Supporting Information

Impact of Cesium in Phase and Device Stability of Triple Cation Pb-Sn Double Halide Perovskite Films and Solar Cells

G. A. Tosado, Y.-Y. Lin, E. J. Zheng, Prof. Q. M. Yu
Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA

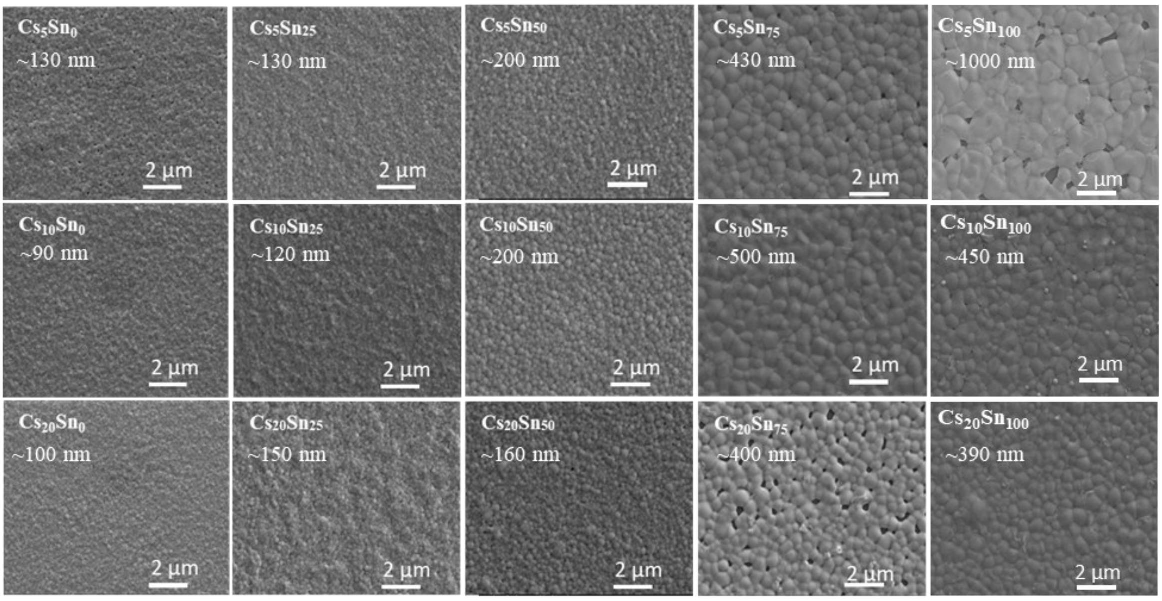

Figure S1. SEM images of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ perovskite thin films at 40,000 magnification with the average grain size of each film.

