

High Efficiency Rubidium Incorporated Perovskite Solar Cells by Gas Quenching

Meng Zhang^{*1}, Jae S. Yun¹, Qingshan Ma¹, Jianghui Zheng¹, Cho Fai Jonathan Lau¹, Xiaofan Deng¹, Jincheol Kim¹, Dohyung Kim², Jan Seidel², Martin A. Green¹, Shujuan Huang¹ and Anita W. Y. Ho-Baillie^{*1}

¹Australian Centre for Advanced Photovoltaics, School of Photovoltaic and Renewable Energy Engineering, University of New South Wales, Sydney 2052, Australia

²School of Materials Science and Engineering, University of New South Wales, Sydney 2052, Australia

*Corresponding Authors' e-mail: meng.zhang@unsw.edu.au; a.ho-baillie@unsw.edu.au

Supporting Information:

Experimental details:

Device fabrication:

Pre-etched FTO glass (Pilkington, $7 \Omega \text{ cm}^{-1}$) was cleaned with soap water, acetone and 2-propanol sequentially. The FTO substrate was further cleaned by a UVO cleaner for 15 min. Compact TiO_2 layer was deposited by spray-pyrolysis using a solution of titanium diisopropoxide bis(acetylacetonate) in isopropanol at 450°C . After cooling, the substrate was cut into $12 \text{ mm} \times 20 \text{ mm}$ pieces and mesoporous TiO_2 layer was then spin-coated with a diluted TiO_2 paste (Dyesol, 18 NR-T) followed by annealing at 500°C for 30 min.

Prior to deposition of perovskite film, the substrates were cleaned by a UVO cleaner for another 15 min and then transferred to a N_2 filled glovebox. The lead concentration in

perovskite precursor solutions is 1.33 M, which were prepared by dissolving FAI (Dyesol), RbI (Sigma-Aldrich), CsI (Sigma-Aldrich), MABr (Dyesol) and PbI₂ (Alfa Aesar), stoichiometrically in a mixed solvent of DMF (Sigma-Aldrich) and DMSO (Sigma-Aldrich) with a volume ratio of 4:1. The perovskite film was deposited by gas-quenching method (gas-assisted spin coating). After the perovskite precursor solution was spread on the mesoporous TiO₂ layer, the substrate was spun firstly at 1000 rpm for 10 s and then 4000 rpm for 30 s. N₂ stream (6 bar) was blown over the spinning substrate for 15 s after spinning at 4000 rpm for 5 s. The perovskite film was then annealed at 150 °C (FA system)/110 °C (FAMA system) for 20 min on a hot plate.

The hole transporting layer was deposited by spin-coating a 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-MeOTAD) solution at 3000 rpm. The solution was prepared by dissolving 72.3 mg spiro-MeOTAD (Lumtec), 28.8 µl, 4-tert-butylpyridine (Sigma-Aldrich), 17.5 µl lithium bis(trifluoromethylsulphonyl)imide (Sigma-Aldrich) solution (520 mg/ml in acetonitrile) and 8 µl FK209-cobalt(III)-TFSI (Lumtec) solution (300 mg of FK209-cobalt(III)-TFSI in 1 ml of acetonitrile) in 1 ml chlorobenzene (Sigma-Aldrich). The device was completed by depositing 100 nm of gold by thermal evaporation. To maximize the PCE, some of the devices had an antireflection layer of MgF₂ was sputtered on the glass side.

Gas-quenching process:

Gas-quenching set up was based on a spin-coater with lid-cover removed in a N₂ filled glovebox. A N₂ gas gun was connected to the glovebox with a pressure of 6 bar. For gas-quenching of perovskite film: 25 µl of perovskite precursor was dropped on the substrate, first spin at 1000 rpm for 10 s and then spin at 4000 rpm for 30 s. After spin at 4000 rpm for

5 s, a N₂ gas stream was blown from the N₂ gun towards the surface at a distance of 1 cm for 15 s with maximum pressure.

Characterisation:

The current density–voltage (*J–V*) measurements were performed using a solar cell I–V testing system from Abet Technologies, Inc. (using class AAA solar simulator) under an illumination power of 100 mW/cm² with a 65 mm² aperture. The FTO electrode is soldered for *J–V* measurements. The *J–V* curves are normally scanned from 1.2 V to -0.1 V with a scan rate of 0.1 V/s or 0.6V/s. The shunt resistances of the devices was obtained from software of the testing system.

