SUPPORTING INFORMATION

On the prospects of high-entropy organic A-site halide perovskites

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CONTENTS

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Supplementary Note 1: Precursor and perovskite masses

Table S1 - Weighted reaction precursors and recovered perovskite masses ($r.m.$). Values in parentheses are the molar quantities (in mmol). Yield is the ratio between the HP obtained and expected (sum of precursors) masses.

x	m MAI (g)	m GAI (g)	m FAI (g)	m EAI (g)	m ACI (g)	m PbI_2 (g)	$r.m.$ (g)	Yield (%)
0.00	0.259_3 (1.61_5)	- (0.00)	- (0.00)	- (0.00)	- (0.00)	0.752_4 (1.61_6)	0.909_5	89.9
0.01	0.248_4 (1.54_7)	0.003_6 (0.01_9)	0.003_2 (0.01_8)	0.003_3 (0.01_9)	0.003_1 (0.01_6)	0.751_3 (1.61_3)	0.920_9	90.9
0.02	0.238_6 (1.48_6)	0.006_2 (0.03_3)	0.006_2) (0.03_6)	0.006_3 (0.03_6)	0.006_0 (0.03_2)	0.750_5 (1.61_2)	0.916_1	90.4
0.03	0.227_2 (1.41_5)	0.009_2 (0.04_9)	0.008_2 (0.04_7)	0.009_2 (0.05_2)	0.009_4 (0.05_0)	0.749_7 (1.61_0)	0.918_2	90.7
0.04	0.217_0 (1.35_1)	0.012_1 (0.06_4)	0.011_6 (0.06_7)	0.011_1 (0.06_3)	0.012_1 (0.06_4)	0.748_0 (1.60_6)	0.902_0	89.1
0.05	0.207_3 (1.29_1)	0.015_2 (0.08_0)	0.014_4 (0.08_3)	0.014_0 (0.07_9)	0.015_2 (0.08_0)	0.747_0 (1.60_4)	0.913_5	90.2
0.06	0.195_5 (1.21_7)	0.018_2) (0.09_6)	0.017_3 (0.10_0)	0.017_2 (0.09_7)	0.018_3 (0.09_6)	0.745_9 (1.60_2)	0.875_4	86.5
0.07	0.185_8 (1.15_7)	0.021_0) (0.11_1)	0.019_4 (0.11_2)	0.020_3 (0.11_5)	0.021_3 (0.11_2)	0.745_0 (1.60_0)	0.922_7	91.1
0.08	0.174_6 (1.08_7)	0.024_3 (0.12_9)	0.022_2 (0.12_8)	0.023_2 (0.13_1)	0.024_4 (0.12_9)	0.744_0 (1.59_8)	0.931_4	92.0
0.09	0.164_3 (1.02_3)	0.027_0 (0.14_3)	0.025_3 (0.14_6)	0.025_3 (0.14_3)	0.027_4 (0.14_4)	0.742_8 (1.59_5)	0.924_0	91.3
0.10	0.153_4 (0.95_5)	0.030_6 (0.16_2)	0.028_4 (0.16_3)	0.028_4 (0.16_1)	0.030_3 (0.16_0)	0.741_9 (1.59_3)	0.938_6	92.7

