Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Insight into the structure-property relationship of two-dimensional lead-free halide perovskite $Cs_3Bi_2Br_9$ nanocrystals under pressure

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Experimental section

Chemicals: All reagents were used as received without further purifications: CsBr (cesium bromide, 99.9%, Alfa Aesar), $BiBr_3$ (bismuth tribromide, 99%, Alfa Aesar), DMSO (analytical grade, Sinopharm Chemical Reagent Co., Ltd, China), oleic acid (OA, technical grade 90%, Sigma), OAm (Oleylamine, technical grade 70%, Sigma), ethanol anhydrous (analytical grade, Sinopharm Chemical Reagent Co., Ltd, China).

Synthesis of $Cs_3Bi_2Br_9$ nanocrystals: The $Cs_3Bi_2Br_9$ nanocrystals was synthesized following a reported method.[1] 42.6 mg (0.2 mmol) CsBr and 60.1mg (0.134 mmol) $BiBr_3$ as well as 33 μL OAm were dissolved in 3 mL DMSO to form a clear precursor solution. 0.5 mL precursor solution was slowly dropped into a mixture of 5 mL ethanol and 0.5 mL OA with vigorous stirring at 80 ℃. After vigorous stirring for 10 min. The solid powders of $Cs_3Bi_2Br_9$ nanocrystals were obtained by gradient centrifugation at 5000 rpm and then 10 000 rpm both for 10 min.

Characterization: The $Cs_3Bi_2Br_9$ samples were characterized by transmission electron microscopy (TEM) and high-resolution TEM(HRTEM) images were obtained on a JEM-2200FS equipped with an emission gun operated at 200 kV.

High-Pressure Generation. High-pressure experiments were carried out with a symmetric diamond anvil cell (DAC), and the culets size of the diamond anvils was 400 μm. The sample was loaded into a 130 μm-diameter chamber of the T301 stainless steel gasket pre-indented to a thickness of 40 μm. A small ruby ball was placed in the sample compartment for in situ pressure calibration. The pressure

calibration was determined utilizing the standard ruby fluorescent technique.[2] In high-pressure experiments, silicon oil was utilized as the pressure transmitting medium (PTM) for in situ high-pressure optical absorption and XRD experiments, while the argon was employed as PTM for Raman measurements. These PTM did not have any detectable effect on the behavior of $Cs_3Bi_2Br_9$ under pressure. All of the measurements were performed at room temperature.

Optical Measurements. In situ absorption photographs of the samples were obtained using a camera (Canon Eos 5Dmark II) equipped on a microscope (Ecilipse TI-U, Nikon). The camera can record the photographs under the same conditions including exposure time and intensity. In situ high-pressure optical absorption spectra measurements were carried out between 250 and 1000 nm using a deuterium-halogen light source and recorded with an optical fiber spectrometer (Ocean Optics, QE65000) with the data-collection time of 8 s. Each new acquisition was carried out several minutes later after elevation of the pressure, aiming to account for any kinetic dependence during measurements. In situ high pressure angle-dispersive X-ray diffraction (ADXRD) patterns were obtained with a wavelength of 0.6199 Å at beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF), China. CeO_2 was used as the standard sample to do the calibration. In situ high-pressure Raman spectra were recorded using a spectrometer equipped with liquid nitrogen cooled CCD (iHR 550, Symphony II, Horiba Jobin Yvon). A 785 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}. All the high-pressure experiments were performed at room

temperature.

