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Correlation of recombination and open circuit voltage in planar heterojunction perovskite solar cells

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Mixed-cation and halide perovskite solar cells have shown superior photovoltaic performance than mono-cation based representatives. Their remarkable photovoltaic performance is the effect of best compositional engineering along with their unique optoelectronic properties. However, there is still a lack of understanding in the working principles of multi-cation based perovskite solar cells. In this study, we employ the state-of-the-art multiple-cation perovskites $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ and $\text{Cs}_2(\text{MA}_{0.17}\text{FA}_{0.83})_{95}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ as absorber layers and investigate their intrinsic and interfacial dynamics in planar TiO_2 -based PSCs. We demonstrate that the incorporation of Cs^+ in $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ leads to an increase in power conversion efficiency, improved perovskite phase stability and reduced recombination. However, these devices along with these excellent characteristics is still suffer from the lower open circuit voltage (V_{oc}) as compared to $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ based devices. By analysing the morphological properties and capacitance versus frequency responses, we show that the higher grain size and higher accumulation of photogenerated charges manifest the high open circuit voltage in $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ based devices. Our results demonstrate that the values of V_{oc} not only depend on the recombination, but also on charges accumulation phenomena.

Introduction

Metal halide perovskite semiconductors have recently taken a dominant position in the field of photovoltaic due to their outstanding optical and electronic properties such as high optical absorption, band gap tunability, high charge-carrier mobility and long diffusion lengths.^{1–3} Along with a solar conversion efficiency certified exceeding 23%, perovskite solar cells (PSCs) have exhibited a performance level that is comparable to state-of-the-art copper indium gallium diselenide (CIGS) and are approaching the commercial monocrystalline silicon.⁴ The main improvements towards high-performance and stable PSCs were achieved through compositional engineering,^{5,6} development of thin film deposition methods^{7–9} and selective contact materials,^{10,11} design of device structure,^{12–14} interface engineering,^{15–17} and so on. The state-of-the-art perovskite solar cells are based on

Pb^{2+} ions and comprise a mixture of monovalent cations (MA, FA and Cs), and a mixture of halides (I and Br); various combinations and ratios of these species have been explored to achieve both high efficiency and stability.^{18–24} For example, the Cs cation additives have been shown to induce a preferable crystallization of photoactive phase of FAPbI_3 perovskite enabling higher stability of PSC.^{18,25} Along with high stability, Cs-intercalation also changes the electronic processes occurring within PSCs such as charge carrier transport and recombination within the absorber layer and across various interfaces.^{26,27} Recently, we have discussed the interfacial characteristics of Cs-based PSCs with both planar and mesoporous architecture providing a deeper insight into the charge accumulation mechanism and the origin of open-circuit voltage (V_{oc}).²⁸ It was also reported that the addition of Cs cation to $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ perovskite composition results in an improvement in solar cell performance,¹⁸ however, the analysis of processes that leads to differences in PV parameters between the undoped and Cs-doped PSCs has been rarely discussed in the literature. Moreover, in literature there is lots of inconstancy in device parameters, which we believe is mainly due to the difference in environmental conditions.^{26,29}

In this work, we investigate the effect of Cs cation on the intrinsic and interfacial dynamics of planar TiO_2 -based PSCs. Our results show that Cs-addition to $\text{FA}_{0.83}\text{MA}_{0.17}\text{Pb}(\text{I}_{0.83}\text{Br}_{0.17})_3$ (MAFA) perovskite composition improves the overall device

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performance by reducing the series resistance and recombination current and decreasing the hysteresis. Moreover, the capacitance–frequency analyses under dark and illumination conditions reveal that a higher accumulation of charges is responsible for the higher V_{oc} observed in MAFA PSCs. These results illustrate a convenient way for in-depth characterization and analysis of efficient PSCs, which is very crucial for the further understanding of PSCs device mechanism.