Supplementary Note 2: Setup for the light-accelerated degradation test

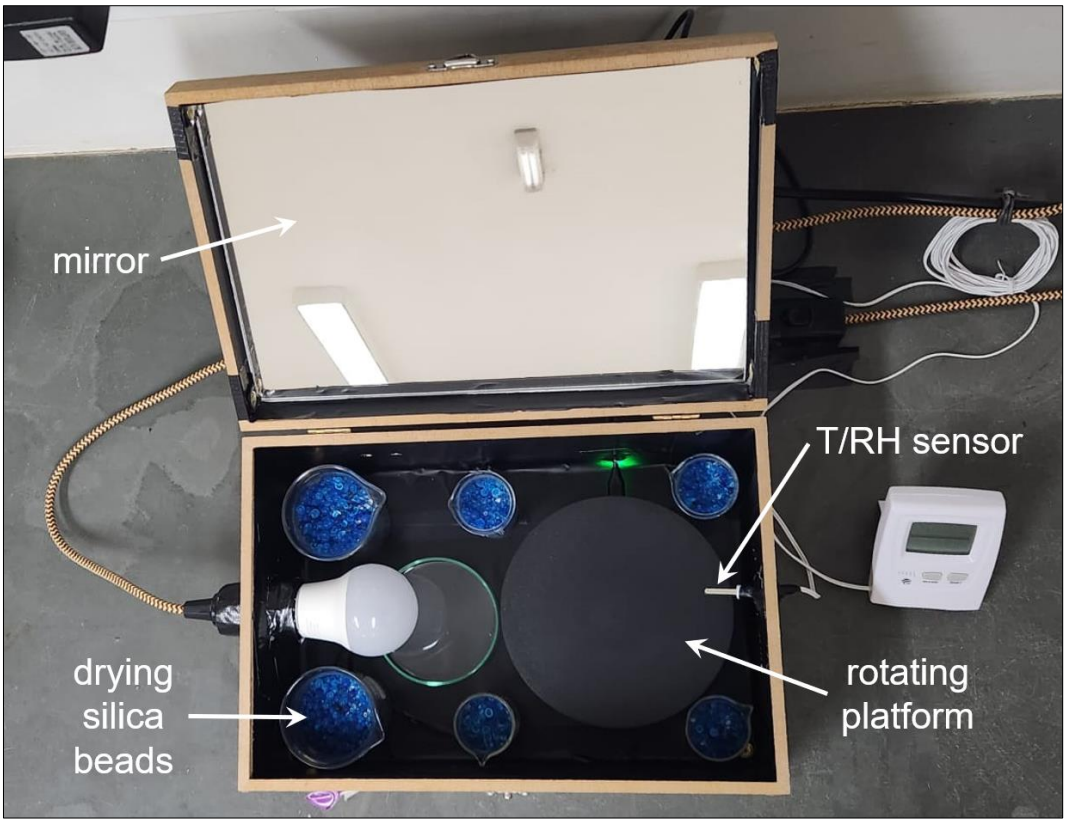

Figure S1 - Homemade setup used for the light-accelerated degradation test. The samples were distributed uniformly in the Petri dish, which was positioned in the center of the rotating (6 Hz clockwise) platform and submitted to direct and mirror-reflected illumination from the LED lamp. The lamp specifications are a power of 6 W, luminous flux of 560 lm, and color cold white (6500 K). The box (30 x 20 x 15 cm) remained closed and sealed with masking tape during the test. Inside humidity was kept as low as possible by drying silica beads. Temperature and relative humidity were constantly monitored, ranging from 25 to 32 °C and 35 to 50 % throughout the experiment.

Supplementary Note 3: Effective A-site characteristics

The effective characteristics of the A-site cations in the studied perovskites were taken as the weighted average, as preconized by Vegard's law. The expressions for the effective A-site ionic radii, dipole moment, and number of N-H bonds are respectively given by:

$$r_{eff} = x(r_{GA} + r_{FA} + r_{EA} + r_{AC}) + (1 - 4x)r_{MA}$$
$$d_{eff} = x(d_{GA} + d_{FA} + d_{EA} + d_{AC}) + (1 - 4x)d_{MA}$$
$$n_{eff} = x(n_{GA} + n_{FA} + n_{EA} + n_{AC}) + (1 - 4x)n_{MA}$$

where r_A, d_A, and n_A are the properties of each A-site cation shown in Figure 1a of the main text. The Goldschmidt tolerance factor of compositions was calculated from its definition using the effective ionic radii:

$$\tau = \frac{r_{eff} + r_I}{\sqrt{2}(r_{Pb} + r_I)}$$

where r_{Pb} = 119 pm and r_I = 220 pm are the ionic radii of Pb^{2+} and I^- [1], respectively. The results are given in Figure S2.