Refinements. Refinements of XRD patterns were accomplished using the Reflex module combined in Materials Studio 8.0 program. All refinements were performed using four refinement cycles fine convergence criteria. First, the pattern was indexed by means of the peak picking option of the software package. Then, a Pawley profile-fitting procedure was applied to refine cell parameters and search space group. The refinements were performed to obtain the crystal structural parameters. The quality of the fitting between the experimental and calculated profile is assessed by the various R parameters like Rp (profile factor) and Rwp (weighted profile factor).[3]

$$R_P = \left\{ \frac{\sum_i \left| I_i^{obs} - I_i^{cal} \right|}{\sum_i I_i^{obl}} \right\}$$

$$R_{\mathrm{wp}} = \left\{ \frac{\sum_i w_i \left(I_i^{obs} - I_i^{cal} \right)^2}{\sum_i w_i \left(I_i^{obs} \right)^2} \right\}^{\frac{1}{2}}$$

Where I_i^{obs} , I_i^{cal} and "i" indicate the experimental, calculated and total number of points respectively. And the " w_i " is the reciprocal of the variance of observation I_i^{obs}.

First-principles calculations. Calculations were performed within the framework of density functional theory (DFT) by using plane-wave pseudopotential methods. Geometry optimization was calculated using the plane-wave pseudopotential method with the generalized gradient approximation (GGA) based on density functional theory with CASTEP package. The plane-wave cutoff energy of 350 eV and

Monkhorst-Pack grid for the electronic Brillouin zone integration was 5×5×3. The self-consistent field (SCF) tolerance was set as 1.0×10-6 eV/atom. The convergence thresholds between optimization cycles for maximum force, maximum stress and maximum displacement are set as 0.03 eV/Å, 0.05 GPa, and 1.0 ×10-3 Å, respectively. The partial density of states (DOSs) were collected by adopting the identical pseudopotential of the GGA that is implemented in the Vienna ab initio simulation package (VASP).

References

(1) M. Leng, Y. Yang, K. Zeng, Z. Chen, Z. Tan, S. Li, J. Li, B. Xu, D. Li, M. P. Hautzinger, Y. Fu, T. Zhai, L. Xu, G. Niu, S. Jin and J. Tang, *Adv. Funct. Mater.,* 2018, **28**, 1704446.

(2) (2) H. K. Mao, J. Xu, P. M. Bell, J. *Geophys. Res.* 1986, **91**, 4673.

(3) E. Jansen, W. Schafer, G. Will, J. *Appl. Crystallogr.* 1994, **27**, 492.

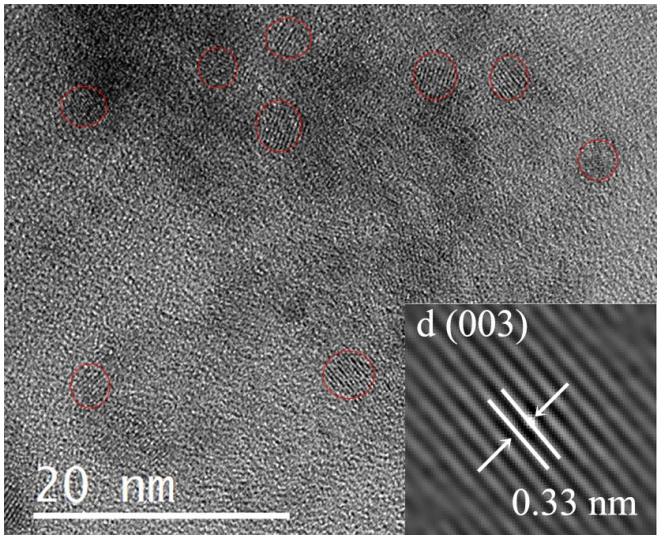

Fig. S1 TEM and HRTEM images of $Cs_3Bi_2Br_9$ NCs.

