Supporting Information

Pressure-Induced Bandgap Engineering of Lead-Free Halide Double Perovskite (NH$_4$)$_2$SnBr$_6$

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Experimental Section

Sample Preparation and High Pressure Generation. (NH$_4$)$_2$SnBr$_6$ was prepared by combing 39.17 mg of NH$_4$Br (0.4 mmol, Macklin, 99%) and 87.66 mg of SnBr$_4$ (0.2 mmol, Alfa Aesar, 99%) in 1 mL of 57% (w/w) HBr, which was stirred for 30 min.[1] The resulted pale yellow powder was washed three times with hydrobromic acid and vacuum-dried overnight. High pressure experiments are carried out using a symmetric diamond anvil cell (DAC) with static pressure in the sample chamber to ensure equal pressure was applied to each crystal direction of the particle.. The culet diameter of the diamond anvils was 400 μm. The sample was loaded into a 150 μm diameter hole of the T301 steel gasket, which was preindented to a thickness of 40 μm. A small ruby chip was inserted into the sample compartment for in situ pressure calibration, utilizing the R1 ruby fluorescence method. Silicon oil was utilized as the pressure transmitting medium (PTM) for optical absorption and XRD experiments, while the argon and KBr were employed as PTM for Raman and IR measurements, respectively. All of the experiments were performed at room temperature.

In situ High Pressure Measurements. High pressure angle-dispersive X-ray diffraction (ADXRD) experiments with a wavelength of 0.6199 Å beam were carried out at BL15U1, Shanghai Synchrotron Radiation Facility (SSRF), China. CeO$_2$ was used as the standard sample to do the calibration. The collected two-dimensional images were integrated on the basis of FIT2D program, yielding one-dimensional intensity versus diffraction angle 2-theta patterns. Refinements of the XRD patterns were accomplished by using the Reflex module in Materials Studio program. High-pressure absorption spectra (250-1000 nm) were measured in the exciton absorption band region by a deuterium-halogen light source and recorded with an optical fiber spectrometer (Ocean Optics, QE65000). The transmission spectrum of silicon oil around the sample was subtracted as the background. High-pressure Raman spectra were recorded using a spectrometer equipped with liquid nitrogen cooled CCD (iHR 550, Symphony II, Horiba Jobin Yvon). A 532 nm single-mode DPSS laser was utilized to excite the sample, and the output power was 10 mW. The resolution of the system was 1 cm^{-1}. High pressure IR spectra measurements were conducted using a Nicolet iN10 FT-IR micro-spectrometer.

Computational Methodology. The first-principles calculations based on density functional theory (DFT) were performed using the plane-wave pseudopotential as implemented in the Vienna Ab-initio Simulation Package

(VASP).[2,3] The electron−core interactions were described with the frozen-core projector-augmented wave pseudopotentials.[4] The generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof (PBE) as the exchange correlation functional with cutoff energies of 520 eV was chosen in all of our calculations.[5] A reciprocal space sampling with a 6×6×6 and 8×8×6 k-points is set in the Brillouin zone for cubic and tetragonal phase. The total energy convergence criteria of 1.0×10^{-5} eV and the force on each atom converge to 0.01 eV Å^{-1} in optimizing the geometric structure. The vdW interaction is considered by using the DFT-D2 method of Grimme.[6] The DFT PBE method are used to obtain total energy and pressure trend. The Heyd-Scuseria-Ernzerhof (HSE06) method is used to get the bandgap values and electronic structure.[7] Pressure was modeled with a fixing volume and shape of the crystal while allowing all lattice constants and atomic positions to relax. The internal pressure values were calculated through the relation: $p=-\dfrac{\partial E}{\partial V}$, where E is the total energy and V is the cell volume of the crystal, respectively.

