Supporting information for Physical Chemistry Chemical Physics

The Role of PbI_2 on $CH_3NH_3PbI_3$ Perovskite Stability, Solar Cell Parameters and Device Degradation

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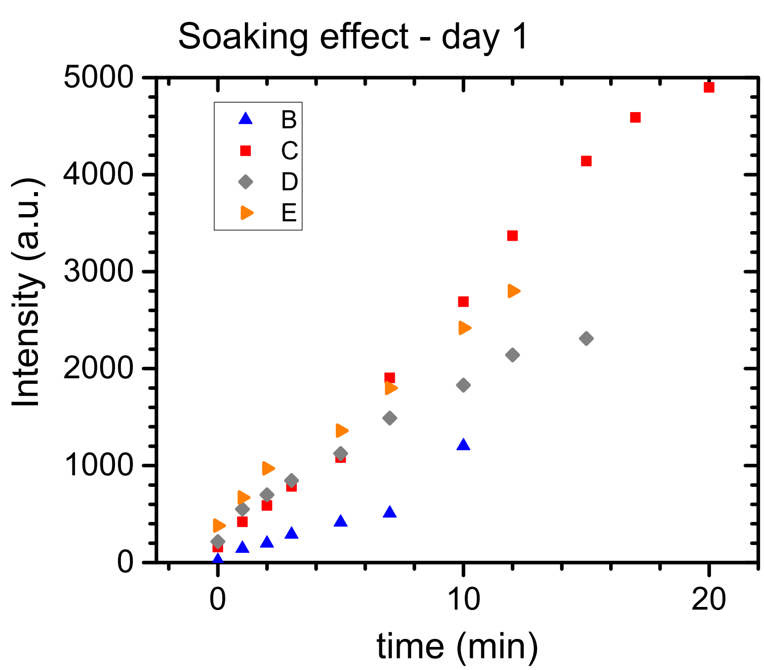

Figure S1. PL peak intensity for samples B to E with light soaking with 485 nm laser light (LDH-D-C-485, PicoQuant GmbH) with an intensity of about 450 $mWcm^{-2}$.

Calculation of PbI_2 content from optical absorption using reference measurements

We prepared six reference samples from PbI_2 and after complete conversion to $CH_3NH_3PbI_3$, we measured the optical density of these reference films. By comparing the optical density at 520 nm of these reference films and our samples A to E, a correlation of the real amount of $CH_3NH_3PbI_3$ in each sample could be obtained. From these calculated values, the amount of PbI_2 in A to E (in nm) is further calculated by using the calibration curve shown in fig.S2 a) using the conversion factor of 1.78 (slope of curve).

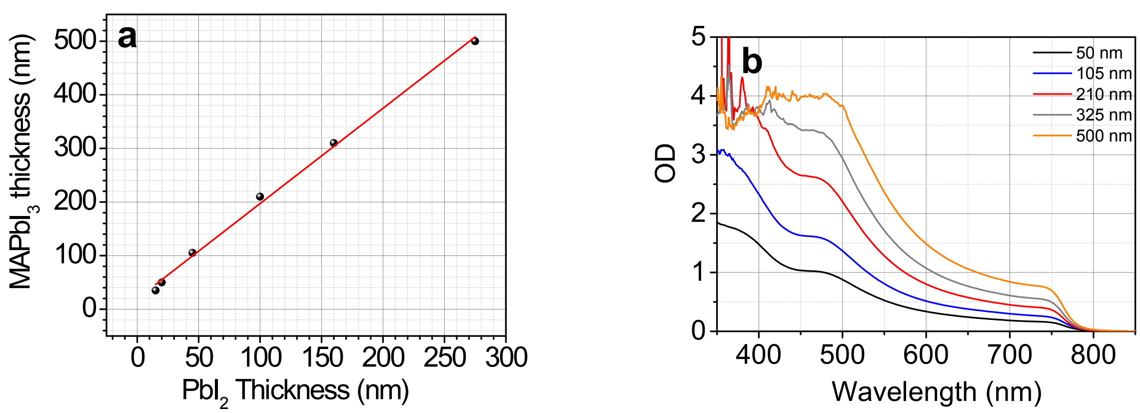

Figure S2. (a) Final perovskite film thickness as a function of the thickness of the precursor PbI_2 film, as measured by dektak profilometry; (b) absorbance spectra of these reference films from (a).