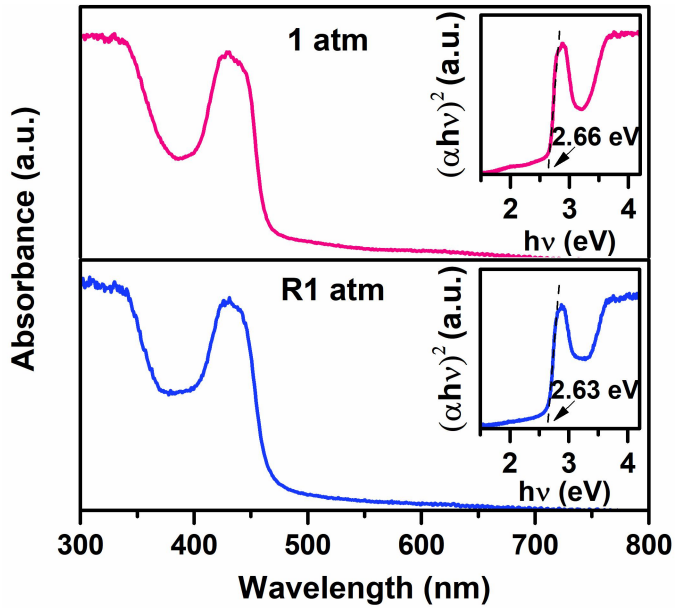

Fig. S2 UV/Vis absorption spectra of the $Cs_3Bi_2Br_9$ NCs at ambient conditions and decompression, respectively.

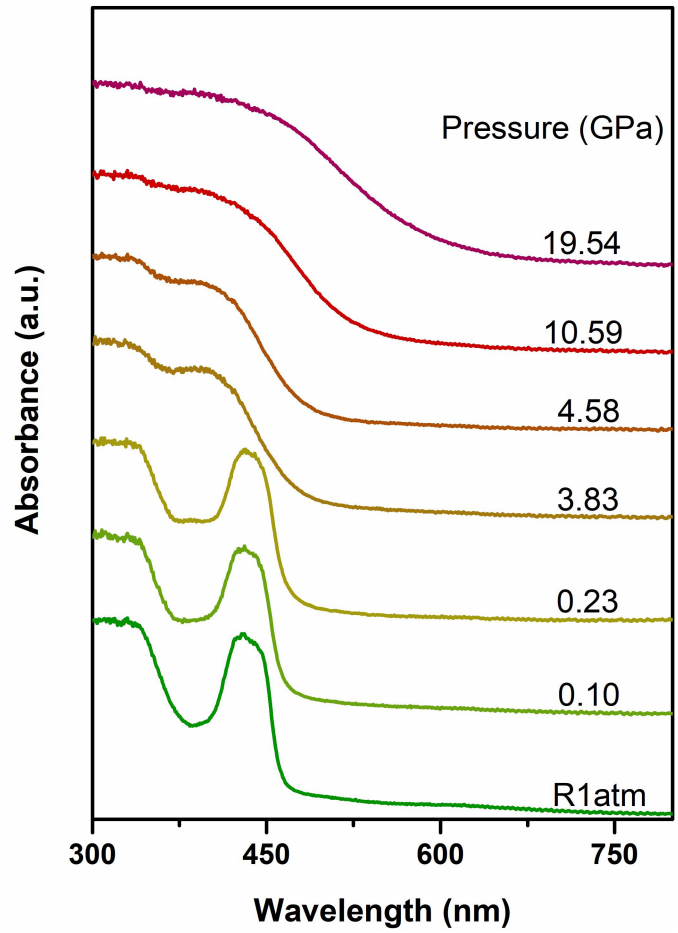

Fig. S3 In situ UV/Vis absorption spectra of $Cs_3Bi_2Br_9$ NCs upon the release of external pressure to the ambient environment.

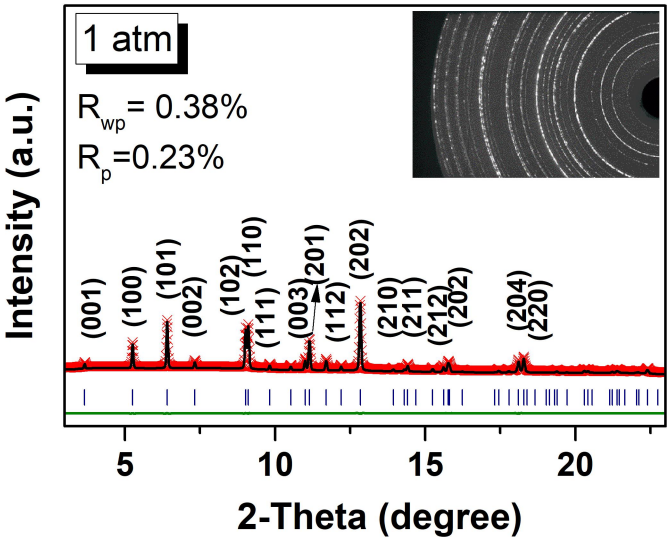

Fig. S4 Refinements of $Cs_3Bi_2Br_9$ NCs at ambient conditions.

