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Supplementary Information

Triple-Cation Low-Bandgap Perovskite Thin-Films for High-Efficiency Four-Terminal All-Perovskite Tandem Solar Cells

Somayeh Moghadamzadeh,[a,b,*] Ihteaz M. Hossain,[b,a] The Duong,[c] Saba Gharibzadeh,[b,a] Tobias Abzieher,[a,b] Huyen Pham,[d] Hang Hu,[b,a] Paul Fassl,[b,a] Uli Lemmer,[a,b] Bahram Abdollahi Nejand,[b,a,*] and Ulrich W. Paetzold[b,a,*]

[a] Light Technology Institute (LTI), Karlsruhe Institute of Technology (KIT), Engesserstrasse 13, 76131, Karlsruhe, Germany

[b] Institute of Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Karlsruhe, Germany

[c] Research School of Electrical, Energy and Materials Engineering, The Australian National University, Canberra 2601, Australia

[d] Department of Electronic Materials Engineering, Research School of Physics, The Australian National University, Canberra 2601, Australia

* To whom correspondence should be addressed email: somayeh.moghadamzadeh@kit.edu, bahram.abdollahi@kit.edu, ulrich.paetzold@kit.edu

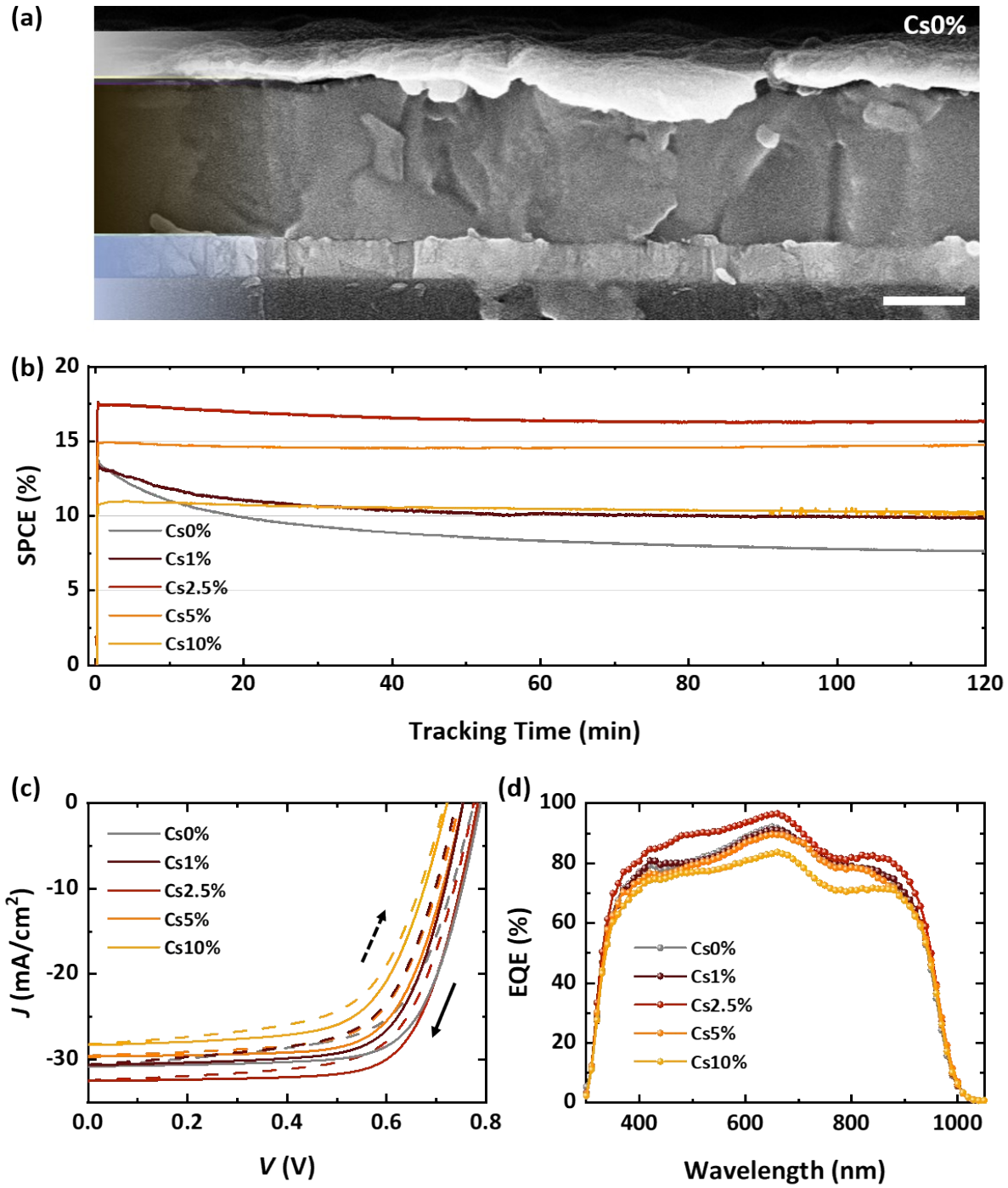

Fig. S1. (a) Cross-sectional SEM image of a PSC with a layer stack of glass / ITO / PTAA / $Cs_x(FA_{0.8}MA_{0.2})_{(1-x)}Sn_{0.5}Pb_{0.5}I_3$ / PCBM / C_{60} / BCP / Ag, for which x = 0 (denoted as Cs0%). The scalebar on the bottom-right is indicative of 300 nm. (b) Absolute values of stabilized power conversion efficiency (SPCE) at the MPP tracking conditions for 120 min, (c) current-density–voltage (J–V) scans measured at a fixed rate of 0.6 V/s from the open-circuit voltage (V_{OC}) to the short-circuit current (J_{SC}) (solid lines) and from J_{SC} to V_{OC} (dashed lines) under AM 1.5G illumination (100 mW/cm^2) at 25°C, of the best performing LBG PSCs prepared with different Cs concentrations varying from 0% to 10% (denoted as Cs0% to Cs10%). Comparing figure a with b demonstrates that the actual PCEs of the PSCs lie in the middle between the forward and backward scans. (d) the external quantum efficiency (EQE) of devices with perovskite thin-films prepared with different Cs concentrations.

