Electronic supplementary information (ESI)

Synthesis of two-dimensional phenylethylamine tin-lead halide perovskites with bandgap bending behavior

Shiqi Sui,[a] Jian Zhou,[b] Aifei Wang,[c] Guangcai Hu,[a] Wen Meng, [a] Chuying Wang,[a] Yao Liu, [a] Jiajing Wu [a] and Zhengtao Deng *[a]

[a] College of Engineering and Applied Sciences, State Key Laboratory of Analytical Chemistry for Life Science, National Laboratory of Microstructures, Nanjing University, Nanjing, Jiangsu, 210023, P. R. China.

[b] Department of Materials Science and Engineering, Nanjing University, National Laboratory of Solid-State Microstructures, Nanjing, Jiangsu 210023, People's Republic of China

[c] Institute of Advanced Materials (IAM), Nanjing Tech University (NJ Tech), 5 Xinmofan Road, Nanjing 210009, P.R. China

Experimental

Materials

Lead bromide ($PbBr_2$, 99 %), stannous oxide (SnO, 99 %), phenylethylamine (PEA, 99 %) hydrobromic acid (HBr, 99 %), hypophosphite acid (H_3PO_2, 99 %) were purchased from Aladdin-reagent. All chemicals were used as received.

Synthesis of $PEA_2Sn_xPb_{1-x}Br_4$

$PEA_2Sn_xPb_{1-x}Br_4$ was synthesized by SnO and $PbBr_2$ with specific ratio. Herein, we took $PEA_2Sn_{0.5}Pb_{0.5}Br_4$ as an example. First, SnO (0.5 mmol) was added in HBr (4 ml) with ultrasonic shaking. After several seconds, the black powder dissolved and yellow solution was received. Then, $PbBr_2$ (0.5 mmol) and H3PO2 (10 ml) were added into the yellow solution with vigorous stirring. Subsequently, 0.25 ml PEA were injected into the light-yellow solution and yellow precipitate appeared rapidly with soaring temperature. The mixed solution was centrifuged with 10000 rpm for 5 min. Yellow precipitates were collected and dried off in 80 ^oC for 2 h in order to get powder samples for following characterization. Samples with Sn/Pb ratios were adjusted by different amount of SnO and $PbBr_2$.

DFT calculation methods

The electronic properties and density of states (DOS) of $PEA_2Sn_xPb_{1-x}Br_4$ are calculated by the density functional theory (DFT) in the generalized gradient approximation implemented in the Vienna ab initio simulation package (VASP) code[48, 49], in which the projected augmented wave method[50, 51] and the Perdew-Burke-Ernzerhof exchange correlation[52] are used. The plane-wave cutoff energy was 400 eV throughout the calculations. The spin-orbit coupling is considered in the calculation due to the heavy atomic mass of Sn and Pb. The HSE06 hybrid functional[53, 54] is also used in DOS calculations in order to overcome the underestimation of band gaps in the normal DFT calculations.

Characterization

Steady state absorbance spectra were collected with a Shimadzu UV-3600 plus spectrophotometer equipped with an integrating sphere under ambient conditions. The high scanning rate model was used with 0.1 s integration and 20 nm slit width. The luminescence spectra were collected with Thorlabs CCS-175 compact CCD spectrometers with corresponding fiber bundles under ambient-condition operating. Wavelength of exciting laser was 385 nm and integration time was 1000 ms. X-ray diffractions spectra were collected with a Bruker D8 ADVANCE X-ray Powder Diffractometer equipped a Cu Kα. Measurement range was from 5^o to 50^o. Step size was 0.0195^o.

