

Supporting Information

Stabilized Wide Bandgap Perovskite Solar Cells by Tin Substitution

*Zhibin Yang^{†, ‡}, Adharsh Rajagopal^{†, ‡}, Sae Byeok Jo[†], Chu-Chen Chueh[†], Spencer Williams[†],
Chun-Chih Huang[§], John K. Katahara[§], Hugh W. Hillhouse[§] and Alex K.-Y. Jen^{†, *}*

[†]Department of Materials Science and Engineering, University of Washington, Seattle, WA, 98195-2120, USA

[§]Department of Chemical Engineering, Molecular Engineering and Sciences Institute, University of Washington, Seattle, WA 98195-1750, USA

[‡] These authors contributed equally to this work

^{*} Corresponding author. E-mail: ajen@u.washington.edu

Keywords: perovskite, wide bandgap, phase segregation, Sn substitution

Time resolved PL measurement. The experimental set up used for time resolved PL measurements were adapted from previous work.^{S1} Spectra were acquired using a modified Horiba LabRAM HR-800, a 532 nm laser diode excitation source, and a 10x objective (NA=0.25). The adjustable confocal hole before the monochromator was set at 800 μm . A 150 gr/mm Czerny-Turner monochromator blazed at 1200 nm was used, and the emitted light was collected with a silicon CCD array detector. For maps, the PL collection time was set to 1 s, and the amount of time that the laser stayed at any given location was set to 1 s. This reduces the effects of any transient behavior and gives the initial condition of each perovskite composition. Spectral artifacts caused by the detector and the optical path between the sample and detector were accounted for by creating a relative correction file with a black body source (IR-301, Infrared Systems Development Corporation) set to 1050 °C. A 10 μm pin-hole was used to fix the spectral photon flux to the detector and allow an absolute photons per count calibration factor to be measured. The laser diameter was measured to be 10 μm and the FWHM of the Gaussian distributed laser intensity was measured to be 6 μm . All PL measurements were conducted with the perovskite samples in a nitrogen-filled cell (P=250 mm-Hg) with a quartz window.

The N-Suns illumination intensity The N-Suns illumination intensity in the PL and TAS measurement was calculated by dividing the photon flux (number of photons per second per area) inside the FWHM of excitation laser by the above-bandgap (of initial perovskite) photon flux of the AM1.5 GT solar spectrum rather than comparing energy density (in W/cm^2) as previously reported. An Oriel optical power meter and beam profilometer were used to measure the illumination intensity and excitation diameter (2 mm circle), respectively, for various laser power through neutral density (ND) filters.

Williamson-Hall analysis method:

According to Williamson-Hall analysis, the line broadening (β) can be expressed as a simple sum of contributions from crystallite size (D) and micro-strain (ε). Thus we have, $\beta = \frac{\kappa\lambda}{D \cos \theta} + 2\varepsilon \tan \theta$ (where β is the line broadening at FWHM, D is the mean size of crystallite domains, ε is the micro-strain, λ is the X-ray wavelength, θ is the Bragg angle and κ is a dimensionless shape factor). By re-arranging the terms we have: $\beta \cos \theta = \frac{\kappa\lambda}{D} + 2\varepsilon \sin \theta$. The slope (2ε) and intercept ($\kappa\lambda/D$) obtained from a linear fit of $\beta \cos \theta$ vs $\sin \theta$ are expressed as strain and size contributions, respectively. The strain contribution is directly proportional to micro-strain and the size contribution is inversely proportional to crystallite size. Uniform deformation model was used based on assumption of isotropic strain.

