

# Large grain size with reduced non-radiative recombination in potassium incorporated methylammonium-free perovskite solar cells

Gabriela S. Anaya Gonzalez,<sup>1,2‡</sup> Jose J. Jeronimo-Rendon,<sup>3‡</sup> Qiong Wang,<sup>1</sup> Guixiang Li,<sup>1</sup> Agustin O. Alvarez,<sup>5</sup> Francisco Fabregat-Santiago,<sup>5</sup> Hans Köbler,<sup>1</sup> Alberto Alvarado,<sup>2</sup> Hector Juárez-Santesteban,<sup>2</sup> Silver-Hamill Turren-Cruz,<sup>1,5\*</sup> Michael Saliba<sup>3,4</sup> and Antonio Abate<sup>1</sup>

<sup>1</sup> Department of Novel Materials and Interfaces for Photovoltaic Solar Cells, Helmholtz-Zentrum Berlin für Materialien und Energie, Kekuléstrasse 5, 12489 Berlin, Germany

<sup>2</sup> Benemérita Universidad Autónoma de Puebla. CIDS, Av. San Claudio y 18 Sur, Col. San Manuel, Ciudad Universitaria, CP 72570, P.O. Box 1067, Puebla, Pue., 7200, México

<sup>3</sup> University of Stuttgart, Institute for Photovoltaics, Pfaffenwaldring 47, 70569 Stuttgart, Germany

<sup>4</sup> Helmholtz Young Investigator Group FRONTRUNNER, IEK5-Photovoltaics Forschungszentrum Jülich, 52425 Jülich, Germany

<sup>5</sup> Institute of Advanced Materials (INAM), Universitat Jaume I, Avda. V. Sos Baynat s/n, 12006 Castellón de la Plana, Spain.

\*Corresponding authors: [turren@uji.es](mailto:turren@uji.es)

‡These authors contributed equally

Keywords: Perovskite solar cell, photovoltaics, Potassium Iodide

## **Abstract**

Organic–inorganic hybrid halide perovskites are widely considered to be one of the most promising materials in photovoltaic technology, and the use of this semiconductor as an absorber layer in solar cells has attracted considerable interest due to their excellent properties. It has been reported that the incorporation of potassium ions is a powerful strategy to tune the properties of perovskites, notwithstanding there has been some disagreement regarding the role of this monovalent alkali metal within the perovskite structure. Here, we investigated the impact of  $K^+$  on the film properties and photovoltaic performance in double-cation perovskite solar cells  $CS_{0.1}FA_{0.9}PbI_3$ . Our results show that  $K^+$  intervenes in the crystallization process, inducing the extraction of non-reactive  $PbI_2$  from the bulk, resulting in a notable enhancement in morphology and reduced non-radiative recombination. The solar cells fabricated with 3% of  $K^+$  content achieve a PCE of 19.3%, showing a significant improvement in  $J_{sc}$ ,  $V_{oc}$  and stability values compared with control devices.

## Introduction

Organic-inorganic halide perovskites have been attracting considerable interest for over a decade; since their first appearance in 2009, there has been a rapid rise in using this novel material as a photo-active layer in solar cells <sup>[1,2]</sup>. Properties like a tunable bandgap, high defect tolerance, and long carrier diffusion length make this material suitable for optoelectronics and photovoltaics applications <sup>[3-5]</sup>. As a result of continuous research and engineering, perovskite solar cells performance (PSCs) has overtaken other photovoltaics technologies such as dye-sensitized, organic, CdTe, or CIGS-based solar cells, reaching more than 25% of power conversion efficiency (PCE) <sup>[6,7]</sup>. Despite the high efficiency and lower production cost compared with silicon solar cells, some constraints remain before industrialization can be achieved, e.g. toxicity, hysteresis, degradation, and instability <sup>[6,7]</sup>.

Compositional engineering is an effective strategy to improve the properties of perovskite and suppress undesirable characteristics. In this regard, different approaches have been proposed. One of the most applied strategies is the cations mixing in the perovskite chemical formula  $ABX_3$  where the A-cations methylammonium ( $(CH_3NH_3)^+$ , MA), formamidinium ( $(CH_3(NH_2)_2^+$ , FA) and  $Cs^+$  have been extensively used.  $MAPbI_3$  and  $FAPbI_3$  were among the first perovskites used as a photo-active layer in solar cells and the most studied so far <sup>[8-11]</sup>.  $MAPbI_3$  based solar cells have achieved high efficiencies but undergoing rapid decomposition when they are exposed to light or in dry air due to the volatile nature of MA <sup>[12]</sup>. On the other hand,  $FAPbI_3$  can crystallize in the non-perovskite hexagonal phase  $\delta$ - $FAPbI_3$ , which does not have photo-active behavior. Nevertheless, FA-based perovskite generates considerable interest due to its wider bandgap and superior thermal stability compared to MA-based perovskites. Incorporating smaller cations such as  $Cs^+$  and  $Rb^+$  stabilize the  $\alpha$ - $FAPbI_3$  cubic phase; the inorganic cations addition also enhance thermal and

moisture stability<sup>[13]</sup>. In recent years, there has been growing interest in adding smaller alkali cations into perovskite to boost solar cells performance and enhance their stability<sup>[14–16]</sup>. In particular, potassium ion ( $K^+$ ) has shown outstanding results tuning the properties of MAFA and CsMAFA perovskites<sup>[17,18]</sup>. Some researchers suggested that the enhancement exhibited after the addition of  $K^+$  is due to the trapping defects reduction at the interface and ion migration suppression<sup>[19,20]</sup>. Studies on how the  $K^+$  addition affects the device's performance have been carried out[21]. However, the role of this ion in solar cells properties and mechanisms is still being investigated; its location in perovskite lattice is still being discussed as well as its influence on the crystallization process.

Further work is therefore required, and a broader application of this cation on mixed perovskites is needed to elucidate its role and maximize the potential to modulate the properties of perovskite films and enhance the solar cell performance.

In this work, we examine and discuss the influence of  $K^+$  on the morphological and electronic properties of CsFAPbI<sub>3</sub> perovskite. In previous works, we have shown that MA-free perovskites are promising materials due to their favorable bandgap and stability. Importantly, it appears that simple CsFA double cation perovskites suffer from an uncontrolled crystallization process with intermediate wide-bandgap contaminants that make reproducibility challenging to achieve. The addition of Rb, MA or Cs, respectively, has been shown to avoid this less controlled crystallization pathway. Thus, this triple cation approach appears to emerge as key for increased reproducibility. [13,22,23].