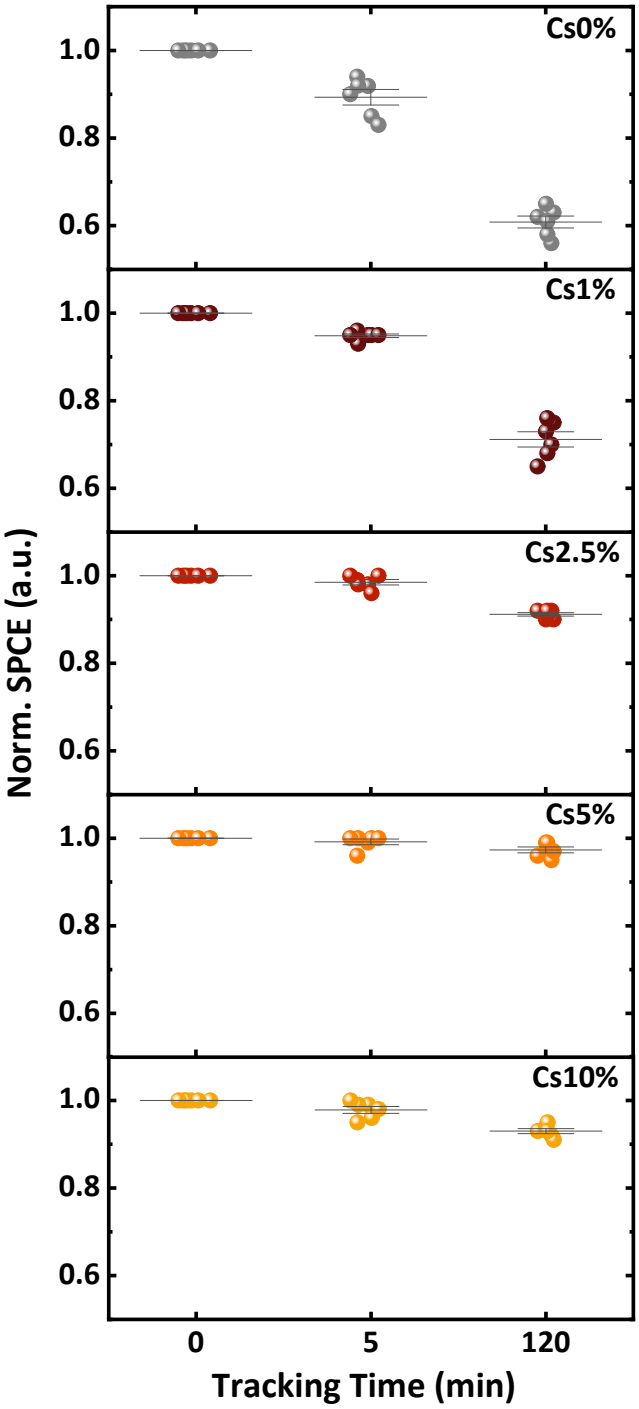

Fig. S2. Stabilized power conversion efficiency (SPCE) at 0 min (when the lamp is switched on), and after 5 and 120 min of maximum power point (MPP) tracking, derived from six low-bandgap perovskite solar cells (LBG PSCs) with different Cs concentrations varying from 0% (top) to 10% (bottom) which were identically-prepared in different batches. The initial values (at 0 min) are normalized to 1.