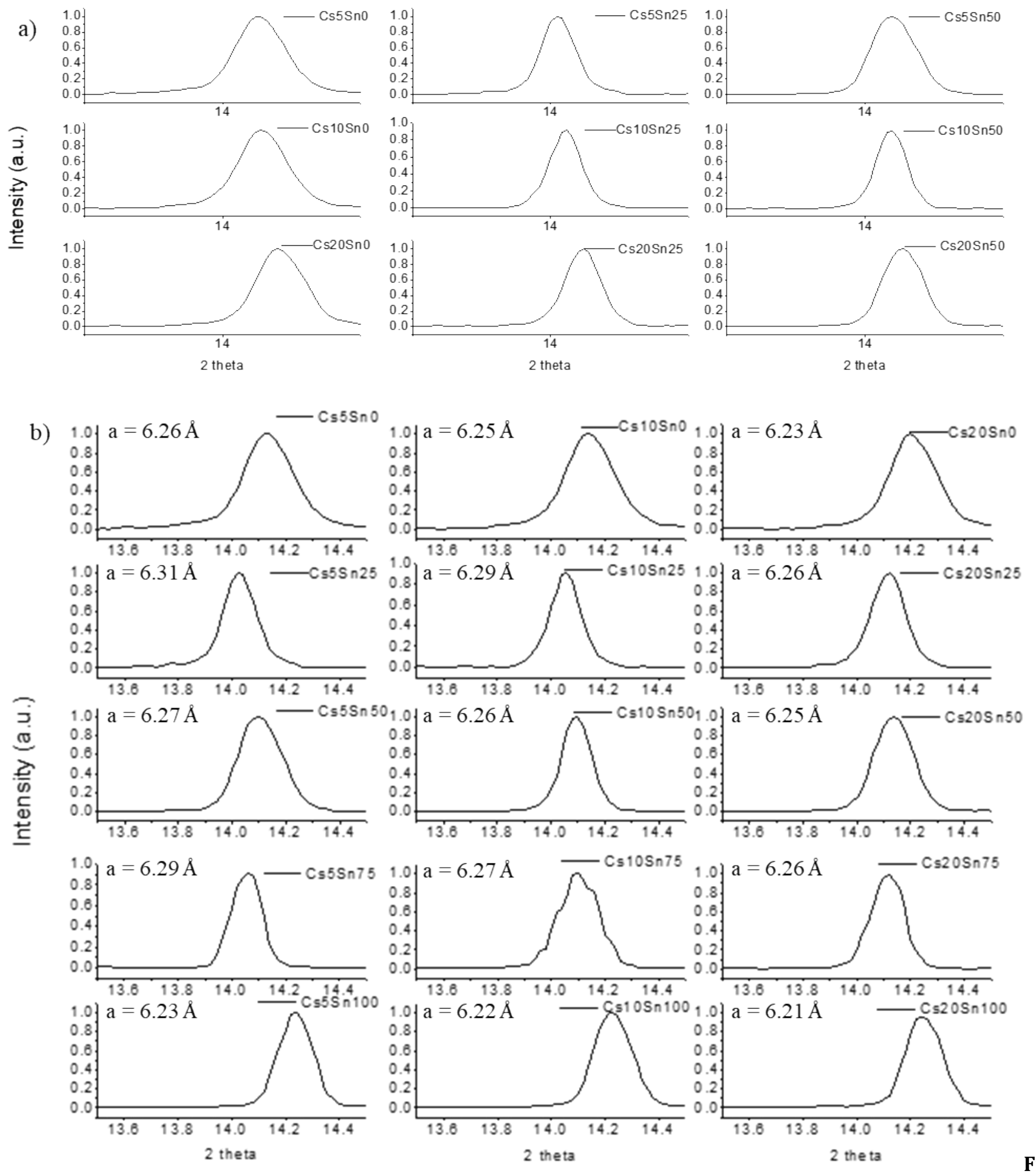

Figure S2. Shift of the (100) diffraction peak of perovskite thin films with the composition formula of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ for a) columns with constant Sn and increasing Cs, and .b) columns with constant Cs and increasing Sn. The cubic lattice parameter of each composition perovskite was calculated using the Bragg's Law.