Comparing the thicknesses PbI_2 and $CH_3NH_3PbI_3$, it can be seen that the thickness of the perovskite is almost twice that of the PbI_2 precursor (slope= 1.78). Thus the calibration curve presented in Fig. S2a) gives an excellent method to calculate the amount of $CH_3NH_3PbI_3$ thickness arising from a definite thickness of PbI_2. Figure S2 b shows the absorption spectra of the perovskite films for different film thickness of $CH_3NH_3PbI_3$.

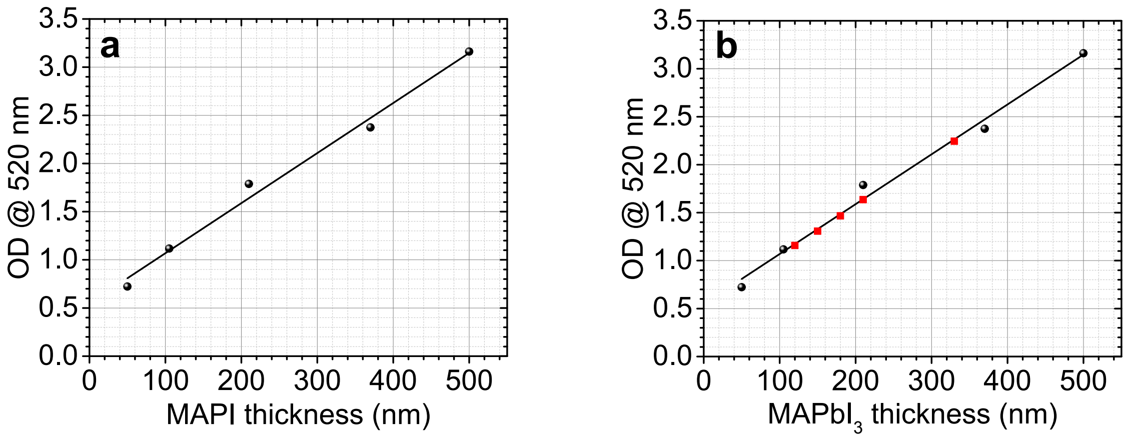

Figure S3. (a) Optical density at 520 nm as a function of the thickness $CH_3NH_3PbI_3$ reference films and (b) optical density values of samples A, B, C, D and E at 520 nm plotted as red points. Plot b) clearly shows that we can assess the amount of real $CH_3NH_3PbI_3$ existing in the films.

In fig. S3 a), the optical density at 520 nm of the reference films are increasing monotonically with $CH_3NH_3PbI_3$ thickness. The linear increase in optical density demonstrates the excellent control over film thickness. We extrapolated the optical density on graph a) and obtained thickness of $CH_3NH_3PbI_3$ and PbI_2 and listed in Table S1.

Table S1. Extraction of PbI_2 wt% from annealed $CH_3NH_3PbI_3$ films. All samples have initial thickness of about 330 nm of $CH_3NH_3PbI_3$.

Sample	$CH_3NH_3PbI_3$ thickness (nm) calculated from OD	$CH_3NH_3PbI_3$ thickness consumed (nm)	Calculated PbI_2 thickness (nm)[a]	Calculated PbI_2 (wt%)	
				from absorption	from XRD
A	330	0	0	0	0
B	210	120	67.54	24.34	21
C	180	150	84.43	31.93	34.3
D	150	180	101.31	40.31	46.5
E	120	210	118.20	49.62	47.6