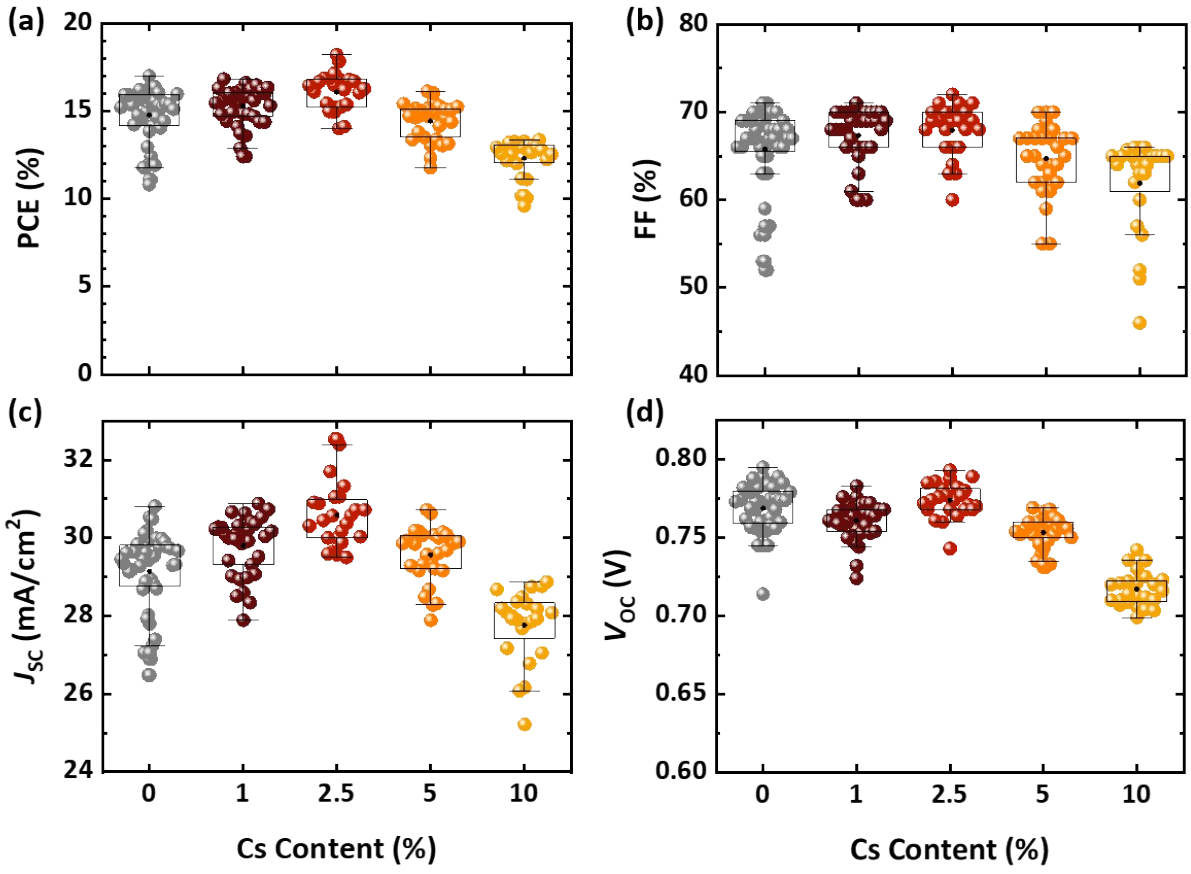

Fig. S3. (a) Power conversion efficiency (PCE), (b) fill factor (FF), (c) short-circuit current (J_{SC}), and (d) open-circuit voltage (V_{OC}) of 30 low-bandgap perovskite solar cells (LBG PSCs) with different Cs concentrations varying from 0% to 10%, identically-prepared in 10 different batches. The black dots show the average values.

Table S1. Photovoltaic parameters (champion (Ch.) and average (Ave.) values) of low-bandgap perovskite solar cells (LBG PSCs) with different Cs concentrations varying from 0% to 10%, derived from current-density–voltage (*J–V*) scans measured at a fixed rate of 0.6 V/s from the open-circuit voltage (V_{OC}) to the short-circuit current (J_{SC}) (backward scan) and from J_{SC} to V_{OC} (forward scan) under AM 1.5G illumination (100 mW/cm^2) at 25°C. The average (Ave.) values are derived from 30 LBG PSCs identically-prepared in 10 different batches.

Cs concentration	**Scan direction**	**V_{OC} (V)**		**J_{SC} (mA/cm^2)**		**FF (%)**		**PCE (%)**	
		Ch.	*Ave.*	*Ch.*	*Ave.*	*Ch.*	*Ave.*	*Ch.*	*Ave.*
Cs0%	Backward	0.79	0.77	30.8	29.1	70.6	65.8	17.2	14.8
	Forward	0.77	0.76	30.9	28.9	63.3	60.5	15.2	13.2
Cs1%	Backward	0.75	0.76	30.7	29.8	69.2	67.3	16.0	15.3
	Forward	0.74	0.75	30.6	29.7	63.4	62.0	14.3	13.8
Cs2.5%	Backward	0.78	0.78	32.5	30.6	71.8	68	18.2	16.1
	Forward	0.77	0.77	32.5	30.4	66.5	63.7	16.7	14.8
Cs5%	Backward	0.75	0.75	29.7	29.6	68.9	64.7	15.4	14.4
	Forward	0.75	0.75	29.6	29.3	65.7	61.2	14.5	13.3
Cs10%	Backward	0.72	0.72	28.3	27.8	65.3	62.0	13.3	12.3
	Forward	0.72	0.73	28.3	26.5	61.4	61.1	12.4	11.9

