Incorporation of γ-butyrolactone (GBL) dramatically lowers the phase transition temperature of formamidinium-based metal halide perovskites

Shuai Ruan, Rong Fan, Narendra Pai, Jianfeng Lu, Nathan A. S. Webster, Yinlan Ruan, Yi-Bing Cheng, and Christopher R. McNeill*

Electronic Supplementary Information (ESI)

***Materials and Methods*:** Unless specified otherwise, all materials were purchased from Sigma-Aldrich and used as received. The perovskite single crystals were grown via a modified anti-solvent vapour-assisted crystallization (AVC) method. 1.0 M $MAPbI_3$/$FAPbI_3$ perovskite precursor solutions were prepared by dissolving equimolar PbI_2 and MAI/FAI in g-butyrolactone (GBL), whereas the mixed cation perovskite precursor solution was blended with $MAPbI_3$ and $FAPbI_3$ precursor solutions in the corresponding ratio. The solutions were filtered using a PTFE filter with a 0.2 mm pore size. Prepared precursors were individually stored in a container full of dichloromethane (DCM) vapour at room temperature. Crystals up 0.5 cm in size were obtained, and these crystals were finely grounded before further use. All procedures were conducted under ambient conditions with humidity of 45–55%.

Ex-situ XRD were collected with a Bruker D8 Advance diffractometer (Bragg–Brentano geometry) equipped with a Cu Ka X-ray tube operated at 40 kV and 40 mA using a step size of 0.02° and a time per step of 2 s.

In-situ XRD were performed using an INEL MPG diffractometer fitted with an Anton Paar HTK10 high-temperature chamber incorporating a Pt resistance strip heater. Perovskite crystals were ground by using a mortar and pestle, before being pressed onto the Pt strip. Samples were heated from room temperature to 200 °C at 5 °C min^{-1} under a flow of air. XRD datasets were collected continuously during heating, with individual datasets collected for 30 seconds. The Co tube was operated at 40 kV and 35 mA. Phase identification was performed using PANalytical Highscore Plus, which integrates with the International Centre of Diffraction Data's (ICDD) PDF 4+ database. The *in-situ* XRD 2θ values (for Co Kα radiation, λ = 1.789 Å) have been converted to 2θ values for Cu radiation (λ = 1.5406 Å) so that the peak positions of the *in-situ* XRD data match with the figures for and the *ex-situ* data.

Raman spectrometer manufactured by Raman Systems is used to obtain the Raman spectrum of various samples. This spectrometer utilizes a 1064 nm laser to excite the molecular vibrations. It also comes with a probe to hold the sample to be examined.

Thermogravimetric and differential scanning calorimetry (TG-DSC) analysis were carried out for single crystals in 70 µL alumina pans within the (25 ~ 250 °C) temperature range (heating rate (5 °C min^{-1})) in dinitrogen atmosphere using TGIR equipped STA 8000 system.

Absorbance spectra were obtained using a Perkin Elmer Lambda 950 UV/VIS/NIR spectrophotometer.

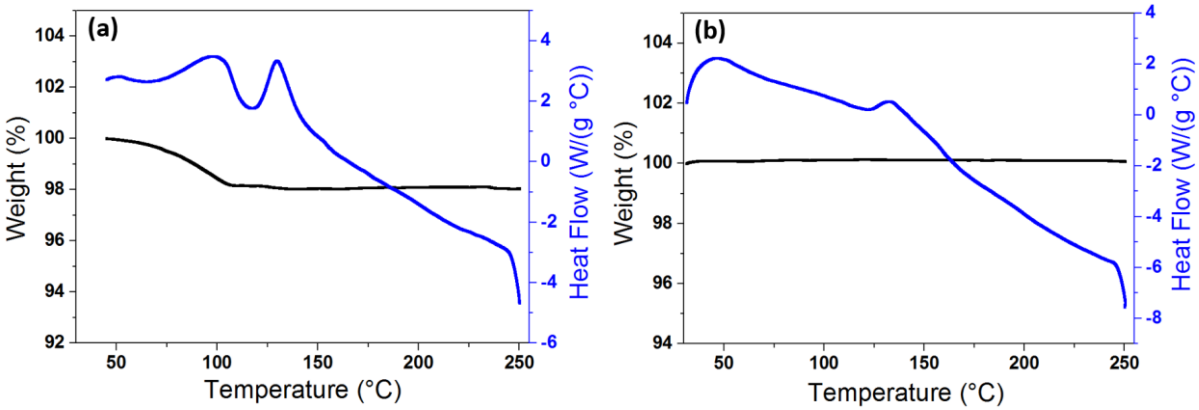

Figure S1. TG-DSC analysis for the $FAPbI_3$ crystal that intercalated with GBL (a), and $FAPbI_3$ crystal that vacuumed overnight to eliminate the residual GBL solvent (b).