[a] calculated from fig. S2 a) using the conversion factor of 1.78

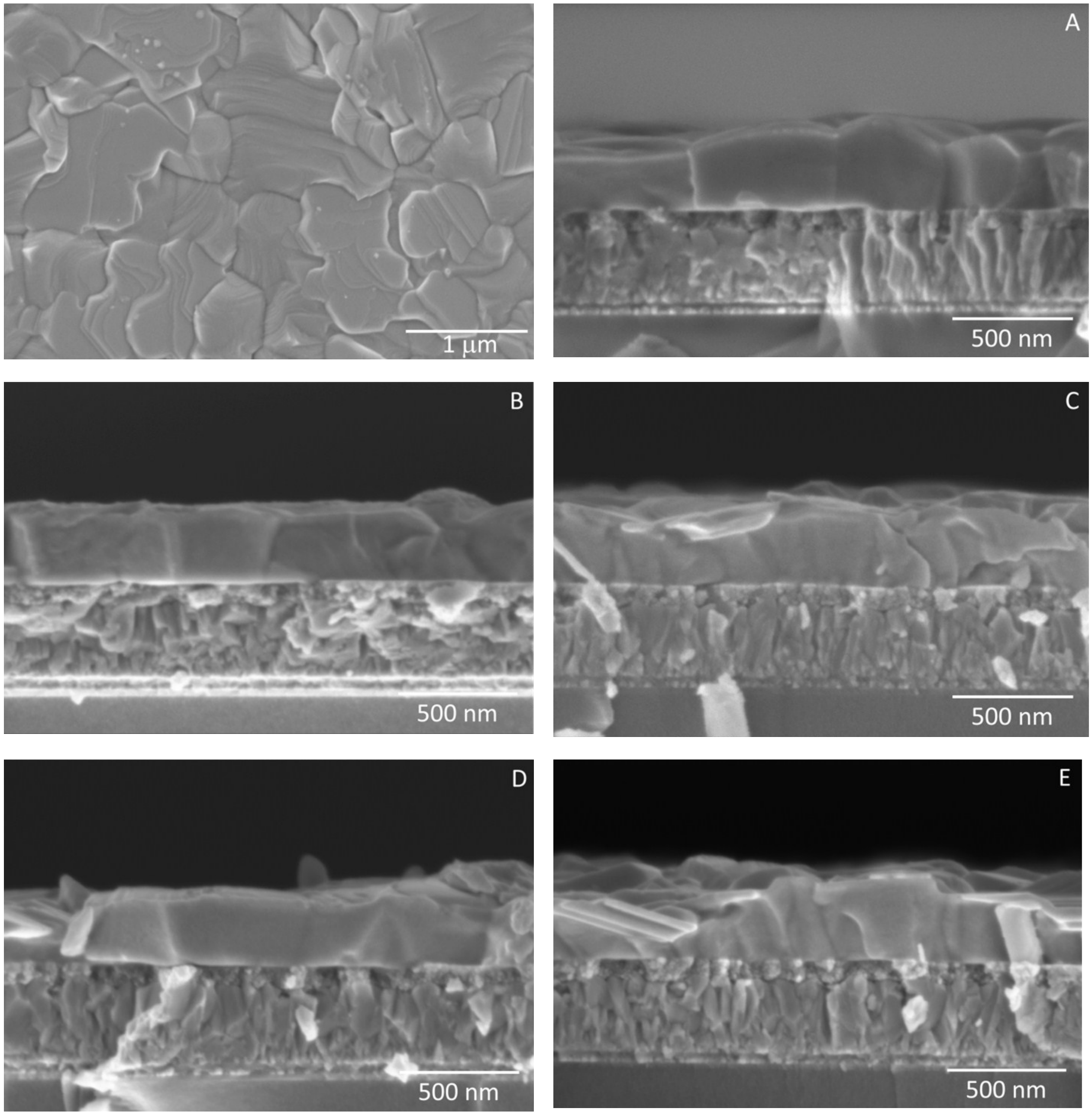

Figure S4. Surface SEM of sample D and cross-section SEM of samples A to E.