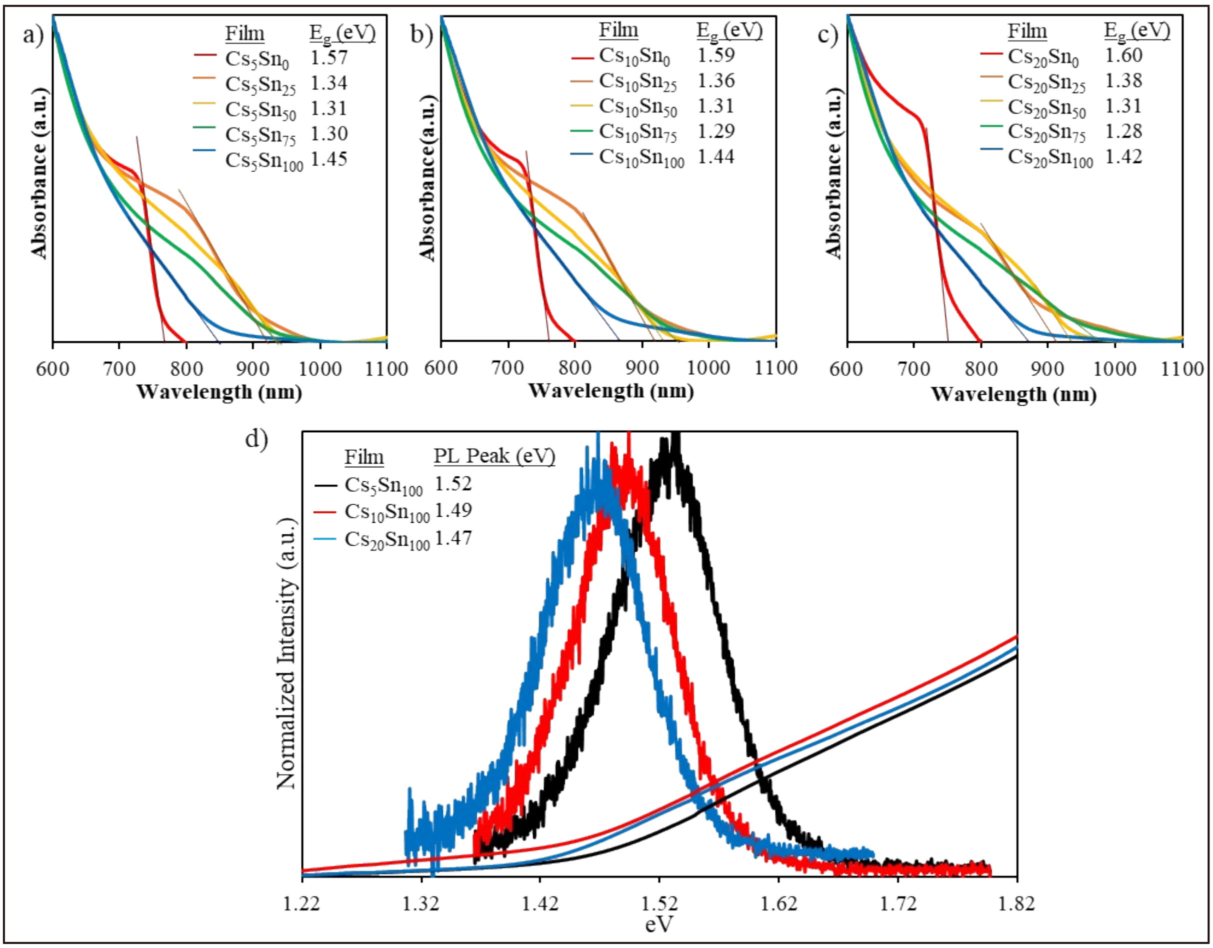

Figure S3. UV-vis absorption spectra of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ perovskite thin films for (a) x = 0.05, (b) x = 0.10, and (c) x = 0.20 with y = 0, 0.25, 0.50, 0.75, and 1.0 for each x. The optical band gaps derived from the absorption onsets are also shown. (d) Normalized PL spectra overlaped with UV-Vis spectra for 100% Sn perovskites with different Cs contents. The band gaps were derived from the peaks of PL spectra. .