Additional Figures:

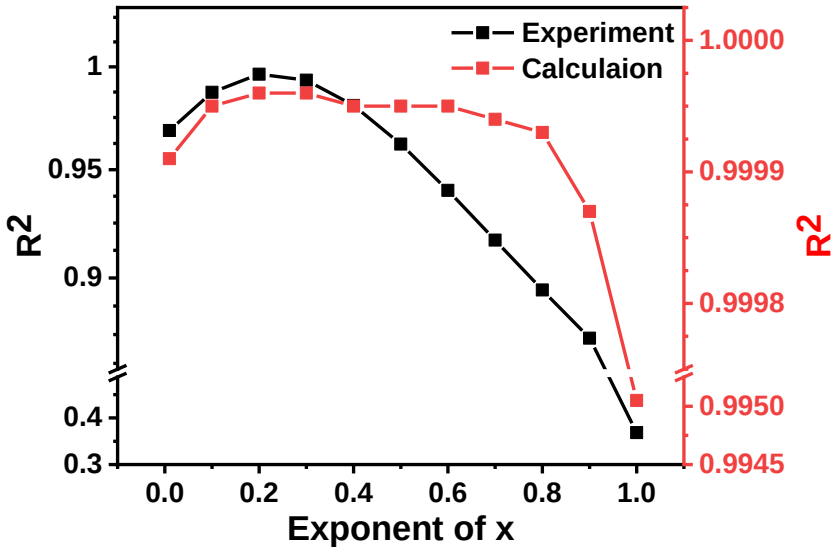

Figure S1. The fitting degree of Eq. 3 in different exponent of x. Different colour indicated experiment and calculation data.

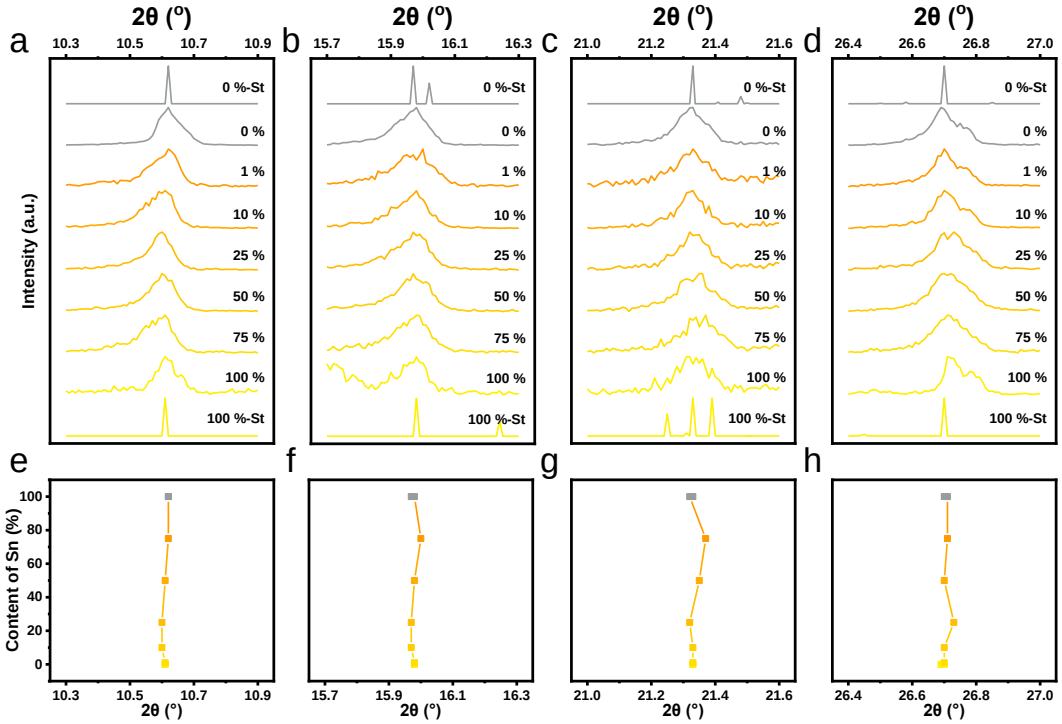

Figure S2. (a-d) Detailed patterns for the characteristic peaks. 0 %-St and 100 %-St indicated standard patterns of pure-Pb and pure-Sn. (e-h) Positions shifts of XRD patterns in different contents of Sn.

