

Supporting Information

Direct Observation of Ferroelectric Domains in Solution-Processed CH₃NH₃PbI₃ Perovskite Thin Films

Yasemin Kutes,^{†,||} Linghan Ye,^{†,||} Yuanyuan Zhou,^{‡,||} Shuping Pang,[§]
Bryan D. Huey,^{†,*} and Nitin P. Padture^{‡,*}

[†] Department of Materials Science and Engineering,
University of Connecticut,
Storrs, CT 06269, USA
(*bhuey@ims.uconn.edu)

[‡] School of Engineering,
Brown University,
Providence, RI 02912, USA
(*nitin_padture@brown.edu)

[§] Qingdao Institute of Bioenergy and Bioprocess Technology,
Chinese Academy of Sciences,
Qingdao 266101, P.R. China

^{||}These authors contributed equally.

Synthesis

Methylammonium iodide (CH₃NH₃I or MAI) was prepared using a process described elsewhere [1]. In a typical procedure, 24 ml of 33 wt% methylamine (CH₃NH₂) solution in anhydrous ethanol was reacted with 10 ml of 57 wt% hydroiodic acid (HI) in water, in 100 ml of ethanol (excess CH₃NH₂) in a dry Ar atmosphere at room temperature (all reagent grade chemicals obtained commercially from Sigma-Aldrich, St. Louis, MO). The solvent and the excess CH₃NH₂ were removed using a rotary evaporator, and the resulting MAI powder was washed and collected. To make a compact MAPbI₃ thin film, first, 30 wt% PbI₂ (Acros Organics) in N,N'-dimethylformamide (DMF; Sigma-Aldrich, St. Louis, MO) was spin-coated (6000 rpm, 40 s) onto fluorine-doped tin oxide (FTO) coated glass substrates to form a smooth PbI₂ thin film which was then dried. Second, 10 mg/ml MAI in 2-propanol was spin-coated (6000 rpm, 40 s) onto the as-prepared PbI₂ layer, and it was then annealed at 150 °C for 1 min. MAI spin-coating and annealing processes were then repeated 3-4 times. The excess MAI was washed away using isopropanol, and the final thin films were annealed at 150 °C for 3 min to obtain a dark-colored β-MAPbI₃ perovskite. Typically thin films were prepared in ambient air (~40% RH) and they were stored in a dry box. Thin films were also prepared in a N₂-filled glovebox, but we did not observe any obvious difference between the two.

Characterization

The as-deposited β-MAPbI₃ thin films were characterized using X-ray diffraction (XRD; D8-Advance, Bruker, Karlsruhe, Germany) using Cu Kα₁ radiation (λ=1.5406 Å) with a 2θ range of 10°-60° and a step size of 0.02°. The surface of the as-deposited β-MAPbI₃ thin films was observed using a scanning electron microscope (SEM; LEO 1530VP, Carl Zeiss, Munich,

Germany). The local roughness of the β -MAPbI₃ thin films was characterized using a conventional atomic force microscope (MFP-3D Origin, Asylum Research, Santa Barbara, CA).

Piezo-Force Microscopy (PFM)

PFM was performed with a different AFM (Cypher, Asylum Research, Santa Barbara, CA). A function generator (Agilent Technologies 33220A, Santa Clara, CA) was used to bias the tip with AC and/or DC signals, while the back electrode of the specimen was grounded. The synchronization channel was used as the reference signal for a lock in amplifier (HF2LI-MF, Zurich Instruments, Zurich, Switzerland) to determine and map the relative phase and amplitude of the cantilever deflection, *i.e.* the local piezoresponse. Typical driving frequencies were on the order of 500-1600 kHz with peak-peak AC biases of 2-4 V, while DC biases for poling ranged ± 8 V. The measurements were performed with conductive diamond coated probes (Nanosensors CDT, NanoAndMore USA, Lady's Island, SC). Note that all PFM images are acquired with an AC signal only, while poling is separately achieved by scanning with DC biases only. The multiple images in Fig. 3 have been aligned using FIJI image processing software.

All PFM experiments were performed in ambient air (RH $\sim 40\%$) the same day the thin films were prepared (vacuum packed for transportation). The thin films did decompose after several hours in ambient air, resulting in MAI and PbI₂, which showed no PFM contrast.

Reference

- (1) Lee, M.M.; Teuscher, J.; Miyasaya, T.; Murakami, T.N.; Snaith, H.J. Efficient Hybrid Solar Cells Based on Meso-Superstructured Organometal Halide Perovskites. *Science*, **2012**, 338, 643-647.