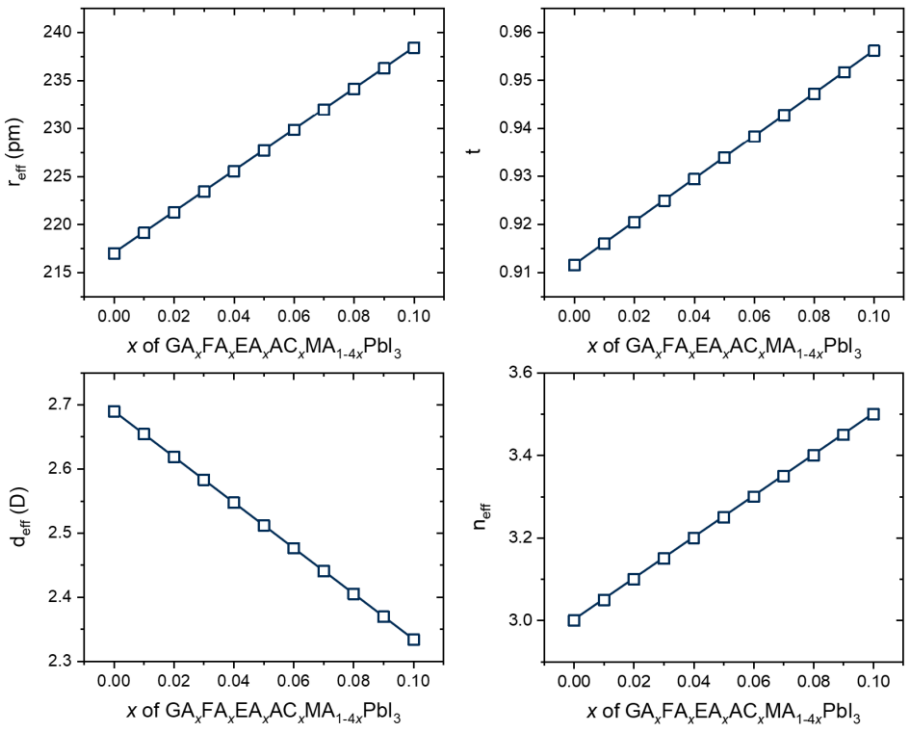

Figure S2 - Effective properties of the studied halide perovskites.

Supplementary Note 4: DSC measurements

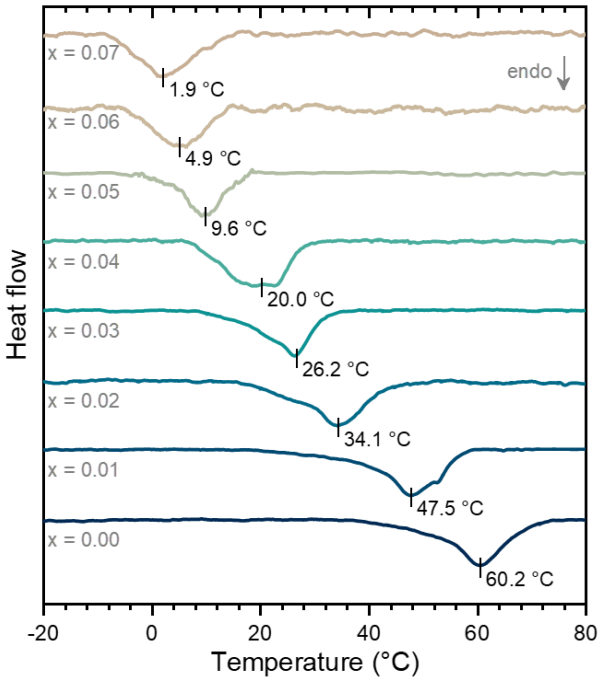

Figure S3 - Experimental thermograms obtained through differential scanning calorimetry measurements from the $GA_xFA_xEA_xAC_xMA_{1-4x}PbI_3$ studied samples.