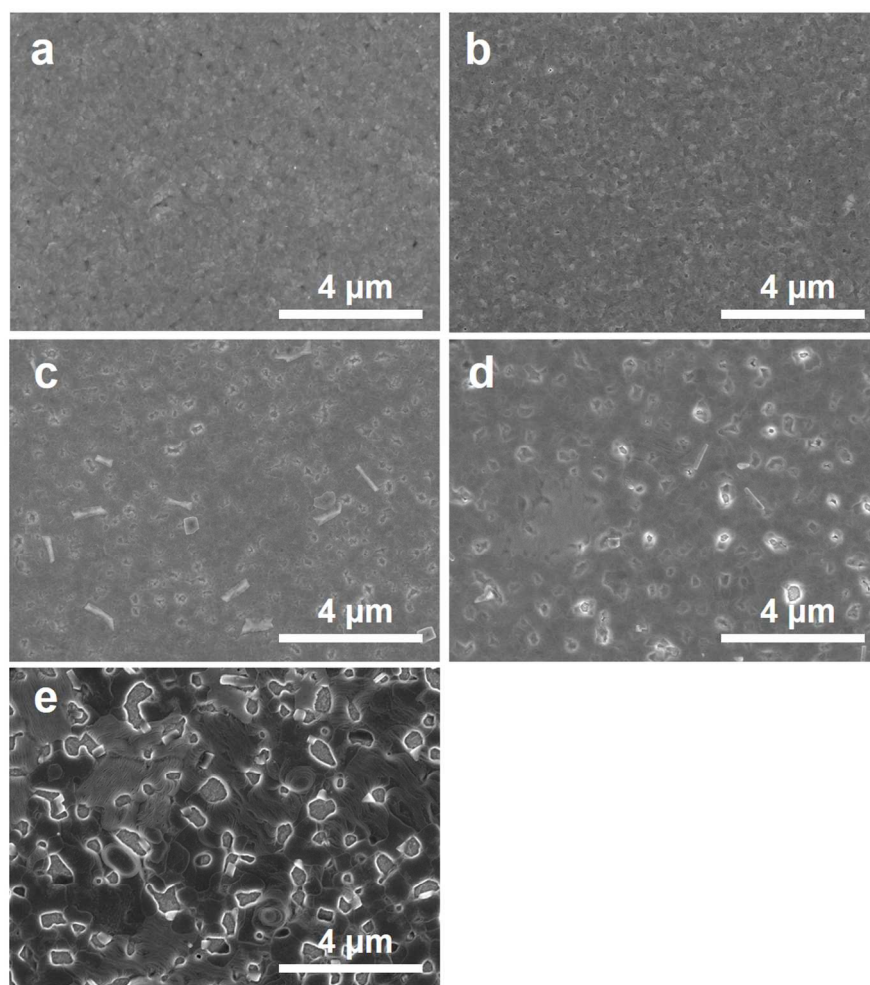


Figure S1. SEM images of the MAPb_{1-x}Sn_x(I_{0.6}Br_{0.4})₃ perovskites with Sn content of 0% (a), 25% (b), 50% (c), 75% (d) and 100% (e).

