Supporting Information

Spontaneous Phase Transition from 3D Perovskite to 1D Non-perovskite in CsPbBr$_{2.7}$I$_{0.3}$

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Experimental details

2.9 g CsBr (0.013 mol, 99.999%, Alfa Aesar), 5 g $PbBr_2$ (0.013 mol, 99.999%, Aladdin), 0.39 g CsI (0.0015 mol, 99.999%, Aladdin) and 0.69 g PbI_2 (0.0015 mol, 99.99%, Aladdin) were mixed, and then loaded into a customized 12 mm inner diameter ampoule. The ampoule was vacuum-sealed and mounted in a horizontal tube furnace. The ampoule was soaked at 700 °C for 48 h to ensure complete reaction and then cooled to room temperature. Finally, the polycrystalline sample of γ-$CsPbBr_{2.7}I_{0.3}$ was obtained. The single crystalline γ-$CsPbBr_{2.7}I_{0.3}$ ingot was grown in a vertical three-zone Bridgman furnace, and the temperature profile of the furnace is shown in Fig. S3. Based on the DSC curve shown in Fig. 2e, the ampoule was heated to 650 °C to ensure complete melting, and then held for 48 h. The descent rate of the ampoule was set as follows: the ampoule was translated downward at a rate of 0.5 mm·h^{-1} until it completely passed through the solidification point (487 °C), translated downward at a rate of 8.0 mm·h^{-1} to the phase transition points (151 °C), and then translated downward at a rate of 0.5 mm·h^{-1} until it completely passed through phase transition points, and finally translated downward at a rate of 8.0 mm·h^{-1} until the ampoule was discharged from the bottom of the growth furnace.

Characterization measurements

Powder samples of γ- and δ-$CsPbBr_{2.7}I_{0.3}$ were used to characterize properties, such as the powder X-ray diffraction (PXRD), differential scanning calorimetry (DSC), UV-vis optical absorption, steady state photoluminescence and time-resolved transient photoluminescence (TRPL) spectra, X-ray fluorescence (XRF), temperature-dependent photoluminescence, and energy dispersive spectroscopy (EDS).

The PXRD measurements for the powder samples of γ- and δ-$CsPbBr_{2.7}I_{0.3}$ were performed on a D8 ADVANCE powder X-ray diffractometer produced by Bruker. The testing was performed using a Cu target as the X-ray source, with a work voltage of 20 kV and a current of 20 mA. The DSC measurement was carried out on the NETZSCH STA 449F3. The material was flame-sealed in a tiny ampoule. A similar vacuum-sealed ampoule without any contents was used as a reference. The sample was heated to 650 °C and then cooled to 30 °C at a rate of 10 °C·min^{-1}. The UV-vis optical absorption spectrums of the powder samples of γ- and δ-$CsPbBr_{2.7}I_{0.3}$ were conducted using HITACHIUH4150. The steady state photoluminescence and TRPL spectrums of the powder samples of γ- and δ-$CsPbBr_{2.7}I_{0.3}$ were carried out using Edinburgh FLS1000 photoluminescence spectrometer. The tests were performed using a 375 nm laser as the excitation source at room temperature. The XRF spectrum in room temperature was measured using OmniFluo 900 equipped with a W X-ray tube. The temperature-dependent photoluminescence spectra were measured using Edinburgh FLS1000, which were conducted in the temperature range of 100 to 300 K, with an interval of every 20 K. EDS was carried out on a HITACHI Regulus8230 equipped with Bruker XFlash Detector 6.

Moreover, for γ-$CsPbBr_{2.7}I_{0.3}$, the single-crystal X-ray diffraction data were collected by the Bruker D8 Venture diffractometer. The crystal structures were solved and refined by the Apex and Olex2.[1-4] Crystallographic data were contained in CCDC 2353805 in crystallographic information file format.

Table S1: Rietveld refinement results of lattice parameters for δ-CsPbBr$_3$ and δ-CsPbBr$_{2.7}$I$_{0.3}$.

	a (Å)	b (Å)	c (Å)	V (Å^3)	References
δ-CsPbBr$_3$	4.60	9.72	16.81	752.12	5
δ-CsPbBr$_{2.7}$I$_{0.3}$	4.61	9.78	16.90	762.95	This work

Table S2. Crystallographic data of γ-CsPbBr$_{2.7}$I$_{0.3}$.