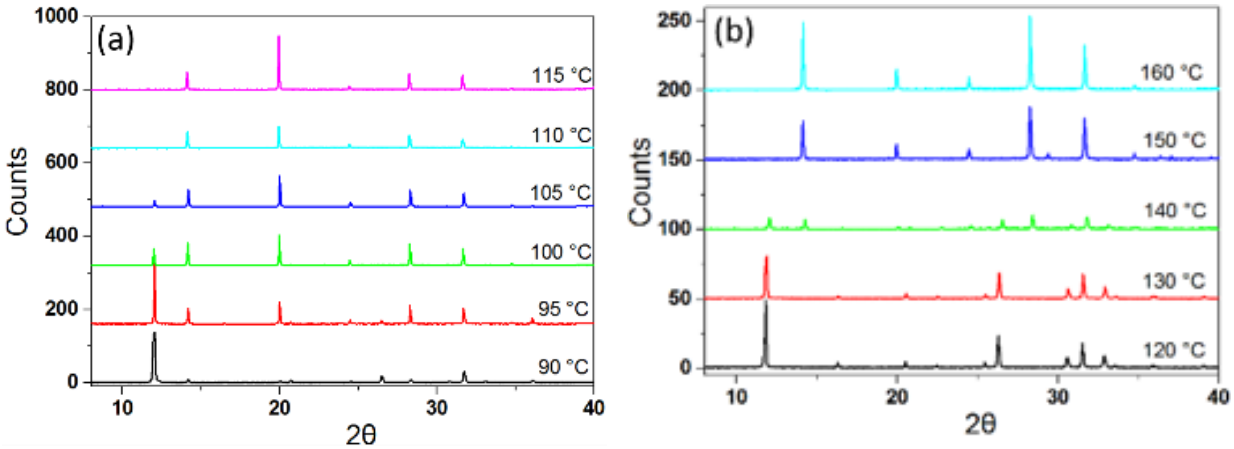

Figure S2. *Ex-situ* XRD study for $FAPbI_3$ (GBL) (a) and $FAPbI_3$ (DMF) (b) films annealed at varied temperature.

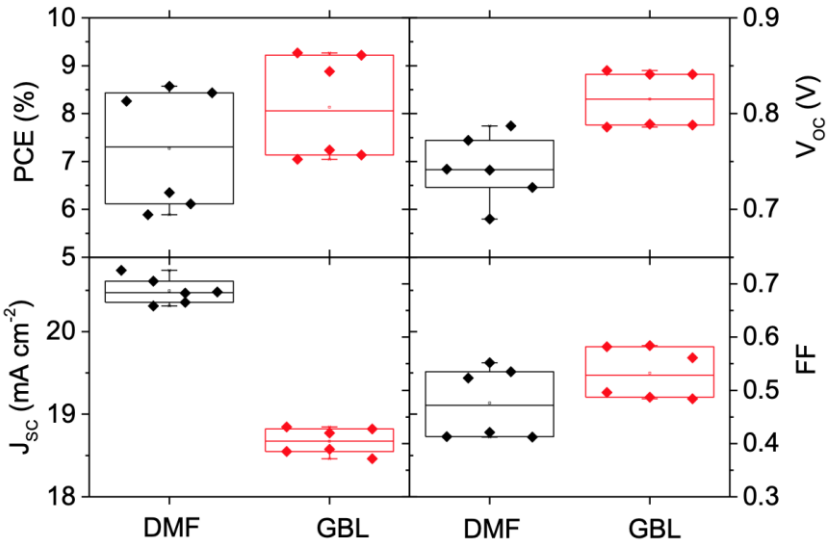

Figure S3. The $FAPbI_3$ solar cell performance comparison by preparing in GBL and DMF. Solar cell fabricating procedure is based on previous study.[1] Briefly, 1.25 M perovskite precursor solutions are successively spin-coated on the ITO glass substrates at 1000 rpm for 10 s and 5000 rpm for 30 s, respectively. Perovskite films were annealed at 125 °C for 10 min.