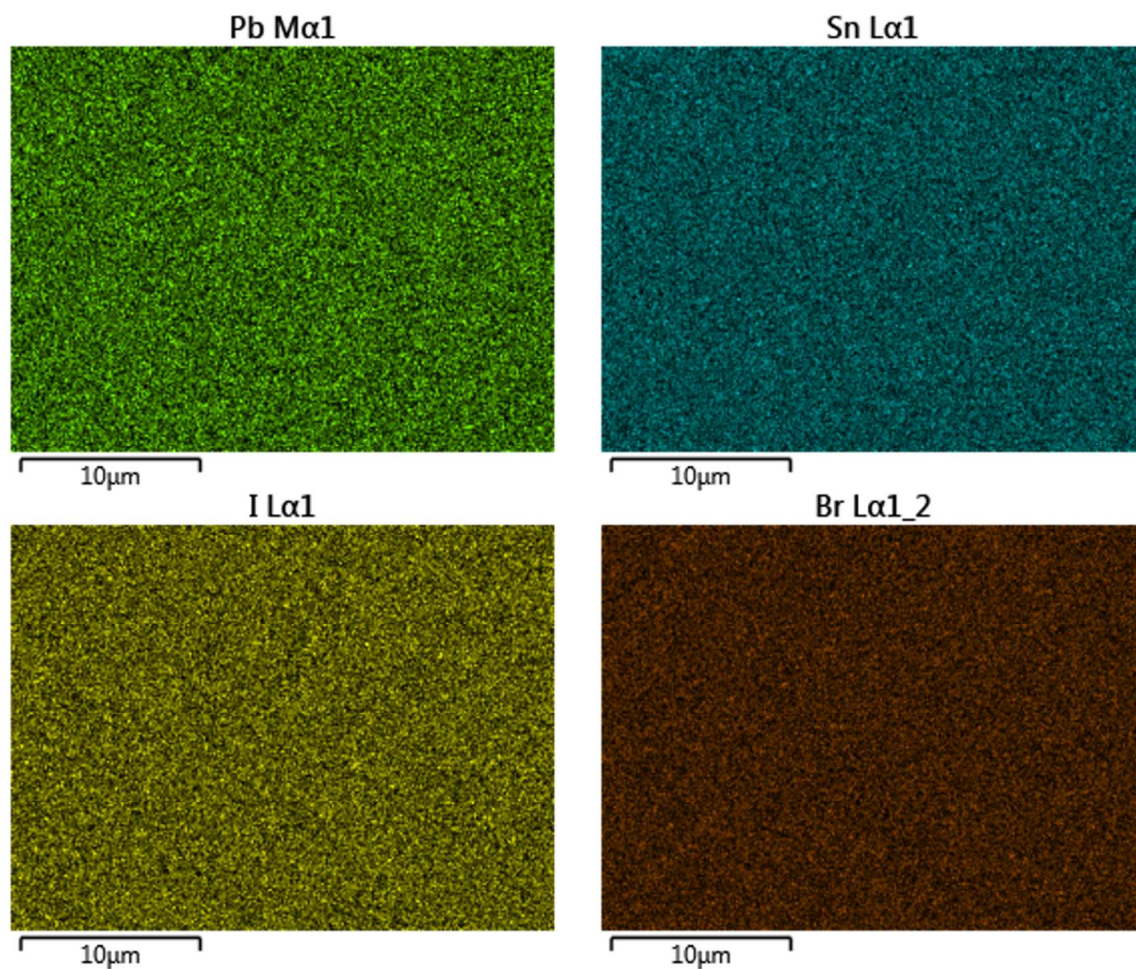


Figure S2. SEM energy dispersive spectroscopy (EDS) mapping (Pb, Sn, I and Br) of $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite film.

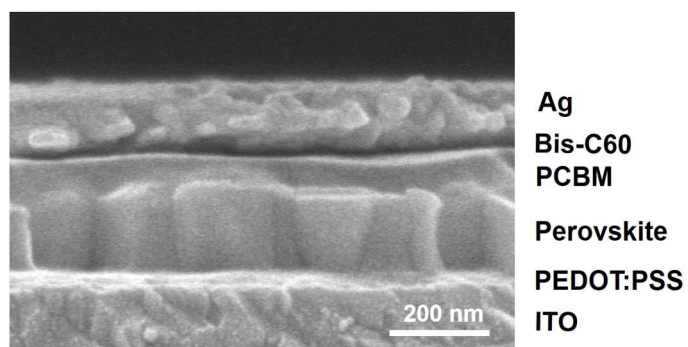


Figure S3. Cross sectional SEM images of the $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite solar cells.