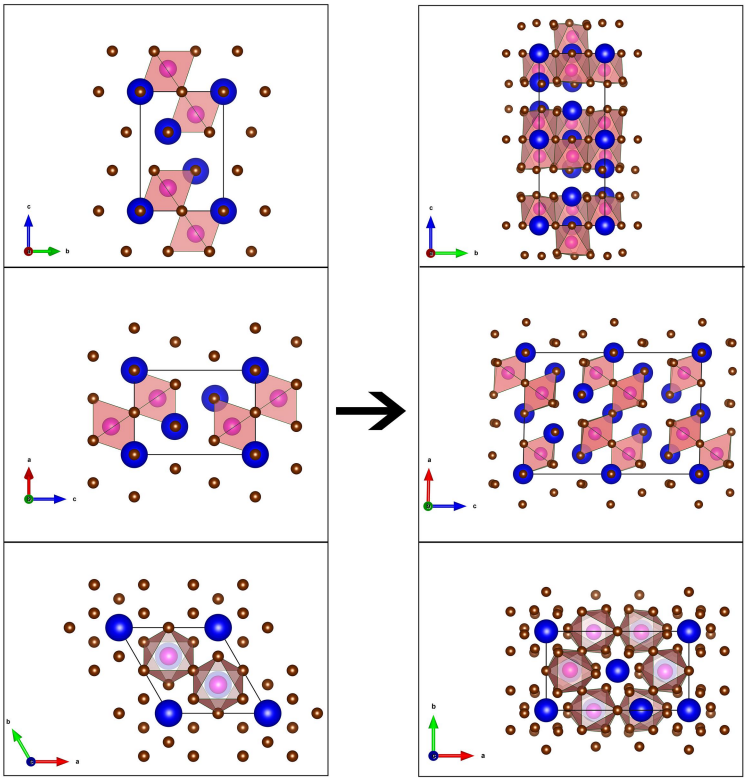

Fig. S5 Crystal structure unit cell viewed in the bc, ac and ab plane of $Cs_3Bi_2Br_9$ NCs. The left shows the trigonal crystal structure and the right shows the monoclinic structure. Cs, Bi and Br atoms are shown as blue, pink and brown spheres, respectively; Bi coordination polyhedra are shown in light pink.

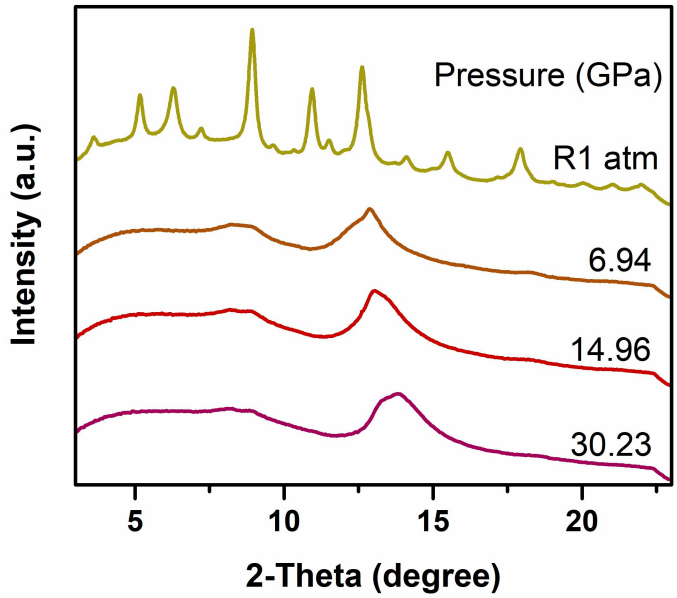

Fig. S6 Selected ADXRD patterns of $Cs_3Bi_2Br_9$ NCs upon decompression.