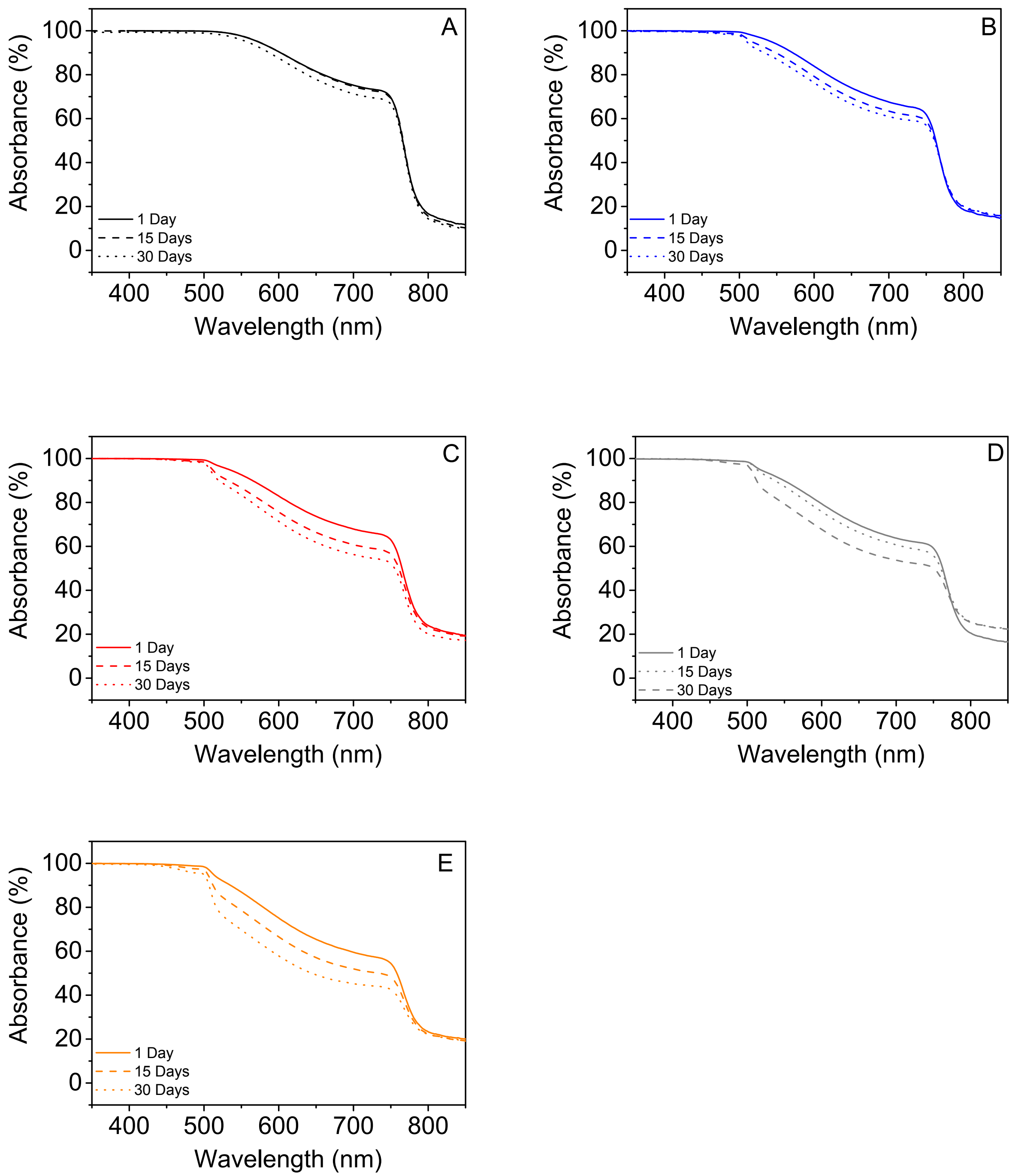

Figure S5. UV-Visible absorption spectra of the $CH_3NH_3PbI_3$ layers for different period of air exposure (at 50% humidity) for samples A, B, C, D and E.

Table S2. Polynomial fit parameters y=a*x^2+b*x+c

Sample	a	b	C
A	330	6243	-30589
B	-1174	82547	-345213
C	-2453	97215	-219069
E	-2692	73276	512

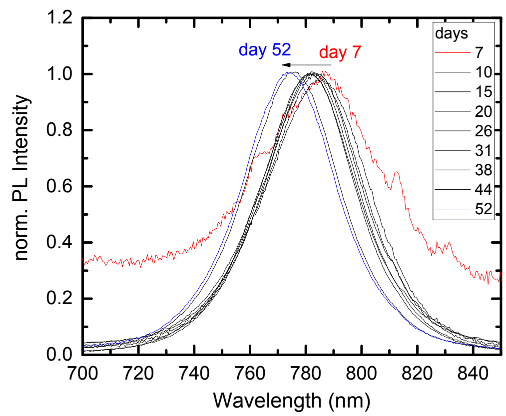

Figure S6. Normalized PL emission spectra for sample B stored under 50% % relative humidity for 7-52 days