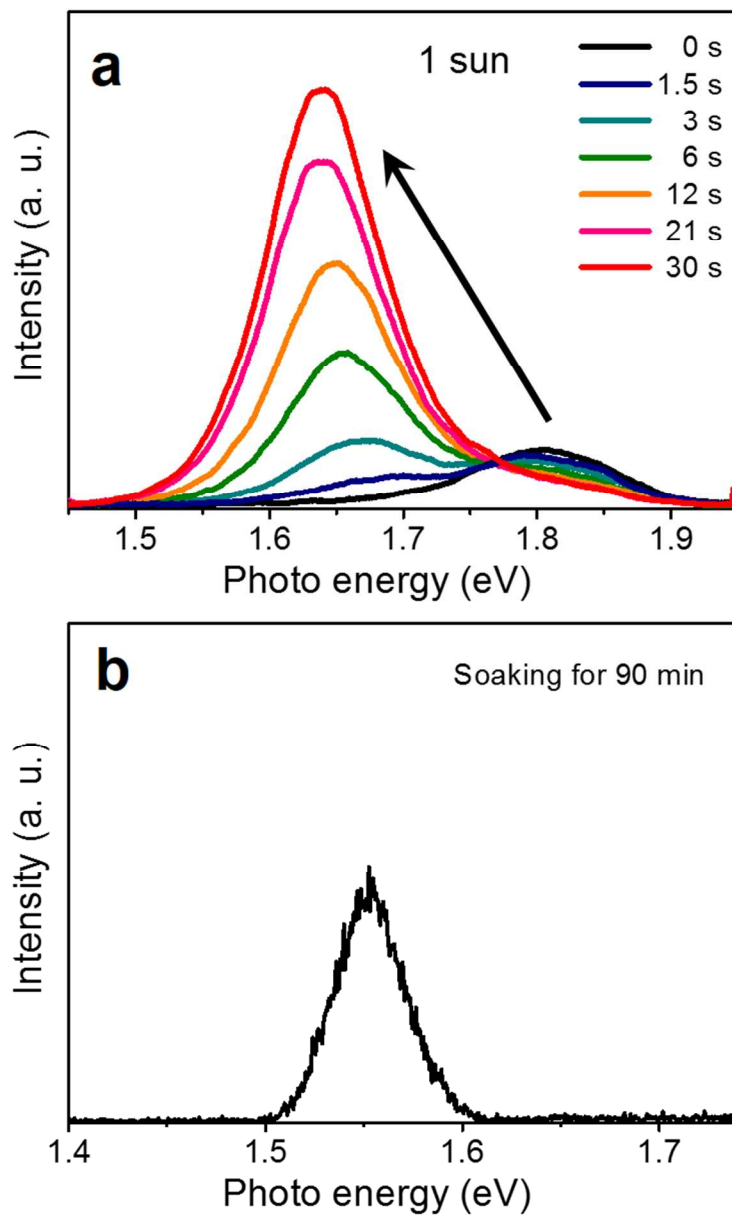


Figure S4. **a**, Time resolved steady state PL of the $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite film under an illumination of one sun-intensity 532 nm laser. **b**, PL of the $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{0.6}\text{Br}_{0.4})_3$ perovskite film under an illumination of one sun-intensity 532 nm laser after soaking and iteration for 90 min.

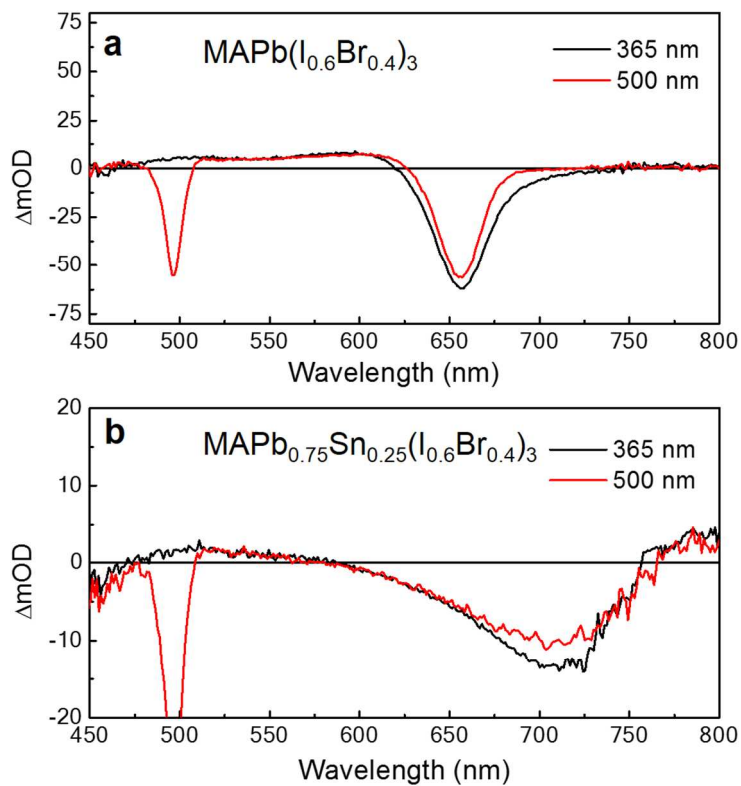


Figure S5. Transient absorption spectra of $\text{MAPb}(\text{I}_{0.6}\text{Br}_{0.4})_3$ (a) and $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{0.6}\text{Br}_{0.4})_3$ (b) perovskite films under different wavelength of pump laser.

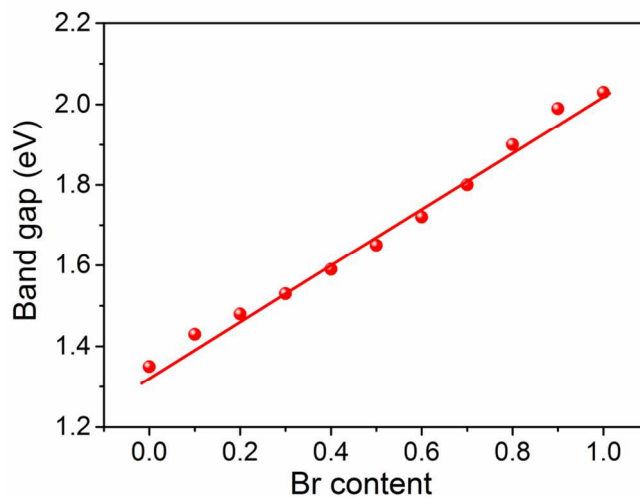


Figure S6. Tunable bandgap of the $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{1-y}\text{Br}_y)_3$ perovskites with different Br contents.