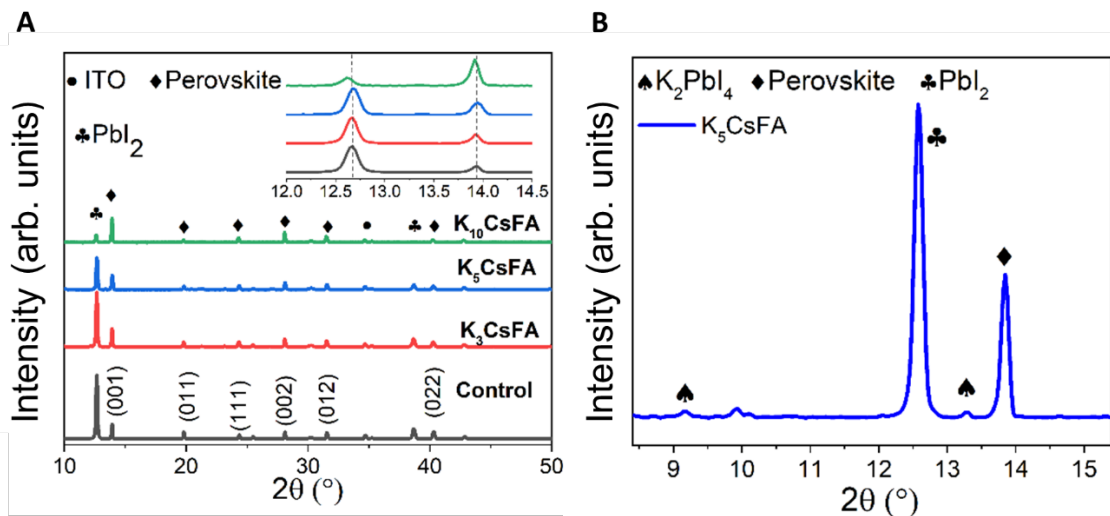
In this context, we realize a triple cation composition by adding KPbI<sub>3</sub> solution into a CsFAPbI<sub>3</sub> perovskite precursor. The perovskite films  $K_x(\text{Cs}_{0.1}\text{FA}_{0.9})_{1-x}\text{PbI}_3$  with ratios 0% (control film), 3%, 5% and 10% were obtained through one-step solution method. In addition,

planar solar cells with structure Glass/ITO/SnO<sub>2</sub>/Perovskite/Spiro-OMeTAD /Gold were fabricated to provide an experimental comparison from the photovoltaic behavior for solar cells with and without K<sup>+</sup>.

Our results reveal that when the K<sup>+</sup> content is increased, perovskite grain size is notably enlarged which is associated to the XRD peaks, becoming more defined. This behavior suggests the PbI<sub>2</sub> by-product segregation from the perovskite film what eases the grain growth as we saw in SEM images. We also found that 3% K<sup>+</sup> concentration leads to a luminescence quantum yield of 0.65 and the highest PCE of 19.3% due to an enhancement in short circuit current and open-circuit voltage. Using impedance measurement, we extracted the characteristics values using an equivalent circuit from the two arcs spectra response, our results showed that V<sub>oc</sub> follows the τ<sub>rec</sub> response, reaching the highest value for the 3% K<sup>+</sup> device, this results means that at this concentrations more charge accumulation is achieved and as a consequence higher QFLS and V<sub>oc</sub> values are reached.

### **Results and discussion**

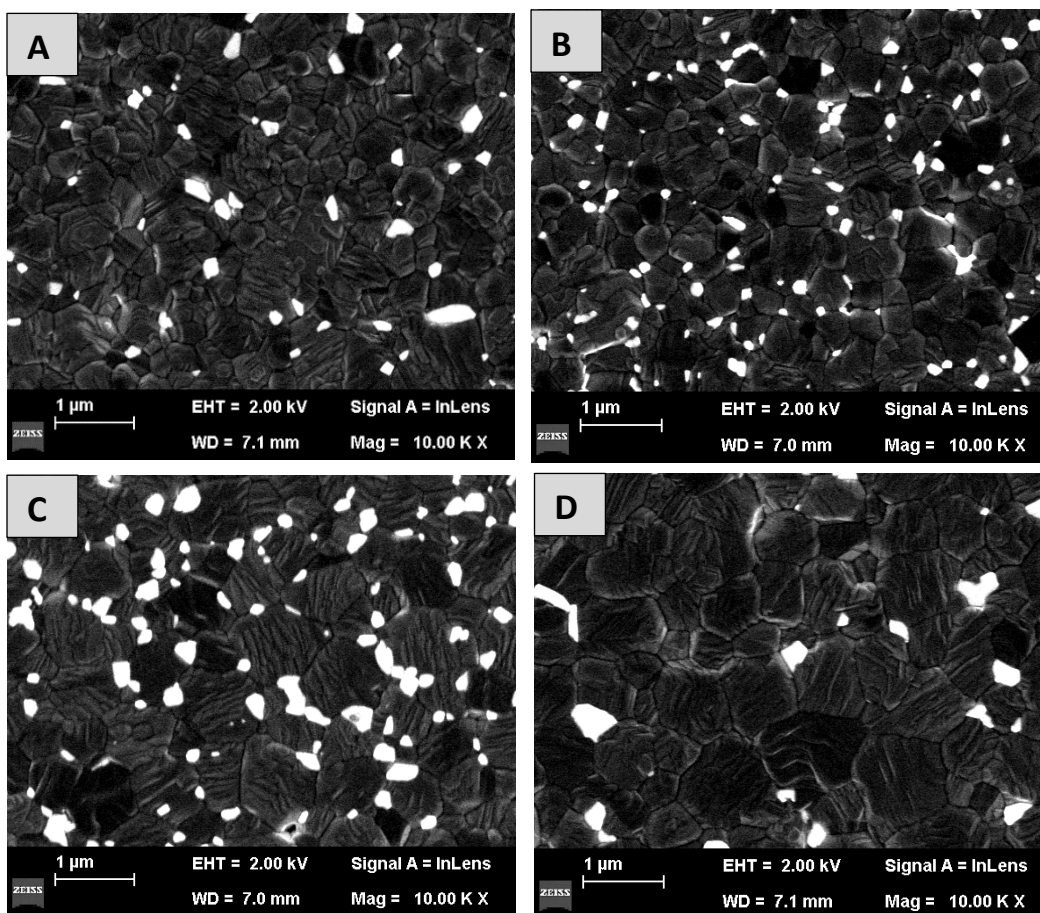
In this study, we investigated the effect of potassium content in the CsFAPbI<sub>3</sub> perovskite crystal structure. As it is further detailed in the experimental section, the perovskite film composition is figured as “K<sub>x</sub> (Cs<sub>0.1</sub>FA<sub>0.9</sub>)<sub>1-x</sub>PbI<sub>3</sub>”, abbreviated for convenience as K<sub>x</sub>CsFA where  $x$  is a percentage of KI added in the precursor solution. With our fabrication procedure that is detailed in the experimental section, we obtained devices with PCE approaching 20% with high reproducibility, as we report in this work.



**Figure 1.** A. XRD spectra for  $K_x(Cs_{0.1}FA_{0.9})_{1-x}PbI_3$  series (Control and after addition of 3%, 5% and 10% of KI in the precursor solution). 1A Inset image on top, B. XRD spectra for low intensity peaks (took it from figure 1A).