X-ray diffraction (XRD) patterns were measured using a PANalytical Xpert Materials Research diffractometer system with a Cu K α radiation source ($\lambda = 0.1541$ nm). Secondary electron image and backscattered electron image of both top and cross-sectional morphology were recorded using a field emission scanning electron microscope (NanoSEM 230). The optical absorbance spectra were measured using Perkin Elmer Lambda1050 UV/Vis/NIR spectrophotometer. Photoluminescence (PL) spectra were measured using a back scattering geometry with laser excitation of 405 nm and a thermo-electrically cooled Si-CCD detector. The detector temperature is -60 °C and exposure time is 100 ms.

KPFM measurements were performed using a AIST-NT SmartSPM system with gold coated Si tips (HYDRA6R-100NG, APPNANO) as the probe in a non-contact mode with an AC voltage of -1 to +1 V. Kelvin mode is based on the two-pass technique. In the first pass, the topography is acquired using standard semi-contact mode (mechanical excitation of the cantilever). In the second pass, the tip is retraced at a set lift height from the sample surface to detect the electric surface potential. In this work, the CPD measured is the contact potential difference between the FTO layer and the gold probe tip.

Supplementary figures:



Figure S1. A photo of $\text{FA}_{0.95}\text{Rb}_{0.05}\text{PbI}_3$ (left) and $\text{FA}_{0.95}\text{Cs}_{0.05}\text{PbI}_3$ (right) annealed at 110°C for 20 min.

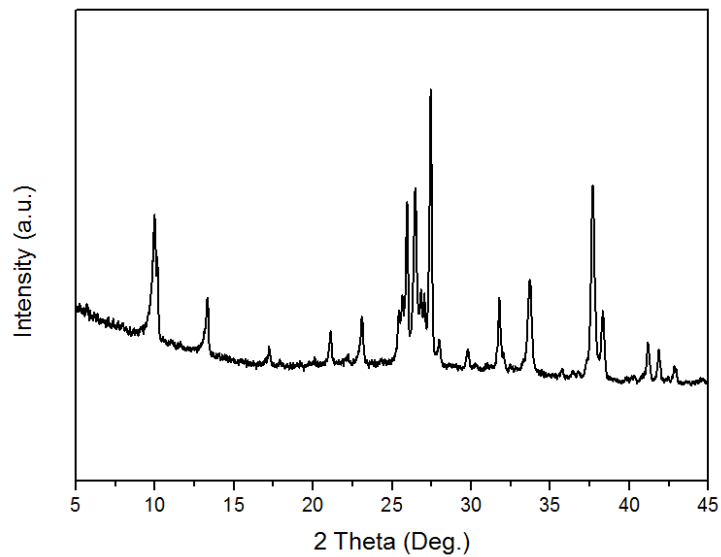


Figure S2. XRD pattern of gas-quenched RbPbI_3 film (RbPbI_3 cannot maintain a perovskite structure due to a $t < 0.8$)

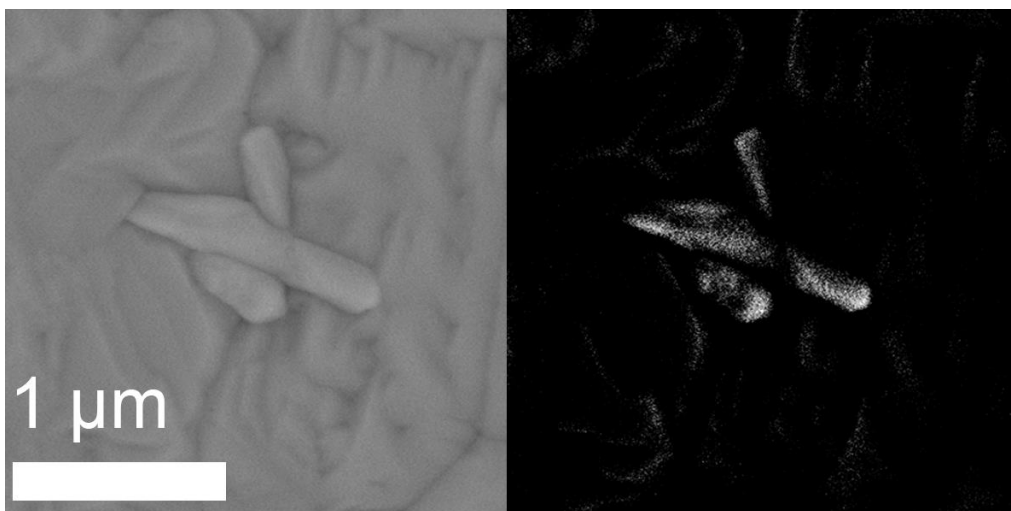


Figure S3. Backscattered electron SEM images of the “bright” particle in $\text{FA}_{0.85}\text{Rb}_{0.15}\text{PbI}_3$ perovskite film with brightness and contrast adjusted for the same image.