Supplementary Note 5: Le Bail fits of XRD data

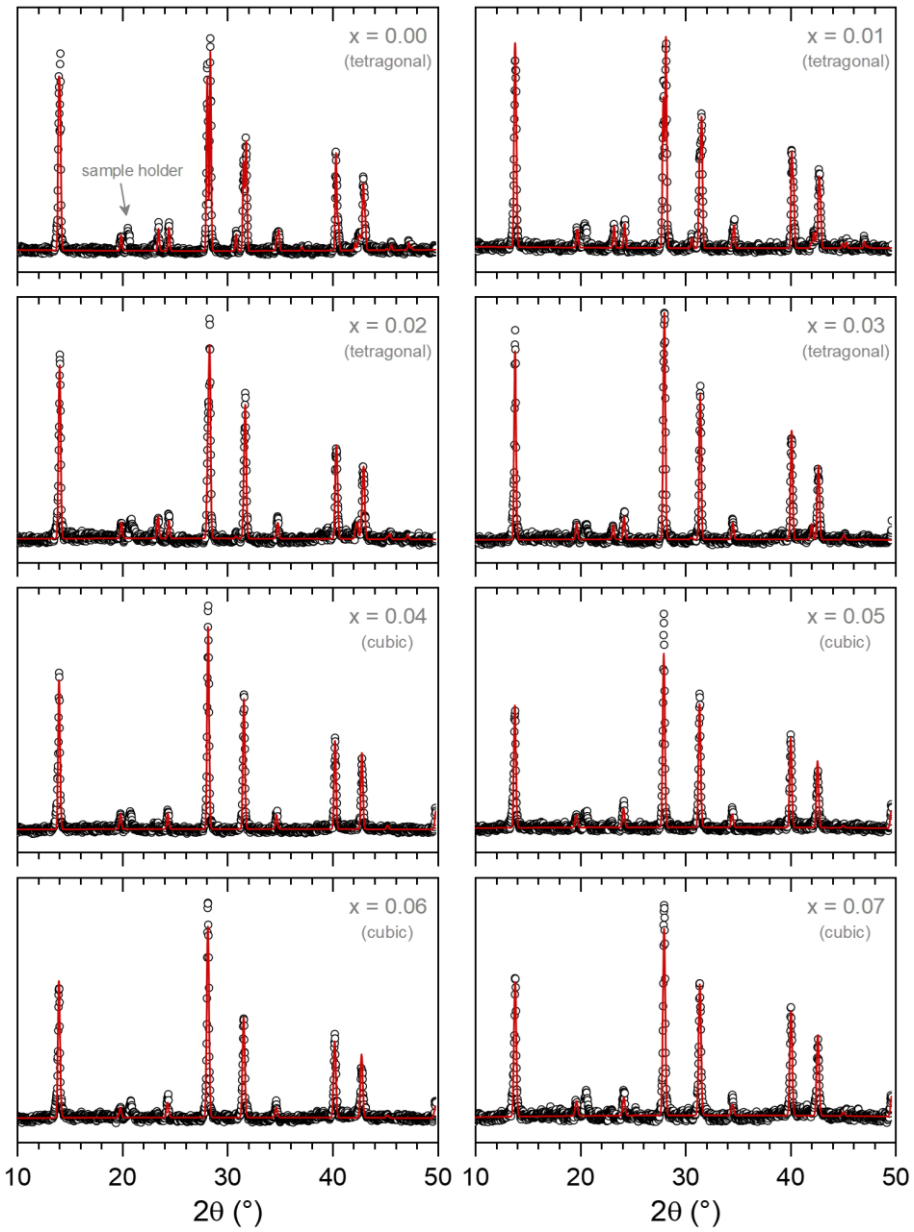

Figure S4 - Experimental XRD patterns (black dots) and Le Bail fits (red lines) of the $GA_xFA_xEA_xAC_xMA_{1-4x}PbI_3$ studied compositions. Fits were calculated using the WinPLOTR package as implemented in the Fullprof software (version of April 2024) considering the $I4cm$ (tetragonal) and $Pm\bar{3}m$ (cubic) space groups.