	1 atm	6.3 GPa
temperature/K	293(2)	293(2)
crystal system	cubic	tetragonal
space group	*Fm-3m*	*P*42
a / Å	10.6046	6.9765
b / Å	10.6046	6.9765
c / Å	10.6046	10.0451
$\alpha=\beta=\gamma$ /°	90	90
Volume/ Å^3	1192.58	488.91
θ range /°	5-21	5.2-20.9
Wavelength / Å	0.6199	0.6199
R_{wp} / %	1.26	1.52
R_p / %	0.69	1.01

Figure S1. Refinement lattice parameters and refinement statistics at ambient pressure and 6.3 GPa for $(NH_4)_2SnBr_6$ crystal.
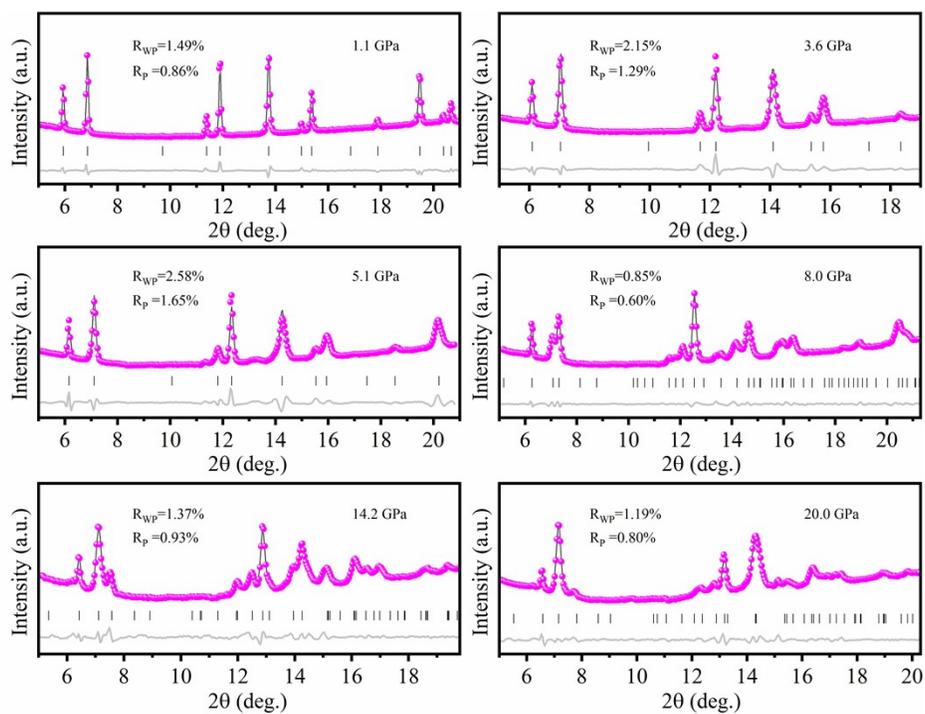
Figure S2. Rietveld refinements of $(NH_4)_2SnBr_6$ at different pressures.

	Pressure (GPa)	a (Å)	b (Å)	c (Å)	V (Å³)
	0	10.6046	10.6046	10.6046	1192.58
	0.4	10.4908	10.4908	10.4908	1154.57
	1.1	10.3641	10.3641	10.3641	1113.26
Cubic	1.8	10.2809	10.2809	10.2809	1086.65
(*Fm-3m*)	2.6	10.1947	10.1947	10.1947	1059.55
	3.6	10.1040	10.1040	10.1040	1031.52
	4.0	10.0864	10.0864	10.0864	1026.15
	5.1	9.9949	9.9949	9.9949	998.47
	6.3	6.9765	6.9765	10.0451	488.91
	6.6	6.9535	6.9535	10.0395	485.42
	8.0	6.8745	6.8745	10.0371	474.34
	10.7	6.7730	6.7730	10.0196	459.63
Tetragonal	12.1	6.7213	6.7213	10.0052	451.99
(*P42*)	14.2	6.6364	6.6364	9.9907	440.00
	16.4	6.5744	6.5744	9.9838	431.52
	17.8	6.5132	6.5132	9.9700	422.94
	20.0	6.4313	6.4313	9.9385	411.07

Figure S3. The lattice parameters and unit cell volume of $(NH_4)_2SnBr_6$ at different pressures.

