Electronic Supplementary Information

Tuning Cesium-Guanidinium in Formamidinium Tin Triiodide Perovskites with Ethylenediammonium Additives for Efficient and Stable Lead-Free Perovskite Solar Cells

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Figure S1. (a) SEM images and (b) XRD patterns of (CsGA)$_x$FA$_{1.2}$SnI$_3+y$% EDAI$_2$ perovskite thin films with $x = 5$ and 10, and $y = 0$, 0.5, 1.0, 1.5 and 2.0. (c) The cubic lattice parameter and (d) the (100)/(111) peak intensity ratio as a function of percent EDAI$_2$ for each (CsGA)$_5$ and (CsGA)$_{10}$ perovskite thin films. (e) Zoomed in (100) peak of XRD patterns for (CsGA)$_{15}$ where EDAI$_2$ ranges from 0-2.0%.
Figure S2. Low magnification SEM images of (CsGA)$_{x}$FA$_{1-x}$SnI$_3$+$y$% EDAI$_2$ perovskite thin films with $x$ = 5, 10, and 15, and $y$ = 0, 0.5, 1.0, 1.5, and 2.0.
Figure S3. XRD pattern of (CsGA)$_{15}$+1.0% EDAI$_2$ thin film along with simulated XRD patterns of cubic and orthorhombic phases of FASnI$_3$. 

Intensity (au) vs. 2θ (degree) plot showing the experimental XRD pattern compared to simulated patterns of cubic and orthorhombic phases of FASnI$_3$. The red line represents the experimental data, while the green and blue lines represent simulated cubic and orthorhombic phases, respectively.
Table S1. Average A-site cation radius (Ra) and Goldschmidt tolerance factors (GTF) for \((\text{CsGA})_x\) with \(x = 0, 5, 10, 15, 20,\) and 25. The average A-site cation radius was calculated as \(Ra = (x(R_{\text{Cs}} + R_{\text{GA}}) + (1-2x)R_{\text{FA}})/100,\) where \(R_{\text{Cs}}\) is the radius of \(\text{Cs}^+\) (1.67 Å), \(R_{\text{GA}}\) is the radius of \(\text{GA}^+\) (2.78 Å), and \(R_{\text{FA}}\) is the radius of \(\text{FA}^+\) (2.53 Å). The EDAI\textsubscript{2} effect was not included in the calculations.

| Sample          | Ra (Å) | GTF  |
|-----------------|--------|------|
| FASnI\textsubscript{3} | 2.53   | 0.998|
| \((\text{CsGA})_5\)  | 2.50   | 0.992|
| \((\text{CsGA})_{10}\) | 2.47   | 0.986|
| \((\text{CsGA})_{15}\) | 2.44   | 0.979|
| \((\text{CsGA})_{20}\) | 2.41   | 0.973|
| \((\text{CsGA})_{25}\) | 2.38   | 0.966|

For the perovskite structure \(\text{ABX}_3,\) the inorganic components (B and X) are in-plane covalently bonded, while the cation component (A) interacts with the metal-halide cage through van der Waals forces and hydrogen bonding. The possible crystal structure phase range of the perovskite can be estimated by the Goldschmidt tolerance factor (GTF). GTF was first used for metal-oxide perovskites and has been applied to metal-halide perovskites as a way to quasi-quantify the stability of various composition perovskites.\textsuperscript{1,2} The GTF of a 3D cubic \(\text{ABX}_3\) perovskite is represented by:

\[
\text{GTF} = \frac{(r_A + r_X)}{\sqrt{2(r_B + r_X)}}
\]

where \(r_A, r_B\) and \(r_X\) are the ionic radii of the monovalent cation, divalent transition metal cation, and halide anion, respectively. Stable cubic \(\alpha\)-phase perovskites are expected to exhibit a GTF between 0.8 to 1.\textsuperscript{3} Experimentally, perovskites are more cubic stable when GTF is between 0.9
and 1 as GTF > 1 enters the hexagonal/tetragonal phase and GTF < 0.8 enters the orthorhombic phase. The tetragonal and orthorhombic structure are affected by more severe octahedral tilting, pushing the bond angles to be less linear.
Figure S4. (a) XRD patterns and (b) SEM images of (CsGA)$_{30}$+$y$% EDAI$_2$ with $y =$ 0, 0.5, and 1.0.
Figure S5. Percent change in lattice parameter of (CsGA)$_5$, (CsGA)$_{10}$ and (CsGA)$_{15}$ thin films comparing the percent lattice parameter change of adding 0.5, 1.0, 1.5 and 2% EDAI$_2$ relative to 0% EDAI$_2$. 
Figure S6. PL spectra and normalized UV-Vis absorption spectra of (CsGA)$_x$+y% EDAI$_2$ thin films for (a) $x = 5$ and (b) $x = 10$ with $y = 0$ and 1.0 for each x. Tauc plots for (c) (CsGA)$_5$, (d) (CsGA)$_{10}$, and (e) (CsGA)$_{15}$ are displayed with $y = 0$ and 1.0 for each x. The optical band gaps are derived from the Tauc plots.
Figure S7. The photocurrent density–voltage (J–V) characteristics of PVSCs with the active layer containing (a) (CsGA)$_x$+y% EDAL$_2$ and (b) (CsGA)$_{10}$+y% EDAL$_2$ thin films with y = 0, 0.5, 1.0, 1.5 and 2.0 under AM 1.5G illumination scanned from -0.1 to 0.6 V at a scan rate of 0.01 V s$^{-1}$.

