Electronic Supplementary Information (ESI)

Combining Theory and Experiment in the Design of a Lead-Free
(CH₃NH₃)₂AgBiI₆ Double Perovskite

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Supporting Information

Methods

Theoretical calculation

The ground state of structure was determined by using density functional theory (DFT) implemented in the Vienna ab initio simulation package (VASP). All calculations were performed by Perdew-Burke-Ernzerh of (PBE) generalized gradient approximation (GGA) exchange-correlation. Projector augmented-wave method (PAW) method was used to describe the interaction between core electrons and valence electrons. Valence configurations included the Bi 5d6s6p, Ag 4d5s, I 5s5p, C 2s2p, N 2s2p and H 1s states. In particular, the kinetic energy cut off for plane wave basis set was set to 500 eV. The cell parameters and atomic positions were fully relaxed until an energy convergence of $10^{-4}$ eV and a force convergence on atoms of $0.02$ eV/Å was achieved, respectively. The Brillouin zone was sampled with $6\times6\times4$ Monkhorst-Pack grid.

Synthesis of $(\text{CH}_3\text{NH}_3)_2\text{AgBiI}_6$ perovskite powders

Methyl ammonium iodide was synthesized by mixing 15 mL of hydriodic acid (57% in water, Sigma-Aldrich) with 13.5 mL of methylamine solution (CH$_3$NH$_2$, 40% in water, Sigma-Aldrich), and the white powder was washed with diethyl ether three times and dried in vacuum oven (24 h, 60 °C). BiI$_3$ (99.99%) and AgI (99.99%) were purchased from Alfa aesar and used as received. The $(\text{CH}_3\text{NH}_3)_2\text{AgBiI}_6$ compounds were prepared by mixing MAI, BiI$_3$ and AgI in the molar ratio of 2: 1: 1, fully ground and mixed in a mortar in a nitrogen glove box. The solid powders were sealed in quartz ampules under certain vacuum and heated to 200 °C for 2 hours to complete the reaction.

Material Characterization

PA Nalytical Empyrean using Cu Kα radiation ($\lambda = 1.54056$ Å) was operated for X-ray analysis at room temperature, and the acquisition was done for every 0.04° increment over the Bragg angle range of 10°–70°. A UV-Vis (JASCO V-550) spectrometer equipped with an integrating sphere was used to collect absorption data of the synthesized perovskite powder. Field Emission Scanning Electron Microscope (FESEM, JEOL, JSM-7800F, 3kV) was used to record surface morphology of the film. XPS measurement was done with a Thermo Scientific Escalab 250 Xi instrument using monochromatic AlKα radiation ($h\nu = 1486.7$ eV). Thermo gravimetric analyses (TGA) were performed with a Netzsch STA 449 F3 Jupiter Thermo-Microbalance at a heating rate of 10 °C/min, using 11.56 mg samples in alumina pans. Atomic force microscopy was performed using a Veeco Multimode 3D instrument to probe the work function of samples.
**Figure S1.** Valence level spectra of the (CH$_3$NH$_3$)$_2$AgBiI$_6$ samples measured by XPS. The fermi level is set to be zero by blue line.

**Figure S2.** Overview XPS spectra of (CH$_3$NH$_3$)$_2$AgBiI$_6$ film. The spectra were measured with photon energy of 1486.6 eV.
Figure S3. Band energy diagram of (MA)$_2$AgBiI$_6$.

Figure S4. Thermogravimetric analysis (TGA) thermogram of (CH$_3$NH$_3$)$_2$AgBiI$_6$ perovskite.

References