	Pressure (GPa)	Sn-Br (Å)
	0	2.5981
	0.4	2.5703
Cubic	1.1	2.5392
	1.8	2.5188
(*Fm-3m*)	2.6	2.4977
	3.6	2.4755
	4.0	2.4712
	5.1	2.4488
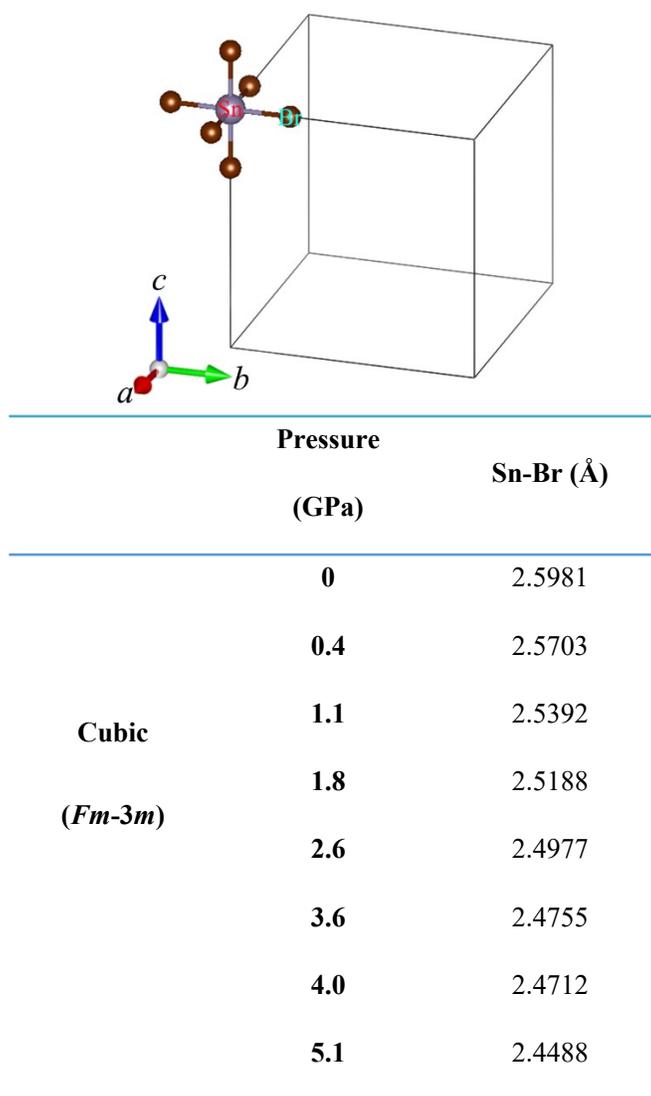
Figure S4. Refined Sn-Br bond distance of $(NH_4)_2SnBr_6$ before phase transition.
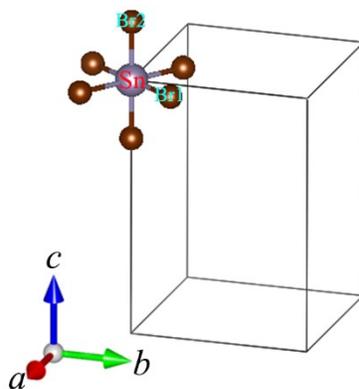
Pressure (GPa)	Sn-Br1 (Å)	Sn-Br2 (Å)
6.3	2.4427	2.3054
6.6	2.4346	2.3041
8.0	2.4070	2.3035
10.7	2.3715	2.2995
12.1	2.3533	2.2962
14.2	2.3236	2.2929
16.4	2.3019	2.2913
17.8	2.2805	2.2881
20.0	2.2518	2.2809

Tetragonal (P42)