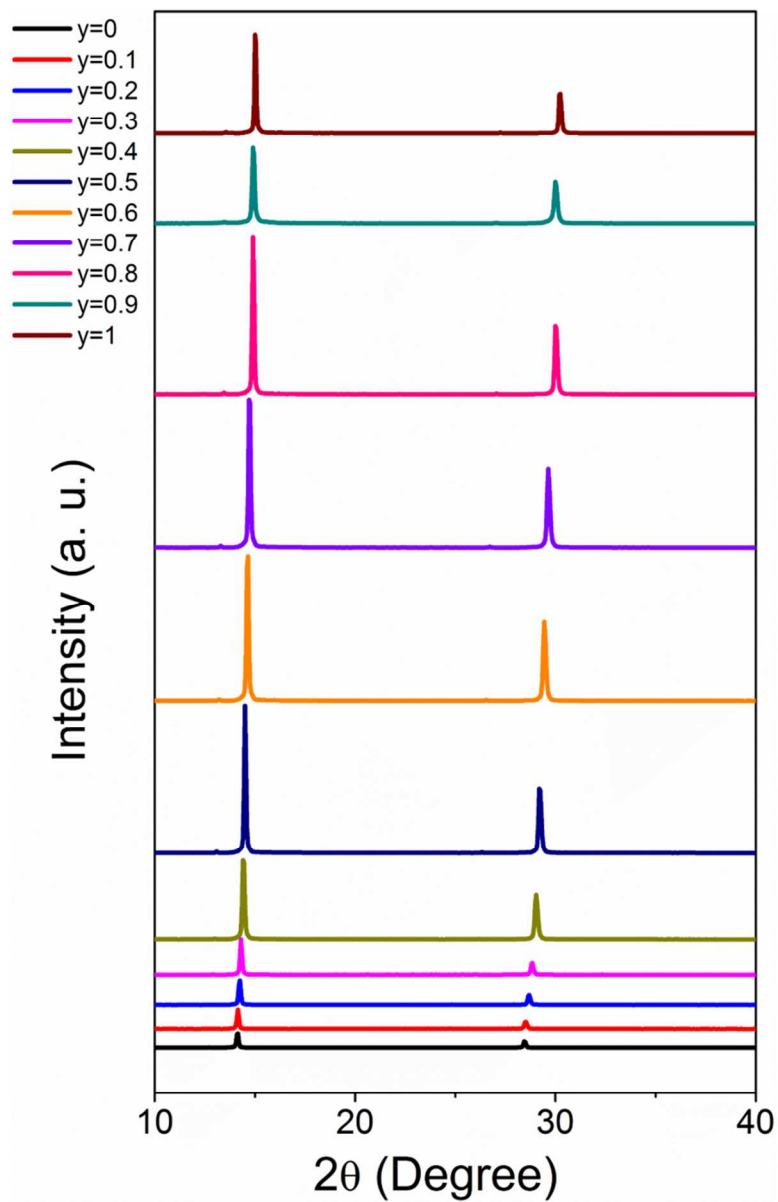


Figure S7. XRD spectra of the $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{1-y}\text{Br}_y)_3$ perovskites with different Sn contents.

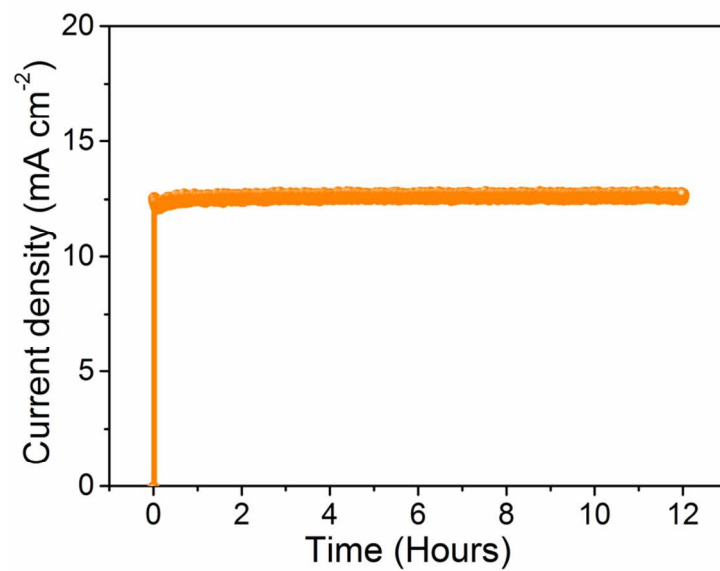


Figure S8. The steady-state photocurrent measurement of $\text{MAPb}_{0.75}\text{Sn}_{0.25}(\text{I}_{0.4}\text{Br}_{0.6})_3$ PVSCs at maximum power point of 0.82 V for 12 hours under AM 1.5 illumination.