Table S2 - Original lattice parameters obtained through the Le Bail fit.

x	a (Å)	c (Å)	χ^2
0.00	8.8652 ± 0.0004	12.6677 ± 0.0007	2.12
0.01	8.8769 ± 0.0004	12.6624 ± 0.0008	1.87
0.02	8.8873 ± 0.0005	12.6461 ± 0.0014	2.17
0.03	8.9095 ± 0.0006	12.6393 ± 0.0013	2.11
0.04	6.3131 ± 0.0002	-	2.37
0.05	6.3169 ± 0.0003	-	2.14
0.06	6.3175 ± 0.0003	-	2.54
0.07	6.3169 ± 0.0003	-	2.01

Supplementary Note 6: Band gap energies

To determine band gap energies (E_g) of studied materials, we fitted UV-Vis diffuse reflectance data with the modified Tauc equation, expressed as [2]:

$$(F(R).h\nu)^{1/\gamma} = B(h\nu - E_g)$$

where $h\nu$ is the incident photon energy, γ a factor that depends on the nature (direct or indirect) of the electron transition, and $F(R)$ is the Kubelka-Munk function, given by:

$$F(R) = \frac{(1-R)^2}{2R}$$

where R is the reflectance of an infinitely thick sample. In our analysis, we considered electronic transitions related to a direct band gap ($\gamma = 1/2$), as reported for halide perovskites [3]. The modified Tauc plots used to estimate the band gap energies are shown in Figure S5.

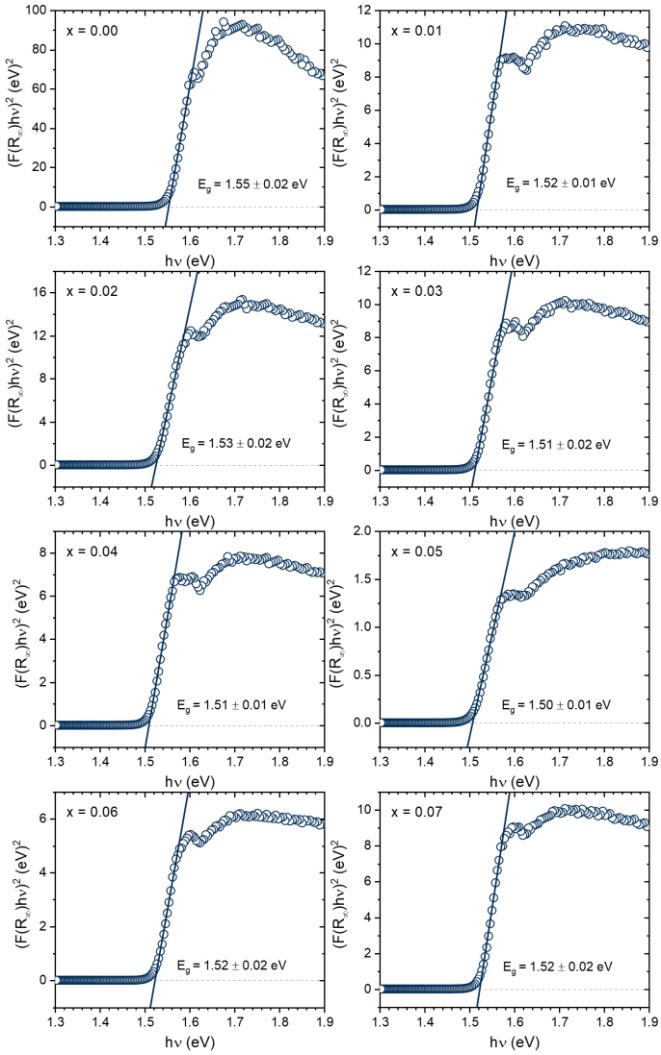

Figure S5 - Modified Tauc plots and respective linear fits of the $GA_xFA_xEA_xAC_xMA_{1-4x}PbI_3$ studied perovskites.