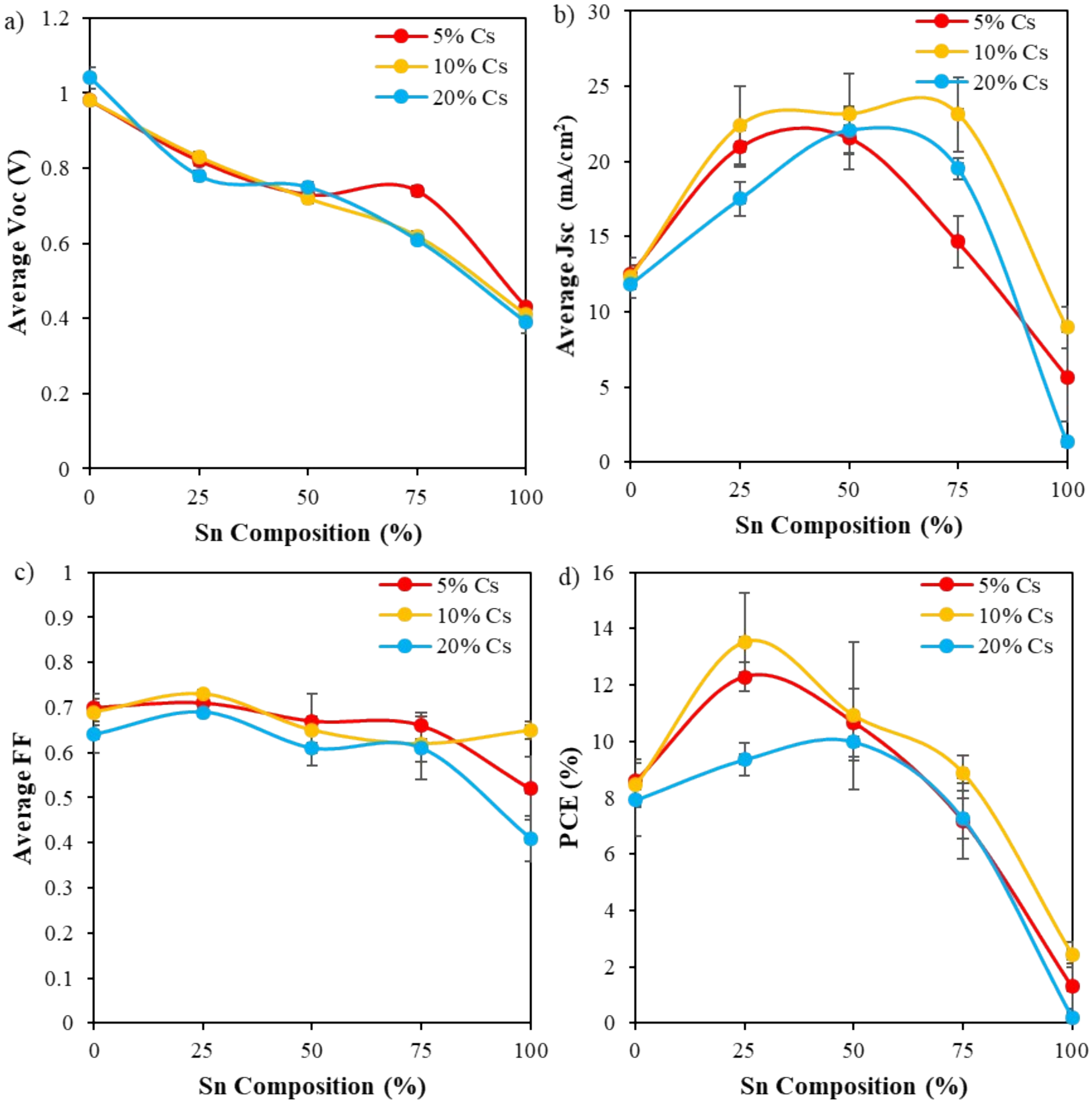

Figure S4. The averages of a) V_{oc}, b) J_{sc}, c) FF, and d) PCE of PVSCs as a function of Sn composition for different Cs contents with $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ perovskite thin films as the active layers.