Results and Discussion

Fig. 1a shows the schematic representation of the planar architecture of PSC consisting of FTO/comp-TiO₂/perovskite absorber layer/spiro OMeTAD/Au. In this study, we employed the mixed-halide and mixed-cation formulation FA_{0.83}MA_{0.17}Pb(I_{0.83}Br_{0.17})₃ (further denoted as MAFA) and Cs₅(MA_{0.17}FA_{0.83})₉₅Pb(I_{0.83}Br_{0.17})₃ (further denoted as CsMAFA) as perovskite absorber layers. The fabrication process of solar cells was carried out at a same time to maintain the same experimental conditions. We believe that by utilization of same conditions for preparation of TiO₂, Spiro-OMeTAD, gold electrode, and using the same amount of perovskite solution for both MAFA and CsMAFA perovskites, the observed differences in the photovoltaic parameter of the resulted devices is only due to the different optoelectrical properties of absorber layers and the nature of interfaces with subsequent layers. Moreover, we note that the elucidation of exact phenomena responsible for better understanding the device working mechanisms is really reliable, when the devices exhibit similar efficiency and other photovoltaic parameters are close to each other. Further details regarding the device preparation and characterization are given in the Experimental Section.

The cross-sectional SEM image of the corresponding CsMAFA device is shown in Fig. 1b. The thickness of the electron transport layer, perovskite layer and hole transport layer are about 250 nm, 400 nm and 80 nm, respectively. The current-voltage (J-V) characteristic curves of the fabricated PSCs under 1 Sun illumination under reverse scan direction are shown in Fig. 1c. The champion MAFA based PSC exhibits a PCE of 18.71 % with a J_{sc} of 21.7 mAcm⁻², a V_{oc} of 1.15 V, and a FF of 75 %, whereas for CsMAFA based PSC the PCE is 19.83% with a J_{sc} of 22.7 mAcm⁻², a V_{oc} of 1.12 V and a FF of 78 %. The statistical distributions of all collected photovoltaic parameters are shown in Fig. S1. It shows that CsMAFA devices exhibit higher average value of PCEs than those of the MAFA based devices due to increased values of FF and J_{sc} . However, the addition of CsI to MAFA solution has a detrimental impact on V_{oc} of device. Recently, Sherkar et al., demonstrated that the monomolecular recombination constant k_1 in MAFA PSCs is relatively low and stems from the trap-assisted recombination sources such as pin holes, grain boundaries, impurities, non-perovskite phase, etc.³⁰ Furthermore, it was also revealed by employing hard X-ray photoelectron spectroscopy that the unreacted organic cation (FA) and halides (excess PbI₂, Br-/I-) are the main remained species in MAFA perovskite films.³¹ The

presence of these sites in perovskite films can act as charge trapping centres and leads to the trap-assisted charge carrier recombination. The introduced CsI to MAFA composition is likely react with these unreacted species and transform into the main perovskite phase. Having this in mind, one may expect a higher value of V_{oc} in CsMAFA as compared to MAFA devices, or there is another possibility that V_{oc} in these PSCs is less affected by the defects and the resulted devices have different origin of V_{oc} .

Fig. 1 (A) Schematic representation of the planar architecture of PSC consisting of FTO/TiO₂/perovskite absorber layer/spiro OMeTAD/Au. (B) Cross-sectional SEM image of fabricated CsMAFA PSC device. (C) J-V characteristics of the fabricated PSCs under 1 Sun illumination for reverse scan direction. (D) Dark J-V characteristics of fabricated PSCs measured in reverse scan and plotted in log scale.

To explain the phenomena responsible for the observed difference in V_{oc} , we first measured the recombination in both devices and correlated with the observed V_{oc} . Generally, recombination in solar cell is elucidated by the ideality factor (n). Fig. 1d represents the dark J-V characteristics of MAFA and CsMAFA PSCs measured in reverse scan and plotted in log scale. The measured J-V plot can be represented by the following expression: $J_{dark}(V) = J_0(\exp(eV/n_dkT))^{-1}$.³² From this equation, the ideality factor can be extracted as $n_d(V) = [(kT/e)(d \ln J(V)/d(V))]^{-1}$. The value of n_d is obtained from the exponential region of J-V characteristics or the minimum point of n_d vs V plot (see Fig. S2). The calculated values of $n_d = 2.2$ for MAFA and $n_d = 2$ for CsMAFA PSCs are similar and thus, it is hard to interpret the recombination processes occurring in these devices. It is also possible that the domination of series and shunt resistance at high and low potential restrict the exact determination of n_d .³³ The J-V curves of PSCs measured at 1 Sun illumination under forward and reverse scan directions are shown in Figure S3. In both devices a hysteresis loop was observed when the scan direction is changed from forward to backward, which is typical in TiO₂-based planar device architectures.^{9,34} We found that the hysteresis index is higher in MAFA PSCs, suggesting that the composition of MAFA absorber layer is the main factor responsible for observed hysteresis. In turn, the addition of Cs⁺ to MAFA composition causes a reduction in the observed hysteresis.