Supplementary Note 7: Current-voltage curves

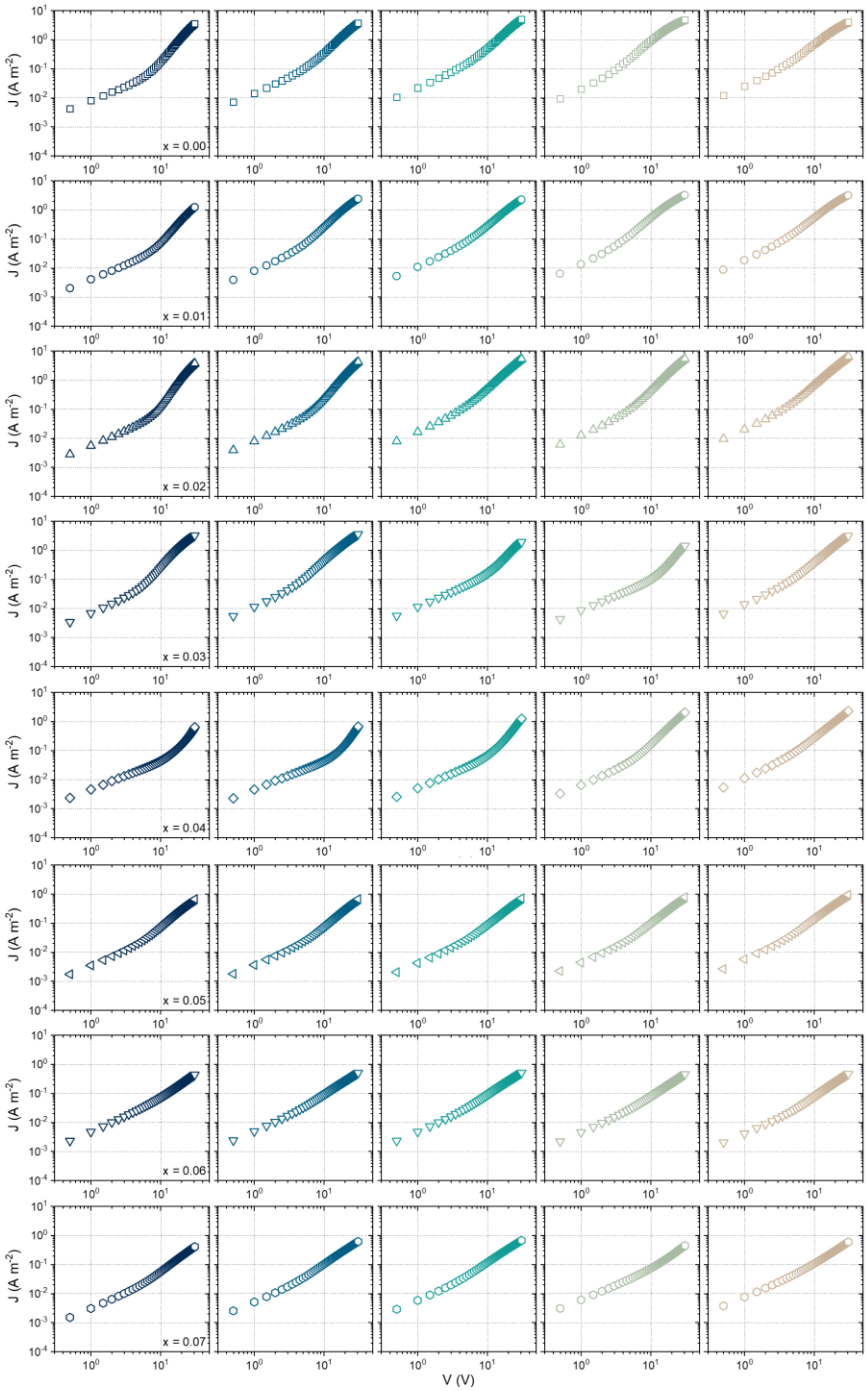

Figure S6 - Experimental current-voltage curves of the $GA_xFA_xEA_xAC_xMA_{1-4x}PbI_3$ compositions. Colors are the data collected in a different electrode on the same sample, given in each row.

References

[1] G. Kieslich, S. Sun and A. K. Cheetham, *Chem. Sci.*, 2014, **5**, 4712–4715.

[2] P. Makuła, M. Pacia and W. Macyk, *J. Phys. Chem. Lett.*, 2018, **9**, 6814–6817.

[3] V. Sarritzu, N. Sestu, D. Marongiu, X. Chang, Q. Wang, S. Masi, S. Colella, A. Rizzo, A. Gocalinska, E. Pelucchi, M. L. Mercuri, F. Quochi, M. Saba, A. Mura and G. Bongiovanni, *Advanced Optical Materials*, 2018, **6**, 1701254.