Figure 1 presents the XRD patterns from control, 3%, 5% and 10 %  $K^+$  films, this analysis runs in order to investigate the effect of potassium in the crystal structure of double cation perovskite. Observing the XRD film series we assure the formation of black phase perovskite, as it is seen on the characteristics peaks at  $13.9^\circ$  and  $24.31^\circ$  in 2 theta degrees, which is attributed to the (100) and (111) cubic phase planes [24]. In the other hand a strong intensity peak located at  $12.7^\circ$  is observed, which is assigned to  $PbI_2$  compound, this is likely ascribed to the high temperature annealing ( $150^\circ C$ ), necessary to get the black phase in FA-based perovskite<sup>31</sup>. This byproduct has an interesting XRD peak evolution, and its presence mainly affects the nature of crystallization and morphology. Here is clearly observed from the XRD patterns that  $K^+$  has strong role on the film, promoting the crystallinity as it is observed in 3 to 10 % perovskite peaks evolution. At the same time the  $K^+$  ion promotes the  $PbI_2$  ripening out from the grain boundaries resulting in  $PbI_2$  peak intensity reduction as well as the formation of metallic like grains over the film observed in SEM images. The ripening effect

can be explained with the formation of a K-Pb compound. Zooming the view of the XRD for small angles (Figure 1B), two low-intensity peaks in  $9.3^\circ$  and  $13.3^\circ$  start growing at 3% K, increasing in intensity for larger concentration of K. These new XRD peaks could correspond to the potassium-rich phase  $K_2PbI_4$  observed by Kuai<sup>[18]</sup>, the low intensities presented by these peaks can be due to the small quantity of  $K^+$  compared to the other elements presented in the film. Moreover, a shift in the XRD peaks to lower angles is observed in Figure 1B, this shift has been observed in previous findings and it is ascribed to a slight change of iodide-bromide ratio, which induces the lattice expansion. In this work pure iodine perovskites are studied, then we associate the shift to lower angles to  $K_2PbI_4$  molecules trapped in the perovskite lattice, generating a structure distortion. This result does not contradict the previous reported research, where it is established that  $K^+$  by itself is not occupying a site in the  $ABX_3$  structure<sup>[21,25]</sup>, since we are proposing the insertion of a  $K_2PbI_4$  molecule in the material rather than the formation of a  $KPbI_3$  perovskite or  $K^+$  taking substitutional sites.



**Figure 2.** Top-view SEM images of samples A. Control film, B.  $K_3CsFA$ , C.  $K_5CsFA$ , and D.  $K_{10}CsFA$ .

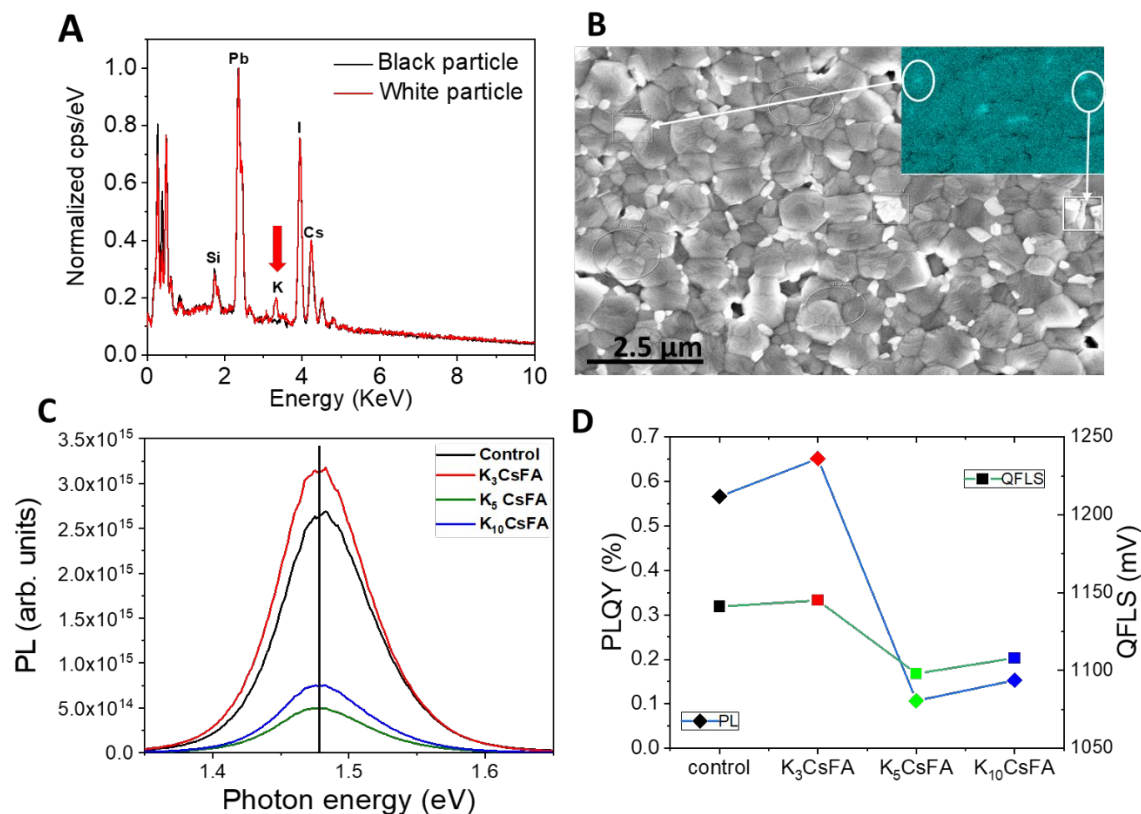
From the SEM images in Figure 2(A-D), it is observed that there is a difference between crystallite size and homogenization. Taking the data from the control sample, there is no uniformity in grain size distribution, which goes from a hundred nanometers to 3 or 4 times that value as it is observed in the figure S1. Additionally, a huge dispersion of brighter grains over the perovskite film is observed that could be due to the  $PbI_2$  metallic like formation, matching the XRD pattern. These particles are growth/crystallized mainly in the grain perovskite boundaries, this could explain the intense peak in the corresponding XRD pattern (see Figure 1 control pattern). As 3% of  $K^+$  content is added, morphological changes are observed, such as an increase in perovskite grain size and the amount of metallic-like



particles, which could be the ripening of  $\text{PbI}_2$  promoted by the monovalent ion. The role played by the K ion could be as an agent that surrounds the perovskite and do not allow the  $\text{PbI}_2$  deposition, probably by suppressing the diffusion of  $\text{PbI}_2$  into the film. It is also observed that some  $\text{PbI}_2$  grains start to coalesce during the crystallization process, this uptake of  $\text{PbI}_2$  is in agreement with the XRD results. When the  $\text{K}^+$  concentration is raised to 5 % the coalescence effect starts governing the metallic like grains letting them grow bigger, simultaneously the perovskite film surface is affected, observing a grain growth and a quasi-homogeneous film that exhibit an average grain size of 600 nm. This monovalent ion not only contributes to the byproduct uptake also subserves the perovskite crystallization as this is observed when the  $\text{K}^+$  concentration is 10% obtaining a 800 nm perovskite grains in average, and  $\text{PbI}_2$  coalescence of 300 nm in size. So according to the X-ray data and the present SEM images; it can be suggested that the  $\text{PbI}_2$  peak intensity is almost diminished when the perovskite solution is saturated with K ion segregating this compound towards perovskite film surface. The domains associated to  $\text{PbI}_2$  compound are only observed at the SEM images surface, and no were detected on the transversal images analysis (metallic-like grains), this could confirm that the  $\text{PbI}_2$  byproduct is only formed on the perovskite film surface due to the effect of K incorporation.