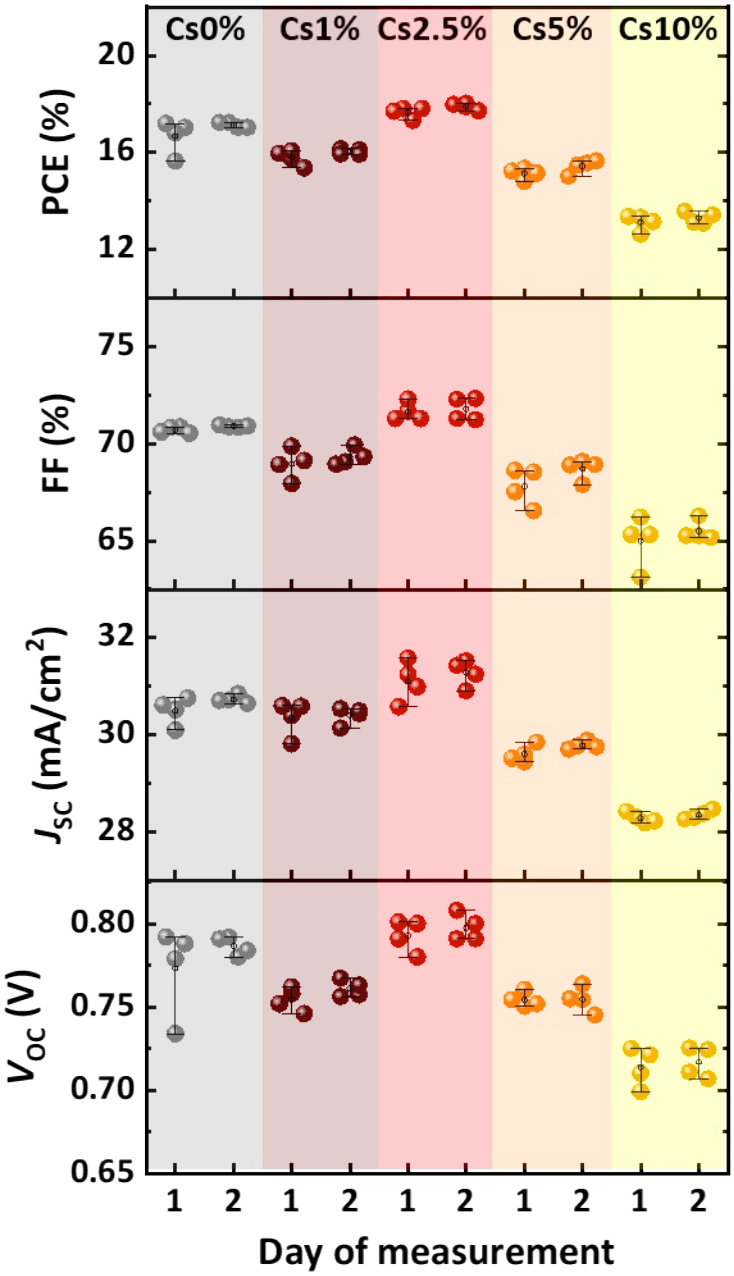

Fig. S4. Power conversion efficiency (PCE), fill factor (FF), short-circuit current (J_{SC}), and open-circuit voltage (V_{OC}) of champion PSCs (from different batches) with different Cs concentrations measured on day 1 (day of device completion) and day 2 (after one night of storage in a dark inert atmosphere).

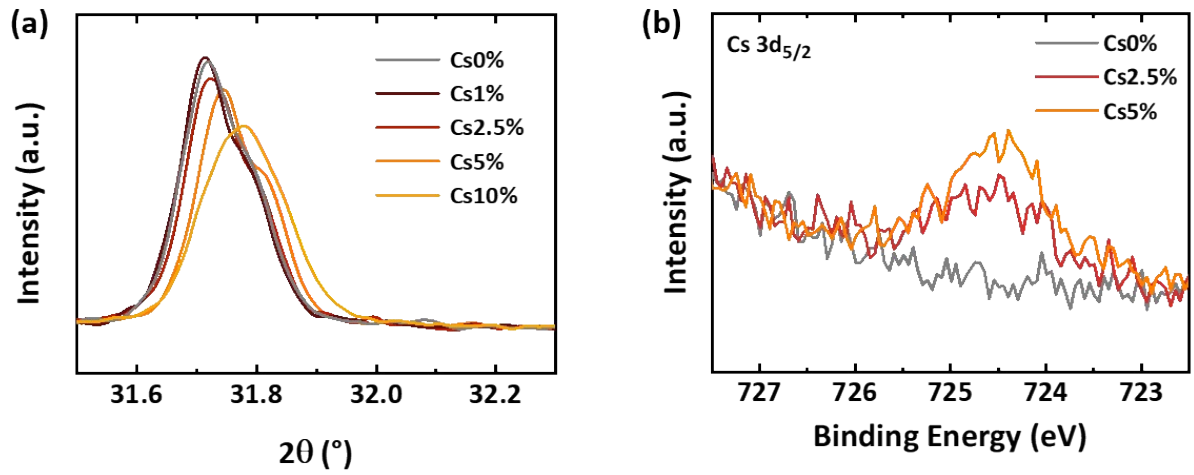

Fig. S5. (a) X-ray diffraction (XRD) peaks assigned to (114)/(310) planes of the $Cs_x(FA_{0.8}MA_{0.2})_{(1-x)}Sn_{0.5}Pb_{0.5}I_3$ low-bandgap perovskite thin-films shifting to higher diffraction angles by increasing *x*. (b) X-ray photoelectron spectroscopy (XPS) spectra of the Cs $3d_{5/2}$ core level of the low-bandgap perovskite thin-films samples with different Cs concentrations varying from 0% to 2.5% and 5%.

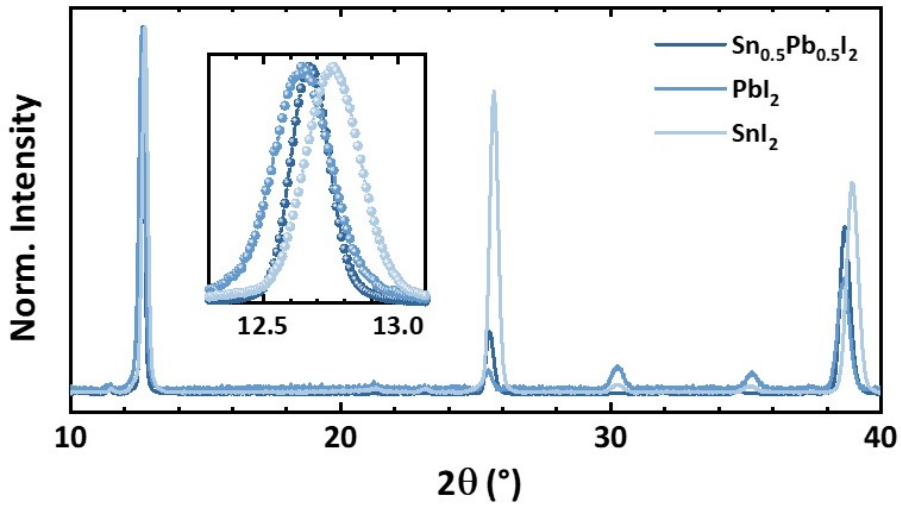

Fig. S6. XRD patterns collected from PbI_2, SnI_2, and $Sn_{0.5}Pb_{0.5}I_2$ thin-films (inset compares the position of the main peak of the three thin-films).