Figure S5. Refined Sn-Br bond distance of $(NH_4)_2SnBr_6$ after phase transition.
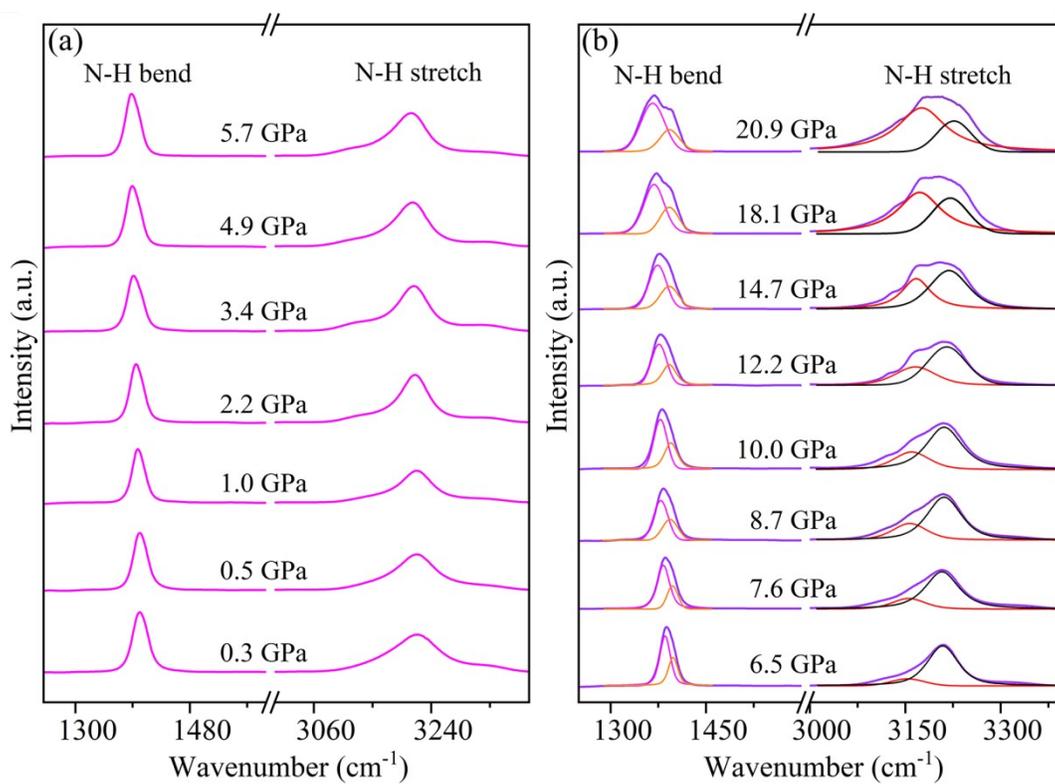
Figure S6. IR spectra of $(NH_4)_2SnBr_6$ at different pressures.
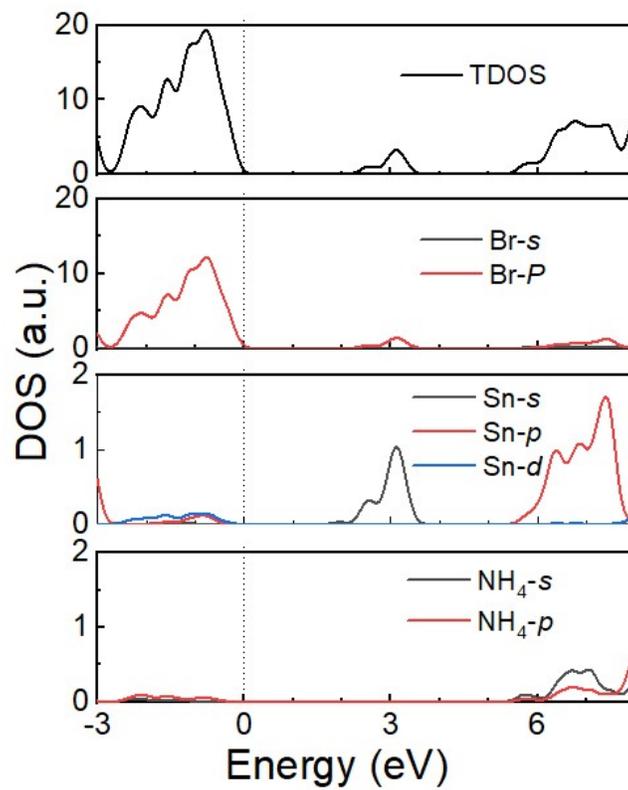
Figure S7. Calculated electronic band structures and projected density of states for

$(NH_4)_2SnBr_6$.

References

1. R. L. Armstrong, R. M. Morra, B. M. Powell and W. J. L. Buyers, *Can. J. Phys.*, 1983, **61**, 997-1002.
2. G. Kresse and J. Furthmüller, *Comp. Mater. Sci.*, 1996, **6**, 15-50.
3. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
4. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
6. S. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787-1799.
7. A. V. Krukau, O. A. Vydrov, A. F. Izmaylov and G. E. Scuseria, *J. Chem. Phys.*, 2006, **125**, 224106.