Focusing on the recombination in these devices, J-V curve of MAFA PSCs under forward sweep shows significantly reduced photovoltaic parameters, i.e., V_{oc} and FF compared to the corresponding parameters observed in CsMAFA PSCs.

Next, we investigate by employing impedance spectroscopy (IS) whether the higher ideality factor observed in MAFA PSCs can be attributed to the effect of series resistance (R_s) or recombination.³⁵ The IS responses were measured under dark and 1 sun illumination as a function of the applied bias. In this measurement, the frequency was set in the range of 100 mHz to 1 MHz with 20 mV perturbation. Fig. 2a and Fig. S4 show the IS spectra of MAFA and CsMAFA PSCs measured under 1 Sun illumination as a function of the applied bias, respectively. Fig. 2b depicts the most commonly used electrical equivalent circuit used for the fitting of IS spectra.^{36,37} In general, the resistive (R_{hf}) and capacitive (C_{hf}) elements represent the recombination and dielectric property of PSCs. The bias dependence of R_{hf} and its interpretation was discussed in more detail in our previous work.²⁸ The R_s element represents the series resistance due to connecting leads or resistive element of PSCs. The R_{lf} and C_{lf} element represents the resistance and capacitance associated with the low frequency loop. The low frequency C_{lf} is associated with the accumulation of charges, which is also responsible for hysteresis in PSCs. The values of R_s were calculated from the high frequency intercept of real axis impedance and found to be 14 Ω and 10 Ω for MAFA and CsMAFA PSCs, respectively. The observed lower value of R_s in CsMAFA device can be assigned to the improved FF and suppressed interruption for the transport of photogenerated charge carriers. The extracted values of R_{hf} for both the devices as a function of applied bias (from knee voltage to V_{oc}) and measured at 1 Sun illumination are shown in Fig. 2c. The higher magnitude of R_{hf} in CsMAFA than that observed in MAFA device attributes to the lower recombination, as R_{hf} is also known as recombination resistance. Interestingly, the value of n_d can also be calculated for both the devices from the obtained curve of R_{hf} . A lower value n_d of 1.9 is obtained for CsMAFA as compared to 2.1 for MAFA.

Fig. 2 (A) IS spectra of MAFA PSCs measured under 1 Sun illumination as a function of the applied bias. (B) Electrical equivalent circuit used for the fitting of

IS spectra of PSC devices and (C) the extracted values of R_{hf} for the fabricated PSC devices as a function of bias from knee voltage to V_{oc} and measured at 1 Sun illumination.

Fig. S5 depicts the plot of R_{lf} for both the devices and a higher value of R_{lf} signifies the lower recombination in CsMAFA device. From the analysis of IS, we found that the addition of Cs^+ to MAFA composition eventually reduces the R_s and recombination in PSCs. Thus, in the line of these results it is really interesting to explain why MAFA devices possess higher V_{oc} as compared to CsMAFA. The possible mechanism that could explain the higher V_{oc} and higher recombination in MAFA devices may stem from the structural and interfacial features of devices.

To get further insight into the structural property, we have characterized the morphologies of MAFA and CsMAFA perovskite films using SEM and atomic force microscopy (AFM). Fig. 3a and 3b show the top-view SEM images of the corresponding films. The average values of grain size are 430 nm and 370 nm for MAFA and CsMAFA films, respectively. A slightly larger grain size in MAFA absorber layer can be correlated to the observed higher V_{oc} value as compared to CsMAFA perovskite layer. AFM images of the corresponding perovskite films are in a good agreement with SEM analysis. The roughness of 38 nm and 31 nm was obtained for MAFA and CsMAFA films, respectively (Fig. 3c and 3d). These results indicate that CsMAFA film has a smoother surface, which can result in a better charge transfer property in contact with hole transporting layer (HTL). This may also explain the observed lower hysteresis loop in CsMAFA PSCs.³⁸

Fig. 3 Top view SEM and AFM images of MAFA (A,C) and CsMAFA (B,D) perovskite films, respectively.

