Electronic Supplementary Information (ESI)

Combining Theory and Experiment in the Design of a Lead-Free $(CH_3NH_3)_2AgBiI_6$ 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).[1] All calculations were performed by Perdew-Burke-Ernzerh of (PBE) generalized gradient approximation (GGA) exchange-correlation.[2] Projector augmented-wave method (PAW) method was used to describe the interaction between core electrons and valence electrons.[3, 4] 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 6×6×4 Monkhorst-Pack grid.

Synthesis of $(CH_3NH_3)_2AgBiI_6$ 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_3NH_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 $(CH_3NH_3)_2AgBiI_6$ 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 (λ = 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 (hν = 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.

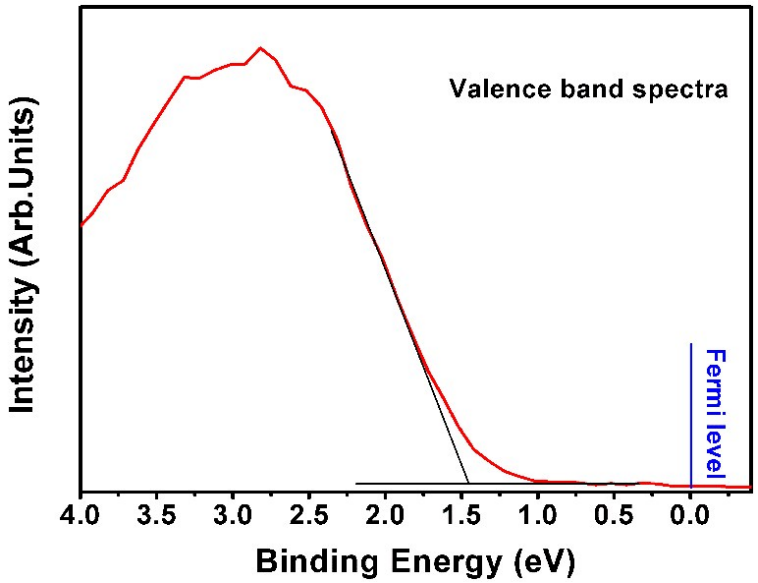

Figure S1. Valence level spectra of the $(CH_3NH_3)_2AgBiI_6$ samples measured by XPS. The fermi level is set to be zero by blue line.

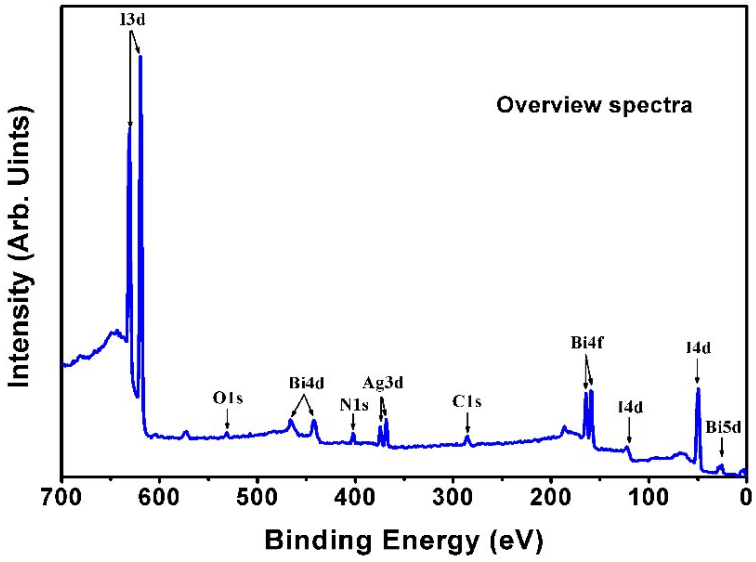

Figure S2. Overview XPS spectra of $(CH_3NH_3)_2AgBiI_6$ film. The spectra were measured with photon energy of 1486.6 eV.

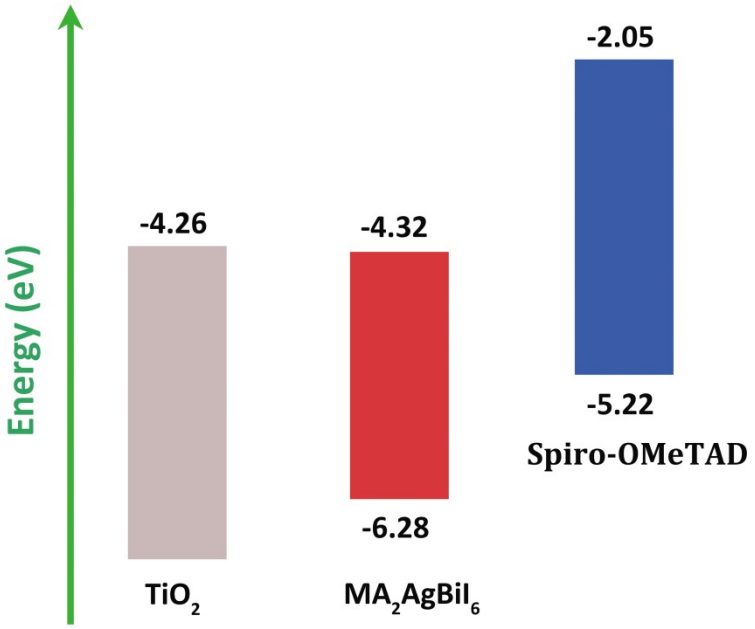

Figure S3. Band energy diagram of $(MA)_2AgBiI_6$.

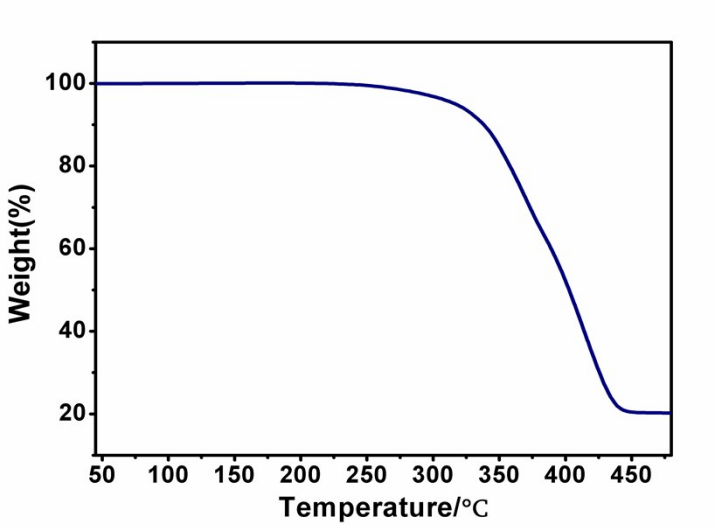

Figure S4. Thermogravimetric analysis (TGA) thermogram of $(CH_3NH_3)_2AgBiI_6$ perovskite.

References

1. G. Kresse and J. Furthmuller, *Phys. Rev. B*, **1996**, 54, 11169-11186.
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4. G. Kresse and D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758-1775.