Supporting Information

In-depth Understanding the Temperature-Dependent Reversible Phase Transition in CsPbI_{3-x}Br_x Perovskites and its Associated Photophysical Properties

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This Supplementary material includes:

- S1 Computational Methods
- S3 Supplementary Figures S1 to S19
- S2 Supplementary Table S1-S3

References

1. Experimental Section

1.1 Materials

PbBr₂ (99.999%) and PbI₂ (99.99%) are purchased from 3A chemical. CsI (99.999%) and CsBr (99.999%) are purchased from Aladdin.

1.2 CsPbI_{3-x}Br_x ($0 \le x \le 3$) perovskite growth

i. Growth of CsPbI₃ Perovskite Crystal

10 mmol CsI and PbI₂ powder were fully mixed after second grinding and transferred into a quartz tube. A plug was welded under 10^{-4} bar vacuum conditions to seal the mixed powder in the quartz tube. Then, the sealed powder was pre-fusion with a flame gun to further mix. After that, the sealed quartz tube was transformed into a programmed temperature control furnace and grown by the Bridgman method.

ii. Growth of CsPbI₂Br Perovskite Crystal

The CsPbI₂Br Perovskite was grown by mixing 10 mmol CsBr and PbI₂ powder and all the other procedures are similar to the growth of CsPbI₃ Perovskite crystal.

iii. Growth of CsPbI_{1.5}Br_{1.5} Perovskite Crystal

The CsPbI_{1.5}Br_{1.5} Perovskite was grown by mixing 5 mmol CsBr, CsI, PbBr₂ and PbI₂ powder and all the other procedures are similar to the growth of CsPbI₃ Perovskite crystal.

iv. Growth of CsPbIBr₂ Perovskite Crystal

The CsPbIBr₂ Perovskite was grown by mixing 10 mmol CsI and PbBr₂ powder and all the other procedures are similar to the growth of CsPbI₃ Perovskite crystal.

v. Growth of CsPbBr₃ Perovskite Crystal

The CsPbBr₃ Perovskite was grown by mixing 10 mmol CsBr and PbBr₂ powder and all the other procedures are similar to the growth of CsPbI₃ Perovskite crystal.

1.3 Characterizations

The determination of unit-cell parameters and data collections were performed on XtaLAB Synergy-i using the scan technique with Mo K α radiation ($\lambda = 0.71073$ Å). The single crystal structure was resolved and refined by SHELXT and OLEX2. ^{1, 2} The perovskite crystal was characterized by Bruker D8 Advance X-ray diffractometer (XRD) with Cu K α radiation at 40 kV and 40 mA. The temperature control unit guarantees the XRD measurement under a steady nitrogen environment with controlled temperature. Differential Scanning Calorimetry (DSC) and Thermogravimetric analysis (TGA) were performed using a TA Instruments SDT Q600 under a nitrogen atmosphere. UV-vis spectra were measured by placing the thin films in a double-beam spectrophotometer equipped with an integrating sphere (UV-3600PLUS, Shimadzu). The Hall effect was characterized by Quantum Design PPMS-9.

2. Computational Methods

2.1 Formation energy of $Cs_4PbI_xBr_{6-x}$ ($0 \le x \le 6$) cluster

The constructed $Cs_4PbI_xBr_{6-x}$ ($0 \le x \le 6$) cluster models were relaxed by Beijing Density Functional (BDF) program package with density functional theory (DFT) method, B3LYP functional and Lanl2dz basis set ³⁻⁶. Here with Cs_4PbI_6 and one Br- ion doping Cs_4PbI_5Br as an example, the formation energy of Cs_4PbBrI_5Br cluster E(FE) is calculated with the formula:

$$E(FE) = E(Cs_4PbI_5Br) - E(Cs_4PbI_6) - E(Br) + E(I)... \quad (1)$$

where $E(Cs_4PbI_5Br)$, $E(Cs_4PbI_6)$, E(Br) and E(I) are the single point energy of Cs_4PbI_5Br and Cs_4PbI_6 cluster, and single point energy of Br and I ions, respectively. For every step of Br-replacing I- ion, all the possible structures of $Cs_4PbI_xBr_{6-x}$ ($0 \le x \le 6$) cluster were constructed and the corresponding formation energy was calculated.

