

Supplemental Information

Bandgap narrowing and piezochromism of doped two-dimensional hybrid perovskites nanocrystals under pressure

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Experimental Section

Materials

PEABr (99.5%, 5g) purchased from Xi'an Polymer Light Technology Corp. and used as received without further purification. PbBr₂(99.99%, 10g), MnBr₂ (95%, 5g), N, N-dimethyl methanamide (DMF, 99.8%), n-octylamine (99%), and Toluene were purchased from Sigma-Aldrich and used as received without further purification.

Typical synthesis of Mn²⁺ doped 2D (PEA)₂PbBr₄ nanocrystals (NCs).

Mn²⁺ doped (PEA)₂PbBr₄ NCs was synthesized according to a modified synthetic approach.¹ During the synthesis of (PEA)₂PbBr₄, 0.4 mmol of PEABr, 0.16 of mmol PbBr₂ and 0.04 mmol MnBr₂ were dissolved in a mixture of 2.5 mL of DMF and 8 μL of n-octylamine to form a perovskite precursor solution. Then, 30 μL of the perovskite precursor solution was quickly dropped into 15 mL of toluene under vigorous stirring. Finally, the Mn²⁺ doped (PEA)₂PbBr₄ NCs were obtained after centrifugation at 4,500 rpm for 5 min to remove the aggregated precipitates.

High pressure generation.

High-pressure were generated by a symmetric diamond anvil cell (DAC) with a culet size of 400 μm. Then we drilled a 150 μm-diameter hole in the center of T301 stainless steel gasket as the sample chamber, which was preindented to 45 μm. The sample and a small ruby ball were loaded into the gasket cavity. The standard ruby fluorescent technique was carried out to determine the actual pressure. Silicon oil (Dow

Corning Corporation, 10 cSt) was used as the pressure transmitting medium to provide the hydrostaticity.

PL and absorption spectra.

The in situ high-pressure PL and absorption spectra were collected with the help of an optical fiber spectrometer (Ocean Optics, QE65000). The pressure-dependent PL spectra were measured by a semiconductor laser with an excitation wavelength of 355 nm. We took the PL micrographs of the samples upon compression with a camera (Canon Eos 5D mark II) installed on a microscope (Ecclipse TI-U, Nikon). A deuterium-halogen light source was used for the absorption measurements during the whole compression.

ADXRD patterns.

In situ high-pressure angle-dispersive X-ray diffraction (ADXRD) patterns were measured at beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF). Portions of this work were performed at the 4W2 High Pressure Station in Beijing Synchrotron Radiation Facility (BSRF). The monochromatic wavelength of the synchrotron radiation was 0.6199 Å and we used CeO₂ as the standard sample for the calibration. The pattern of intensity versus diffraction angle 2θ was plotted based on the FIT2D program, which integrated and analyzed the 2D images collected. All the high-pressure experiments were conducted at room temperature.