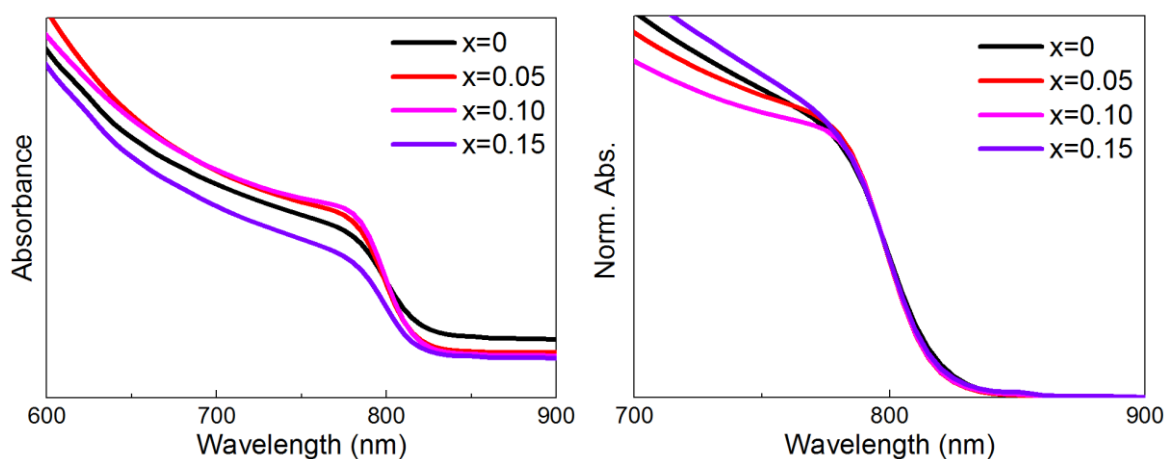


Figure S4. Original and normalized absorption spectra of $\text{FA}_{1-x}\text{Rb}_x\text{PbI}_3$ perovskite films.

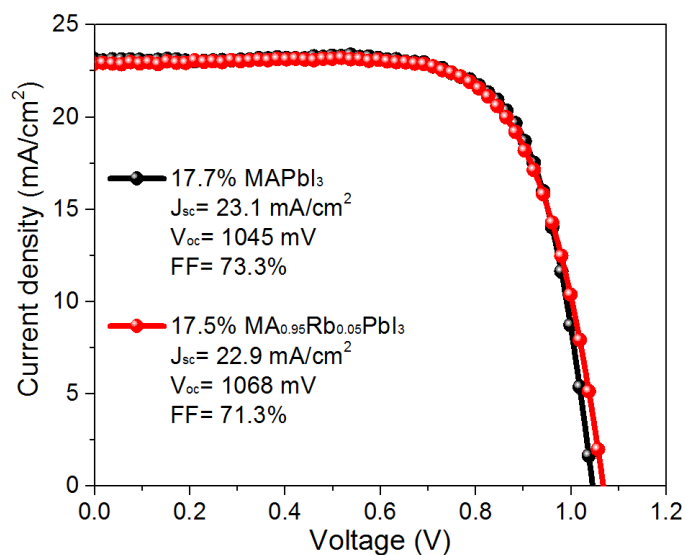


Figure S5. Light J - V curves of 65mm^2 (aperture area) MAPbI_3 device and $\text{MA}_{0.95}\text{Rb}_{0.05}\text{PbI}_3$ devices.