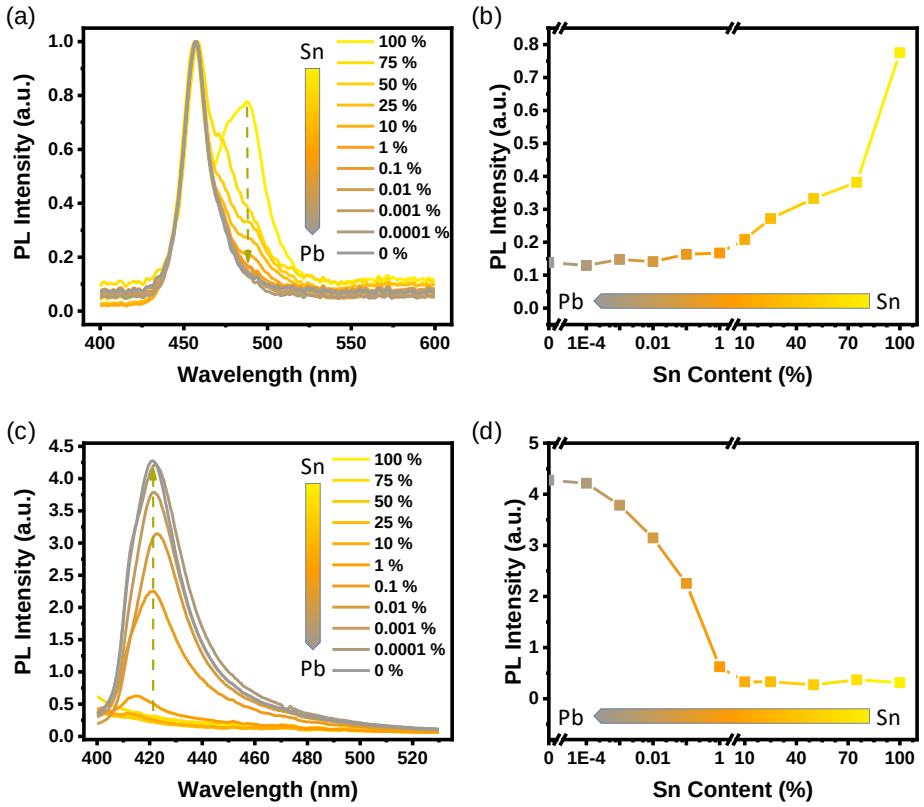

Figure S3. (a, c) Photoluminescence spectra of Sn-Pb bromide perovskites (a: Sn-peak parts; c: Pb-peak parts). (b, d) Photoluminescence intensity of Sn-Pb bromide perovskites (b: Sn-peak parts; d: Pb-peak parts). In all figures above, B-site ingredient changed from total Sn to total Pb were shown with a narrow from yellow to grey.

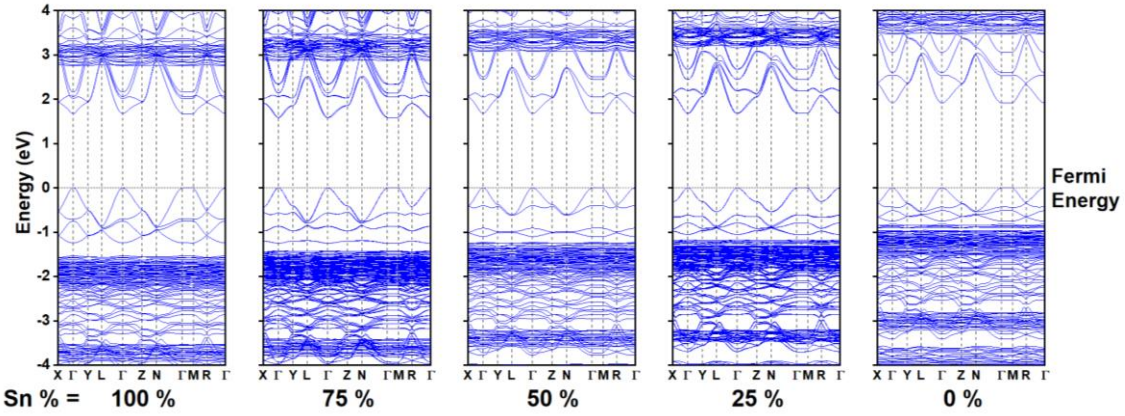

Figure S4. Band structure of Sn-Pb bromide perovskites. The content of Sn was marked in the bottom of each graph. The calculation was not including hybrid functional methods. Fermi energies of each sample were marked with dot-line in each figure.