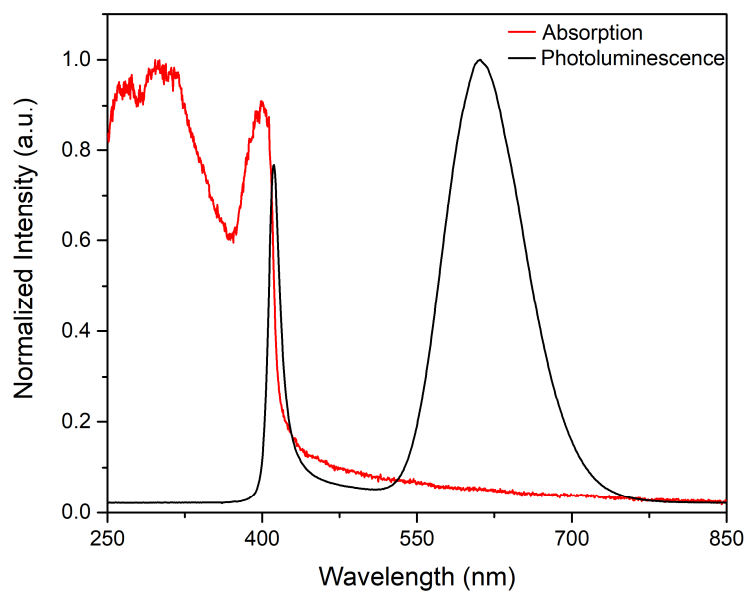


Figure S1. Absorption and PL spectral of Mn-doped (PEA)₂PbBr₄ NCs under ambient condition.

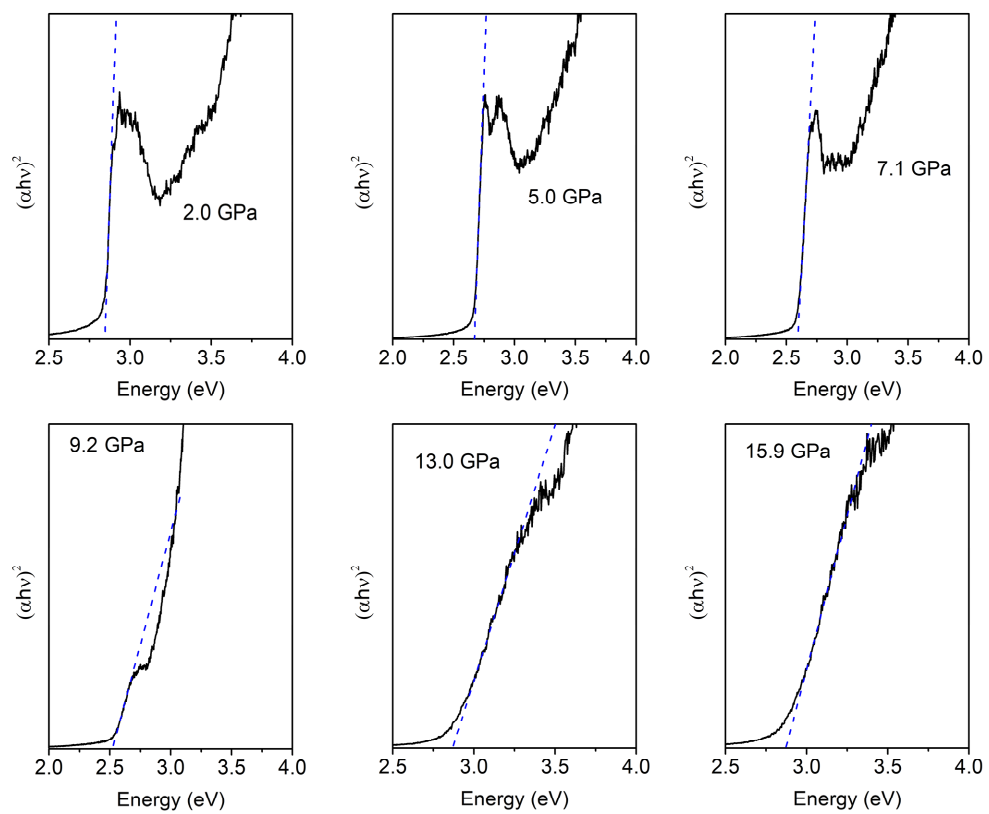


Figure S2. Tauc plot of Mn-doped $(\text{PEA})_2\text{PbBr}_4$ NCs at 2.0, 5.0, 7.1, 9.2, 13.0 and 15.9 GPa.