Table S2. Average photovoltaic parameters and the best performance device photovoltaic parameters in parenthesis along with series resistance, $R_s$ and Shunt resistance, $R_{sh}$ of PVSCs containing (CsGA)$_x$FA$_{1-2x}$SnI$_3$+y% EDAL$_2$ with x = 0.05 and 0.10, and y = 0, 0.5, 1.0, 1.5 and 2.0 measured under AM 1.5G illumination obtained from forward J–V measurements.

| Device       | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF    | PCE (%) | $R_s$ (Ω cm$^2$) | $R_{sh}$ (Ω cm$^2$) |
|--------------|--------------|-------------------------|-------|---------|------------------|---------------------|
| (CsGA)$_x$+0%| 0.30±0.02 (0.29) | 15.75±2.80 (20.71) | 0.54±0.05 (0.61) | 2.58±0.60 (3.71) | 3.51              | 45.56               |
| (CsGA)$_x$+0.5% | 0.31±0.01 (0.31) | 13.26±3.44 (17.46) | 0.55±0.07 (0.64) | 2.29±0.73 (3.40) | 4.22              | 66.59               |
| (CsGA)$_x$+1% | 0.32±0.04 (0.36) | 12.70±2.79 (9.81)  | 0.38±0.08 (0.46) | 1.50±0.17 (1.61) | 16.22             | 73.08               |
| (CsGA)$_x$+1.5% | 0.36±0.00 (0.32) | 22.55±2.35 (22.61) | 0.57±0.02 (0.70) | 4.61±0.61 (5.14) | 5.35              | 57.19               |
| (CsGA)$_x$+2%  | 0.36±0.01 (0.37) | 21.21±2.03 (21.89) | 0.53±0.07 (0.59) | 4.01±0.68 (4.78) | 5.59              | 57.95               |
| (CsGA)$_{10}$+0% | 0.36±0.04 (0.39) | 14.91±1.18 (16.27) | 0.36±0.13 (0.51) | 2.01±1.10 (3.26) | 7.70              | 53.40               |
| (CsGA)$_{10}$+0.5% | 0.34±0.02 (0.36) | 15.82±2.89 (18.66) | 0.63±0.04 (0.68) | 3.44±0.94 (4.56) | 3.63              | 84.17               |
| (CsGA)$_{10}$+1% | 0.39±0.01 (0.42) | 11.90±1.99 (14.19) | 0.56±0.03 (0.55) | 2.61±0.5 (3.24)  | 10.19             | 86.07               |
| (CsGA)$_{10}$+1.5% | 0.42±0.01 (0.43) | 11.77±2.53 (13.93) | 0.61±0.03 (0.61) | 3.05±0.80 (3.66) | 8.47              | 109.60              |
| (CsGA)$_{10}$+2%  | 0.40±0.01 (0.39) | 13.49±4.55 (15.02) | 0.57±0.03 (0.59) | 3.03±0.90 (3.50) | 8.42              | 93.10               |
Calculations of $R_s$ and $R_{sh}$:

This method utilizes the fact that the J-V curve at $J_{sc}$ and $V_{oc}$ are free from resistance effects. We can calculate series resistance using the equation outlined in 1963 by Wolf:

$$R_s = \frac{(V_{oc} - V_{mpp})}{J_{mpp}}$$

The following equation was used to calculate shunt resistance:

$$R_{sh} = \frac{(J_{sc} - J_{mpp})}{V_{mpp}}$$
Figure S8. UPS spectra for (a) the valence band edge region and the Fermi levels and (b) the secondary electron energy cut off region for (CsGA)$_5$, (CsGA)$_{10}$ and (CsGA)$_{15}$ with 1.5% EDAI$_2$ thin films.
References:

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