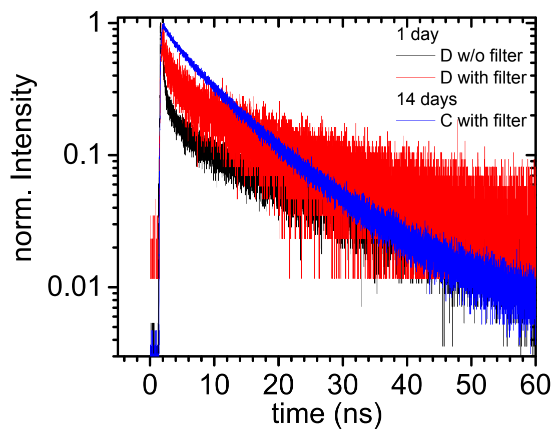

Figure S7. TRPL transients for sample D with (red line) and without (black line) filter for the laser scatter. Blue line shows sample C aged for 14 days period in air exposure (at 50% humidity).

Figure S8. a) The influence of scan rate and b) hysteresis along with c) steady state output at V_{mmp} of device A are shown.

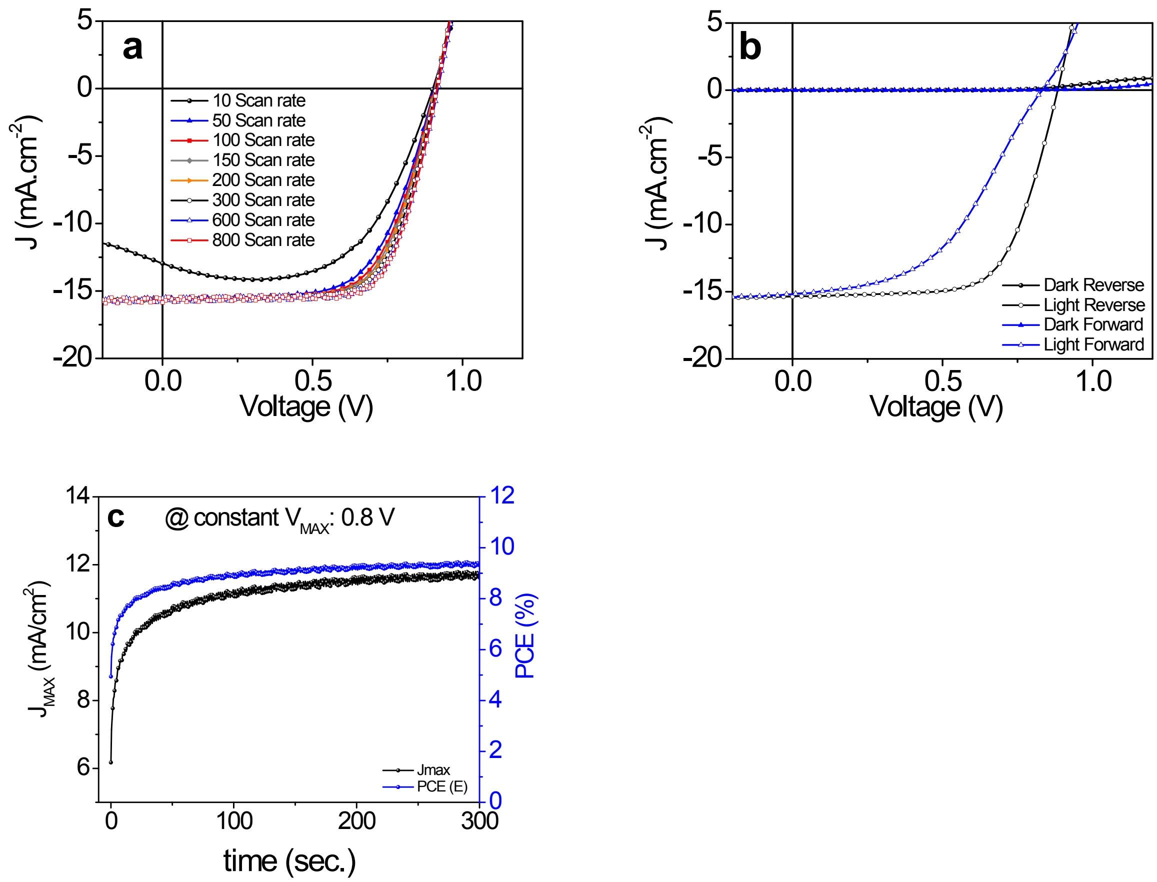

Table S3. Statistics regarding photovoltaic parameters of 8 devices (2 batches of 4 each) measured under 100 $mW.cm^{-2}$ simulated AM1.5G illumination for sample A, B, C, D and E at scan rate 100 $mV.S^{-1}$.