EDX mapping of  $\text{K}_x\text{CsFA}$  samples is presented in Figure 3. The EDX analysis was measured on the white and black particles. Those particles we selected explicitly, as we can see in Figure 3B, and S2. EDX spectra have confirmed the presence of elements such as potassium (K), lead (Pb), iodide (I), and cesium (Cs), which corresponds to the perovskite material presented in this work. From the EDX mapping we confirm that  $\text{K}^+$  is not occupying a site within the perovskite structure, since we did not find any content of this metal in the grains

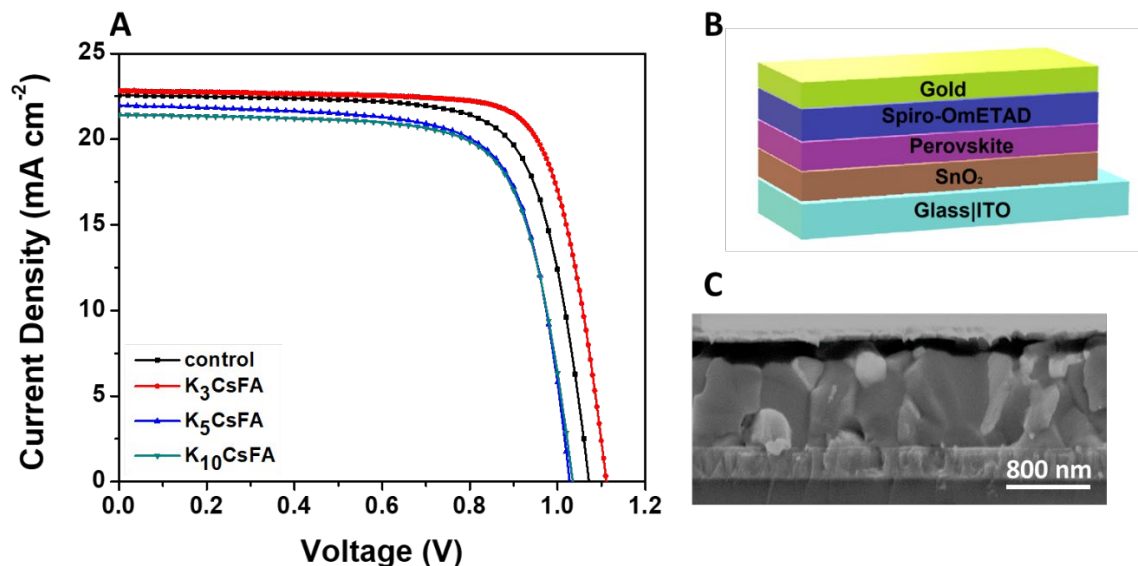
associated to perovskite material, nevertheless small  $K^+$  signal was found in the white dots, as expected from previous results. Optical properties were studied through photoluminescence (PL) emission, photoluminescence quantum yield (PLQY), and quasi-fermi level splitting characterization (QFLS). The perovskite precursor solution was deposited on glass without hole or electron transport layers to show no interference or contribution from another material. It can be observed from Figure 3C an increase in the PL emission intensity after the addition of 3%  $K^+$ , this enhancement is associated with a non-radiative recombination process reduction, primarily due to defects passivation. In previous results it has been reported that  $PbI_2$  originates recombination centers in the perovskite films, triggering detrimental effects in photoluminescence properties. Hence the enhanced PL emission in 3 %  $K^+$  has strengthened our hypothesis that at this level,  $K^+$  is suppressing the diffusion of  $PbI_2$  into the film diminishing non-radiative recombination.



**Figure 3.** EDX results of potassium-added and Photoluminescence of perovskite films **A.** EDX mapping of a white particle with excess of potassium and black particle with low content of potassium. **B.** SEM top view image of potassium-based perovskite film, showing the white and black particle. **C.** Photoluminescence spectra for pristine perovskite films deposited on quartz with no adjacent charge selective contacts, **D.** PL quantum yield (PLQY), and quasi-Fermi level splitting (QFLS) characterizations extracted from absolute PL measurement given in A.

When  $K^+$  concentration was further increased to 5% and 10%, a dramatic PL quenching was observed, even though these films exhibit larger grains and therefore, grain boundaries reduction, as we have seen in SEM images. This apparent lack of correlation can be justified; if at this stage the higher amount of PbI-K compound is originating deep traps at grain boundaries and surface, accelerating carrier losses. We propose that for 5%, 10% and higher concentration of  $K^+$  the surface trap states are the predominant pathways that contribute to non-radiative recombination losses, due to the excess of metallic-like compound at the surface (Fig. S3) and K-PbI molecules passivating the perovskite near the surface. This

mechanism is schematically described in the image S4. Nevertheless, broad research is needed to estimate the different defect contributions in the recombination process. It is well known that the presence of non-radiative losses in the absorbent layer limits the performance of solar cells [26]; PLQY quantifies the ratio between radiative and total recombination, values of PLQY closer to the unity are required for radiative recombination. As shown in Figure 3D, 3%  $K^+$  exhibits the highest value of PLQY, which implies this concentration shows the lower non-radiative recombination rate, compared to the other concentrations. Meanwhile the quasi-Fermi level splitting (QFLS) (Figure 3D) for this concentration is 1.14 V, this value is the higher achievable open-circuit voltage that can be reached and was calculated from PLQY (SI), but  $V_{oc}$  in perovskite solar cell is always lower due to nonradiative losses phenomena, e.g., non-radiative recombination in bulk and at interfaces, parasitic absorption and disparities in energy alignments at perovskite/charge extraction interfaces[27].



**Figure 5.** **A.** Current density–voltage ( $J$ – $V$ ) curves of champion solar cells for each concentration. **B.** Schematic image of the planar solar cell. **C.** Cross-sectional SEM of a planar perovskite solar cell ITO/SnO<sub>x</sub>/perovskite/spiro-MeOTAD/gold with 3% of K<sup>+</sup>.

Figure S5, shows the films absorbance spectra. The control film exhibited the highest absorption, decreasing proportionally as the K<sup>+</sup> content is increased from 3% to 5%. It is noteworthy that the differences among control, 3%, and 5% films are negligible. However, at 10% K<sup>+</sup> film, we can observe a more significant decrease in intensity. As shown in Figure S6, the perovskite layer thickness has an increment with the addition of K<sup>+</sup>, then the reduction in absorption could be associated with this increment and with a detrimental film quality or a less tightly covered surface observed promoted by the presence of high content of K-PbI (brighter domains). Table S2 shows the differences thickness on the different amount of K, the material with 3% of K have 660 nm (see Fig. 5C).

To study the K<sup>+</sup> impact on the device performance, perovskite films were prepared with identical concentrations as previously mentioned and incorporated into a solar cell with tin oxide (SnO<sub>2</sub>) and Spiro-OMeTAD as ETM and HTM, respectively. The device architecture and the corresponding complete device cross-sectional SEM images are shown in Figures 5B and C, respectively.

The perovskite solar cells photovoltaic performance was measured under 1 sun illumination condition (as it is described in supplementary information). Figure 5A show K<sub>x</sub>CsFA series presenting the champion devices J-V scans, the corresponding photovoltaic parameters for each concentration are displayed in Table 1. The statistics performance of the planar perovskite solar cells is shown in Figure 7.