2.2 Effective mass and exciton binding energy

The Nanodcal, a state-of-the-art nonequilibrium quantum transport calculation package, was employed to calculate effective mass. The Nanodcal uses the mixture of the nonequilibrium Green's function (NEGF) theory and DFT as the theoretical framework. The linear combination of atomic orbitals (LCAO) method was chosen to implement the calculation, and the Perdew-Burke-Ernzerhof of generalized gradient approximation (GGA-PBE96) exchange-correlation functional was selected to define the exchange-correlation potential. The cutoff energy was 80 Hartree and the self-consistent calculations did not reach convergence until the Hamiltonian and charge density matrix differences were less than 10⁻⁵ eV and 10⁻⁵, respectively. The spin condition was not into account. The exciton binding energy was calculated based on the calculated effective mass with the weak Mott-Wannier model, as elucidated in the main text.

Electron localization function (ELF): The ELF calculation in our study is used to visualize the covalency of Pb-X (X = Br and I) bond and is defined as: 7

$$ELF = \left[1 + \left(\frac{D}{D_h}\right)^2\right]^{-1} \tag{2}$$

where

$$D = \frac{1}{2} \sum_{i} |\nabla \phi_i|^2 - \frac{1 |\nabla \rho|^2}{8 \rho}$$
(3)

and

$$D_h = \frac{3}{10} (3\pi^2)^{\frac{5}{3}} \rho^{\frac{5}{3}}$$
(4)

here ρ is the electron density and ϕ_i are the Kohn-Sham functions.

2.3 Noncovalent interactions (NCI):

Reduced density gradient (RDG) is a dimensionless parameter used to describe the nonuniformity of electrons in DFT method, and is defined as: ⁸

$$s = \frac{1}{2(3\pi^2)^{1/3} \rho^{4/3}}$$
(5)

here ρ is electric charge density. Based on the RDG strategy, NCI analysis could be used to describe interatomic or intermolecular non-bonded interactions. The First-principles computing software Quantum ESPRESSO 7.1 was employed to implement the DFT calculation. The Troullier-Martines norm-conserving pseudopotential was used to approximate the potential field produced by the atomic cores. The RDG grid point was extracted from the real space charge density calculated after self-consistent iteration. The convergence threshold is 1×10^{-6} with kinetic energy cutoff for wavefunctions of 50 Ry and kinetic energy cutoff for charge density of 300 Ry.

The RDG scattering plot is based on the concept of the RDG, which is a local property of the electron density distribution. In the RDG scattering plot, the RDG is plotted along the x-axis, while the Laplacian of the electron density is plotted along the y-axis. The plot is divided into different regions that correspond to different types of chemical bonding, such as covalent bonds, noncovalent interactions, and van der Waals interactions. Each region is characterized by specific values and patterns in the plot. The RDG scattering plot provides valuable insights into the nature and strength of chemical bonding, as well as the presence of weak interactions in a molecular or solid system.

2.4 The ab initio Boltzmann-transport formalism

The election mobility tensor reads: 9

$$\mu_{e,\alpha\beta} = -\frac{e}{n_e \Omega} \sum_{n \in CB} \int \frac{dK \,\partial f_{nK}}{\Omega_{BZ} \partial \varepsilon_{nK}} \nu_{nK,\alpha} \nu_{nK,\beta} \tau_{nK}$$
(6)

where n_e is the electron density and e is the electron charge; Ω_{BZ} and Ω are the first Brillouin zone and the volume of the crystalline unit cell and, respectively. The sum consists of the conduction bands (CB) with energy ε_{nK} , wavevector k and band index n. $\nu_{nK,\alpha}$ is the electron band velocity along long the Cartesian direction α and f_{nK} is the Fermi-Dirac function. What's more, the relaxation time τ_{nK} , associated with phonon, is defined as:

$$\frac{1}{\tau_{nK}} = \frac{2\pi}{\hbar} \sum_{m\nu\sigma} \int \frac{dq}{\Omega_{BZ}} |g_{mn\nu}(k,q)|^2 [\frac{1+\sigma}{2} - \sigma f_{mk+q} + n_{q\nu}] \delta(\varepsilon_{nk} - \varepsilon_{mk+q} - \sigma \hbar \omega_{q\nu})$$
(7)

here $g_{mnv}(k,q)$ is the matrix element representing the scattering of an excited electron via a phonon of branch v, frequency ω_{qv} , and wavevector q. n_{qv} is the Bose-Einstein occupation of this phonon. utions. The hole mobility is obtained analogously by restricting the summation in equation 6 over the valence bands.



