Supporting information

Balanced change in crystal unit cell volume and strain leads to stable halide perovskite with high guanidinium content

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Experimental section

Materials

Materials: All materials were reagent grade and were used as received. Lead iodide (PbI₂, > 98%, from TCI), methylammonium iodide (MAI, 98%, from Greatcellsolar), Guanidinium iodide (GuI, > 99%, from Greatcellsolar), 2-propanol (99.7% from Carlo Erba), ethanol (96%) and acetone (99.25%) from PanReac, hydrochloric acid (HCl 37%), dimethyl sulfoxide (DMSO anhydrous 99.9%), chlorobenzene (CB anhydrous 99.8%), acetonitrile (MeCN anhydrous 99.8%), ethylacetate (EA anhydrous 99.8%), 4-tert-butylpirididine (TBP 96%), zinc powder (99.995%) and lithium bis(trifluoromethylsulfonyl)imide (Li-TFSI 99.95%) from Sigma aldrich, while 2,20,7,70-tetrakis [N,N-di(4-methoxyphenyl)amino]-9,90-spirobiﬂuorene (spiro-OMeTAD 99% from Feiming chemical limited), and SnO₂ colloid precursor from Alfa Aesar (15% in H₂O colloidal dispersion). Indium tin oxide (ITO) coated glass substrates (Pilkington TEC15, ~ 15 Ω sq⁻¹).
Device fabrication

Substrates (indium tin oxide, ITO) were etched by using zinc powder and pour over it drops of HCl 2 M. Then glass was cleaned with deionized water, acetone and ethanol in an ultrasonic cleaner for 15 min for each solvent. After being dried by air flow, the substrates were put in an ultraviolet–ozone for 15 min to remove organic residues. Once cleaned, the electron transport layer ETL (SnO\textsubscript{2}) was deposited from dissolution of SnO\textsubscript{2} 3% from colloid precursor. Then, it is spin-coated onto the ITO substrates with an acceleration of 3,000 rpm for 30 s, and heated at 150 °C for 30 min. Once the ETL is prepared, substrates are submitted to 20 min of UV-Ozone before perovskite deposition. A quantity of 50 μl of perovskite is deposited over SnO\textsubscript{2} ETL by one-step spin coating at 4,000 rpm for 20 s. Perovskite solutions were prepared by weighting the MAI precursors and PbI\textsubscript{2} at 1.4 M concentration and mix them to obtain MAPbI\textsubscript{3} 1.4 M concentration in 4:1 DMF:DMSO (v:v). The same procedure was followed for GuPbI\textsubscript{3} by weighting GuI 1.4 M and PbI\textsubscript{2} 1.4 M. Once both solutions were prepared they were mixed in different proportions. According to this, the perovskite mixtures MAPbI\textsubscript{3}:GUPbI\textsubscript{3} where mixed in the following volume ratio: 1:0, 0.98:0.02, 0.95:0.05, 0.93:0.07, 0.90:0.10 and 0.85:0.15. Then, the sample was moved to a hotplate and annealed for 10 min at a temperature of 130 °C. After perovskite deposition, 50 μl of hole transporting layer made with spiro-OMeTAD in chlorobenzene (85.5 mg/mL), doped with 28.8 μL of TBP and 17.8 μL of a stock solution of 520 mg mL\textsuperscript{-1} of Li-TFSI in acetonitrile, is spin-coated at 4,000 rpm for 20 s onto the top annealed perovskite layers as hole transport material (HTM). Finally, Au electrode with a thickness of 80 nm is deposited by thermal evaporation.

Film characterization
**Optical Characterization:** UV-VIS absorption of the thin films are measured using a UV-VIS-absorption spectrophotometer (Varian, Cary 300) in the wavelength range of 400-850 nm.

**Steady state photoluminescence emission (PL):** PL of the films were carried out by using the 514 nm excitation wavelength coupled with a CCD detector (InGaAsAndor-iDUS DU490A-2.2) with an adaptive focus imaging spectrograph (Kymera KY-193i-B2). A commercial continuous laser (532 nm, GL532RM-150) was used as an excitation source.