<i>Sample</i>	<i>J<sub>sc</sub> (mA cm<sup>-2</sup>)</i>	<i>Integrated J<sub>sc</sub> (mA cm<sup>-2</sup>)</i>	<i>V<sub>oc</sub> (V)</i>	<i>FF (%)</i>	<i>PCE (%)</i>
<i>Control</i> <i>Champion</i> <i>mean ± SD<sup>a</sup></i>	22.6 21.75 ± 0.1	22.7	1.07 1.03 ± 0.007	73.6 73.6 ± 0.3	17.8 16.45 ± 0.2
<i>K<sub>3</sub>CsFA</i> <i>Champion</i> <i>mean ± SD<sup>a</sup></i>	22.8 22.4 ± 0.09	23.6	1.11 1.04 ± 0.006	76.4 72.8 ± 0.3	19.39 17.2 ± 0.1
<i>K<sub>5</sub>CsFA</i> <i>Champion</i> <i>mean ± SD<sup>a</sup></i>	22.5 21.5 ± 0.1	21.2	1.03 0.97 ± 0.007	71.5 69.65 ± 0.4	16.5 14.85 ± 0.2
<i>K<sub>10</sub>CsFA</i> <i>Champion</i> <i>mean ± SD<sup>a</sup></i>	21.4 21.9 ± 0.1	20.0	1.03 1.02 ± 0.006	72.8 68.7 ± 0.8	16.1 15.75 ± 0.2

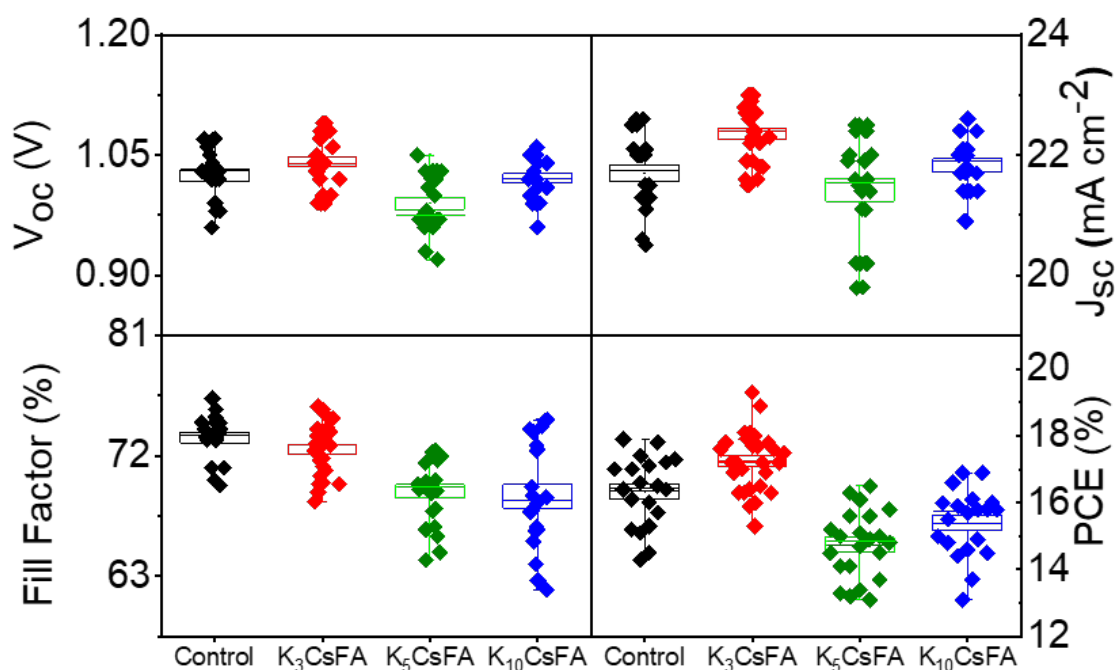
<sup>a</sup> The mean values are calculated from a batch of 20 devices each.

**Table 1.** Photovoltaic parameters for champion devices and mean values for each concentration.

The best photovoltaic performance was obtained from 3% K<sup>+</sup> based devices, achieving a PCE of 19.39 % for the champion solar cell. The short-circuit current (J<sub>sc</sub>) and open-circuit voltage (V<sub>oc</sub>) values show a significative enhancement after the alkali metal addition. As was mentioned previously small amount of K<sup>+</sup> promotes mitigation of non-radiative recombination pathways and improves crystallinity, thus the JV results show that J<sub>sc</sub> and V<sub>oc</sub> evolves accordingly to the film properties. Additionally, detrimental effects in photovoltaic parameters were observed for higher K<sup>+</sup> devices. The control solar cells showed the best FF values among the four concentrations, with a mean value of 73.6%. The FF exhibited a gradually decrease for 3%, 5% and 10% K<sup>+</sup> devices; this was possibly due to PbI<sub>2</sub>

accumulation at the surface, hindering charge extraction between perovskite and charge transport layers, inducing a minimized PCE of 16% for 10% K<sup>+</sup> solar cells.

Additionally, the photostability test of the PSCs was conducted with constant illumination with an adjusted light intensity of 100 mW cm<sup>-2</sup> at room temperature. In Figure S8A we can see the stability measure of the best pixel for each devices, where the PSCs with high concentration of K<sup>+</sup> (K<sub>10</sub>CsFA) rapidly lost more than 80% of their initial PCE (15%) after 7000 seconds of maximum power point tracking (MPPT), on the other hand, the PSCs with 3% of K<sup>+</sup> (K<sub>3</sub>CsFA) exhibit excellent higher stability and retain 80% of the initial efficiency (17%) after 7000 seconds of continuous MPPT, comparing also with the control devices gradually decrease until they reach 70% of the initial PCE (15%) after 7000 seconds followed by devices with 5% K<sup>+</sup> addition (K<sub>5</sub>CsFA) retained 40% of the initial PCE (16%), also in the figure S8B we can see the average values form different pixel from each K content, where the composition of K<sub>3</sub>CsFA shows better stability losing only 20% in comparison to the others and the improvement in device stability with 3% K<sup>+</sup> addition can be attributed to the enlarged grain size and facilitated charge separation, reducing carrier accumulation at interfaces.