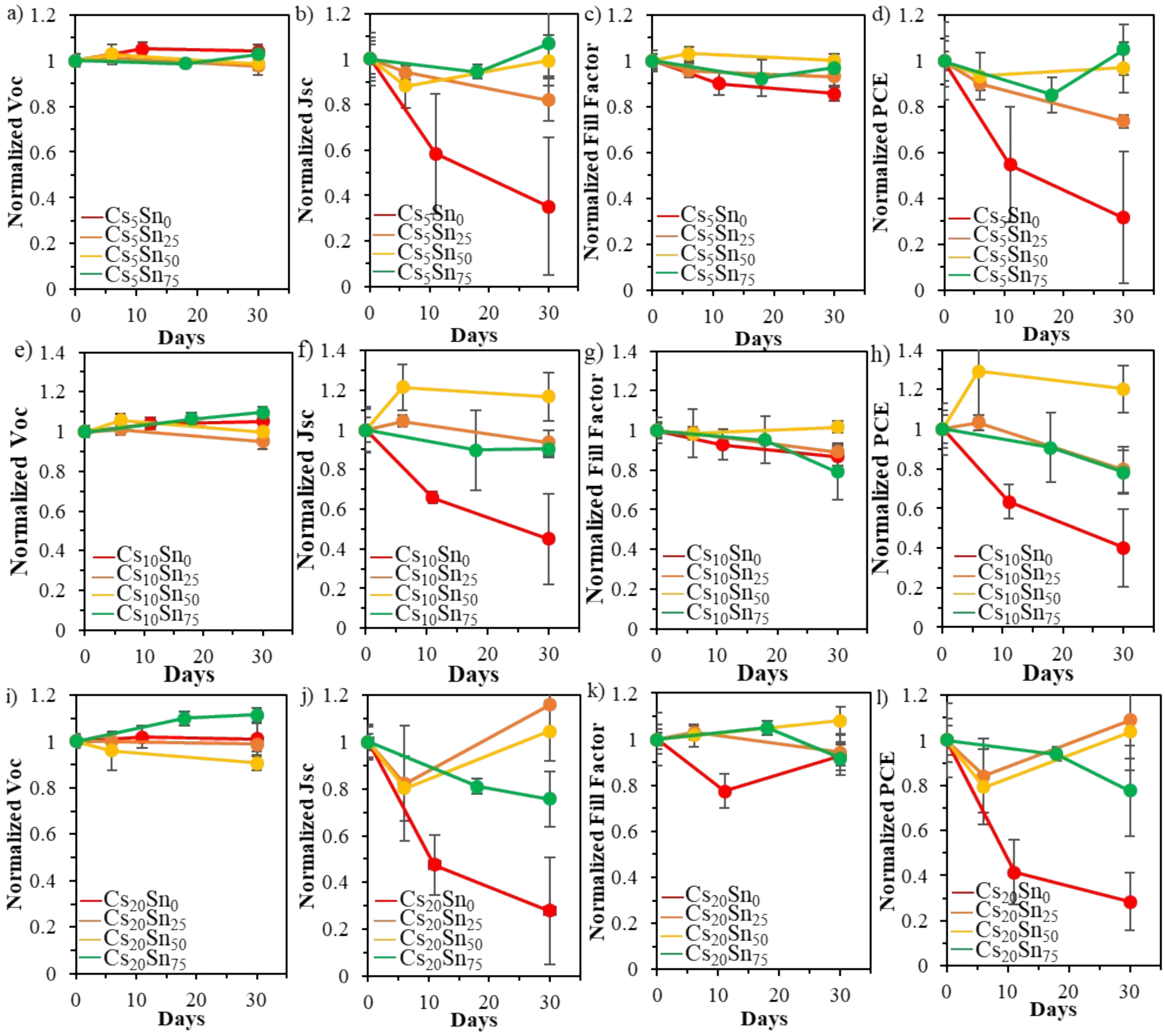

Figure S5. Normalized (a, e and i) V_{oc}, (b, f and j) J_{sc}, (c, g and k) FF, and (d, h and l) PCE of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ PVSCs for 5, 10 and 20% Cs, respectively, with Sn from 0 to 75% for each Cs composition, over time in the glovebox.