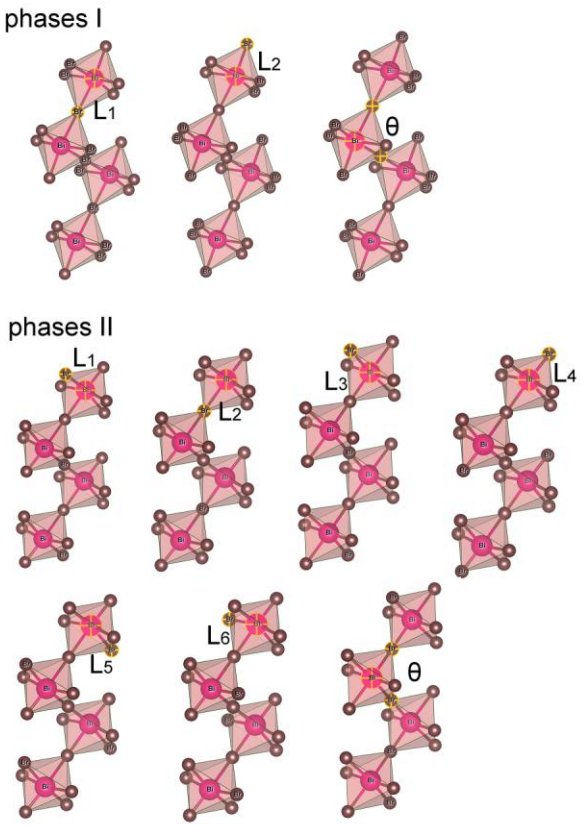

Fig. S7 Inorganic framework of $[Bi_2Br_9]^{3-}$ of phase I and phase II.

Table S1. Raman peaks of $Cs_3Bi_2Br_9$ NCs.

Raman modes	Frequency(cm^{-1})	Symmetry	Assign
ν_1	189.2	A_{1g}	ν_a $BiBr_3$
ν_2	163.3	E_g	ν_a $BiBr_3$
ν_3	89	A_g	ν_s $BrBi_2$
ν_4	74		
ν_5	61.5		

Table S2. Extracted pressure coefficient (χ) and frequency difference (Δυ) for $Cs_3Bi_2Br_9$ NCs.

Raman modes	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
χ (cm^{-1}/GPa)	6.04	5.60	3.83	4.68	6.24	4.05	4.88
Δυ (cm^{-1})	33.99	51.25	15.00	26.45	44.84	16.25	25.66

Table S3. Refinement cell parameters and refinement statistics at ambient pressure and 10.1 GPa for $Cs_3Bi_2Br_9$ NCs.

	1 atm	10.1 GPa
Temperature (K)	293 (3) K	293 (3) K
Crystal system	Trigonal	monoclinie
Space group	*P*3*m*1	C 2/c
a (Å)	7.957(5)	12.972(5)
b (Å)	7.957(5)	7.176(3)
c (Å)	9.836(2)	18.786(3)
α (°)	90	90
β (°)	90	88.84
γ (°)	120	90
Volume ($Å^3$)	539.40	1692.48
Z	1	4
range (°)	3-25	3-25
Wavelength (Å)	0.6199	0.6199
Rwp (%)	0.38	1.31
Rp (%)	0.23	0.84

Table S4. Grüneisen parameter (γ) of the corresponding Raman modes for different phases of $Cs_3Bi_2Br_9$ NCs under high pressure.

Raman modes	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7
Phase I	1.79	1.38	0.78	0.52	0.60	n/a	n/a
Phase II	n/a	1.38	n/a	n/a	n/a	10.20	10.94

n/a means “not applicable”.