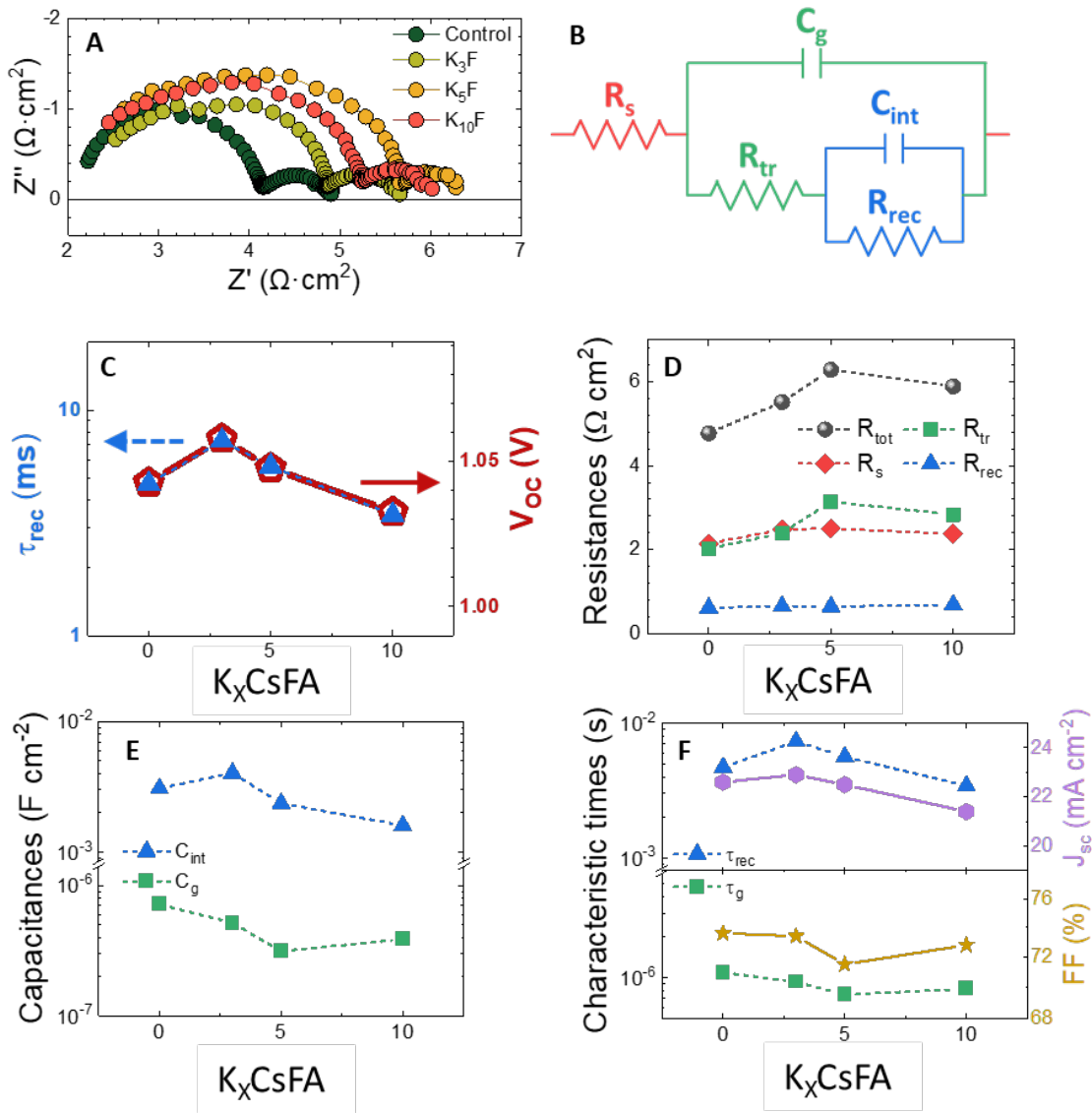
**Figure 7.** Statistic of photovoltaic parameters for 20 solar cells for each concentration. The data have been collected over ten different batches.

Additionally, the devices external quantum efficiency (EQE) curves at different K<sup>+</sup> concentration were measured (Fig. S7). As is usually reported in EQE characterization for solar cells, the spectra can be subdivided in three distinct regions: for short wavelengths all EQE curves show an edge, this is related to front reflection and parasitic absorption due to ITO and the ETL. Between 450 and 650 nm, EQE reaches the highest values, with a slighting increment at 3% K<sup>+</sup> compared to control device, this increase, evidences the K<sup>+</sup> role as passivating agent, increasing the probability of charge collection due to a lower recombination rate. The devices show a slightly weaker signal over 650 nm, where an EQE decrement in this region is related to a charge extraction reduction at perovskite/HTL interface mainly due to surface recombination, this is consistent with our assumption that K-



PbI accumulation at the perovskite surface triggers a detrimental effect creating recombination pathways at perovskite/spiro interface. This effect can be observed more clearly for 5% K<sup>+</sup> and 10% K<sup>+</sup> devices, where the EQE values for wavelengths above 650 nm are noticeable lower. The integrated J<sub>sc</sub> of the best devices from external quantum efficiency measurement (EQE) integration is shown in Figure S7 and Table 1.

To investigate in detail the effect of incorporating K<sup>+</sup> during the solar cell operation, we have measured impedance spectroscopy (IS). Figure 8A shows the impedance spectra for different K<sub>x</sub> configurations, measured around V<sub>oc</sub>. Usually, these spectra are analyzed with an equivalent circuit (EC), allowing the extraction of quantitative parameters. However, the election of this EC is particularly complicated for perovskite solar cells because many have been proposed in the literature. Different ECs were needed to explain different IS responses, including inductive loops[28], negative capacitances[29,30], and diffusion-like arcs[31]. On the other hand, different ECs reproduce the same impedance response, which requires complementary techniques to differentiate them [32,33]. The spectra in Figure 8A present only two arcs, which is the most typical response for perovskite solar cells. We selected the EC in Figure 8B because it generates two arcs and has been widely implemented for perovskite solar cells<sup>[33,34]</sup>. R<sub>s</sub> is the series resistance corresponding to the high-frequency limit in this EC. The high-frequency arc is generated by R<sub>tr</sub> and C<sub>g</sub>, mainly associated with transport resistance and the geometrical capacitance of the perovskite device. Finally, the low-frequency arc is generated by R<sub>rec</sub> and C<sub>int</sub>, associated with the recombination resistance and an internal capacitance. The parameters obtained from the spectra fitting in Figure 8A with the EC in Figure 8B are shown in Table S1.



**Figure 8.** A. Impedance Spectroscopy responses for the different concentrations of  $\text{K}^+$ , measured around  $V_{oc}$ . B. Equivalent circuit used to fit these responses, with  $R_s$ : series resistance,  $C_g$ : geometrical capacitance,  $R_{tr}$ : transfer resistance,  $R_{rec}$ : recombination resistance and  $C_{int}$ : internal capacitance. C. Compare the characteristic recombination time ( $\tau_{rec} = R_{rec} \cdot C_{int}$ ) with the  $V_{oc}$ , for the different concentrations. D. Shows the evolution of the resistances in the equivalent circuit, together with the total resistance ( $R_{tot} = R_s + R_{tr} + R_{rec}$ ), as a function of the  $\text{K}^+$  concentration, E. Capacitance data obtained from the fitting and F. characteristic times,  $J_{sc}$  and FF vs K concentration.

Figure 8C shows the characteristic recombination time ( $\tau_{\text{rec}} = R_{\text{rec}} \cdot C_{\text{int}}$ ) compared with the  $V_{\text{oc}}$  for the devices with different K concentrations. The fact that the  $V_{\text{oc}}$  follows the response of  $\tau_{\text{rec}}$  implies that it is related to non-radiative recombination kinetics. When  $\tau_{\text{rec}}$  increase means that non-radiative recombination process is slower, which allows a higher charges accumulation and a consequent increment in the  $V_{\text{oc}}$ . The  $V_{\text{oc}}$  obtained for these samples have a similar trend to the corresponding samples in Figure 5 and Figure 7, showing an increase for 3%  $\text{K}^+$  compared with the control a pronounced decrease for high  $\text{K}^+$  concentrations. Note in Figure 8E that it is  $C_{\text{int}}$ , rather than  $R_{\text{rec}}$ , the parameter that provides the characteristic shape observed for  $t_{\text{rec}}$ , suggesting a larger charge accumulation which is determining to the higher displacement in Fermi level and thus larger  $V_{\text{oc}}$ , the same trend as the one found in chemical capacitances[35].

