Electronic Supplementary Material (ESI) for Materials Advances. This journal is © The Royal Society of Chemistry 2020

Electronic Supplementary Information

Tuning Cesium-Guanidinium in Formamidinium Tin Triiodide Perovskites with

Ethylenediammonium Additives for Efficient and Stable Lead-Free Perovskite Solar Cells

Gabriella A. Tosado, Erjin Zheng and Qiuming Yu*

Department of Chemical Engineering, University of Washington, Seattle, WA 98195, USA

Email: qyu@u.wwashington.edu



Figure S1. (a) SEM images and (b) XRD patterns of $(CsGA)_xFA_{1-2x}SnI_3+y\%$ EDAI₂ 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 EDAI₂ for each (CsGA)₅ and (CsGA)₁₀ perovskite thin films. (e) Zoomed in (100) peak of XRD patterns for (CsGA)₁₅ where EDAI₂ ranges from 0-2.0%.

0% EDAI ₂	0.5% EDAI ₂	1.0% EDAI ₂	1.5% EDAI ₂	2.0% EDAI ₂	
(CsGA)5	(CsGA) _j	(CsGA)₅	(CsGA) ₅	(CsGA)₅	
5 μm	5 µm	5 µm	5 µm	5 µm	
(CsGA) ₁₀	(CsGA) ₁₀	(CsGA) ₁₀	(CsGA) ₁₀	(CsGA) ₁₀	
5 µm	5 µm	5 µm	5 µm	n Sµn	
(CsGA) ₁₅	(CsGA) ₁₅	(CsGA) ₁₅	(CsGA) ₁₅	(CsGA) ₁₅	
5 µm	5 µm	5 µm	5 µm	5 µm	

Figure S2. Low magnification SEM images of $(CsGA)_xFA_{1-2x}SnI_3+y\%$ EDAI₂ 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 $(CsGA)_{15}+1.0\%$ EDAI₂ thin film along with simulated XRD patterns of cubic and orthorhombic phases of FASnI₃.

Table S1. Average A-site cation radius (Ra) and Goldschmidt tolerance factors (GTF) for (CsGA)_x with x = 0, 5, 10, 15, 20, and 25. The average A-site cation radius was calculated as Ra = (x(R_{Cs} + R_{GA}) + (1-2x)R_{FA})/100, where R_{Cs} is the radius of Cs⁺ (1.67 Å), R_{GA} is the radius of GA⁺ (2.78 Å), and R_{FA} is the radius of FA⁺ (2.53 Å). The EDAI₂ effect was not included in the calculations.

Sample	Ra (Å)	GTF
FASnI ₃	2.53	0.998
(CsGA) ₅	2.50	0.992
(CsGA) ₁₀	2.47	0.986
(CsGA) ₁₅	2.44	0.979
(CsGA) ₂₀	2.41	0.973
(CsGA) ₂₅	2.38	0.966

For the perovskite structure ABX₃, 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 Goldschmid tolerance factor (GTF). GTF was first used for metal-oxide perovskites and has been applied to metal-halide perovskites as a way to quasiquantify the stability of various composition perovskites.^{1,2} The GTF of a 3D cubic ABX₃ 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 α -phase perovskites are expected to exhibit a GTF between 0.8 to 1.³ 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 $(CsGA)_{20}+y\%$ EDAI₂ 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% EDAI₂ relative to 0% EDAI₂.



Figure S6. PL spectra and normalized UV-Vis absorption spectra of $(CsGA)_x+y\%$ EDAI₂ 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) $(CsGA)_5+y\%$ EDAI₂ and (b) $(CsGA)_{10}+y\%$ EDAI₂ 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 $(CsGA)_xFA_{1-2x}SnI_3+y\%$ EDAI₂ 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 (%)	$R_s \Omega.cm^2$	$R_{sh}\Omega.cm^2$
(CsGA) ₅ +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) ₅ +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) ₅ +1.0%	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) ₅ +1.5%	0.36±0.00 (0.32)	22.35±2.35 (22.61)	0.57±0.02 (0.70)	4.61±0.61 (5.14)	5.35	57.19
(CsGA) ₅ +2.0%	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%	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%	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: ⁴

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

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% EDAI₂ thin films.

References:

- 1 Z. Li, M. Yang, J.-S. Park, S.-H. Wei, J. J. Berry and K. Zhu, Chem. Mater., 2015, 28, 284–292.
- 2 V. Goldschmidt, *Naturwussenschaften*, 1926, 14, 477–485.
 3 B. Saparov and D. B. Mitzi, *Chem. Rev.*, 2016, 116, 4558–4596.
- 4 M. Wolf, H. Raushenbach, Adv. Energ. Conversion 1963, 3, 455-479.