Further, ultraviolet photoelectron spectroscopy (UPS) measurement of both the MAFA and CsMAFA layers was performed to get information of absorber layer energetics (Fig. 4 and S6). These results show that the valance band maxima

(VBM) for MAFA are energetically same as than that of CsMAFA, which is consistent with previous report.³⁹ The authors have also shown that the incorporation of 10 % of Cs⁺ in MAFA resulted in the shifting of the Fermi level toward conduction band and makes CsMAFA more n-type compared to MAFA. This observation is well understood and can justify the observed difference in device parameters. However, in case of 5% incorporation of Cs⁺ in MAFA no such phenomena is observed; this may be attributed to the limitation of UPS measurement or the some other phenomena is associated.⁴⁰ Moreover, from the obtained UPS results and previous report by other authors we believed that the difference in the observed values of V_{oc} for MAFA and CsMAFA is not possible to explain by the interface energetics.³⁹

Fig. 4 UPS measurements of (A) MAFA and (B) CsMAFA films to get insights about absorber layer energetics.

Fig. 5a depicts the capacitance-frequency (C-F) response of both the PSCs measured under dark in a frequency range of 0.1 Hz to 1 MHz. In general, the C-F response of PSCs is defined by the term of low (< 1 kHz) and high frequency (> 1 kHz). Generally, the high-frequency capacitance rely on the geometrical capacitance of PSCs, whereas low frequency capacitance is due to charge and ion accumulation at the interfaces.⁴¹ We found that the C-F response curves for both devices exhibit similar trend, which suggest that under dark condition the interfacial behaviour in both the PSCs are the same. However, the C-F response curves recorded under illumination have a totally distinguish response in compared to analyses under dark (Fig. 5b). A higher value of low frequency capacitance observed in MAFA PSCs attributes that PV device parameters difference from CsMAFA PSCs stem from the influence of illumination. The studies by Jacobs et al., demonstrated that the increased in the low frequency capacitance under illumination can be simply explain as a consequence of larger recombination rates, which in turn contribute to both the real and imaginary parts of the admittance or impedance.⁴² The increased in recombination primarily affects the real part (conductivity), however, the contributions to the imaginary part (capacitance) also appear at lower frequencies due to ion-induced delay. These results demonstrate that the MAFA device exhibits a significantly higher value of low frequency capacitance as compared to CsMAFA device. The higher capacitance in MAFA PSCs is assigned to the excess accumulation of ions or charges at the interface. The recent study by Zarazua et al., has shown that the accumulated charges in PSCs increase the surface

recombination, which may be the one of the phenomena responsible for the resulted higher ideality factor in MAFA PSCs.⁴³ More importantly, the extra accumulated charges not only increase the surface recombination, but also enlarge the electrostatic potential at surface that could eventually add in series with open circuit potential.^{44–50} The low frequency capacitance or accumulated capacitance is expressed by the given equation:

$$C_s = dQ/dV = q(p_b/2)^{1/2} (\epsilon_r \epsilon_0 / kT)^{1/2} e^{qV/2kT}$$

In this equation, the higher value of accumulation is accepted for a large value of doping density. In order to get information of the doping density, Mott-Schotky measurements of both devices under dark and illumination conditions were performed, as shown in Fig. S7. We found that MAFA and CsMAFA PSCs exhibit a comparative value of doping density, but under illumination a higher value is observed for MAFA PSCs. This increase number of carrier density is correlated with the higher accumulation of charges in MAFA PSCs.

Fig. 5 Capacitance-frequency response of both the PSCs in a frequency range of 0.1 Hz to 1MHz measured under (A) light and (B) dark conditions.

Conclusions

In conclusion, we have addressed the influence of Cs⁺ addition on the intrinsic and interfacial dynamics of state-of-the-art multiple-cation PSCs. We have shown that Cs-addition to

MAFA perovskite composition improved the overall device performance by reducing the series resistance and recombination current and decreasing the hysteresis. Moreover, the analysis of the morphological properties and capacitance-frequency responses under dark and illumination conditions of the investigated PSCs demonstrated that the higher grain size and higher accumulation of photogenerated charges manifest the high open circuit voltage found in the MAFA based devices. The present study provides an in-depth analysis of processes that lead to differences in PV parameters between the undoped and Cs-doped PSCs.

