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Supplementary Information

White-Light Emission Triggered by Pseudo Jahn-Teller Distortion at the Pressure-Induced Phase Transition in Cs_4PbBr_6

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Table S1. Selected crystallographic and refinement data for the structures of Cs_4PbBr_6.

Crystal formula	Cs_4PbBr_6				
Color	colorless				
Pressure (GPa)	0.0001	1.25	2.09	2.9	3.84
Crystal system Space group Z	Trigonal $R\bar{3}c$ 6			Orthorhombic *Cmce* 4	Tetragonal *P*4/*mnc* 2
Crystal size (mm)	0.2 × 0.2 × 0.2	0.11 × 0.07 × 0.04	0.11 × 0.07 × 0.04	0.11 × 0.07 × 0.04	0.11 × 0.11 × 0.05
a (Å) *b* (Å) *c* (Å)	13.6949(2) 13.6949(2) 17.3030(3)	13.2866(11) 13.2866(11) 16.921(2)	13.1280(13) 13.1280(13) 16.780(3)	13.202(4) 12.76(4) 9.4879(18)	8.8515(12) 8.8515(12) 9.3867(13)
Volume ($Å^3$)	2810.43(9)	2587.0(5)	2504.5(6)	1598(5)	735.4(2)
ρ (g cm^{-3})	4.319	4.692	4.846	5.062	5.502
μ (mm^{-1})	29.423	31.965	33.017	34.488	37.479
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	7629, 897, 836	4172, 407, 309	3984, 393, 299	3064, 294, 156	3014, 272, 211
R_{int}	0.032	0.052	0.066	0.204	0.062
R_1 [$I > 2\sigma(I)$], R_1(*all*)	0.022, 0.024	0.036, 0.060	0.046, 0.069	0.097, 0.159	0.044, 0.060
wR_2 [$I > 2\sigma(I)$], wR_2 (*all*)	0.057, 0.058	0.060, 0.069	0.088, 0.099	0.257, 0.306	0.101, 0.109
S	1.104	1.165	1.112	1.090	1.082

Table S2. Comparison of the unit cell parameters of the colourless and yellow Cs_4PbBr_6 at atmospheric pressure.

	Colorless Cs_4PbBr_6	Yellow Cs_4PbBr_6
Crystal system Space group Z	Trigonal $R\bar{3}c$ 6	
Crystal size (mm)	0.2 × 0.2 × 0.2	0.10 × 0.07 × 0.07
a (Å)	13.6949(2)	13.6776(6)
b (Å)	13.6949(2)	13.6776(6)
c (Å)	17.3030(3)	17.2585(8)
Volume (Å^3)	2810.43(9)	2796.1(3)

The thermal stability of Cs_4PbBr_6 was verified by the thermogravimetric analysis (TGA) method using a TGA Q50 apparatus (TA Instruments) and by differential scanning calorimetry (DSC) with a Q2000 calorimeter (TA Instruments). TGA was performed on powdered crystals heated with a rate of 10 K min^{-1} in a stream of gaseous nitrogen. TGA has shown that Cs_4PbBr_6 is thermally stable up to about 800 K, where the onset of a decay was detected (Fig. S1a). The DSC cooling/heating runs were measured with the same rate of temperature changes in the range 100–500 K. Under ambient pressure, the trigonal phase of the crystal is preserved in a studied temperature range (Fig. S1b).