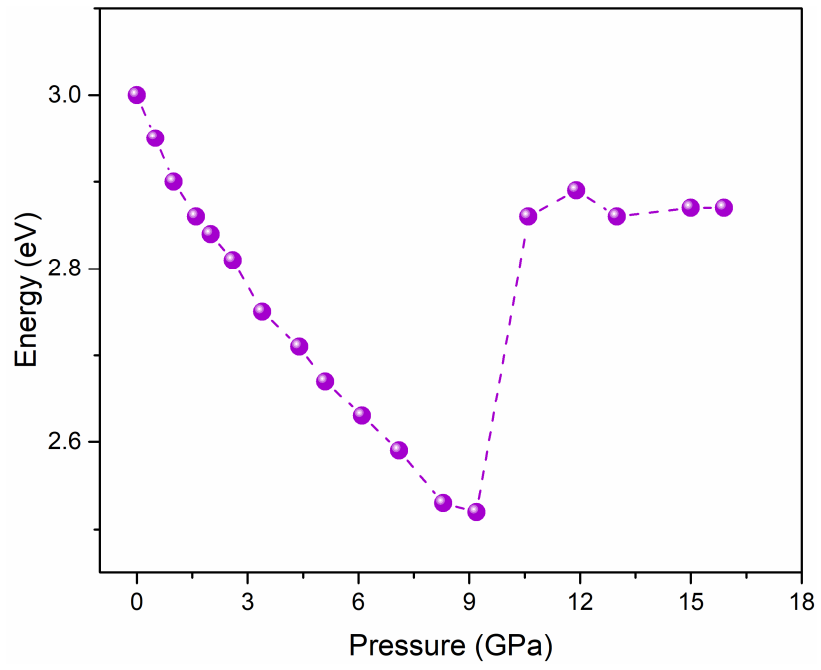


Figure S3. Pressure dependence of bandgap energy from 1 atm to 15.9 GPa.

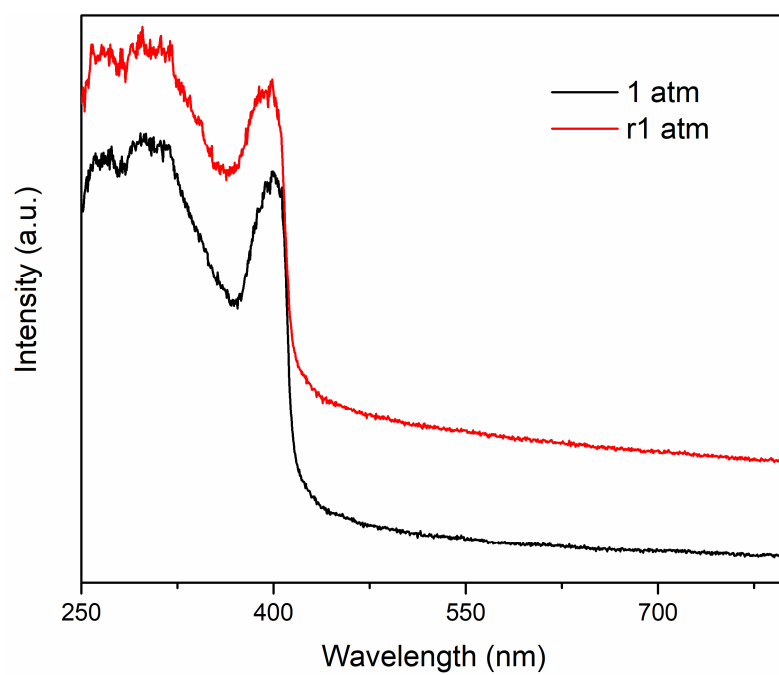


Figure S4. Contrast of absorption spectra between ambient condition and decompression.