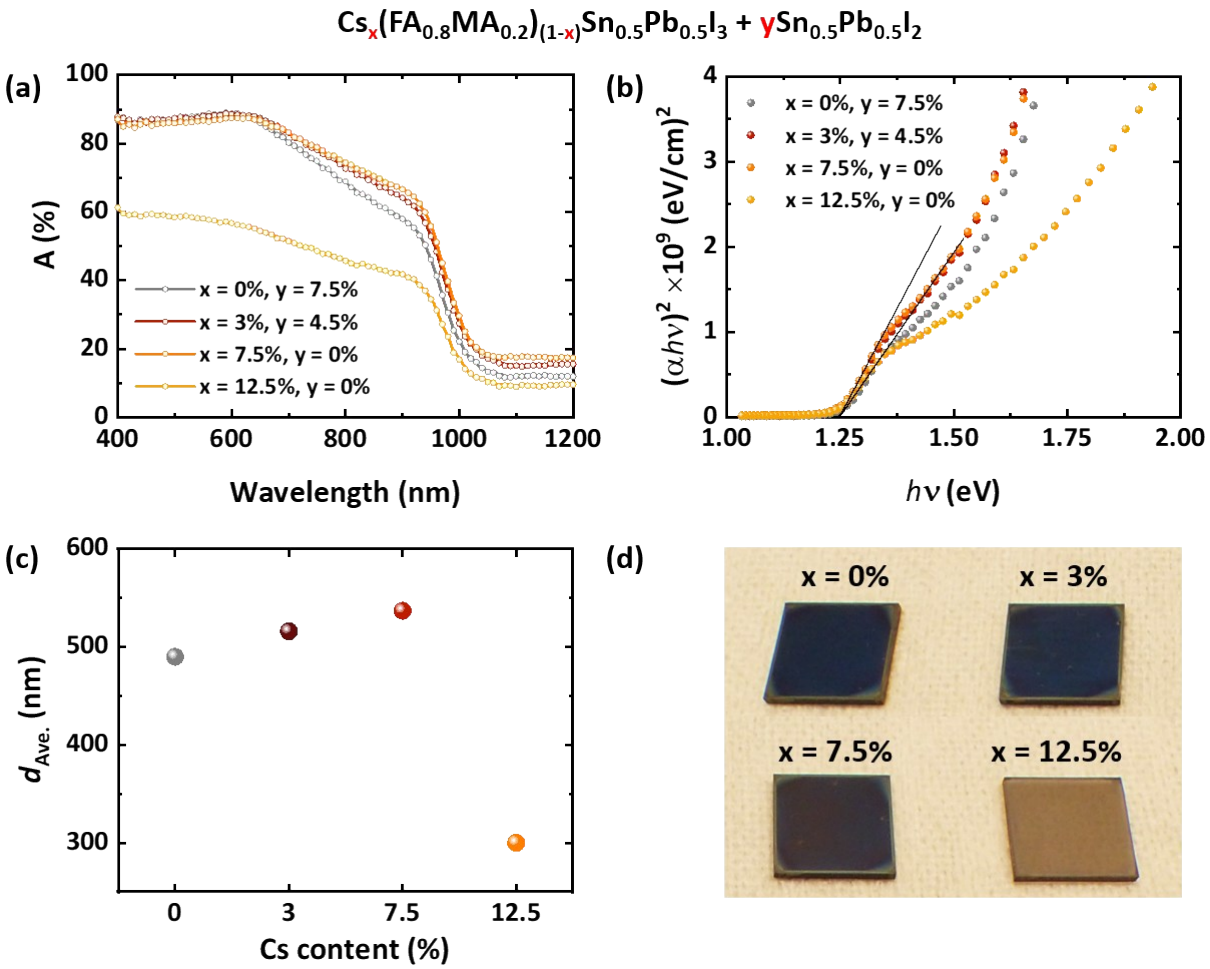

Fig. S7. (a) Absorptance spectra (A), (b) Tauc plot, (c) the average thickness ($d_{Ave.}$), and (d) picture of Cs$_x$(FA$_{0.8}$MA$_{0.2}$)$_{(1-x)}$Sn$_{0.5}$Pb$_{0.5}$I$_3$ thin-films prepared with excess Sn and Pb for different Cs concentrations of x = 0%, 3%, 7.5%, and 12.5%. All the thin-films are deposited on glass substrates. The average thickness (d_{Ave}) of each thin-film is an average of ten values obtained from two different samples on five different spots on each.

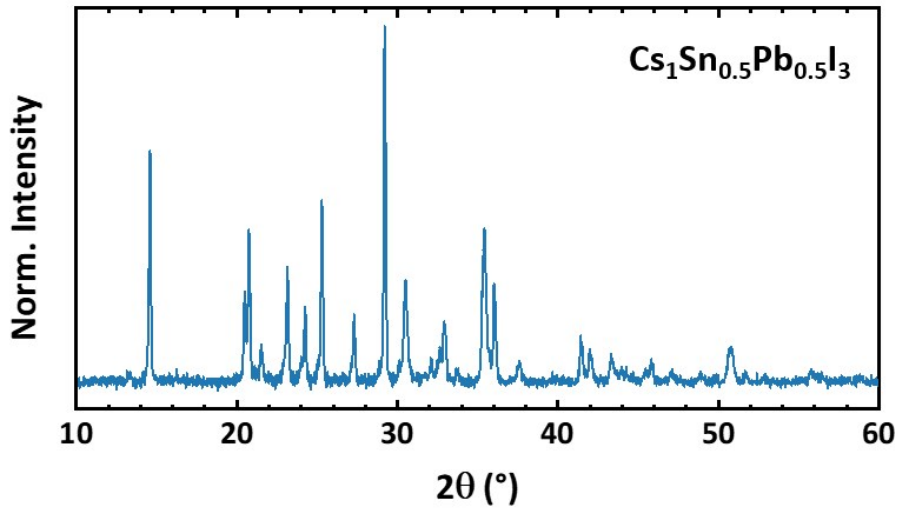

Fig. S8. X-ray diffraction (XRD) patterns of $Cs_1Sn_{0.5}Pb_{0.5}I_3$ perovskite thin-film.