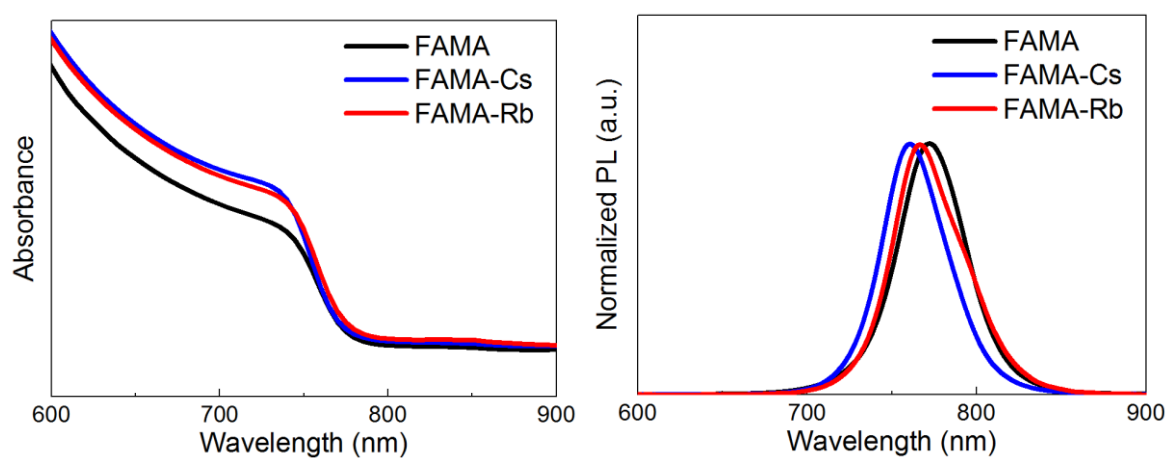


Figure S6. Absorption and normalized PL emission spectra of FAMA, FAMA-Cs and FAMA-Rb perovskite films.

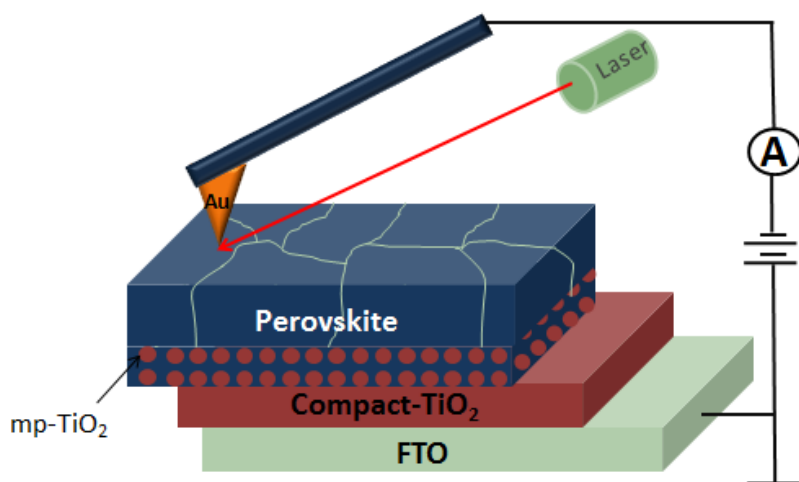


Figure S7. Schematic of the KPFM measurement set up.

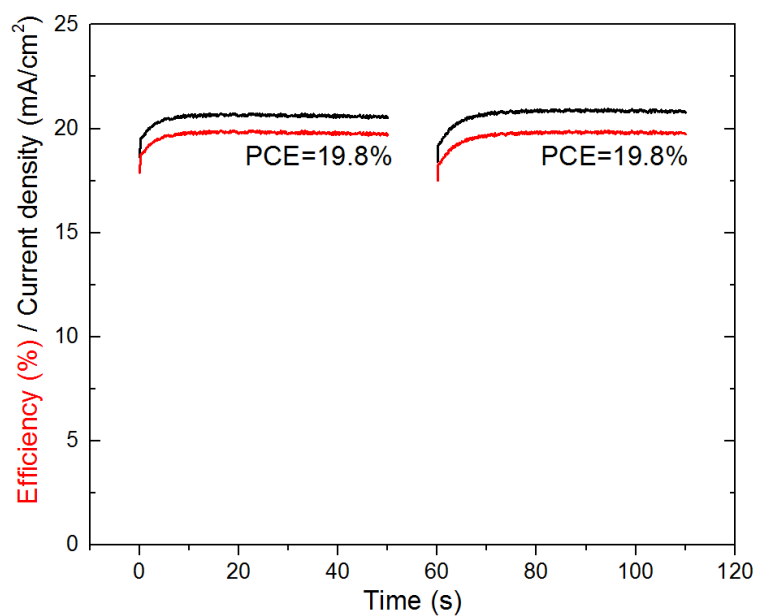


Figure S8. Steady-state photocurrent density and power conversion efficiency of the FAMA-Rb device with antireflection layer, obtained by holding the device at a fixed voltage near the maximum power point (0.957V).