**Scanning electron microscopy (SEM):** SEM is performed by the equipment JEOL 3100 F equipped with an electron gun employing 5 kV which allow us to magnifications from 5000X up to 50000X to analyze surface. By using INCA 350 (Oxford) and INCA Wave 200 (Oxford) it was employed microanalysis by X-ray energy dispersion (EDX) or by wavelength dispersion (WDX) respectively.

**X-Ray Diffraction (XRD):** The x-ray diffraction (XRD) profiles were registered by a diffractometer (Bruker AXS, D8 Advance) equipped with a primary monochromator of Ge. Measurements were taken using Cu Kα radiation (wavelength of λ= 1.5406 Å) over a 2θ range between 5° and 70° with a step size of 0.02°.

**Device characterization**

**Current-voltage (J-V) measurement:** n-i-p devices parameters are obtained using Abet sun 2000 solar simulator which gives an AM 1.5G (100 mW/cm²) light illumination conditions coupled with a Keithley 2612 sourcemeter to measure current-voltage. Each measured was taken with Tracer software and done at ambient conditions (T=25°C, RH~40-60%) using a scan rate of 10 mV/s and a shadow mask of 0.121 cm².
**Incident photon to current efficiency (IPCE):** IPCE measurements are performed using a Xenon lamp with a monochromator Oriel Cornestone 130 which was used to measure along the wavelength of the spectrum. Before measurement, calibration is done using a reference photodiode of silicon and each measurement is obtained using TRACQ BASIC software. Finally, IPCE scans were taken from 300 nm to 810 nm in steps of 10 nm.

**Chronoamperometry:** data is obtained by a Potentiostat Autolab PGSTAT30 employing 1 sun illumination over devices at ambient conditions of 40 % R.H measuring at mpp for 1 Hour.

**Impedance spectroscopy (IS):** The IS is measured by using a Potentiostat Autolab PGSTAT30 employing different filters to change light intensity up to 1 sun. For each voltage point ($V_{OC}$) IS was measured with an AC 10mV voltage perturbation from 1 MHz to 100 mHz. Nova software was used to generate data and Z-View software for modelling the equivalent circuit model used to fit the spectra, respectively.

**Volume calculation**

On the basis of the tetragonal phase of MAPbI$_3$ the characteristic peak at approximately 14° was considered to correspond to the plane (110) and the peak at 20° to the plane (112). These peaks can be observed for the references and MA$_{1-x}$Gu$_x$PbI$_3$ samples with Gu content of up to 20% preserving the same crystalline structure and increasing its volume. In consequence, the tetragonal phase will consist of a square base of side “a” and height “c” that will result in a volume of “a$^2$c”. However for higher values than 20% peaks at ~8.5° and ~11°, which are related to 2D structures appear, and the volume cannot be calculated as a tetragonal structure.
**PbS QDs synthesis and ligand exchange procedure**

PbS QDs were synthesized and added according to previous reports. In a three-necked round-bottom 0.9 g (4 mmol) of PbO, 2.0 g (7 mmol) of Oleic acid and 36 ml of 1-octadecene (ODE) were mixed and heated at 150 °C under N₂ while stirring. After 1 h, 3 ml (6.7 mmol) of trioctylphosphine (90%) were injected. Then, 0.42 ml (2 mmol) of hexamethyldisilathiane (HMDS) and 4 ml ODE were introduced once flask decreases its temperature to 110°C. Finally, solution was left to decrease its temperature to room temperature. QDs were obtained after performed three time washes with ethanol/acetone (1:1, v/v), centrifuged (3000 rpm for 10 minutes) and dispersed in toluene (100 mg/ml).

To perform the ligand exchange PbS in octane is mixed with 0.25 M of perovskite in 1:3 volume ratio. The latter leaves one phase of PbS in octane separated from another phase of perovskite in its solvents. Then, after stirring by 30 min the ligand exchange is produced leading to one phase of PbS/perovskite in the bottom and octane in the upper part. To recover the QDs with perovskite capping ligand it is perform three washing and finally the QDs are precipitated with toluene. Then, the remainder is dried by vacuum pump for 2 hours. Finally, perovskite solution is added in proper way to have PbS/perovskite embedded in perovskite solution. To have mixed cation/perovskite capping ligand the same procedure was followed.