In Figure 8D each device resistances obtained fitted with the equivalent circuit (Figure 8B) is shown. The  $R_s$  is approximately constant, which is expected because the same contacts were used for all samples. Interestingly,  $R_{\text{rec}}$  is also approximately constant, which is associated with all measurements being taken at  $V_{\text{oc}}$ . As observed, the high-frequency arc, given by  $R_{\text{tr}}$ , mainly dominates the total resistance ( $R_{\text{tot}} = R_s + R_{\text{tr}} + R_{\text{rec}}$ ). This transfer resistance combines transport resistance at the perovskite layer, charge transfer at perovskite interfaces, and high-frequency contribution to recombination resistance[36]. As seen in Figure 8D,  $R_{\text{tr}}$  increases with the K incorporation. The simultaneous drop in FF observed in Fig 8F, suggest that the serial resistance contribution to  $R_{\text{tr}}$  (transport and charge transfer at contacts) dominate over recombination contributions. We may associate this change either to surface passivation with increased  $\text{K}^+$  amount or to a reduction in the charges mobility at the perovskite layer, in this case both effects combination may not be discarded. At 3%  $\text{K}^+$ , the

$R_{tr}$  increase is small, and so is the decrease in FF. At 5%  $K^+$   $R_{tr}$  peaks and FF makes a minimum. The 10% slight change could be due to the growth of the metallic-like grains observed in the SEM images. The differences observed in the geometrical capacitance ( $C_g$ ) follow the opposite behavior of  $R_{tr}$ . combined with the SEM results, suggesting that the K incorporation increases film thickness, and thus  $C_g$  should decrease and  $R_{tr}$  increase in the perovskite composition.

## **Conclusions**

In summary, we have investigated the effects of KI adding into the perovskite precursor solution on the properties of CsFAPbI<sub>3</sub> films and its impact on the photovoltaic performance. We conclude that the incorporation of potassium ion strongly influences the crystallization process and induces the growth of larger grains on the films, this through the uptake of PbI<sub>2</sub> byproduct out the perovskite structure. In short, we conclude that, from our findings we propose a twofold impact of  $K^+$  addition on CsFAPbI<sub>3</sub> film, the first one at 3%,  $K^+$  prevents the byproduct deposition on the bulk, and the corresponding uptake near the film surface. But for a higher  $K^+$  concentration, not only contributes to this uptake, the relative excess of this ion start to passivate the perovskite grains surface, this passivation and the bulk-trapped KPbI<sub>4</sub> molecules induce a lattice expansion, that is clearly observed on the diffraction peaks shift to lower angles. We found that 3% concentration of  $K^+$  reduces the non-radiative recombination on the film, inducing high values of  $J_{sc}$  and  $V_{oc}$  for devices fabricated with this concentration. Impedance measurement further confirms our results, from the typical two arc model we observed that  $\tau_{rec}$  presented the highest value for the 3%  $K^+$  device due to the reduction of non-radiative recombination, matching with  $V_{oc}$  and QFLS measurement. Thus, the  $K^+$  incorporation improves significantly the performance of perovskite solar cells,

showing a PCE increment of 17.7% for the control device to 19.39 % for the 3% K<sup>+</sup> concentration with better stability in a constant measurement. This paper highlights the suitability of K addition into CsFAPbI<sub>3</sub> perovskite as a technique to tune the film morphology and optical properties, modulating the solar cell performance simultaneously.

### **Acknowledgements**

Gabriela S. Anaya Gonzalez thanks the Consejo Nacional de Ciencia y Tecnología (CONACYT) for financial support and The Helmholtz-Zentrum Berlin for materials and energy. M. Saliba received funding from the Helmholtz Young Investigator Program at Forschungszentrum Jülich, Germany. M. Saliba acknowledge funding from the German Research Foundation (DFG), SPP2196 and GRK 2642. A.O.A and S.F.F acknowledge funding from the European Union's Horizon 2020 MSCA Innovative Training Network under grant agreement No 764787, from the Ministerio de Economía y Competitividad (MINECO) of Spain under the project ENE2017-85087-C3-1-R and from the Generalitat Valenciana under the project PROMETEO/2020/028. S.H.T.C would like to thank the Spanish Ministry of Economy, Industry and Competitiveness (postdoctoral contract Juan de la Cierva Formación FJC2019-041835-I) for the financial support during this work.

## References

- [1] Gao X-X, Luo W, Zhang Y, Hu R, Zhang B, Züttel A et al. Stable and High-Efficiency Methylammonium-Free Perovskite Solar Cells. *Advanced materials* (Deerfield Beach, Fla.) 2020;32(9):e1905502.
- [2] Best Research-Cell Efficiency Chart; Available from: <https://www.nrel.gov/pv/cell-efficiency.html>.
- [3] Yin W-J, Shi T, Yan Y. Unusual defect physics in CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> perovskite solar cell absorber. *Appl. Phys. Lett.* 2014;104(6):63903.
- [4] Steirer KX, Schulz P, Teeter G, Stevanovic V, Yang M, Zhu K et al. Defect Tolerance in Methylammonium Lead Triiodide Perovskite. *ACS Energy Lett.* 2016;1(2):360–6.
- [5] Hwang B, Gu C, Lee D, Lee J-S. Effect of halide-mixing on the switching behaviors of organic-inorganic hybrid perovskite memory. *Scientific reports* 2017;7:43794.
- [6] Li D, Bretschneider SA, Bergmann VW, Hermes IM, Mars J, Klasek A et al. Humidity-Induced Grain Boundaries in MAPbI<sub>3</sub> Perovskite Films. *J. Phys. Chem. C* 2016;120(12):6363–8.
- [7] Lee J-W, Kim S-G, Bae S-H, Lee D-K, Lin O, Yang Y et al. The Interplay between Trap Density and Hysteresis in Planar Heterojunction Perovskite Solar Cells. *Nano letters* 2017;17(7):4270–6.
- [8] Lee SJ, Shin SS, Kim YC, Kim D, Ahn TK, Noh JH et al. Fabrication of Efficient Formamidinium Tin Iodide Perovskite Solar Cells through SnF<sub>2</sub>-Pyrazine Complex. *Journal of the American Chemical Society* 2016;138(12):3974–7.
- [9] Lv S, Pang S, Zhou Y, Padture NP, Hu H, Wang L et al. One-step, solution-processed formamidinium lead trihalide (FAPbI<sub>3-x</sub>Cl<sub>x</sub>) for mesoscopic perovskite-polymer solar cells. *Physical chemistry chemical physics PCCP* 2014;16(36):19206–11.
- [10] Xi J, Wu Z, Xi K, Dong H, Xia B, Lei T et al. Initiating crystal growth kinetics of  $\alpha$ -HC(NH<sub>2</sub>)<sub>2</sub>PbI<sub>3</sub> for flexible solar cells with long-term stability. *Nano Energy* 2016;26:438–45.
- [11] Wang Y, Zhang H, Zhang T, Shi W, Kan M, Chen J et al. Photostability of MAPbI<sub>3</sub> Perovskite Solar Cells by Incorporating Black Phosphorus. *Sol. RRL* 2019;3(9):1900197.
- [12] Ouyang Y, Li Y, Zhu P, Li Q, Gao Y, Tong J et al. Photo-oxidative degradation of methylammonium lead iodide perovskite: mechanism and protection. *J. Mater. Chem. A* 2019;7(5):2275–82.
- [13] Turren-Cruz S-H, Hagfeldt A, Saliba M. Methylammonium-free, high-performance, and stable perovskite solar cells on a planar architecture. *Science* (New York, N.Y.) 2018;362(6413):449–53.
- [14] Zhao W, Yao Z, Yu F, Yang D, Liu SF. Alkali Metal Doping for Improved CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> Perovskite Solar Cells. *Advanced science* (Weinheim, Baden-Wuerttemberg, Germany) 2018;5(2):1700131.
- [15] Tang Z, Uchida S, Bessho T, Kinoshita T, Wang H, Awai F et al. Modulations of various alkali metal cations on organometal halide perovskites and their influence on photovoltaic performance. *Nano Energy* 2018;45:184–92.