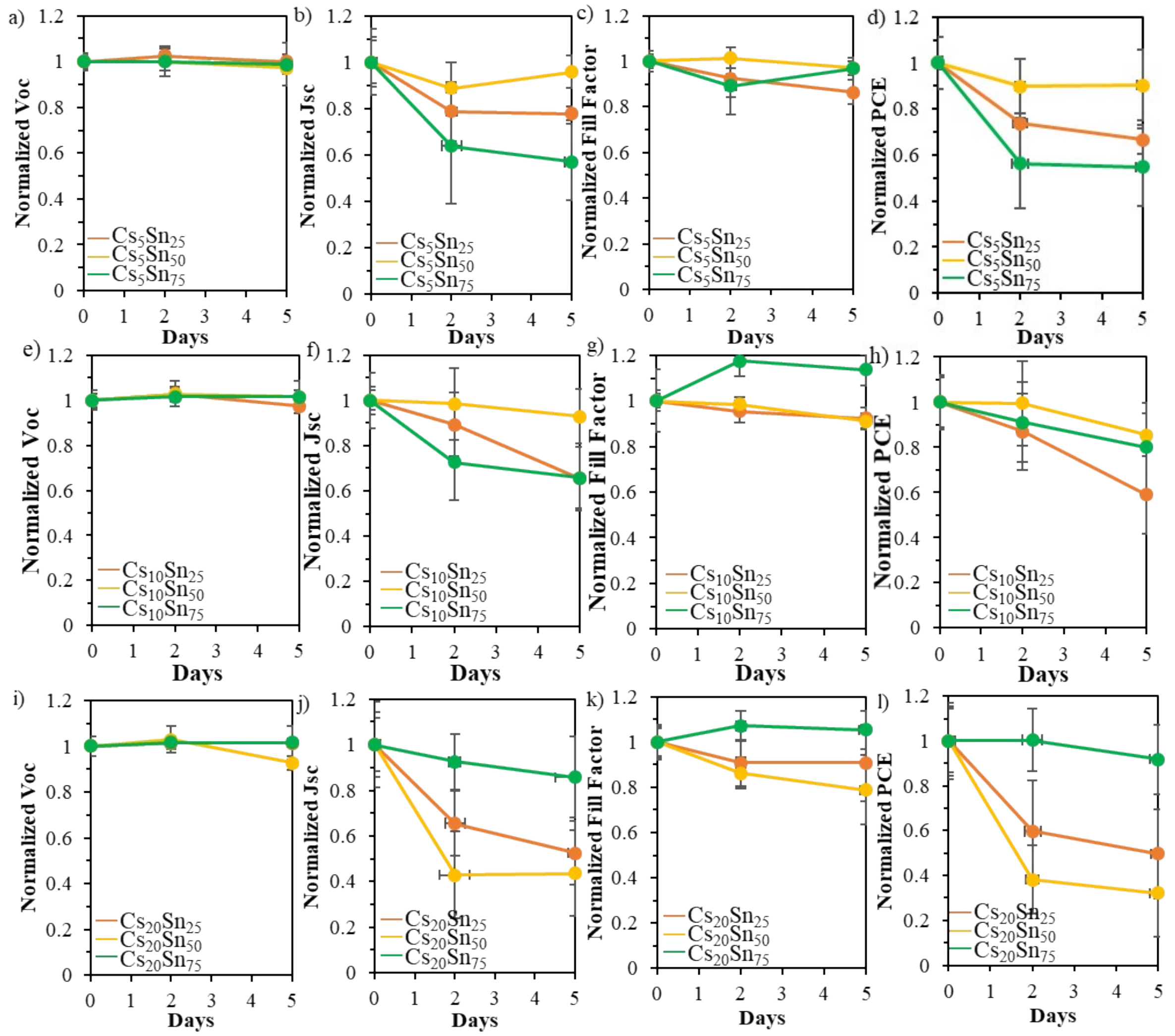

Figure S6. Normalized (a, e and i) V_{oc}, (b, f and j) J_{sc}, (c, g and k) FF, and (d, h and l) PCE of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ PVSCs for 5, 10 and 20% Cs, respectively, with Sn from 0 to 75% for each Cs composition, over time in ambient conditions after stored in golve box for 30 days.

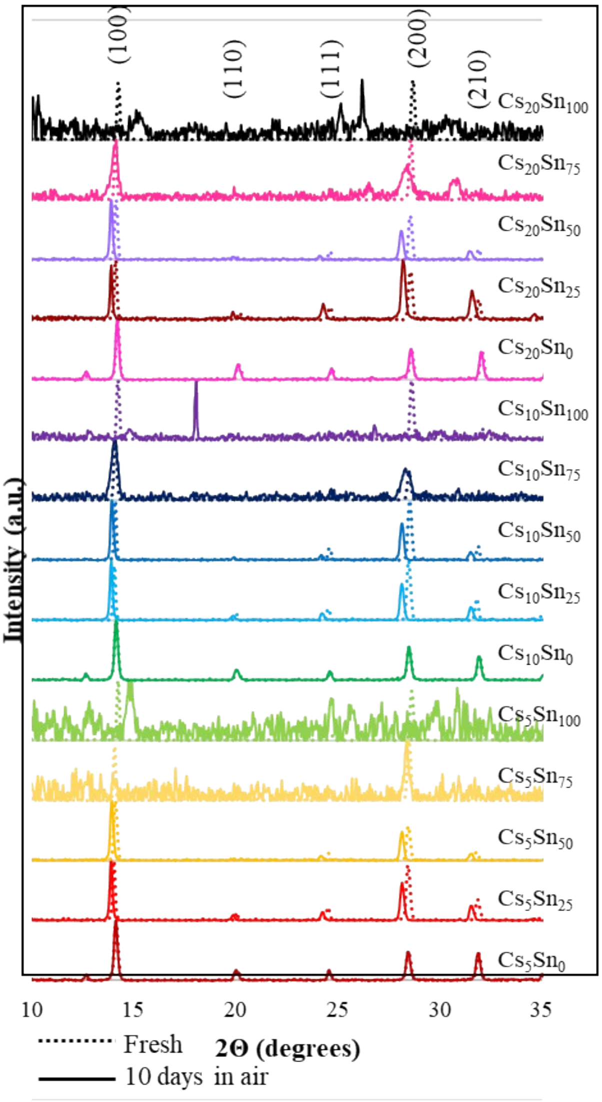

Figure S7. XRD patterns of pristine (dashed lines) and after 10 days of air exposure (solid lines) of the $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ perovskite thin films.