Empirical formula	CsPbBr$_{2.7}$I$_{0.3}$
Formula weight	593.93
Wavelength (Å)	0.71073
Temperature (K)	300
Crystal system	Orthorhombic
Space group, Z	*Pnma*, 4
a (Å)	8.2876(17)
b (Å)	11.814(3)
c (Å)	8.2579(18)
Volume (Å^3)	808.5(3)
Density (calculated) (g·cm^{-3})	4.879
Absorption coefficient (mm^{-1})	39.676
F (000)	990.0
Theta range for data collection	3.010 to 27.578
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-10 \leq l \leq 10$
Reflections collected/ unique	6178 / 971 [R(int) = 0.0707]
Completeness (%)	99
Data/ restraints/ parameters	971 / 0 / 28
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2$sigma(I)][a]	$R_1 = 0.0437$, $wR_2 = 0.0893$
R indices (all data)[a]	$R_1 = 0.0787$, $wR_2 = 0.1069$
Largest diff. peak and hole (e·Å^{-3})	1.80 and -1.69

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$ for $F_o^2 > 2\sigma(F_o^2)$

Table S3. Atomic coordinates ($\times 10^4$), equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) and bond valence sum (BVS) for γ-CsPbBr$_{2.7}$I$_{0.3}$.

Atom	x	y	z	U(eq)	BVS[a]
Cs1	9709(3)	7500	9926(3)	93.0(8)	0.93
Pb1	10000	5000	5000	29.8(2)	2.14
I1/Br1	10037(5)	7500	4533(4)	90.9(12)	1.01
I2/Br2	7088(3)	5245(2)	7078(2)	76.1(7)	1.03

[a]BVS[6,7] are calculated by using the bond-valence model ($S_i = \exp [(R_o - R_i / b]$, where R_o is an empirical constant with values 3.18 for Cs-I bonds, 3.06 for Cs-Br bonds, 2.83 for Pb-I bonds, and 2.56 for Pb-Br bonds, R_i is the length of bond i (in angstroms), and $b = 0.37$ Å).

Table S4. Selected bond lengths (Å) and bond angles (°) for γ-CsPbBr$_{2.7}$I$_{0.3}$.

Pb1-I1/Br1	2.979(9)	Cs1-I1/Br1	4.462(4)	Cs1-I2/Br2#5	3.987(3)
Pb1-I1/Br1#10	2.979(9)	Cs1-I2/Br2	4.165(3)	Cs1-I1/Br1#9	3.813(4)
Pb1-I2/Br2	2.976(2)	Cs1-I2/Br2#4	4.165(3)	Cs1-I1/Br1#7	4.438(5)
Pb1-I2/Br2#1	2.983(2)	Cs1-I1/Br1#8	3.898(5)	Cs1-I2/Br2#1	3.705(3)
Pb1-I2/Br2#2	2.976(2)	Cs1-I2/Br2#6	3.987(3)	Cs1-I2/Br2#7	3.705(3)