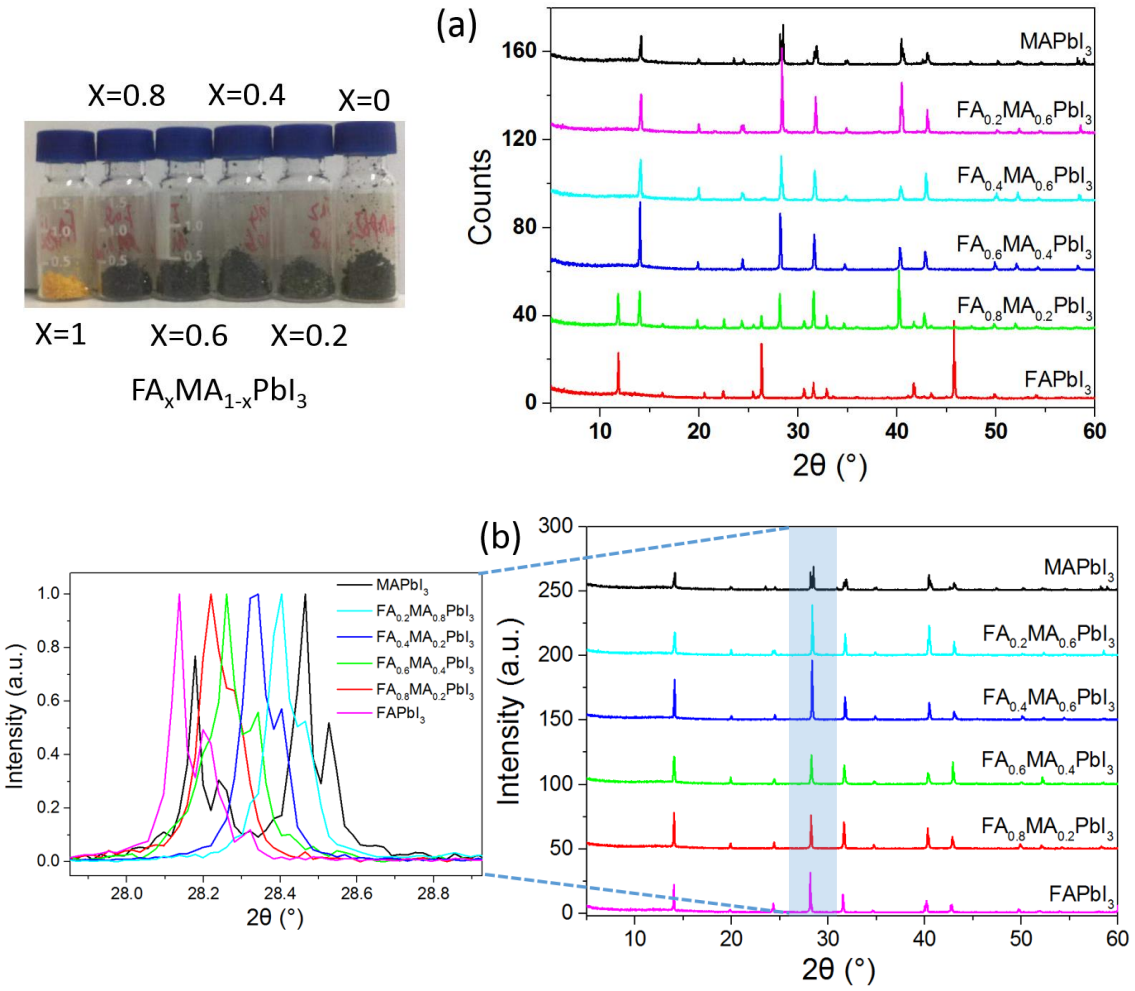

Figure S4. Ex-situ XRD for the freshly prepared and finely grounded $FA_xMA_{1-x}PbI_3$ single crystal powder (a), and the same powder that annealed at 150 °C for 5 min in the air (b).