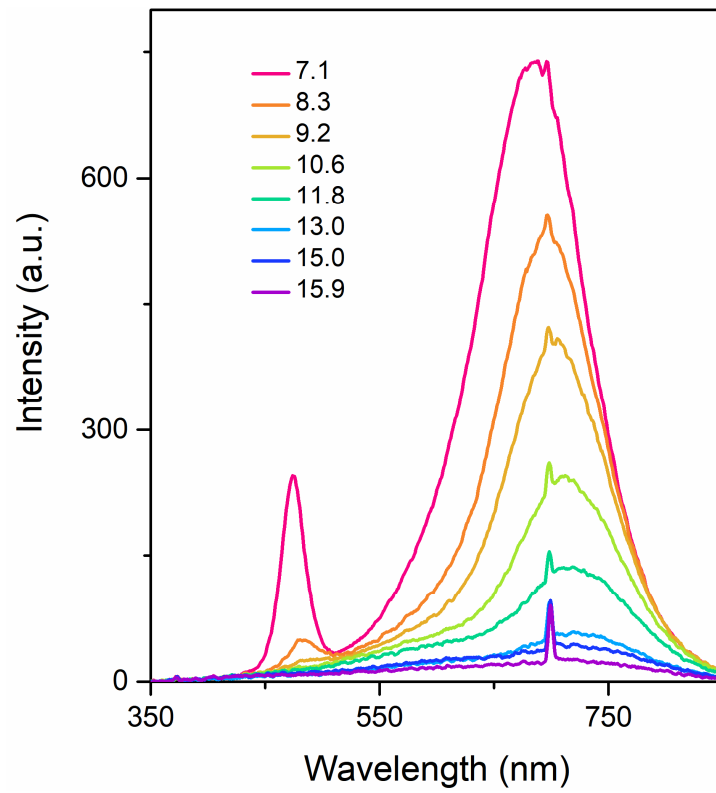


Figure S5. PL spectra of Mn-doped (PEA)₂PbBr₄ under high pressure. (Sharp peak near 700 nm was ruby peak).

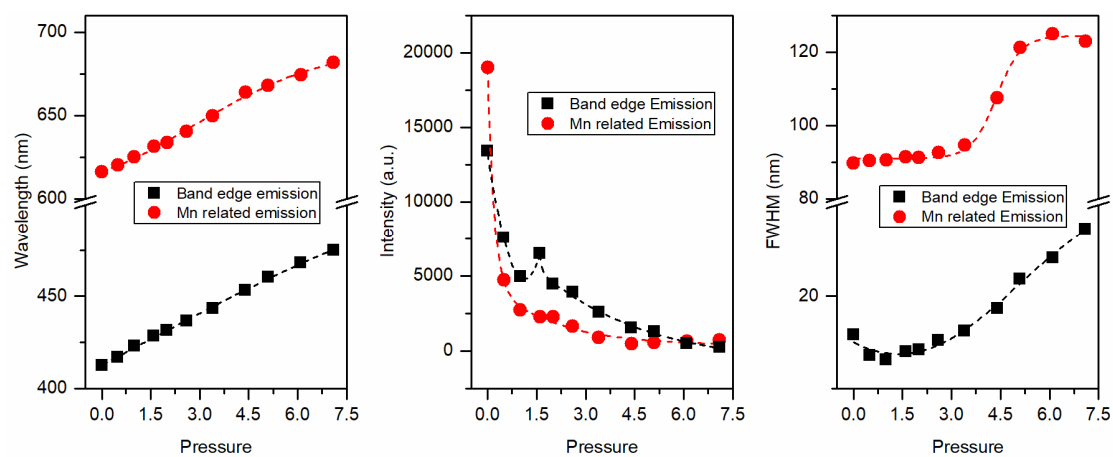


Figure S6. Emission locations, intensity and FWHM of Mn-doped (PEA)₂PbBr₄ NCs against pressures.

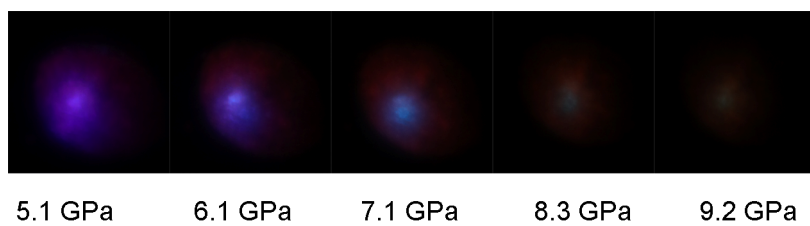


Figure S7. PL micrographs of Mn-doped (PEA)₂PbBr₄ NCs upon compression at selected pressures.