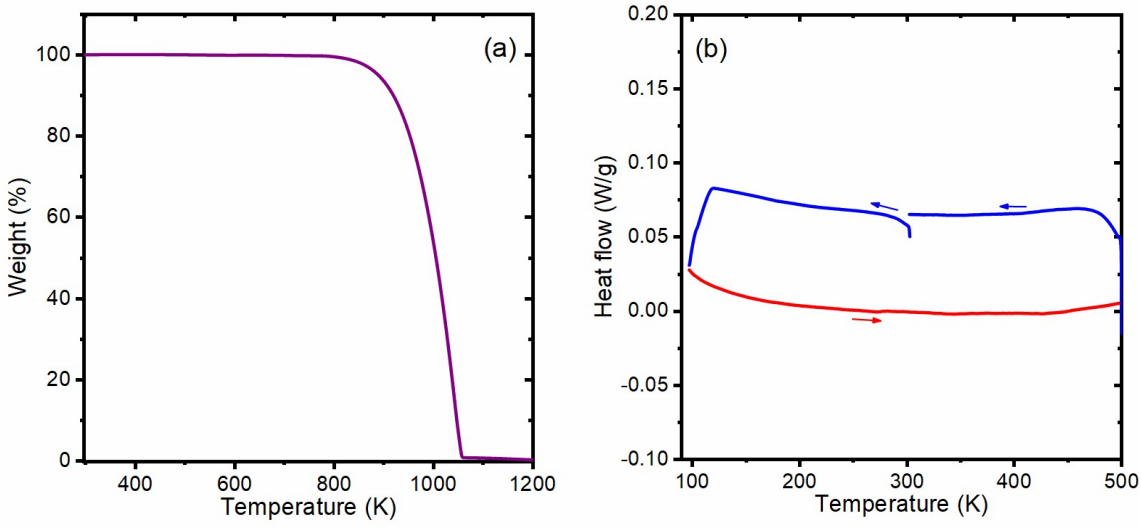

Fig. S1 TGA curve (a), and DSC runs (b) measured for powdered Cs_4PbBr_6 at a temperature rare of 10 K/min.

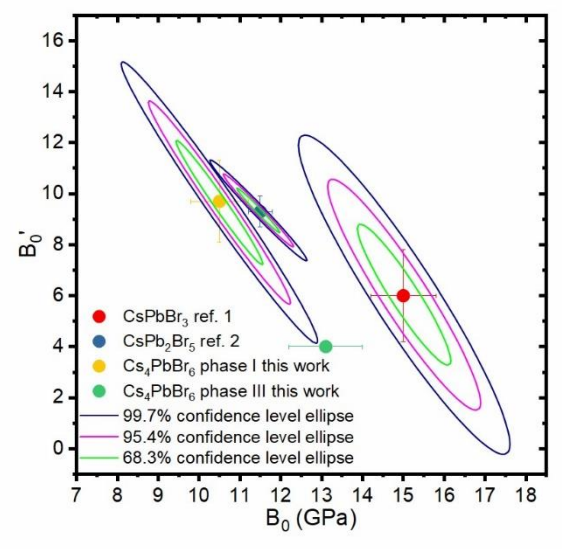

Fig. S2 Values of B_0' plotted versus B_0 for Cs_4PbBr_6, $CsPb_2Br_5$ and $CsPbBr_3$. The different confidence level ellipses are shown. For Cs_4PbBr_6 in phase III the second-order Birch–Murnaghan equation of state was used.

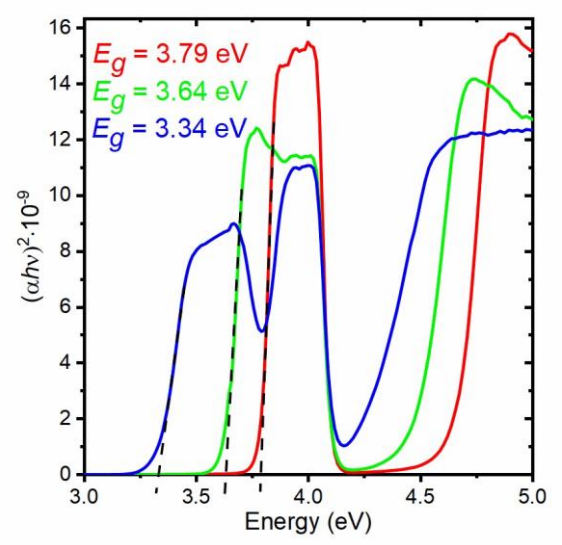

Fig. S3 Tauc plots and energy gaps determined from the absorption spectra measured for the 1.7 μm thick pure Cs_4PbBr_6 single-crystal plate.

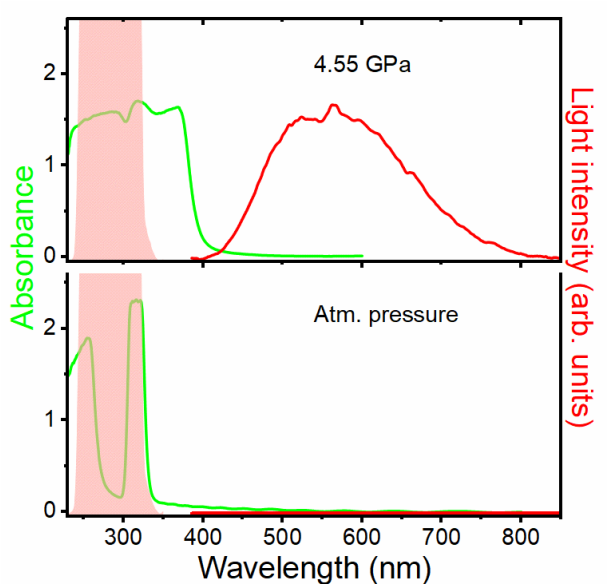

Fig. S4 Comparison of the absorption and emission spectra of pure Cs_4PbBr_6 at atmospheric pressure and 4.55 GPa. Light red colour area represents the excitation spectrum.

