Supplementary Information

Investigation of High Contrast and Reversible Luminescence Thermochromism of Quantum Confined Cs_4PbBr_6 Perovskite Solid

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Full width half maximum (FWHM) broadening can be described with addition of temperature-independent inhomogeneous broadening term and homogeneous photoluminescence (PL) emission broadening terms. In case of homogeneous PL broadening terms, acoustic homogeneous PL emission broadening term is proportional to the temperature, while optical (LO) phonon related to the function of Bose-Einstein distribution. Therefore, FWHM broadening depending on the temperature changes can be described as following equation.

$$\Gamma(T) = \Gamma_0 + \gamma_{ac}T + \frac{\gamma_{LO}}{e^{\frac{E_{LO}}{k_B T}} - 1}$$

Equation S1.

Γ_0 : Temperature-independent inhomogeneous broadening

γ_{ac} : Homogeneous term from acoustic phonon

γ_{LO} : Homogeneous term from LO phonon

E_{LO} : Weakly dispersive LO phonon generation energy

The PL intensity of semiconductors can be expressed with radiative recombination rate, trap related exciton dissociation rate, thermal dissociation rate, and the thermal escape rate. Furthermore, contribution of PL intensity enhancement above 200 K due to the thermal escape of carriers through quantized energy was considered.

$$I(T) = \frac{I_0 + I' e^{-\frac{\Delta E_t}{k_B T}}}{1 + Ae^{\left(-\frac{E_a}{k_B T}\right)} + Be^{\left(-\frac{E_b}{k_B T}\right)} + C\left(e^{\frac{E_{LO}}{k_B T}} - 1\right)^{-m}}$$

Equation S2

I_0 : PL intensity at 0 K

I' : Density of trap state produced inside QDs

ΔE_t : Activation energy for carrier generated from shallow trap

E_a : Shallow trap related thermal activation energy

E_b : Exciton binding energy

k_B : Boltzmann constant

E_{LO} : Weakly dispersive LO phonon generation energy

m : Number of LO phonons involved in the thermal escape

$A,\ B, C$: Proportional coefficient

The parameters, γ_{ac}, γ_{LO} and E_{LO} are determined by fitting equation S1 to the temperature-dependent full width half maximum (FWHM) as shown in Fig. S1.

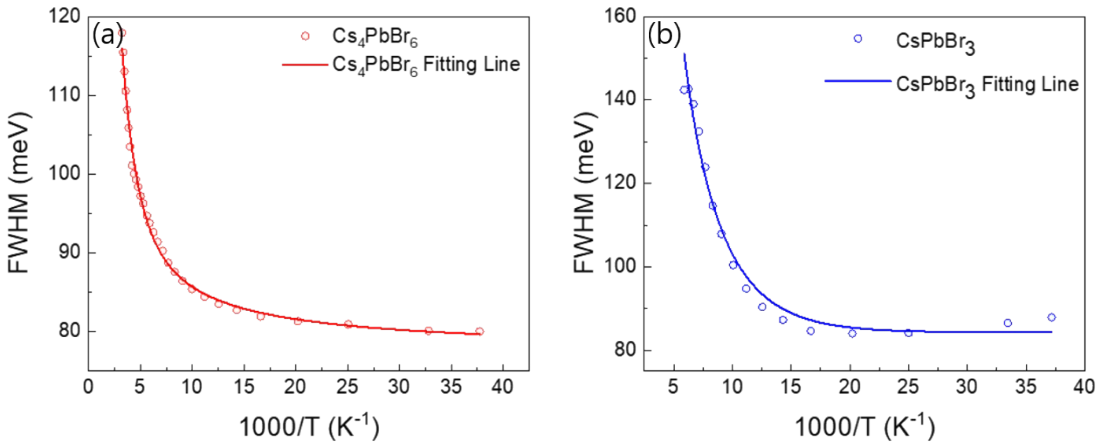

Fig. S1. Temperature-dependent FWHM of (a) Cs_4PbBr_6 and (b) $CsPbBr_3$.

With the obtained E_{LO}, the exciton binding energy, E_b was determined by fitting equation S2 to the temperature-dependent integrated PL intensity.

As stated in the manuscript, the photoluminescence of Cs_4PbBr_6 originates from its zero-

dimensional structure, where the $[PbBr_6]^{4-}$ octahedrons are surrounded by Cs. In this structure, Cs prevents interactions among the Pb^{2+} ions and the Br vacancy defects ($[PbBr_5]^{3-}$) formed in the isolated $[PbBr_6]^{4-}$ octahedrons serving as radiative states for green light emission. Therefore, the Cs_4PbBr_6 PL is solely dependent on the Br vacancy defects (zero-dimensional)-related radiative states, and is not affected by structural defect (three-dimensional) ones. For this reason, the parameters, A and E_a in equation S2 are ignored for Cs_4PbBr_6 and the fitting equation used for Cs_4PbBr_6 was,

$$I(T) = \frac{I_0 + I' e^{-\frac{\Delta E_t}{k_B T}}}{1 + Be^{-\frac{E_b}{k_B T}} + C\left(e^{\frac{E_{LO}}{k_B T}} - 1\right)^{-m}}$$

Equation S3

On the other hands, like other bulk semiconductors, the radiative state of the $CsPbBr_3$ perovskite is dependent on the structural defect states, and thus, A and E_a were considered. Meanwhile, because of the thermal relaxation of carriers in such bulk materials, the thermal escape process is ignored for $CsPbBr_3$ and thus, parameters C and m are not considered in equation S2. Therefore, the fitting equation for $CsPbBr_3$ is,

$$I(T) = \frac{I_0}{1 + Ae^{-\frac{E_a}{k_B T}} + Be^{-\frac{E_b}{k_B T}}}$$

Equation S4

where all the results are represented in the Table S1.

Table S1. The resultant fitting parameters for Cs_4PbBr_6 and $CsPbBr_3$.

	A	B	C	E_a [meV]	E_b [meV]	E_{LO} [meV]	I'	m	Δ_{E_t} [meV]
Cs_4PbBr_6	-	124616	2093	-	368.15	61.97	4.16	3.96	84.62
$CsPbBr_3$	7.08	238.72	-	9.78	73.15	23.24	-	-	-

Table S2. PL lifetime of Cs_4PbBr_6 films in different temperature. The monitored wavelength was 520 nm. The PL decay curves were fitted by a tri-exponential function. The intensity-weighted average exciton lifetime (τ_{avr}) was $f_1\tau_1 + f_2\tau_2 + f_3\tau_3$, where f_1, f_2 and f_3 are fractional intensities and τ_1, τ_2 and τ_3 are lifetimes.

Film	$\tau_1(f_1)$ [ns]		$\tau_2(f_2)$ [ns]		$\tau_3(f_3)$ [ns]		χ^2	τ_{avr} [ns]
Cs_4PbBr_6 film RT	1.80	(0.08)	10.16	(0.42)	43.00	(0.50)	1.084	25.91
Cs_4PbBr_6 film 90˚C	1.31	(0.07)	9.28	(0.35)	44.50	(0.58)	1.119	29.15
Cs_4PbBr_6 film Re-RT	1.80	(0.09)	9.76	(0.42)	43.01	(0.49)	1.079	25.34