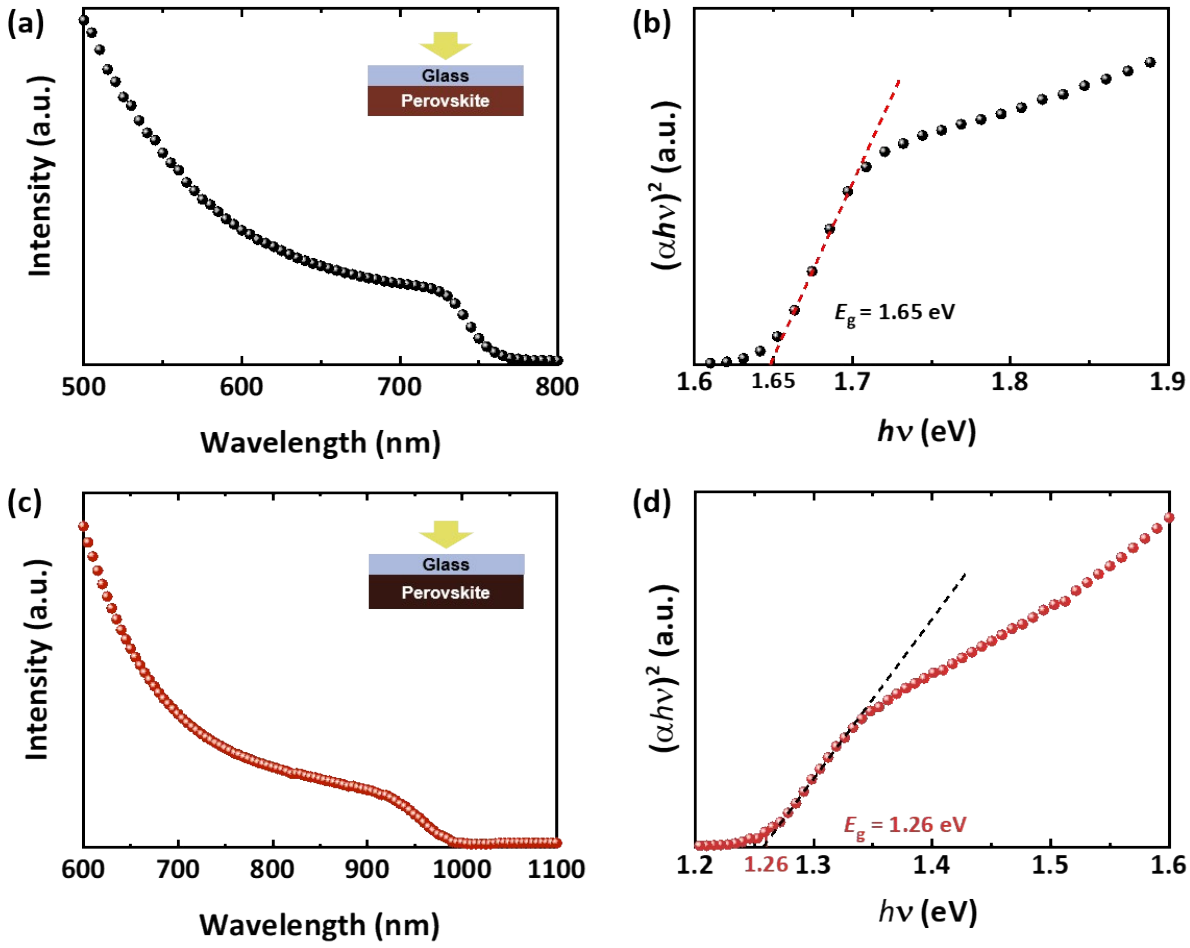

Fig. S9. UV-vis absorbance spectra and Tauc plots of a double-cation $Cs_{0.17}FA_{0.83}Pb(I_{0.76}Br_{0.24})_3$ perovskite thin-film with a bandgap of E_g = 1.65 eV (a and b), and a triple cation $Cs_{0.025}(FA_{0.8}MA_{0.2})_{0.075}Sn_{0.5}Pb_{0.5}I_3$ low-bandgap perovskite thin-film with a bandgap of E_g = 1.26 eV (c and d), both deposited on glass substrates.