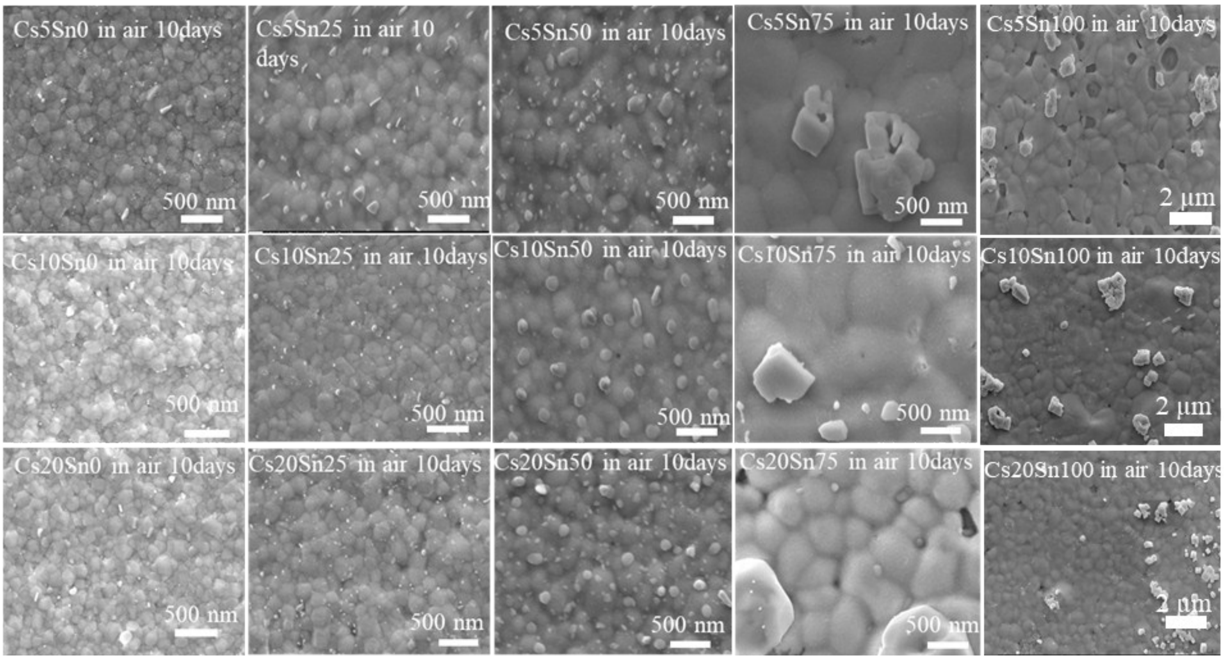

Figure S8. SEM images of $Cs_x(MA_{0.17}FA_{0.83})_{1-x}Pb_{1-y}Sn_y(I_{0.83}Br_{0.17})_3$ perovskite films after 10 days of air exposure.

Table S1. The EDS measured average atomic percentage of elements on rods and background from the $Cs_{20}Sn_{25}$ thin film after 10 days of air exposure.