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Supporting figures

**Figure S1.** A) Absorbance spectra of perovskite with different amount of Gu; Tauc plots and second derivative to determine their bandgap. B) SEM measurements of fresh samples with different quantities of Gu.

**Table S1.** Photoluminescence Full Width Half Maximum (PL FWHM) of perovskite peaks with different Gu %.

| Gu% | FWHM       |
|-----|------------|
| 0   | 44.65 ± 0.36 |
| 2   | 47.18 ± 0.53 |
| 5   | 45.74 ± 1.23 |
| 7   | 44.34 ± 0.26 |
| 10  | 48.94 ± 0.09 |
| 15  | 49.11 ± 0.03 |
Figure S2. Grain size of different mixtures of perovskite observed at surface measured by SEM images.
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Table S2. Photovoltaic parameter of samples measured under 1 sun illumination for different quantities of Gu in the perovskite at day 0.

| Gu %  | Jsc (mA/cm²) | Voc (V)  | FF (%) | PCE (%) |
|-------|--------------|----------|--------|---------|
| 0     | 20.3 ± 0.9   | 1.05 ±0.02 | 72.9 ± 1.8 | 15.6 ± 0.3 |
| 2     | 20.7 ± 0.7   | 1.06 ±0.01 | 74.6 ± 1.8 | 16.3 ± 0.6 |
| 5     | 20.9 ± 0.9   | 1.04 ±0.02 | 76.0 ± 3.0 | 16.6 ± 0.7 |
| 7     | 21.5 ± 0.6   | 1.06 ±0.01 | 76.2 ± 2.1 | 17.4 ± 0.5 |
| 10    | 19.8 ± 1.0   | 1.05 ±0.03 | 74.2 ± 2.3 | 15.4 ± 0.7 |
| 15    | 20.3 ± 0.7   | 1.06 ±0.02 | 71.0 ± 4.0 | 15.2 ± 0.7 |
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Figure S5. Photovoltaic parameters for 15 devices of each Gu percentage for the mixed cation perovskite measured at different days while they remain at 30-40% RH in dark conditions and 22 °C.
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Table S3. Photoluminescence Full Width Half Maximum (PL FWHM) of perovskite peaks with different Gu % with QDs.

| Gu % | FWHM       |
|------|------------|
| 0    | 50.50 ± 0.40 |
| 2    | 48.51 ± 0.06 |
| 5    | 49.90 ± 0.30 |
| 7    | 48.99 ± 0.02 |
| 10   | 50.06 ± 0.15 |
| 15   | 50.83 ± 0.08 |
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Table S4. Photovoltaic parameter of samples measured under 1 sun illumination for different quantities of Gu in perovskite with embedded PbS QDs at day 0.

| Gu (%) | Jsc (mA/cm$^2$) | Voc (V) | FF (%) | PCE (%) |
|-------|----------------|--------|--------|---------|
| 0     | 20.2 ± 0.4     | 0.99 ± 0.01 | 67.7 ± 1.0 | 14.3 ± 0.2 |
| 2     | 19.9 ± 0.6     | 1.01 ± 0.02 | 70.1 ± 1.9 | 14.1 ± 0.5 |
| 5     | 20.7 ± 0.6     | 1.00 ± 0.02 | 73.1 ± 1.8 | 15.1 ± 0.4 |
| 7     | 20.5 ± 0.6     | 1.03 ± 0.02 | 72.0 ± 3.0 | 15.2 ± 0.5 |
| 10    | 19.3 ± 1.0     | 1.04 ± 0.03 | 72.4 ± 2.5 | 14.6 ± 0.6 |
| 15    | 18.7 ± 0.5     | 1.05 ± 0.02 | 74.1 ± 2.3 | 14.6 ± 0.5 |
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References

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