Table S1. Photovoltaic parameters of the MAPb_{1-x}Sn_x(I_{0.6}Br_{0.4})₃ PVSCs measured under AM 1.5 illumination.

MAPb _{1-x} Sn _x (I _{0.6} Br _{0.4}) ₃	Band gap (eV)	V _{OC} (V)	J _{SC} (mA/cm ²)	FF	PCE (%)	V _{OC} /V _{OC} ^{SQ}
x=0	1.80	1.05±0.01	14.34±0.42	0.74±0.02	11.14±0.58	0.69
x=0.25	1.59	0.91±0.01	17.25±0.67	0.76±0.02	11.93±0.74	0.69
x=0.50	1.48	0.57±0.03	6.02±0.56	0.68±0.03	2.34±0.31	0.47
x=0.75	1.34	0.41±0.03	2.76±0.75	0.63±0.05	0.71±0.27	0.38
x=1	1.60	0.15±0.04	1.03±0.69	0.51±0.05	0.07±0.09	0.11

Average values with standard deviation. The data for each sample was obtained from 20 devices. The limit for V_{OC}, V_{OC}^{SQ}, was calculated using the ASTM G-173 standard for the AM1.5GT solar spectrum, a temperature of 298.15 K, and a perfect back reflector.

Table S2. Line broadening parameters calculated based on Uniform Deformation Model (UDM) through Williamson-Hall approach*

	Size Contribution $\frac{\kappa\lambda}{D}$	Strain Contribution 2ε
MAPb(I _{0.6} Br _{0.4}) ₃ Before Illumination	0.0023	0.0080
MAPb(I _{0.6} Br _{0.4}) ₃ During Illumination	0.0036	0.0112
MAPb(I _{0.6} Br _{0.4}) ₃ After Illumination	0.0022	0.0088
MAPb _{0.75} Sn _{0.25} (I _{0.6} Br _{0.4}) ₃ Before Illumination	0.0019	0.0096
MAPb _{0.75} Sn _{0.25} (I _{0.6} Br _{0.4}) ₃ During Illumination	0.0019	0.0096

*Williamson-Hall approach: $\beta \cos \theta = \frac{\kappa\lambda}{D} + 2\varepsilon \sin \theta$ (where β is the line broadening at FWHM, D is the mean size of crystallite domains, ε is the micro-strain, λ is the X-ray wavelength, θ is the Bragg angle and κ is a dimensionless shape factor)

Table S3. Photovoltaic parameters of the MAPb_{0.75}Sn_{0.25}(I_{1-y}Br_y)₃ PVSCs measured under AM 1.5 illumination.

MAPb _{0.75} Sn _{0.25} (I _{1-y} Br _y) ₃	E _g (eV)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
0.0	1.35	0.82±0.01	22.19±0.56	0.78±0.01	14.19±0.63
0.1	1.43	0.85±0.02	21.86±0.87	0.78±0.02	14.49±1.21
0.2	1.48	0.87±0.03	21.05±0.79	0.77±0.03	14.10±1.32
0.3	1.53	0.90±0.04	19.60±0.69	0.76±0.03	13.41±1.53
0.4	1.59	0.91 ±0.04	17.25±0.54	0.76±0.03	11.93±1.22
0.5	1.65	0.94 ±0.04	16.31±0.77	0.75±0.04	11.50±1.37
0.6	1.73	0.99±0.05	15.16±0.67	0.74±0.03	11.11±1.45
0.7	1.80	1.01 ±0.04	9.33±0.97	0.67±0.04	6.31±0.98
0.8	1.90	0.97±0.04	6.21±1.22	0.63±0.05	3.79±0.87
0.9	1.99	0.91±0.06	4.47±0.96	0.62±0.06	2.52±0.73
1.0	2.03	0.76±0.05	3.22±0.54	0.61±0.05	1.49±0.41

Average values with standard deviation. The data for each sample was obtained from 20 devices.

Reference

(S1) Braly, I. L.; Hillhouse, H. W. J. Phys. Chem. C 2016, 120, 893-902.