Sample	Cell	J_{sc} [$mA.cm^{-2}$]	V_{oc} [V]	FF [%]	PCE [%]
A	1	15.14	0.93	66.08	9.32
	2	14.00	0.896	57.08	7.16
	3	14.74	0.94	67.00	9.33
	4	16.72	0.94	68.43	10.80
	5	15.38	0.94	66.76	9.69
	6	14.48	0.88	61.80	7.92
	7	15.18	0.90	69.03	9.39
	8	15.08	0.90	69.36	9.37
	Average	15.10	0.92	65.28	9.12

Sample	Cell	J_{sc} [$mA.cm^{-2}$]	V_{oc} [V]	FF [%]	PCE [%]
B	1	15.16	0.94	67.32	9.64
	2	17.22	0.94	67.70	11.00
	3	15.05	0.90	69.38	9.36
	4	16.19	0.93	66.71	10.06
	5	16.72	0.93	65.93	10.28
	6	16.75	0.93	65.73	10.26
	7	16.33	0.95	65.68	10.19
	8	16.70	0.95	66.56	10.56
	Average	16.26	0.94	66.88	10.17

Sample	Cell	J_{sc} [$mA.cm^{-2}$]	V_{oc} [V]	FF [%]	PCE [%]
C	1	15.46	0.940	62.13	9.03
	2	15.75	0.950	65.67	9.83
	3	16.75	0.93	66.31	10.35
	4	16.13	0.950	57.58	8.82
	5	16.21	0.94	65.43	9.97
	6	16.17	0.95	66.38	10.20
	7	16.59	0.95	67.11	10.58
	8	16.13	0.94	58.66	8.90
	Average	16.15	0.94	63.66	9.71

Sample	Cell	J_{sc} [$mA.cm^{-2}$]	V_{oc} [V]	FF [%]	PCE [%]
D	1	14.63	0.900	52.65	6.93
	2	15.39	0.920	55.96	7.92
	3	14.48	0.884	61.80	7.92
	4	14.59	0.920	62.05	8.33
	5	14.74	0.90	64.19	8.48

	6	14.79	0.90	67.56	8.96
	7	14.85	0.90	68.43	9.11
	8	14.97	0.92	56.06	7.72
	Average	14.81	0.90	61.09	8.17

Sample	Cell	J_{sc} [mA.cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
E	1	13.95	0.840	58.74	6.88
	2	14.33	0.810	47.49	5.51
	3	13.46	0.830	54.19	6.05
	4	12.56	0.860	58.00	6.27
	5	14.50	0.872	54.35	6.87
	6	12.81	0.920	59.01	6.96
	7	14.63	0.900	52.65	6.93
	8	10.19	0.91	66.51	6.15
	Average	13.30	0.87	56.37	6.45

Method to determine the percentage of PbI_2 content in $CH_3NH_3PbI_3$ by XRD

K^{th} peak of phase i

L^{th} peak of phase j

$$\frac{I_{iK}}{I_{jL}} = \frac{G_{iK}}{G_{jL}} \cdot \frac{v_i}{v_j} = \frac{G_{iK}\rho_i}{G_{jL}\rho_j} \cdot \frac{x_i}{x_j}$$

v_i is the volume concentration and x_i the mass concentration of phase i

with $G_i(hkl) = L_i(\theta) \cdot P_i(\theta) \cdot y_i H_i |F_i(hjk)|^2$

Polarization factor for Bragg-Brentano geometry with incident beam monochromator $P(\theta)$

$2\theta_M$ Bragg angle of monochromator $\theta_M = 13.640°$, $2\theta_M = 27{,}28°$, $cos^2(2\theta_M) = 0.789$

$$L(\theta) = \frac{1}{sin^2(\theta)cos(\theta)} \qquad P(\theta) = \frac{1 + cos^2(2\theta_M)cos^2(2\theta)}{1 + cos^2(2\theta)_M}$$

$$\frac{I_{MAPbI_3}}{I_{PbI_2}} = \frac{G_{iK}}{G_{jL}}$$

$$\frac{I_{MAPbI_3}}{I_{PbI_2}} = \left(\frac{L_{MAPbI_3}(\theta)}{L_{PbI_2}(\theta)} \cdot \frac{P_{MAPbI_3}(\theta) H_{MAPbI_3} |F_{MAPbI_3}|^2}{P_{PbI_2}(\theta) \quad H_{PbI_2} \quad |F_{PbI_2}|^2}\right)\left(\frac{\rho_{MAPbI_3}}{\rho_{PbI_2}}\right)^{-1}\frac{x_{MAPbI_3}}{x_{PbI_2}}$$