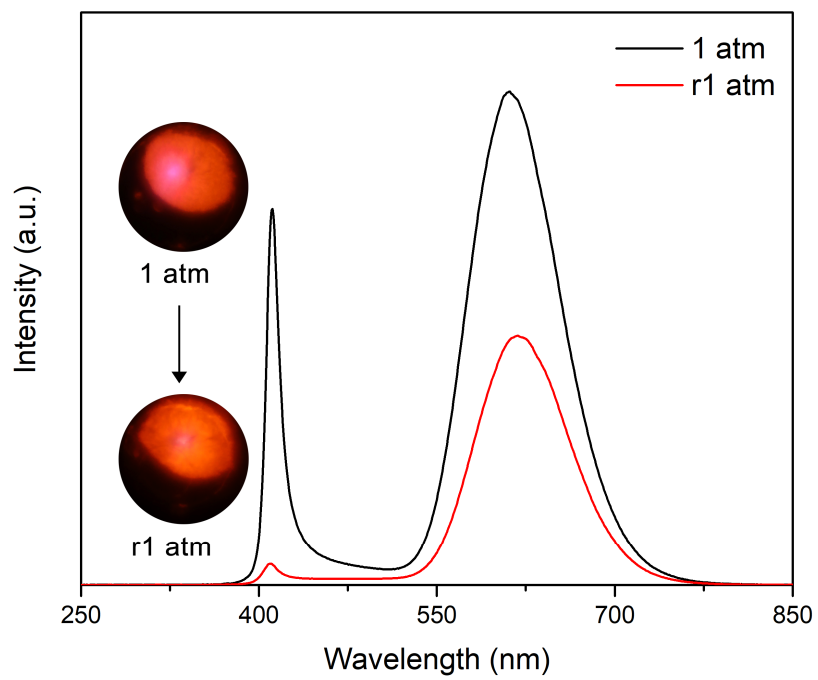


Figure S8. Contrast PL spectra between ambient condition and decompression.

Table S1. Lattice parameter changes under pressure.

Pressure (GPa)	a (Å)	b (Å)	c (Å)	V (Å³)
1 atm	32.7948	8.1174	8.0359	2139.23
0.5	32.7747	8.0835	7.801	2066.77
1.0	32.7736	8.03895	7.7665	2046.2
2.0	32.4124	8.0133	7.7093	2022.93
3.0	32.3504	7.9924	7.6922	1988.89
4.0	32.33	7.985	7.6843	1983.74
4.5	32.309	7.9316	7.6577	1962.38
5.1	32.308	7.9246	7.6082	1947.93
6.0	32.3062	7.9175	7.5984	1943.56
7.0	32.2249	7.8943	7.5734	1926.64
8.1	32.2209	7.8796	7.552	1917.38
9.1	32.189	7.8626	7.5137	1901.64

We also revealed the distortion of Mn–Br and Pb–Br octahedral within inorganic layer under pressure quantitatively (Figure S7 and Figure S8). The degree of octahedral distortions was determined using the following parameters^{2,3}:

$$\text{Distortion of bond length: } \Delta d = \frac{1}{6} \sum_{i=1}^6 [(d_i - d_0)/d_0]^2$$

$$\text{Variance in octahedral angle: } \delta^2 = \frac{1}{11} \sum_{i=1}^{12} (\theta_i - 90)^2$$

The results show that the distortion of octahedron of Pb-Br and Mn-Br were the main reason for the deformation of the inorganic layer under higher pressure.