Experimental Section

Materials: The organic cation halide salts were purchased from Dyesol; the lead compounds from TCI and the CsI from abcr GmbH. Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and 4-tert-butylpyridine (tBP) are received from Sigma-Aldrich.

Solar cell device fabrication: Nippon Sheet Glass 10 Ω/sq was cleaned by sonication in 2% Hellmanex water solution for 30 min. After rinsing with deionised water and ethanol, the substrates were further cleaned with UV ozone treatment for 15 min. Then, a compact thick titanium dioxide layer was deposited by spray pyrolysis of 9 ml ethanol solution containing 0.6 mL titanium diisopropoxide bis(acetylacetonate) solution (75% in 2-propanol, Sigma-Aldrich) and 0.4 mL acetylacetone at 450° C in air. The devices were made of a stacking of FTO/compact TiO_2 -layer/perovskite/spiro-MeOTAD/Au.

The perovskite films of MAFA were deposited from a precursor solution containing FAI (1M), PbI_2 (1.1 M), MABr (0.2 M) and PbBr_2 (0.2 M) in anhydrous DMF/DMSO (4:1 (v:v)) solution. The perovskite solution was spin coated in a two-step programme at 1,000 and 6,000 r.p.m. for 10 and 20 s, respectively. During the second step, 100 ml of chlorobenzene was poured on the spinning substrate 10 s prior the end of the programme. The substrates were then annealed at 100°C for 1 h in nitrogen-filled glove box.

The perovskite films of CsMAFA were deposited from a precursor solution containing FAI (1 M), PbI_2 (1.1 M), MABr (0.2 M) and PbBr_2 (0.2 M) was first prepared in a mixed solvent of DMF:DMSO = 4:1 v/v. Then, a 5 vol% of 1.5 M CsI solution in DMSO was added into the perovskite solution in order to have a triple cation perovskite. The solution was spin-coated at 1000 rpm for 10 s and, continuously at 6000 rpm for 20 s. During the second phase, 100 μL of chlorobenzene or isopropanol was dropped on top film 10 second before end of spinning. Thereafter, the film was annealed at 100°C for 50 min in a dry box.

Hole transporting material (HTM) solution was prepared by dissolving 100 mg spiro-MeOTAD in 1.094 ml chlorobenzene and additionally mixing it with 23 μL of lithium bis(trifluoromethylsulphonyl)imide (stock solution Li-TFSI 520 mg·mL⁻¹ in acetonitrile), 39 μL tert-butylpyridine. HTM was

deposited on top of the perovskite layer by spin coating at 4000 rpm for 20 s. Afterward, the samples maintained in the air (20% relative humidity) for 6 hours for spiro oxidation purpose. Finally, 80 nm of gold top electrode was thermally evaporated under high vacuum. The active area of the devices is approximately 0.16 cm².

Device characterization: The J-V characteristics of the devices were measured under 100 mW/cm² conditions using a 450 W Xenon lamp (Oriol), as a light source, equipped with a Schott K113 Tempax sunlight filter (Prazisions Glas & Optik GmbH) to match the emission spectra to the AM1.5G standard in the region of 350-750 nm. The current-voltage characteristics of the devices were obtained by applying external potential bias to the cell while recording the generated photocurrent using a Keithley (Model 2400) digital source meter and also with a temperature-controlled probe station from LASC. The J-V curves of all devices were measured by masking the active area with a metal mask of area 0.16 cm². AC measurements were performed using a potentiostat Autolab equipped with a frequency response analyser. IS measurements were performed in the DC bias range of 0 to open circuit voltage with an AC perturbation signal of 20 mV in the frequency range of 100mHz to 100 kHz.

Film characterizations: The surface morphology of the perovskite film was explored by a ZEISS Merlin HR-SEM. An electron beam accelerated to 5 kV was used with an in-lens detector. In order to study the surface roughness of perovskite films, atomic force microscopy (AFM, NanoScope IIIa/Dimension 3100) was employed. The band alignment of PSC devices was studied by using ultraviolet photoelectron spectroscopy (UPS, AXIS NOVA, Kratos Analytical Ltd, UK) using He I (21.2 eV) as the photon source.

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