25 °C; R.H.= 30%

Figure. S1. Fresh CsPbI_{3-x}Br_x perovskite prepared with Bridgman method (first line). Corresponding CsPbI_{3-x}Br_x perovskite stored for three months (second line).



Figure. S2. XRD patterns of (a) Fresh and (b) three months later $CsPbI_{3-x}Br_x$ perovskite prepared with Bridgman method.



Figure. S3. DSC plots of (a) CsPbI₃, (b) CsPbI₂Br, (c) CsPbI_{1.5}Br_{1.5}, (d) CsPbIBr₂ and (e)

CsPbBr₃.



Figure. S4. (a) Simulated XRD patterns of CsPbBr₃ that resolves under different temperature.

(b) Magnified image with 2Theta in range $22^{\circ} \sim 30^{\circ}$.



Figure. S5. XRD patterns of (a) $CsPbI_{0.8}Br_{2.2}$, (b) $CsPbI_{0.5}Br_{2.5}$ and (c) $CsPbI_{0.2}Br_{2.8}$ perovskite. Orange and green lines represent the perovskites that are fresh and stored for 2000 h in 30 °C and R.H. = 60% condition, respectively.



Fig. S6. Diffraction patterns of CsPbBr₃ in reciprocal space viewing from different directions. The CsPbBr₃ single crystal is resolved under temperatures of 25°C, 90°C and 140°C, representing the γ , β and α phase, respectively.



Figure. S7. The evolution of diffraction intensity in reciprocal space as the function of temperature.



Figure. S8. (a-b) Temperature dependence of the lattice parameters of CsPbBr₃ perovskite. (c) Evolution of lattice volume of CsPbBr₃ perovskite during control heating from 130 K to 415 K.



Figure. S9. Formation energy of $Cs_4PbI_{6-x}Br_x$ ($0 \le x \le 6$) cluster varying with the number of Br ions. The light-blue line depicts the lowest formation energy of each $Cs_4PbI_{6-x}Br_x$ ($0 \le x \le 6$) cluster and the red line gives the isomerized structures with higher formation energy. The inset picture is all the possible isomerized structures of $Cs_4PbI_{6-x}Br_x$ ($0 \le x \le 6$) cluster.



Figure. S10. Lattice structures of α phase CsPbI_{3-x}Br_x perovskite.



Figure. S11. Projected density of states (PDOS) of α , β and γ phase CsPbI_{1.5}Br_{1.5} perovskites.



Figure. S12. Valence band minimum (VBM) isosurface tuning in α , β and γ phases of (a) CsPbI₃, (b) CsPbI_{1.5}Br_{1.5} and (c) CsPbBr₃.



Figure. S13. PDOS on Pb-6 $p_x/p_y/p_z$, Pb-6s and Br-4 $p_x/p_y/p_z$ for (a) γ , (b) β and (c) α phase CsPbBr₃ perovskites.



Figure. S14. Bandgap evolution of $CsPbI_{3-x}Br_x$ perovskite with phase transition from $\delta \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$.



Figure. S15. (a) Hole and (b) electron effective masses evolution of different phases of CsPbI₃.

_xBr_x perovskite.



Figure. S16. Binding energy evolution of different phases of $CsPbI_{3-x}Br_x$ perovskite.



Figure. S17. Isosurface noncovalent interactions (NCI) plots of γ phase CsPbBr₃ viewing from (a) (100) and (b) (010) directions.



Figure. S18. ELF and RDG isosurface of β and α phase CsPbBr₃ viewing from [001] direction.



Figure. S19. Isosurface NCI plots of (a) γ , (b) β and (c) α phase of CsPbIBr₂ perovskite. PBE

level sign(λ_2) ρ vs. RDG 2D plots (0.5 a.u.) for (d) γ , (e) β , and (f) α phase CsPbIBr₂.



Figure. S20. Experimental temperature-dependent absorption spectra of (a) $CsPbI_2Br$, (b) $CsPbI_{1.5}Br_{1.5}$.



Fig. S21. Schematic of Hall effect measurement.

Table S1. Details of X-ray crystallographic parameters of CsPbBr3 perovskite single crystalssolved under 25 °C, 90 °C and 140 °C.