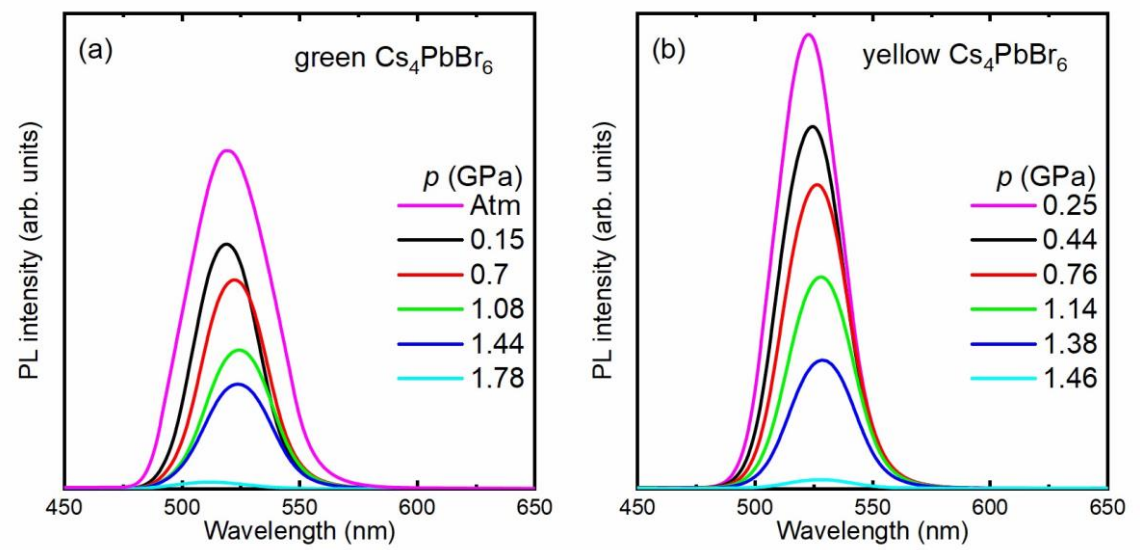

Fig. S5 Pressure dependence of the PL spectra of green (a) and yellow (b) Cs_4PbBr_6.

In Fig. S5, we show the fluorescence spectra of compressed green and yellow Cs_4PbBr_6 samples. With increasing pressure, the PL signal of both forms gradually redshifts and decreases, and finally suddenly disappears around 1.78 and 1.46 GPa, respectively, for the green and yellow crystals. This pressure where PL vanishes corresponds well to the phase transition in $CsPbBr_3$ associated

with PL quenching. This indicates that the green emission of Cs_4PbBr_6 originates in $CsPbBr_3$ inclusions.

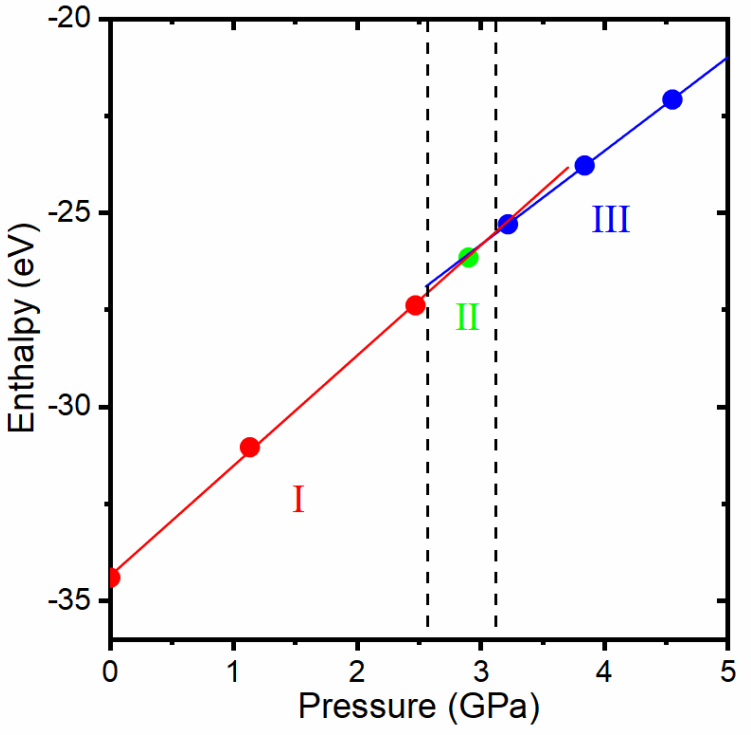

Fig. S6. Free enthalpy calculated for one formula unit as a function of pressure across the phases I, II and III. The solid lines correspond to the best linear fits of the calculated points in phase I (red) and III (blue).

References

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2. V. Drushliak and M. Szafrański, *Inorg Chem*, 2022, **61**, 14389–14396.