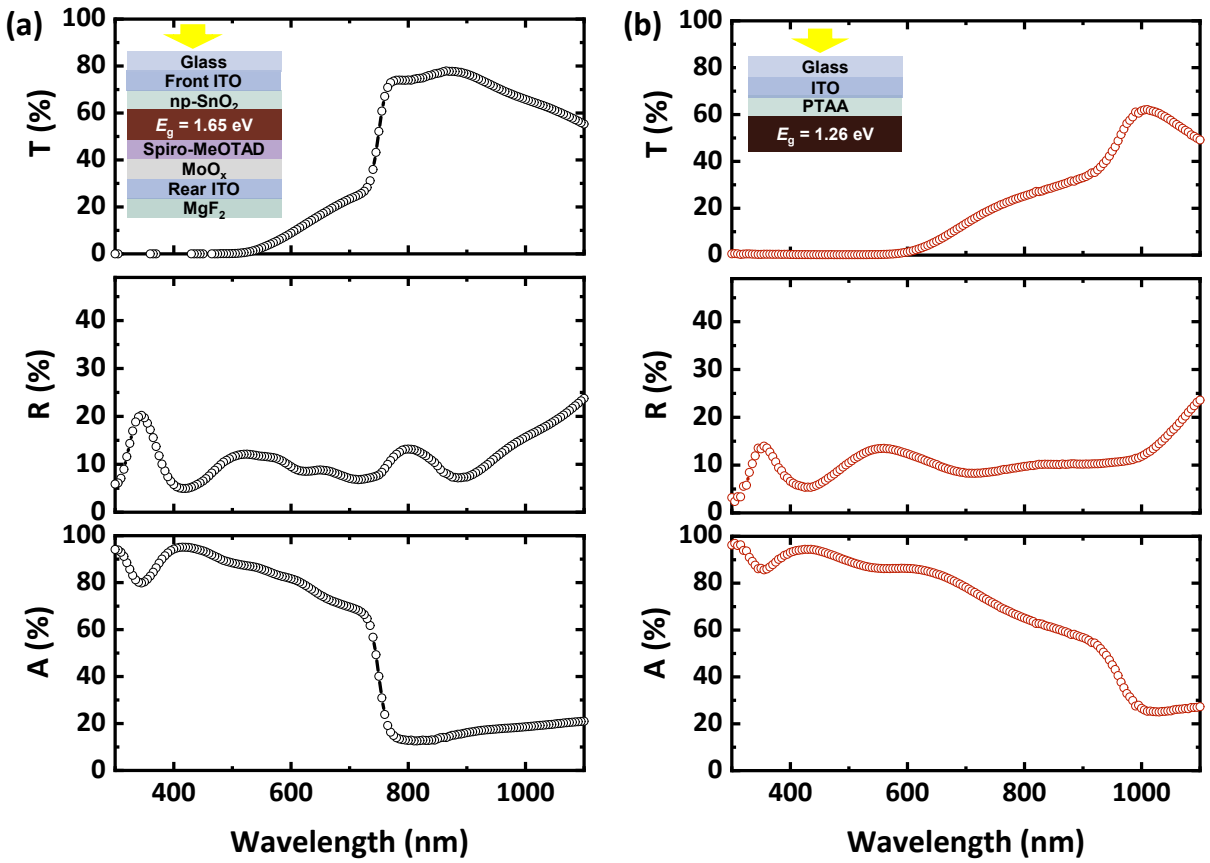

Fig. S10. Transmittance (T), reflectance (R), and absorptance (A) spectra of (a) a semitransparent perovskite filter composed of a double-cation $Cs_{0.17}FA_{0.83}Pb(I_{0.76}Br_{0.24})_3$ perovskite thin-film with a bandgap of E_g = 1.65 eV, and (b) a triple cation $Cs_{0.025}(FA_{0.8}MA_{0.2})_{0.075}Sn_{0.5}Pb_{0.5}I_3$ low-bandgap perovskite thin-film with a bandgap of E_g = 1.26 eV, deposited on PTAA-coated ITO.

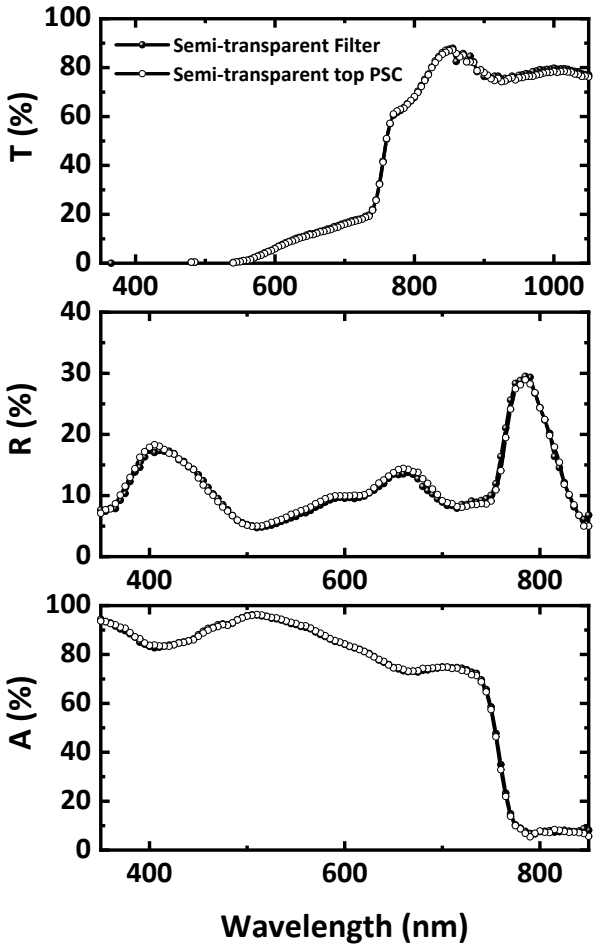

Fig. S11. Transmittance (T), reflectance (R), and absorptance (A) spectra of a semitransparent perovskite filter and a semi-transparent top PSC, composed of a double-cation $Cs_{0.17}FA_{0.83}Pb(I_{0.76}Br_{0.24})_3$ perovskite thin-film with a bandgap of E_g = 1.65 eV. The relative difference in transmittance and reflectance on average (derived from three filters and three PSCs) is equal to ±1.1% and ±0.1%, respectively (weighted to AM1.5G).