CsPbBr ₃ Parameter	25 °C	90 °C	140 °C	
CCDC NO.	2243599	2243598	2243597	
Formula weight	420.026 g/mol	420.01 g/mol	24.16 g/mol	
Crystal system	orthorhombic	tetragonal	cubic	
Space group	P n m a P 4/m b m		P m -3 m	
Unit-cell dimensions	a = 8.2546(3) Å b = 11.7511(4) Å c = 8.2037(3) Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$ $\gamma = 90^{\circ}$	a = 8.2515(2) Å b = 8.2515(2) Å c = 5.8911(2) Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$ $\gamma = 90^{\circ}$	a = 5.8649(5) Å b = 5.8649(5) Å c = 5.8649(5) Å $\alpha = 90^{\circ}$ $\beta = 90^{\circ}$ $\gamma = 90^{\circ}$	
Volume	795.76(5) Å ³	401.11(2) Å ³	201.74(5) Å ³	
Ζ	6	3	24	
ρ(calculated)	5.259	5.216	4.773	
Absorption coefficient	45.910	45.534	40.092	
F(000)	1014.265	516	242	
Crystal size 0.3×0.4×0.3mm ³		0.3×0.4×0.3mm ³	.3mm ³ 0.3×0.4×0.3mm ³	
Radiation	МоКа	МоКа	МоКа	
	$(\lambda = 0.71073 \text{ nm})$	$(\lambda = 0.71073 \text{ nm})$	$(\lambda = 0.71073 \text{ nm})$	
2θ range for data Collection	4.148° to 54.506°	4.148° to 54.506°	4.148° to 54.506°	

	$9 \le h \le 10$,	$-7 \le h \le 10$,	$-7 \le h \le 7$,
Index ranges	-14≤ k≤ 14,	-10≤ k≤ 10,	-7≤ k≤ 7,
	-10≤l≤9	-7≤ l≤ 7	-7≤ l≤ 7
Reflections collected	3203	1822	933
Independent reflections	659 [Rint = 0.0509,	233 [Rint = 0.0396,	70 [Rint = 0.0252,
	Rsigma = 0.0635]	Rsigma = 0.0442]	Rsigma = 0.0252]
Data/restraints/paramet	815/ 0/ 28	264/ 0/ 12	70/ 0/ 5
ers			
Final R indexes	R1 = 0.0509	R1 = 0.0396	R1 = 0.0252
[I>=2σ(I)]	wR2 = 0.1277	wR2 = 0.0937	wR2 = 0.0575
Final R indexes [all	R1 = 0.0635	R1 = 0.0442	R1 = 0.0252
data]	wR2 = 0.1362	wR2 = 0.0963	wR2 = 0.0575
Goodness-of-fit on F2	0.9987	1.148	1.258
Largest difference map	1.5002/ 5.50(0.8.3	1 478/ 2 070 8-3	0.507/ 1.110 8 3
peak/hole	1.5082/ -5.5068 A ⁻⁵	1.4/8/-2.0/0 A ⁻³	0.30// -1.118 A ⁻³

			Carrier		Hall		
	Temper	Carrier				Carrier	
,		Same	Bulk	Resistivit	Coefficie	Mah:1:4	Geometry
/	ature	Surface	Density	v (Ocm)	nt (cm ³ C-	Mobility	factor f
	(°C)	Density (cm ⁻²)	Density	, (eiii)		(cm ² V ⁻¹ s ⁻¹)	inclui i
			(cm ⁻³)		1)		
	25	1.44E+12	1.37E+13	8.55E+04	4.55E+05	5.32E+00	0.95187
	100	1.65E+13	1.57E+14	3.09E+04	3.96E+04	1.28E+00	0.96028
CsPbBr ₃	350	3.69E+15	3.51E+16	1.73E+03	1.78E+02	1.03E-01	0.96633
	500	4.70E+17	4.48E+18	1.41E+02	1.39E+00	9.85E-03	0.97528
	25	2.55E+11	2.12E+12	3.37E+05	2.94E+06	8.72E+00	0.95277
CsPbIBr ₂	350	3.10E+14	2.58E+15	1.12E+04	2.42E+03	2.15E-01	0.96219
	450	4.14E+15	3.45E+16	3.50E+03	1.81E+02	5.16E-02	0.96793
	500	2.03E+16	1.69E+17	1.57E+03	3.70E+01	2.35E-02	0.97604
CsPb15Br15	25	3.90E+11	3.25E+12	2.51E+05	1.92E+06	7.64E+00	0.95318
	350	5.59E+14	4.66E+15	7.30E+03	1.34E+03	1.84E-01	0.96485
1.0 1.0	450	7.93E+15	6.61E+16	1.94E+03	9.44E+01	4.86E-02	0.97153
	500	5.02E+16	4.18E+17	6.98E+02	1.49E+01	2.14E-02	0.97552
	25	1.53E+12	8.48E+12	1.25E+05	7.36E+05	5.90E+00	0.95882
CsPbI ₂ Br	350	3.20E+15	1.78E+16	2.25E+03	3.51E+02	1.56E-01	0.96785
	450	5.09E+16	2.83E+17	6.03E+02	2.21E+01	3.66E-02	0.97352
	500	4.93E+17	2.74E+18	1.77E+02	2.28E+00	1.29E-02	0.97935
	25	2.62E+12	2.18E+13	4.51E+04	2.86E+05	6.35E+00	0.95719
CsPbI ₃	350	4.96E+15	4.14E+16	6.29E+02	1.51E+02	2.40E-01	0.96926
	450	1.00E+17	8.36E+17	1.71E+02	7.46E+00	4.36E-02	0.97661
	500	6.79E+17	5.66E+18	5.35E+01	1.10E+00	2.06E-02	0.97923