	Cs	Pb	Sn	I	Br	F
Rods (%)	4.20±0.78	28.14±9.14	5.82±1.92	44.33±12.47	16.13±4.80	1.38±1.13
Background (%)	5.34±0.62	35.73±10.85	4.66±1.11	44.69±16.84	9.35±4.30	0.23±0.41

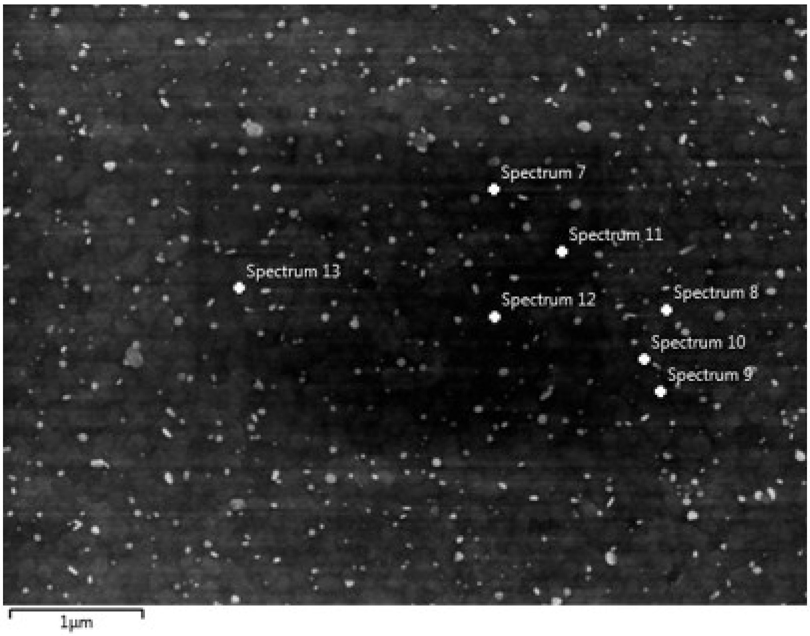

Figure S9. SEM image with the spots where EDS measurements were taken for $Cs_{20}Sn_{25}$ thin film after 10 days of air exposure

Figure S9 shows XRD spectra of perovskite films pristine and after 10 days exposure to air. Previous reports indicate a new peak corresponding to MA_2SnI_6 at 14.9 from Sn oxidation just after 1 day in ambient conditions.[1] For all spectra, no such peak was observed even after 10 days, supporting the previous literature that showed an identical suppression of an oxidation peak with the addition of Cs into the crystal lattice. The Pb-Sn alloyed perovskites exposed to air all have a right shift in peaks signaling an increase in d-spacing. This could be attributed to the phase segregation that occurs with air exposure as shown in the SEM images of air exposed perovskites in Figure S10. Although the air exposed perovskites have intact grains, some large particles ~500 nm appeared on the surfaces of 75 and 100% Sn perovskite thin films. EDS spot measurements on the new white rods and background on $Cs_{20}Sn_{25}$ thin film (Figure S11) showed that the white rods had a higher percentage of Sn, Br and F than those from the background (Table S1), indicating a slow segregation of these components from the perovskite thin film, resulting in an increased d-spacing of the crystal lattice. Previous reports have indicated ion migration of perovskites causing reversible Br and I rich segregation near grain boundaries under illumination and with current bias due to excess charge carriers.[2][3]

We propose that the SnF_2 reducing agent, which for 75 and 100% Sn have a 7.5 and 10% mole excess SnF_2, respectively, create Br and F rich particles through ion migration. This is supported by the lack of lattice shifting in the pure Pb perovskites due to the lack of SnF_2 reducing agent, avoiding the segregation effects. The air exposed XRD spectra for 75% Sn may not have the Sn^{4+} oxidation peak, but the cubic peaks are more broad, lower in intensity, and show splitting, indicating a possible degradation of the crystallinity due to this phase segregation. Unfortunately, after 10 days the pure Sn perovskites had a substantial decrease in the intensities of all cubic perovskites peaks, showing the instability of pure Sn perovskites.

[1] C.-M. Tsai *et al.*, "Role of Tin Chloride in Tin-Rich Mixed-Halide Perovskites Applied as Mesoscopic Solar Cells with a Carbon Counter Electrode," *ACS Energy Lett.*, vol. 1, pp. 1086–1093, Nov. 2016.
[2] X. Tang *et al.*, "Local Observation of Phase Segregation in Mixed-Halide Perovskite," *Nano Lett.*, vol. 18, pp. 2172–2178, Mar. 2018.
[3] I. L. Braly *et al.*, "Current-Induced Phase Segregation in Mixed Halide Hybrid Perovskites and its Impact on Two-Terminal Tandem Solar Cell Design," *ACS Energy Lett.*, vol. 2, pp. 1841–1847, Jul. 2017.