- [16] Li Y, Duan J, Yuan H, Zhao Y, He B, Tang Q. Lattice Modulation of Alkali Metal Cations Doped Cs  $1-x$  R  $x$  PbBr  $3$  Halides for Inorganic Perovskite Solar Cells. *Sol. RRL* 2018;2(10):1800164.
- [17] Ling T, Zou X, Cheng J, Yang Y, Ren H, Chen D. Modulating Surface Morphology Related to Crystallization Speed of Perovskite Grain and Optical Semiconductor and Crystallization Properties of the Absorber Layer Under Controlled Doping of Potassium Ions for Solar Cells. *Materials (Basel, Switzerland)* 2018;11(9).
- [18] Kuai L, Wang Y, Zhang Z, Yang Y, Qin Y, Wu T et al. Passivating Crystal Boundaries with Potassium-Rich Phase in Organic Halide Perovskite. *Sol. RRL* 2019;3(5):1900053.
- [19] Zheng F, Chen W, Bu T, Ghiggino KP, Huang F, Cheng Y et al. Triggering the Passivation Effect of Potassium Doping in Mixed-Cation Mixed-Halide Perovskite by Light Illumination. *Adv. Energy Mater.* 2019;9(24):1901016.
- [20] Chang J, Lin Z, Zhu H, Isikgor FH, Xu Q-H, Zhang C et al. Enhancing the photovoltaic performance of planar heterojunction perovskite solar cells by doping the perovskite layer with alkali metal ions. *J. Mater. Chem. A* 2016;4(42):16546–52.
- [21] Kubicki DJ, Prochowicz D, Hofstetter A, Zakeeruddin SM, Grätzel M, Emsley L. Phase Segregation in Potassium-Doped Lead Halide Perovskites from 39K Solid-State NMR at 21.1 T. *Journal of the American Chemical Society* 2018;140(23):7232–8.
- [22] Saidaminov MI, Williams K, Wei M, Johnston A, Quintero-Bermudez R, Vafaie M et al. Multi-cation perovskites prevent carrier reflection from grain surfaces. *Nature materials* 2020;19(4):412–8.
- [23] Dang HX, Wang K, Ghasemi M, Tang M-C, Bastiani M de, Aydin E et al. Multi-cation Synergy Suppresses Phase Segregation in Mixed-Halide Perovskites. *Joule* 2019;3(7):1746–64.
- [24] Saidi WA, Choi JJ. Nature of the cubic to tetragonal phase transition in methylammonium lead iodide perovskite. *The Journal of chemical physics* 2016;145(14):144702.
- [25] Abdi-Jalebi M, Andaji-Garmaroudi Z, Cacovich S, Stavrakas C, Philippe B, Richter JM et al. Maximizing and stabilizing luminescence from halide perovskites with potassium passivation. *Nature* 2018;555(7697):497–501.
- [26] Pellet N, Gao P, Gregori G, Yang T-Y, Nazeeruddin MK, Maier J et al. Mixed-Organic-Cation Perovskite Photovoltaics for Enhanced Solar-Light Harvesting. *Angew. Chem.* 2014;126(12):3215–21.
- [27] Mahesh S, Ball JM, Oliver RDJ, McMeekin DP, Nayak PK, Johnston MB et al. Revealing the origin of voltage loss in mixed-halide perovskite solar cells. *Energy Environ. Sci.* 2020;13(1):258–67.
- [28] Guerrero A, Garcia-Belmonte G, Mora-Sero I, Bisquert J, Kang YS, Jacobsson TJ et al. Properties of Contact and Bulk Impedances in Hybrid Lead Halide Perovskite Solar Cells Including Inductive Loop Elements. *J. Phys. Chem. C* 2016;120(15):8023–32.
- [29] Ghahremanirad E, Bou A, Olyae S, Bisquert J. Inductive Loop in the Impedance Response of Perovskite Solar Cells Explained by Surface Polarization Model. *The journal of physical chemistry letters* 2017;8(7):1402–6.

- [30] Alvarez AO, Arcas R, Aranda CA, Bethencourt L, Mas-Marzá E, Saliba M et al. Negative Capacitance and Inverted Hysteresis: Matching Features in Perovskite Solar Cells. *The journal of physical chemistry letters* 2020;11(19):8417–23.
- [31] Babu V, Fuentes Pineda R, Ahmad T, Alvarez AO, Castriotta LA, Di Carlo A et al. Improved Stability of Inverted and Flexible Perovskite Solar Cells with Carbon Electrode. *ACS Appl. Energy Mater.* 2020;3(6):5126–34.
- [32] Alvarez AO, Ravishankar S, Fabregat-Santiago F. Combining Modulated Techniques for the Analysis of Photosensitive Devices. *Small methods* 2021;5(10):e2100661.
- [33] Ravishankar S, Aranda C, Sanchez S, Bisquert J, Saliba M, Garcia-Belmonte G. Perovskite Solar Cell Modeling Using Light- and Voltage-Modulated Techniques. *J. Phys. Chem. C* 2019;123(11):6444–9.
- [34] Di Girolamo D, Phung N, Jošt M, Al-Ashouri A, Chistiakova G, Li J et al. From Bulk to Surface: Sodium Treatment Reduces Recombination at the Nickel Oxide/Perovskite Interface. *Adv. Mater. Interfaces* 2019;6(17):1900789.
- [35] Bisquert J. Chemical capacitance of nanostructured semiconductors: its origin and significance for nanocomposite solar cells. *Phys. Chem. Chem. Phys.* 2003;5(24):5360.
- [36] Juarez-Perez EJ, Sanchez RS, Badia L, Garcia-Belmonte G, Kang YS, Mora-Sero I et al. Photoinduced Giant Dielectric Constant in Lead Halide Perovskite Solar Cells. *The journal of physical chemistry letters* 2014;5(13):2390–4.