Pb1-I2/Br2#3	2.983(2)				
I1/Br1-Pb1-I1/Br1#10	179.982(6)	I1/Br1-Cs1-I1/Br1#9	172.420(10)	I1/Br1#8-Cs1-I2/Br2#5	65.026(4)
I1/Br1-Pb1-I2/Br2	89.230(5)	I1/Br1-Cs1-I1/Br1#7	92.284(8)	I1/Br1#8-Cs1-I1/Br1#9	87.505(9)
I1/Br1-Pb1-I2/Br2#1	90.146(5)	I1/Br1-Cs1-I2/Br2#1	61.424(3)	I1/Br1#8-Cs1-I1/Br1#7	167.641(1)
I1/Br1-Pb1-I2/Br2#2	90.770(5)	I1/Br1-Cs1-I2/Br2#7	61.424(3)	I1/Br1#8-Cs1-I2/Br2#1	125.445(4)
I1/Br1-Pb1-I2/Br2#3	89.854(5)	I2/Br2-Cs1-I2/Br2#4	79.530(8)	I1/Br1#8-Cs1-I2/Br2#7	125.445(4)
I1/Br1#10-Pb1-I2/Br2	90.770(5)	I2/Br2-Cs1-I1/Br1#8	63.039(3)	I2/Br2#6-Cs1-I2/Br2#5	108.872(5)
I1/Br1#10-Pb1-I2/Br2#1	89.854(5)	I2/Br2-Cs1-I2/Br2#6	125.260(7)	I2/Br2#6-Cs1-I1/Br1#9	65.291(3)
I1/Br1#10-Pb1-I2/Br2#2	89.230(5)	I2/Br2-Cs1-I2/Br2#5	62.390(3)	I2/Br2#6-Cs1-I1/Br1#7	109.075(4)
I1/Br1#10-Pb1-I2/Br2#3	90.146(5)	I2/Br2-Cs1-I1/Br1#9	126.899(3)	I2/Br2#6-Cs1-I2/Br2#1	169.410(5)
I2/Br2-Pb1-I2/Br2#1	89.689(5)	I2/Br2-Cs1-I1/Br1#7	125.151(3)	I2/Br2#6-Cs1-I2/Br2#7	79.220(5)
I2/Br2-Pb1-I2/Br2#2	180	I2/Br2-Cs1-I2/Br2#1	64.230(4)	I2/Br2#5-Cs1-I1/Br1#9	65.291(3)
I2/Br2-Pb1-I2/Br2#3	90.311(5)	I2/Br2-Cs1-I2/Br2#7	119.020(7)	I2/Br2#5-Cs1-I1/Br1#7	109.075(4)
I2/Br2#1-Pb1-I2/Br2#2	90.311(5)	I2/Br2#4-Cs1-I1/Br1#8	63.039(3)	I2/Br2#5-Cs1-I2/Br2#1	79.220(5)
I2/Br2#1-Pb1-I2/Br2#3	180	I2/Br2#4-Cs1-I2/Br2#6	62.391(5)	I2/Br2#5-Cs1-I2/Br2#7	169.410(5)
I2/Br2#2-Pb1-I2/Br2#3	89.689(5)	I2/Br2#4-Cs1-I2/Br2#5	125.254(4)	I1/Br1#9-Cs1-I1/Br1#7	80.136(9)
I1/Br1-Cs1-I2/Br2	57.869(2)	I2/Br2#4-Cs1-I1/Br1#9	126.899(3)	I1/Br1#9-Cs1-I2/Br2#1	114.058(3)
I1/Br1-Cs1-I2/Br2#4	57.869(2)	I2/Br2#4-Cs1-I1/Br1#7	125.151(3)	I1/Br1#9-Cs1-I2/Br2#7	114.058(3)
I1/Br1-Cs1-I1/Br1#8	100.075(9)	I2/Br2#4-Cs1-I2/Br2#1	119.033(5)	I1/Br1#7-Cs1-I2/Br2#1	61.017(4)
I1/Br1-Cs1-I2/Br2#6	117.885(3)	I2/Br2#4-Cs1-I2/Br2#7	64.236(5)	I1/Br1#7-Cs1-I2/Br2#7	61.017(4)
I1/Br1-Cs1-I2/Br2#5	117.885(3)	I1/Br1#8-Cs1-I2/Br2#6	65.026(4)	I2/Br2#1-Cs1-I2/Br2#7	91.968(5)

