Supporting information:

Influence of mixed organic cation ratio in lead iodide based perovskite on the performance of solar cells

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X-Ray Diffraction of Perovskite Layers

X-ray diffraction measurements from the perovskite film were used to estimate the crystal size as a function of the ratio methylammonium and formamidinium used. XRD spectra are shown in Figure S1 (a-c). The peak positions are in agreement with the previous report¹. It can be clearly observed how the characteristics peaks shift to the lower angle when the amount of FAI increases.





Figure S1. XRD characterization of the $MA_xFA_{(1-x)}PbI_3$ thin-film perovskite grown by solvent engineering one-step method. Magnification views of the characteristic peaks region 13-14.5°, 27.7-29°, 31.2° -31.8° respectively are plotted.

The average crystallite size was estimated from the most intense peak using the software from the equipment (D/MAX-Ultima3 from Rigaku). Crystal size calculation is a complex task mainly due to the different phases present when mixed perovskite is synthesized. Apart from different perovskite crystal structure, depending on the annealing temperature it also affects in the final crystal structure, therefore the analysis and crystal size.



Figure S2. Average crystal size depending on the mixed cation ratio calculated by the XRD software versus FA cation amount in MAPbI₃ perovskite.

XRD and Optical absorption measurements of the $MA_{0.5}FA_{0.5}PbI_3$ perovskite film annealed at different temperature:



Figure S3. X-ray diffraction spectra for the $MA_xFA_{(1-x)}PbI_3$ perovskite film for x=0.5. The perovskite films were annealed at 120 °C, 135°C and 150 °C for one hour respectively. The characteristic and prominent peaks for tetragonal structure can be seen in 120°C annealed sample and increased annealed temperature decreases its intensity and finally peaks disappeared when heated at 150 °C.

UV-Vis Absorption

Absorption spectrum of organohalide perovskite material at the same ratio 50:50 was performed to study the influence of annealing temperature. The importance of this experiment falls on the fact that for the 50-50 ratio of formamidinium and methylammonium is difficult to know the optimum temperature for high quality perovskite conversion. As we can observe in the graph, at 120 °C, better absorption is achieved, however not remarkable differences are appreciated. That could be due to at 120°C, methylammonium based perovskite is predominant because formamidinium is not fully converted in black α -phase but in no-photo- active δ -phase of formamidinium. Nevertheless, at 150°C formamidinium based perovskite is converted but methylammonium cation is partial degraded by temperature. At 135°C, formamidinium is not converted in photo-active phase and methylammonium starts to degrade.



Figure S4. UV-Vis absorbance spectra of a thin film of perovskite on FTO in 50:50 organic cation mixtures thermally annealed at different temperature.



Figure S5. SEM Top-view of perovskite films in 50:50 organic cation mixture at different temperature.





Figure S6. SEM Top-view of perovskite films varying the ratio of organic cations

Hysteresis measurements:

J-V curves were measured at several scan rates for both reverse and forward directions at different dwell time and we found that in our case, 100 mV/s is the optimized scan rate and the pre sweep delay time was 30 s where cell was kept at 1.1 V. for both direction where we observed minimum mismatch between forward and reverse direction. The scan was started at 1.1V to 0 V and then back to 1.1 V. The hysteresis index (HI) was calculated by the formula as reported by Kim et al.¹ which allows us to estimate the degree of hysteresis.

$$Hysteresis Index = \frac{J_{backward}(0.8V_{OC}) - J_{forward}(0.8V_{OC})}{J_{backward}(0.8V_{OC})}$$
(1)

Where, $J_{backward}$ (0.8 V_{oc}) and $J_{forward}$ (0.8 V_{oc}) represent photocurrent density at 80% of V_{oc} for the reverse and forward bias measurements, respectively.

If the value of HI is 0 then it predicts no hysteresis and if the value is 1 then hysteresis is as high as photocurrent. The *J*-*V* curves were measured at 100 mV/s to calculate the degree of hysteresis, photovoltaics parameters and HI are given in Table S1. It was found that the degree of hysteresis decreases with increasing amount of FAI until x=0.60.

Table	S1:	Photovoltaic	parameters	of	the	devices	measured	on	both	directio	on to
calcul	ate tł	he hysteresis	index (HI) u	unde	er 10	00 mW/c	m ² (Active	are	a: 0.1	6 cm ² ,	Scan
rate: 1	00 m	V/s) Forward	l scan, from J	V_{SC} to	$o V_O$; Revers	e scan, fror	n Va	p_C to J	SC	

Mixed catión ratio	Scan direction	V _{OC} (mV)	$ J_{SC} (mA.cm-2) $	FF (%)	PCE (%)	HI
MAI 100:FAI 0	Reverse Forward	987 972	19.79 19.99	74.18 68.47	14.49 13.32	0.16
MAI 85:FAI 15	Reverse Forward	994 977	19.90 19.87	73.32 66.53	14.50 12.92	0.10
MAI 70:FAI 30	Reverse Forward	898 891	19.84 19.91	71.39 66.33	12.73 11.77	0.05
MAI 60:FAI 40	Reverse Forward	975 963	20.87 20.89	69.96 68.8	14.23 13.85	0.005
MAI 50:FAI 50	Reverse Forward	929 899	19.92 18.52	54.99 46.35	10.18 7.72	0.28
MAI15:FAI85	Reverse Forward	802 757	17.55 17.11	65.5 61.3	9.22 7.95	0.029
MAI 0:FAI 100	Reverse Forward	805 773	15.66 15.38	59.80 52.64	7.53 6.26	0.20

¹ H.S. Kim, N.-G. Park, J. Phys. Chem. Lett. **2014**, *5*, 2927–2934.





Figure S7. Current density–voltage (*J-V*) curves showing the hysteresis depending on the MAI:FAI ratio (*Scan rate:* 100 mV/s). The scan starts at 1.1 V to 0 V and back to 1.1 V Forward scan, from J_{SC} to V_{OC} ; Reverse scan, from V_{OC} to J_{SC} . X=0.6 exhibits almost negligible hysteresis due to proper crystal structure formation, however with the increase proportion of formamidinium cation, the hysteresis enlarge considerably.



Figure S8. Series and shunt resistance of $MA_xFA_{(1-x)}PbI_3$ based mesoscopic perovskite solar cells depending upon the molar concentration of FA cation. These resistances were calculated using the Oriel *I-V* software from the slopes of *J-V* curve measured for the best performing cells.

Impedance Measurement

For the interpretation of the impedance spectra the following appropriate equivalent circuit has been chosen. Further, the parameters of the equivalent circuit elements can be determined by fitting of the experimental spectra to the chosen system.



Figure S9. Equivalent circuit used to fit impedance spectra

The equivalent circuit is composed by three resistances in parallel with a constant phase element. The equation for the constant phase element assumed is:

 $Z = 1 / [Qo * (j * \omega)^n]$

The value of the capacitance obtained in the software (Zview) corresponds to a chemical capacitance which is no considering the real one in perovskite based solar cell. Therefore

The equation used to calculate the geometrical capacitance is: $C = (Qo^*R)^{(1/n)}/R$

Where: Qo is the chemical capacitance

R is the resistance

n is a parameter which indicates the fitting quality.

MAI



Figure S10. Nyquist plot of pure MAPbI₃ perovskite based solar cell at different voltages.