and WVP values have been studied by electrochemical impedance spectroscopy at open-circuit potential in the frequency range 10⁻⁴–10⁻² Hz. Two different LED bias wavelengths were used (465 nm (blue) and 635 nm (red)) to establish the impact of different optical penetration depths in the perovskite layer. Because of the high perovskite absorption in the blue region, the 465 nm LED light is absorbed in the 200 nm closest to the titania perovskite interface. In contrast, the 635 nm LED light has a longer penetration depth, so information obtained by red light bias characterizes charge behavior in the perovskite regions further from the titania layer. The impedance spectra were mainly characterized by a high-frequency (HF) signal at 10 Hz (Figure S14), which has been associated with electronic transport and recombination processes in the perovskite layer. The HF signal was analyzed by fitting to a Voight equivalent circuit (inset in Figure S14A). The HF
resistance \((R_{HF})\) extracted from the impedance results are given in Figure 7A as a function of open-circuit potential, while HF capacitance \((C_{HF})\) and time constant are shown in Figure S15. In the case of \(C_{HF}\), blue and red signals agree, showing small \((\sim 10^{-8}\text{ F})\) and almost constant values for all bias voltages close to \(V_{OC}\) (Figure S15A) which are typical for perovskite solar cells.\(^{53}\) By contrast, \(R_{HF}\) varies exponentially with the open-circuit potential following eq 5. From Figure 7A, lower values of \(R_{HF}\) are observed with red light illumination than those for blue light regardless of DMSO ratio. However, when the \(R_{HF}\) is compared for different DMSO ratios, higher values of \(R_{HF}\) are obtained for the lowest DMSO concentration. Taking into account that the red light illumination produces photogenerated charged carriers further away from titania/perovskite interface compared to blue light illumination, the lower \(R_{HF}\) values can be analyzed as a magnification of charge recombination loss close to the perovskite/HTM interface and/or a shorter diffusion length due to a global acceleration of the recombination rate. The ideality factors \((m)\) were obtained from the slopes of the graphs of the resistance \((R_{HF})\) vs potential \((V)\) according to the following equation:\(^{15,50,53}\)

\[
R_{HF} = R_{0HF} \exp \left[ \frac{eV}{mk_BT} \right]
\]

where \(R_{0HF}\) is the resistance at bias potential equal to zero, \(k_B\) is the Boltzmann constant, and \(T\) is temperature. We can clearly see from Figure 7B that the ideality factor becomes higher with higher DMSO concentration. The smallest and best values of the ideality factor \((m\) between 1 and 1.5\) are obtained for 0.24 DMSO:DMF ratio. These ideality factor values are in line with those previously obtained for pure MAPbI\(_3\) in AC conditions.\(^{31}\) The variation of the ideality factor with DMSO concentration can be interpreted as a change of the recombination mechanism (from bulk to surface recombination). This interpretation is supported by a larger shift between red and blue excitation data for a cell with a lower ideality factor.\(^{19}\)

Finally, we have also measured the electrochemical impedance for DC samples. In this case a different configuration was used—the cells were measured both in the dark and under 1 sun illumination at different bias voltages in non-open-circuit conditions, permitting the flow of the charges through the circuit. At such conditions the time constants obtained in the dark correspond to the recombination processes, while those under illumination contain an additional contribution from the transfer of the photogenerated carriers to ETM and HTM. The exemplary results for the cells that differ in photocurrent are presented in Figure S16. The time constants in the dark are similar for all cells, but time constants measured under illumination are significantly shorter for the cells with higher photocurrent. We have observed similar behavior in our recent studies of the mixed MA and FA solar cells,\(^6\) which can be explained by faster carrier injection in better performing cells. This agrees with the findings of time-resolved emission and transient absorption studies probing injection at shorter time scales as discussed in the previous sections.

\section*{CONCLUSIONS}

One of the most efficient configurations of third-generation solar cells is the triple-cation perovskite (methylammonium, formamidinium, and cesium) placed between the mesoporous titania layer (ETM) and spiro-OMeTAD (HTM). In this work a detailed investigation of the properties of such perovskites in contact with both materials is provided, including the studies of charge transfer dynamics at the interfaces using time-resolved fluorescence and femtosecond transient absorption techniques. The results are verified for perovskite solar cells prepared with standard procedure under water-free drybox conditions as well as those fabricated under ambient room humidity. For the samples prepared under ambient room conditions, the charge population decay is significantly faster at the ETM side than at the HTM side. For example, emission half-lifetimes are 1.6 ns at the ETM side vs 2.4 ns at the HTM side for excitation 400 \(\mu\text{W}\) at 407 nm, and transient absorption average decay is 3.5 ns vs 5.5 ns for excitation 10 \(\mu\text{J/cm}^2\) at 505 nm. This indicates asymmetry in the electron and hole injection dynamics induced by the presence of water and/or a different distribution of recombination centers close to the two interfaces. The charge recombination loss observed by electrochemical impedance spectroscopy is found to be slower at the interface with ETM than with HTM (times on the order of milliseconds). For the solar cells prepared under drybox conditions, the hole injection becomes faster for the solar cells.
with higher photocurrent (with the fastest decay emission half-lifetime about 1 ns from HTM side). Grazing incident X-ray diffraction experiments indicate that the content of unreacted PbI₂ phase in the perovskite structure is much higher near the interface with ETM than near the interface with HTM. The stationary emission spectra and transient bleach peaks of perovskites show additional long-wavelength features close to the titania side (e.g., emission maximum shifts from 770 nm at HTM to 784 nm at ETM side). Finally, the effects of varying the DMSO content in the precursor solution or perovskite thickness on the properties of the solar cells prepared under ambient room conditions are also investigated. The ideality factor of the cells is found to increase with increasing DMSO concentration. This can be interpreted as a change of the recombination mechanism from bulk to surface recombination. Our findings reveal that the perovskite structure and charge dynamics are not uniform within the whole perovskite layer, which has significant implications for understanding the operation and optimizing the performance of devices based on this efficient mixed-cation perovskite material.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c07095.

- Figures S1–S16: C–V curves, absorption spectra, TEM-EELS-SAED, TEM-EDX, SEM, and XRD analysis, additional transient absorption spectra, BI kinetics, additional impedance spectroscopy data; Tables S1–S5: Pearson correlations for the cells of similar thickness; emission lifetimes at different wavelength, parameters of the BI fit (PDF)

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