Symmetry transformations used to generate equivalent atoms:

#1 1/2 + X, Y, 3/2 − Z; #2 2 − X, 1 − Y, 1 − Z; #3 3/2 − X, 1 − Y, −1/2 + Z; #4 X, 3/2 − Y, Z; #5 3/2 − X, 1 − Y, 1/2 + Z; #6 3/2 − X, 1/2 + Y, 1/2 + Z; #7 1/2 + X, 3/2 − Y, 3/2 − Z; #8 −1/2 + X, 3/2 − Y, 3/2 − Z; #9 X, Y, 1 + Z; #10 2 − X, −1/2 + Y, 1 − Z.
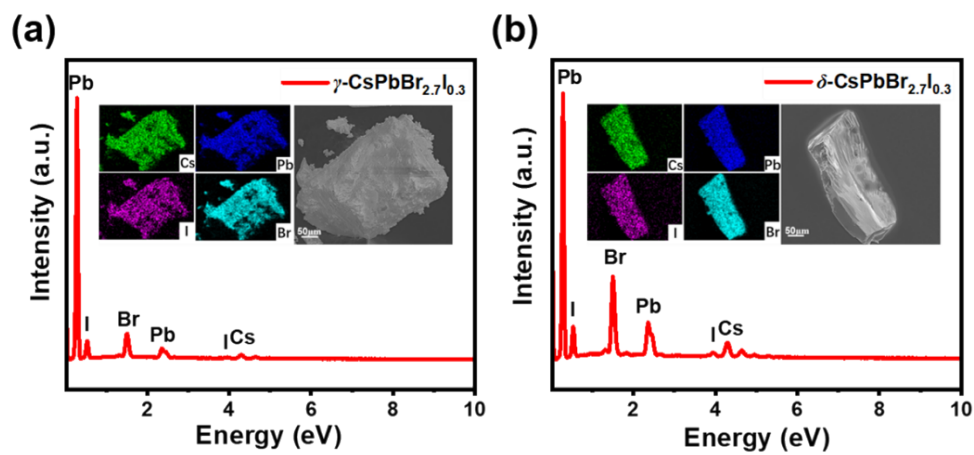
Fig. S1. (a) EDS analysis of γ-CsPbBr$_{2.7}$I$_{0.3}$. (b) EDS analysis of δ-CsPbBr$_{2.7}$I$_{0.3}$.
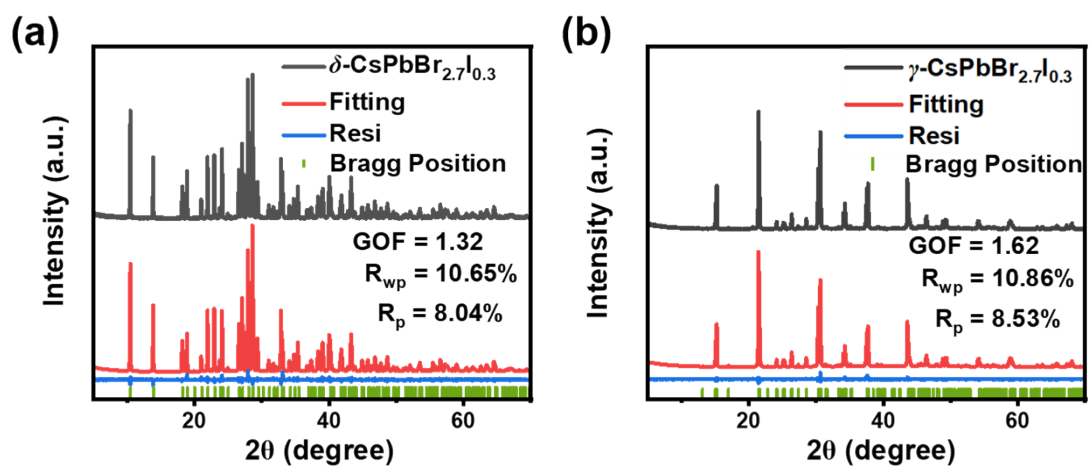
Fig. S2. (a) Rietveld refinement for δ-CsPbBr$_{2.7}$I$_{0.3}$. (b) Rietveld refinement for γ-CsPbBr$_{2.7}$I$_{0.3}$.
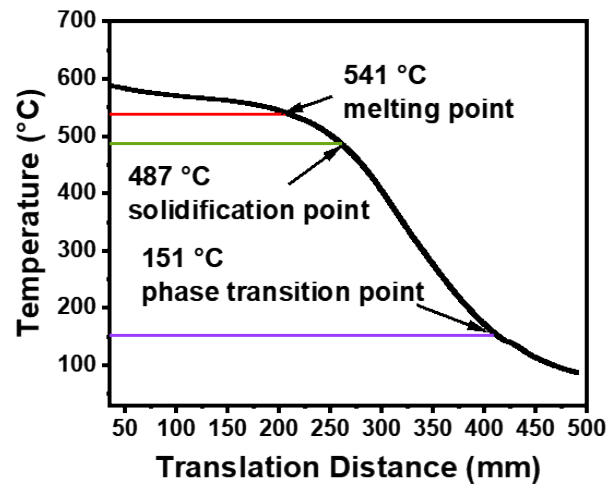
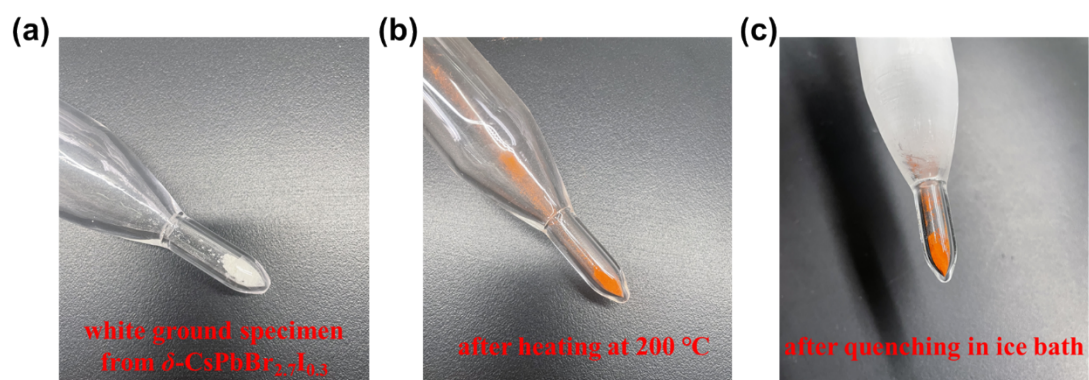**Fig. S3.** Temperature profile of the Bridgeman furnace for crystal growth.

Fig. S4. (a) White δ-CsPbBr$_{2.7}$I$_{0.3}$ sealed in a vacuum silica tube. (b) Orange powder in the fused ampoule after heating at 200 °C in a tube furnace for five hours. (c) Orange powder in the fused ampoule after quenching in an ice-water bath.

References：

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