L() is the Lorentz factor, P is the polarization factor, H(hkl) is the plane multiplicity, F(hkl) is the structure factor of the plane (hkl),

PbI_2:	001	$2\theta = 12.645°$
		$\theta = 6.323°$
$CH_3NH_3PbI_3$:	110	$2\theta = 14.110°$
	002	$\theta = 7.055°$

$$\frac{L_{MAPbI_3}}{L_{PbI_2}} = \left(\frac{82.949}{66.796}\right)^{-1} = \frac{1}{1.242} = 0.805$$

Polarization factor P(θ) with $\theta_M = 13.640°$

$$P(\theta) = \frac{1 + 0.7899 * cos^2(2\theta)}{1.7899}$$

$P_{MAPbI_3}(7.055°) = 0.9738$ $P_{PbI_2}(6.323) = 0.9789$ $\frac{P_{MAPbI_3}}{P_{PbI_2}} = \frac{0.9738}{0.9789} = 0.995$

$$H_{MAPbI_3} \cdot \left|F_{MAPbI_3}\right|^2 = H_{MAPbI_3}(110) \cdot \left|F_{MAPbI_3}(110)\right|^2 + H_{MAPbI_3}(002) \cdot \left|F_{MAPbI_3}(002)\right|^2$$

$$= 4 * 313^2 + 2 * 338^2 = 620364$$

$$H_{PbI_2} \cdot \left|F_{PbI_2}\right|^2 = H_{MAPbI_2}(001) \cdot \left|F_{MAPbI_2}(001)\right|^2 = 2 * 287^2 = 164738$$

Ration of densities

$$\frac{\rho_{MAPbI_3}}{\rho_{PbI_2}} = \frac{4.17 g/cm^3}{6.16 g/cm^3} = 0.677$$

$$\frac{I_{MAPbI_3}}{I_{PbI_2}} = \frac{G_{MAPbI_3}}{G_{PbI_2}} \cdot \left(\frac{\rho_{MAPbI_3}}{\rho_{PbI_2}}\right)^{-1} \frac{x_{MAPbI_3}}{x_{PbI_2}} \rightarrow \frac{x_{MAPbI_3}}{x_{PbI_2}} = \frac{I_{MAPbI_3}}{I_{PbI_2}} \left(\frac{G_{MAPbI_3}}{G_{PbI_2}}\right)^{-1} \frac{\rho_{MAPbI_3}}{\rho_{PbI_2}}$$

$$\frac{x_{MAPbI_3}}{x_{PbI_2}} = \frac{I_{MAPbI_3}}{I_{PbI_2}} \cdot 3.016 \cdot 0.677 = \frac{I_{MAPbI_3}}{I_{PbI_2}} \cdot 2.042$$

$$x_{PbI_2} = \frac{x_{PbI_2}}{x_{MAPbI_3} + x_{PbI_2}} = \frac{1}{\frac{x_{MAPbI_3}}{x_{PbI_2}} + 1}$$

with $x_{MAPbI_3} + x_{PbI_2} = 1$

Sample	rel. Intensities	mass ratio $\frac{x_{MAPbI_3}}{x_{PbI_2}}$	PbI_2 content x_{PbI_2}
A	$I_{MAPbI_3} = 9.1795$ $I_{PbI_2} = -$	-	-
B	$I_{MAPbI_3} = 9.975$ $I_{PbI_2} = 5.4007$	3.7715	0.21
C	$I_{MAPbI_3} = 7.5424$ $I_{PbI_2} = 8.0434$	1.9148	0.343

D	$I_{MAPbI_3} = 5.7247$ $I_{PbI_2} = 10.1689$	1.1496	0.445
E	$I_{MAPbI_3} = 7.865$ $I_{PbI_2} = 14.5852$	1.1011	0.476