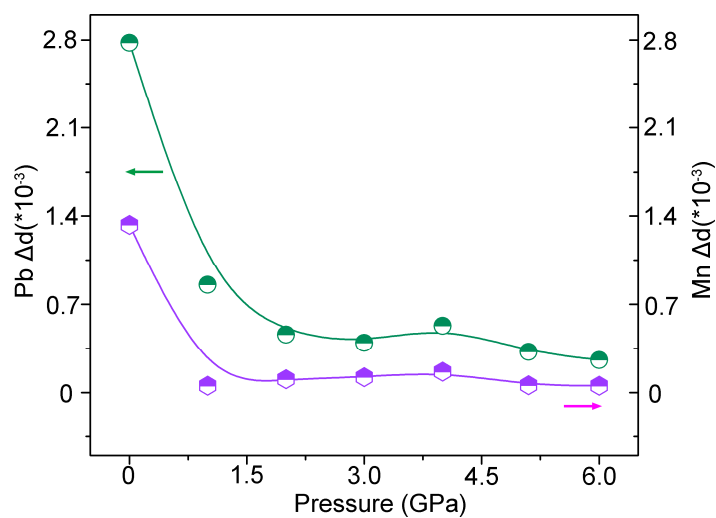


Figure S9. Δd values (distortion in bond length) of Pb and Mn octahedra within Mn-doped (PEA)₂PbBr₄ under pressure.

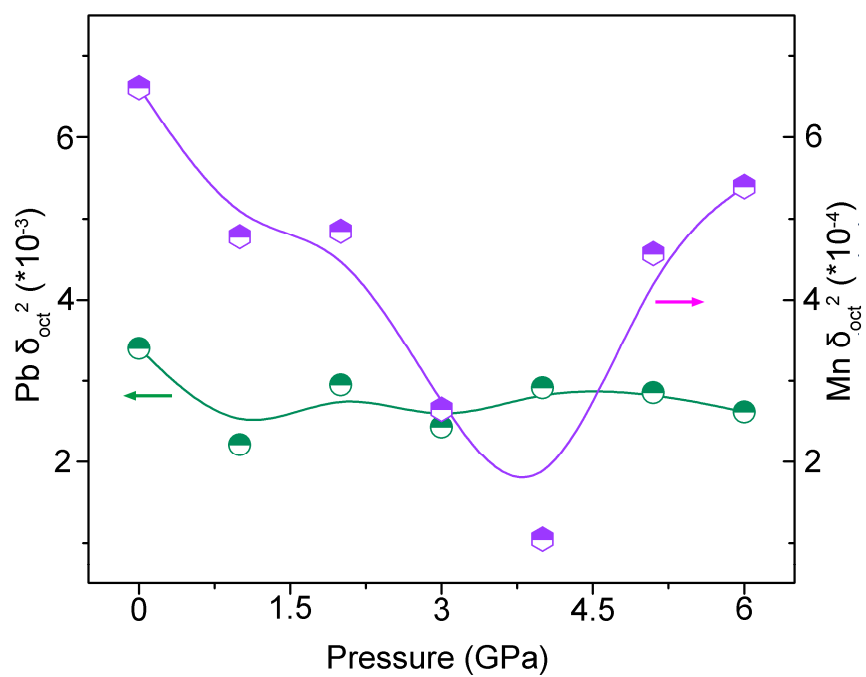


Figure S10. δ^2 values (variance in octahedral angle) of Pb octahedra within Mn-doped $(\text{PEA})_2\text{PbBr}_4$ under pressure.

Reference

1. X. Gao, X. Shen, D. Xue, X. Li, P. Lu, M. Lu, C. Li, W. W. Yu and X. Bai, *Mater. Chem. Front.*, 2021, **5**, 937-943.
2. K. ROBINSON, G. V. Gibbs, P. H. RIBBE, *Science*, 1971, **172**, 567-570.
3. Y. Peng, Y. Yao, L. Li, Z. Wu, S. Wang and J. Luo, *J. Mater. Chem. C*, 2018, **6**, 6033-6037.