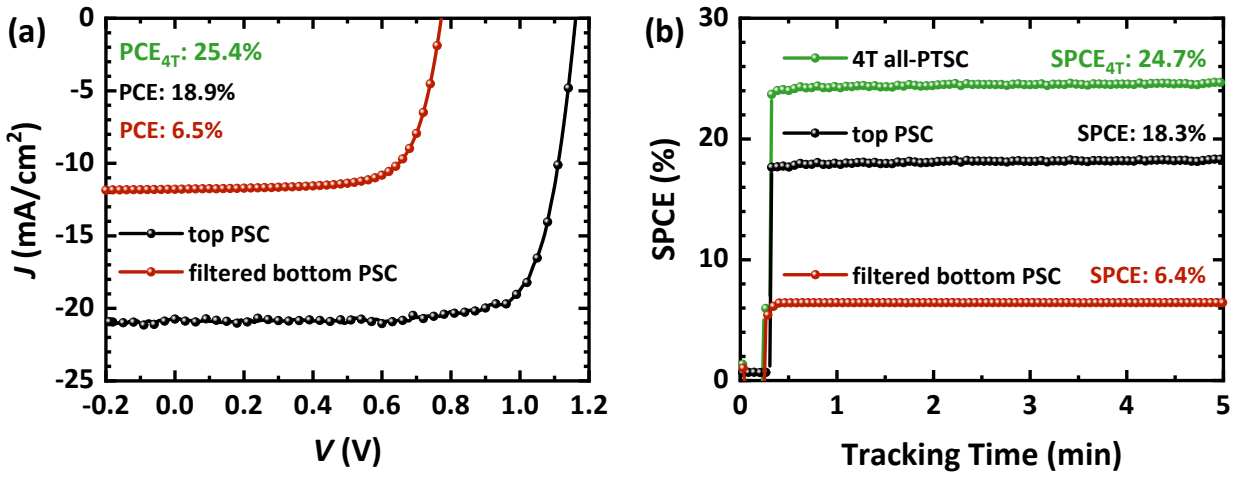

Fig. S12. (a) Current-density–voltage (J–V) scans measured at a fixed rate of 0.6 V/s from the open-circuit voltage (V_{OC}) to the short-circuit current (J_{SC}), and (b) maximum power point (MPP) tracking measurements of a single-junction semi-transparent top PSC (E_g = 1.65 eV), a single-junction filtered LBG bottom PSC (E_g = 1.26 eV) covered with an anti-reflection PDMS foil, under AM 1.5G illumination (100 mW/cm^2) at 25°C. PCE$_{4T}$ and SPCE$_{4T}$ are the calculated PCE and stabilized PCE derived from the J–V scans and MPP tracking measurements for the champion 4T all-PTSC, respectively.

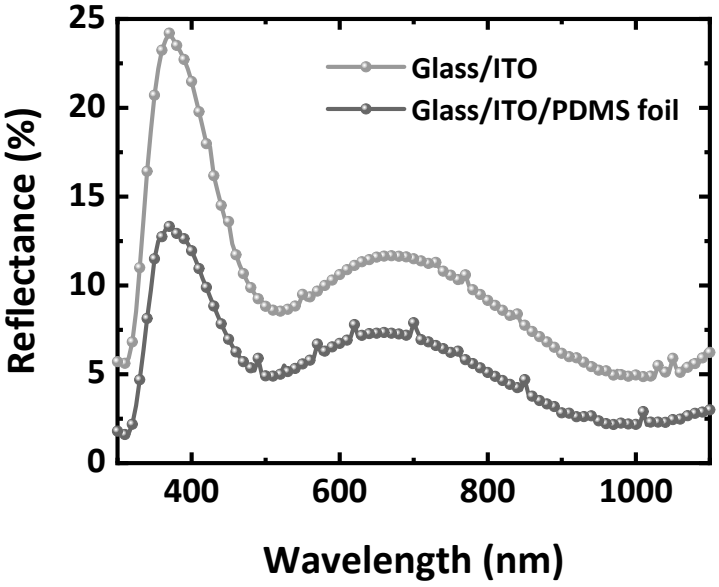

Fig. S13. Reflectance spectra of an ITO glass substrate with and without a textured PDMS foil implemented on the front-side of the ITO glass substrate.

Table S2. Photovoltaic parameters derived from current-density–voltage (*J–V*) scans measured at a fixed rate of 0.6 V/s from the open-circuit voltage (V_{OC}) to the short-circuit current (J_{SC}) (backward scan) and from J_{SC} to V_{OC} (forward scan) for a champion semi-transparent top PSC and a filtered LBG bottom PSC while an anti-reflection PDMS foil was applied in front side of the device. The stabilized PCEs (SPCEs) of the top and filtered bottom PSCs and the corresponding calculated 4T all-perovskite tandem solar cell (all-PTSC) are given in bold.

Perovskite solar cell (PSC)	Scan Direction	V_{OC} (V)	J_{SC} (mA/cm²)	FF (%)	PCE (%)	SPCE (%)
Semi-transparent top PSC (with PDMS)	Backward	1.16	20.7	78.6	**18.9**	**18.3**
	Forward	1.13	21.0	74.4	**17.7**	
Filtered LBG bottom PSC (with PDMS)	Backward	0.77	11.7	72.0	**6.5**	**6.4**
	Forward	0.76	11.7	67.5	**6.0**	
4T all-PTSC (with PDMS)	Backward				**25.4**	**24.7**
	Forward				**23.7**	