Supplementary information

Tunable photoconductivity in bismuth-based hybrid perovskites via precursor stoichiometry and composition

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Experimental details:

Fabrication of thin film:

All thin-films used in this work were fabricated through solution processed spin-coating method. To fabricate bismuth halide, lead free perovskite thin films, a desired amount of organic/inorganic salt (e.g. MAI, CsI or BAI) and BiI_3 were added in a mixed solvent of DMF and DMSO and stirred overnight inside a glovebox. The solution was then spun on a pre-cleaned glass (or quartz) substrates at 2500 rpm for 30s followed by an annealing at 100 ˚C for 30 min.

Characterization of thin films:

Optical absorption spectra and X-ray diffraction patterns of the thin films of were obtained by Carry 6000*i* UV− vis−NIR spectrophotometer and Bruker D8 Advance X-ray powder diffractometer (Cu Kα radiation, λ = 1.54 Å) respectively. The topography measurements were carried out in a Nanosurf C3000 atomic force mocroscope.

TRMC measurements were done on the thin films fabricated on quartz substrate. The samples were placed in a microwave cavity at the end of an X-band waveguide operating at ca. 10 GHz and photoexcited through a grid with a 5 ns laser pulse from an OPO pumped by the third harmonic of an Nd:YAG laser. The interaction between photoinduced electrons and holes with the microwaves induced a change in microwave power (ΔP) in the cavity. The relative change ($\Delta P/P$) in microwave power such as $\Delta P/P = -K\Delta G$ (K is the calibration factor) is correlated with the transient photoconductance ΔG. Considering that the electrons and holes are generated in pairs the peak photoconductance during the laser pulse can be expressed as

$$\Delta G = \beta q_e F_A I_0 (\Phi.\Sigma\mu)$$

where β = 2.2 is the geometric factor for the X-band waveguide used, q_e is the elementary charge, F_A is the fraction of light absorbed at the excitation wavelength, I_0 is the incident photon flux, Φ is the quantum efficiency or yield of free carrier generation per photon absorbed and $\Sigma\mu$ the sum of the mobility of electrons and holes. The details of our experimental set up and procedure are described elsewhere. [1]

The product of free carrier generation per photon absorbed and local mobility of free carriers which is called the yield mobility product is considered as a figure of merit. Tracking this quantity over time after the end of the laser pulse provides insight into the free carrier generation, recombination and transport in the samples.

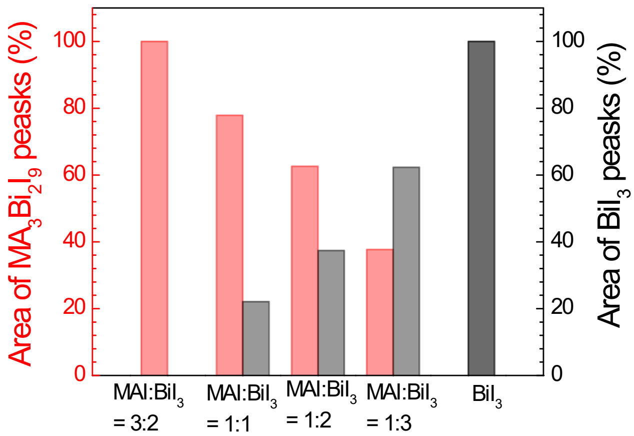

Fig. S1 The relative contribution of the peak areas of $MA_3Bi_2I_9$ (0D phase) and BiI_3 (2D phase) to the total XRD pattern area of MABI thin films with varying MAI/BiI_3 ratios.

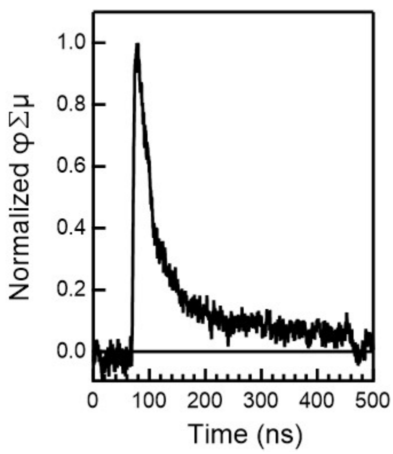

Fig. S2 TRMC transients of BiI_3 thin film.