Table S2. The temperature-dependent Hall effect results for $CsPbI_{3-x}Br_x$ (x = 0, 1, 1.5, 2, 3).

We measured the Hall effect with van der Pauw geometry method using a Quantum Design PPMS system with a magnetic field intensity 1 T. The temperature control unit guarantees the measurement under steady nitrogen atmosphere with controlled temperature. The CsPbI_{3-x}Br_x $(0 \le x \le 3)$ perovskite was squashed to a circle pill about 3mm thick by pressure machine. We selected four corners as test point on one side of the circle pill. The Hall effects measurement mainly contain two values, namely material resistivity ρ and Hall coefficient R_H. The value ρ is determined by formula:

$$\rho_1 = \frac{\pi}{\ln 2} f_1 d \frac{(R_1 + R_2)}{2} \tag{8}$$

$$\rho_2 = \frac{\pi}{\ln 2} f_2 d \frac{(\kappa_3 + \kappa_4)}{2} \tag{9}$$

$$\rho = \frac{(\rho_1 + \rho_2)}{2} \tag{10}$$

Where *d* is material thickness, R_1 , R_2 , R_3 and R_4 are the resistivities by measuring the voltage and current of adjacent test point sequentially with forward and reverse current direction, respectively. f_1 and f_2 are geometry factor, which are determined by the formula:

$$\frac{Q-1}{Q+1} = \frac{f}{0.693} \operatorname{csch}^{-1} \frac{e^{\frac{0.693}{f}}}{2}$$
(11)

Where Q is the resistance ratio that can be obtained by the measured voltage as aforementioned. Then, the Hall coefficient R_H , it can be calculated by formula:

$$R_H = \frac{R_{12} - R_{34}}{B} \tag{12}$$

$$R_{12} = \frac{V_a - V_b}{I_a - I_b}$$
(13)

$$R_{34} = \frac{V_c - V_d}{I_d - I_d}$$
(14)

Where *B* is the magnetic field density perpendicular to the perovskite films. V_a/V_b are the Hall voltage between two interval test point with another two interval test points load forward/reverse current I_a/I_b , respectively. V_c/V_d and I_c/I_d is similar with V_a/V_b and I_a/I_b but were measured under inversed magnetic field. By this way, the unwanted thermoelectric voltage and misalignment voltage could be counteracted. Finally, the carrier type of perovskite films was

determined by sign of the Hall coefficient R_{H} . The Hall mobility μ_{Hall} , bulk carrier density λ can be obtained with formula:

$$\mu_{Hall} = \frac{R_H}{\rho}$$

$$\lambda = \frac{1}{R_H}$$
(15)

$$r = \frac{1}{R_H \times e} \tag{16}$$

Where *e* is unit charge.

/	CsPbI ₃	CsPbI ₂ Br	CsPbI _{1.5} Br _{1.5}	CsPbIBr ₂	CsPbBr ₃
Α	624.51	833.06	1157.88	1310.97	194.51
b	-1.43	-1.54	-1.56	-1.56	-1.12
R-Square	0.9994	0.9997	0.9998	0.9998	0.9955

 Table S3. Fitted coefficients of temperature-dependent Hall mobilities.

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