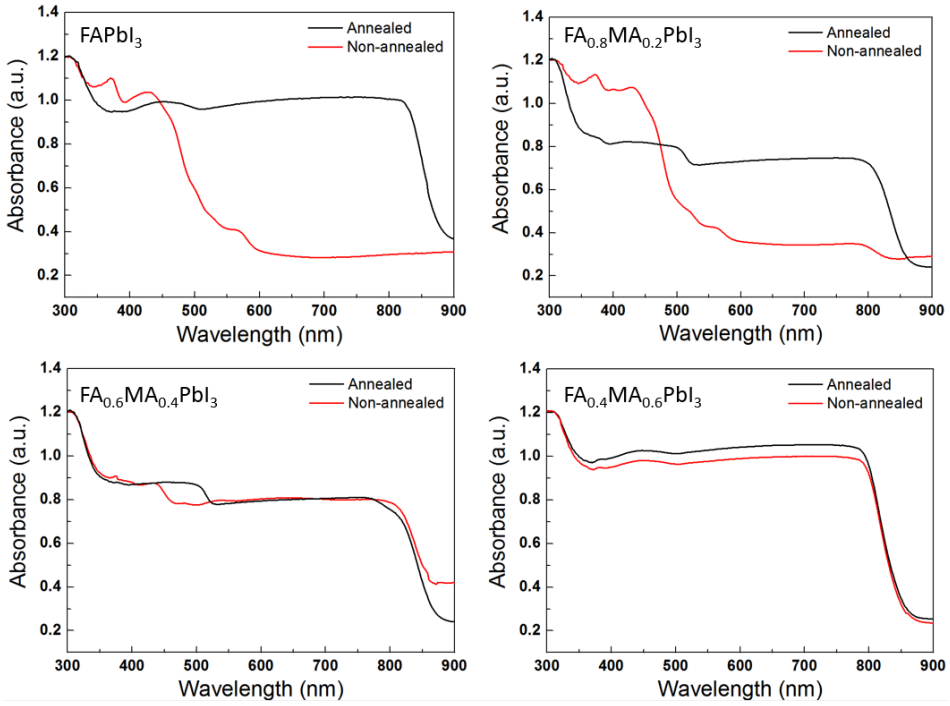

Figure S5. The comparison of absorbance spectra of the freshly prepared $FA_xMA_{1-x}PbI_3$ single crystals at room temperature and annealed at 150 °C for 5 min in the air

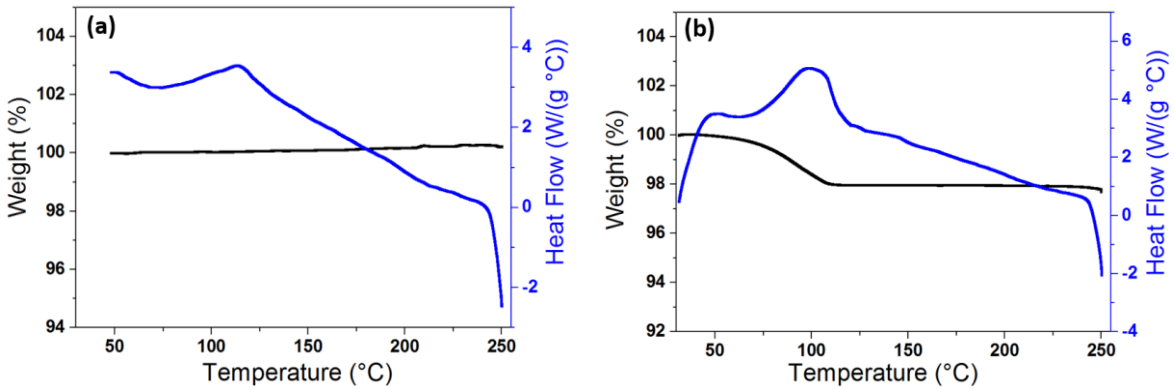

Figure S6. TG-DSC analysis for the $FA_{0.8}MA_{0.2}PbI_3$ crystal that vacuumed overnight to eliminate the residual GBL solvent (a), and $FA_{0.8}MA_{0.2}PbI_3$ crystal that intercalated with GBL (b).

References

1 Y. Zhang, G. Grancini, Y. Feng, A. M. Asiri, M. K. Nazeeruddin, *ACS Energy Letters* **2017**, *2*, 802-806.