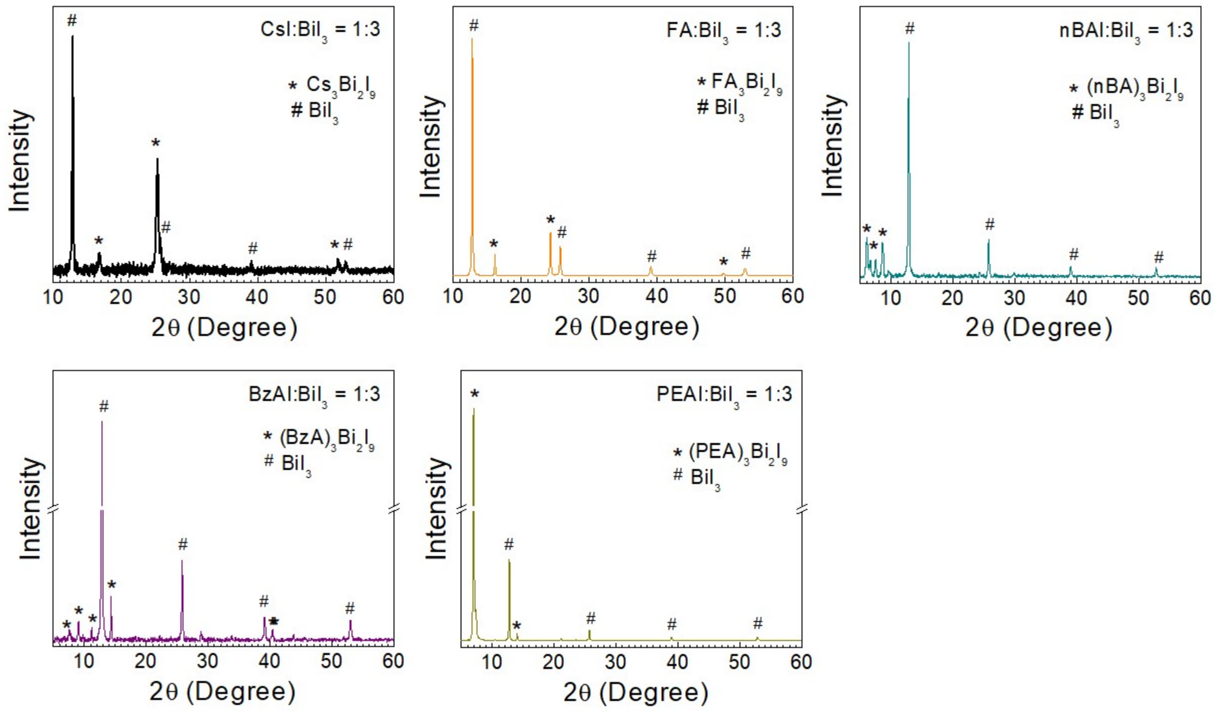

Fig. S3 XRD pattern of Bi-based perovskite derivative thin films having different organic cations.

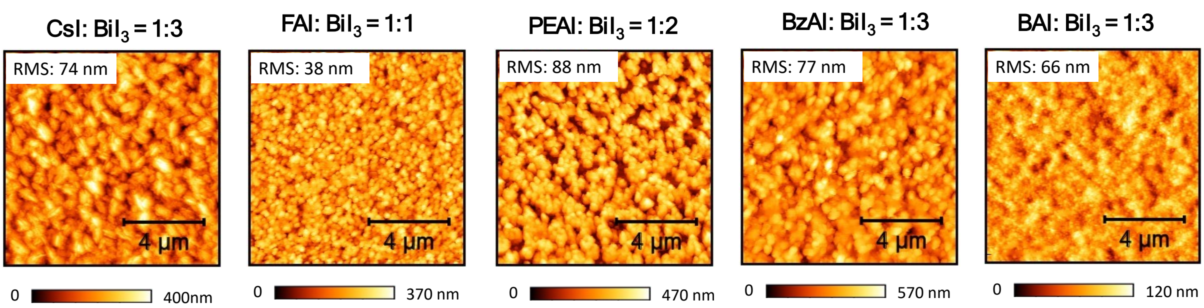

Fig. S4 AFM topography of Bi-based perovskite derivative thin films having different organic cations

References:

1. Microwave photoconductance spectrometer and methods of using the same, B. W. Larson. US Patent 11,563,405, 2023