Supporting Information

Point Defects and Green Emission in Zerodimensional Perovskites

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METHODS

Computational methods. Density functional theory (DFT) calculations were carried out by the projector-augmented wave (PAW) method as implemented in the VASP code.¹⁻² The generalized gradient approximation (GGA) Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was applied. A uniform grid of $6 \times 6 \times 6$ k-mesh in the Brillouin zone was employed to optimize the crystal structures of CsPbBr₃, CsPb₂Br₅, and Cs₄PbBr₆; the optimized crystal parameters of Cs-Br-Pb compounds are given in Table S1). The Hevd-Scuseria-Ernzerhof hybrid functional (HSE06) including spin-orbit coupling (SOC) was also used to calculate the electronic band structures and correct the bandgaps that are underestimated using the PBE+SOC method. The contribution of the Hartree-Fock exchange potential was set to 0.48 for cubic-phase CsPbBr₃, 0.45 for orthorhombicphase CsPbBr₃, and 0.2 for both CsPb₂Br₅ and CsPb₄Br₆. A $3\times3\times2$ supercell for orthorhombicphase CsPbBr₃ (360 atoms), a $3 \times 3 \times 3$ supercell for cubic-phase CsPbBr₃ (320 atoms), and a $2 \times 2 \times 2$ supercell for CsPb₂Br₅ (256 atoms) and Cs₄PbBr₆ (396 atoms) were used for the defect calculations. The Brillouin zone was sampled by a $2 \times 2 \times 2$ k-mesh. The plane-wave basis set cutoffs of the wavefunctions were set at 500 eV for bulk crystal structures and 450 eV for supercells. The atomic positions of all supercells with and without defects were fully relaxed until the supercells had forces on each atom less than 0.01 eV/Å.

The defect formation energies, $\Delta H(\alpha,q)$, for the supercells containing defect α at charge state q can be calculated by

$$\Delta H(\alpha, q) = E(\alpha, q) - E(host) + \sum n_i (E_i + \mu_i) + q(E_{VBM}(host) + E_F)$$

where $E(\alpha, q)$ is the total energy of the supercell containing the defect and E(host) is the total energy of the host supercell without a defect. μ_i is the chemical potential of constituent *i*, with reference to an elemental solid or molecule with energy E_i . Here, μ_{Cs} refers to the Cs solid phase with a Im3m symmetry, μ_{Br} refers to the Br₂ gas molecule, and μ_{Pb} refers to the fcc Pb solid phase. $E_{\text{VBM}}(\text{host})$ is the valence band maximum (VBM) of the perfect supercell, and E_{F} is the Fermi energy that refers to VBM. n_i is the number of atoms taken out of the supercell to form the defects, and q is the number of electrons transferred from the supercell to the Fermi reservoirs in forming the defective supercell. In equilibrium growth conditions, the chemical potential μ_i should satisfy the following equations, which are CsBr, PbBr₂ and elemental solids³:

$$\mu_{Cs} + \mu_{Pb} + 3\mu_{Br} = \Delta H(\text{CsPbBr}_{3}) = -6.87 \text{ eV (cubic)}$$

$$\mu_{Cs} + \mu_{Pb} + 3\mu_{Br} = \Delta H(\text{CsPbBr}_{3}) = -6.95 \text{ eV (orthorhombic)}$$

$$\mu_{Cs} + 2\mu_{Pb} + 5\mu_{Br} = \Delta H(\text{CsPb}_{2}\text{Br}_{5}) = -9.93 \text{ eV}$$

$$4\mu_{Cs} + \mu_{Pb} + 6\mu_{Br} = \Delta H(\text{Cs}_{4}\text{PbBr}_{6}) = -18.23 \text{ eV}$$

$$\mu_{Pb} + 2\mu_{Br} < \Delta H(\text{PbBr}_{2}) = -3.04 \text{ eV};$$

$$\mu_{Cs} + \mu_{Br} < \Delta H(\text{CsBr}) = -3.63 \text{ eV};$$

$$\mu_{Cs} < 0 \text{ eV}, \mu_{Pb} < 0 \text{ eV}, \mu_{Br} < 0 \text{ eV}$$

where $\Delta H(\text{CsPbBr}_3)$, for example, is the formation enthalpy of CsPbBr₃, defined as the total energy difference $\Delta H(\text{CsPbBr}_3) = E(\text{CsPbBr}_3) - E(\text{Cs}) - E(\text{Pb}) - 3E(\text{Br})$, $\Delta H(\text{PbBr}_2)$ is the formation enthalpy of PbBr₂ defined as the total energy difference $\Delta H(\text{PbBr}_2) = E(\text{PbBr}_2) - E(\text{Pb}) - 2E(\text{Br})$, and $\Delta H(\text{CsBr})$ is the formation enthalpy of CsBr defined as the total energy difference $\Delta H(\text{CsBr}) = E(\text{CsBr}) - E(\text{Pb}) - 2E(\text{Br})$, = E(CsBr) - E(Cs) - E(Cs).

The charge-transition levels for defect α were calculated as

$$\varepsilon(q/q') = [E(\alpha,q) - E(\alpha,q') + (q-q')(E_{VBM} + \Delta V)]/(q-q')$$

Materials and synthesis. All reagents were used without any further purification: Cs₂CO₃ (cesium carbonate, 99%, Sigma-Aldrich), PbBr₂ (lead bromide, 99.99%, Alpha Aesar), OA (oleic acid, 90%, Sigma-Aldrich), OAm (oleylamine, 90%, Sigma-Aldrich), DMF (N,N-dimethylformamide, 99.8%, Sigma-Aldrich), and anhydrous n-hexane (99.98%, Sigma-Aldrich). The PbBr₂ precursor and the Cs-oleate precursor were synthesized separately. First, 2.25 g of Cs₂CO₃ and 20 mL of OA was stirred and degassed at 130°C under vacuum for 1 hour to generate a yellowish stock of Cs-oleate precursor.

Green-emissive Cs_4PbBr_6 *nanocrystals:* Green-emissive Cs_4PbBr_6 nanocrystals were synthesized under different conditions by controlling the amount of HBr. 200 µL of Cs-oleate precursor, 10 mL of n-hexane, and 2 mL of OA were loaded in five 20 mL vials. Subsequently, a mixture of 0.107 mL of PbBr₂ (0.3 M, DMF), 0.9 mL of DMF, 0.1 mL OA, 0.05 mL of OAm, HBr

[48% aqueous solution, 12 μ L (Br-poor), 13.5 μ L (Br-slightly poor), 15 μ L (moderate), 16.5 μ L (Br-slightly rich), 18 μ L (Br-rich)] was injected into the vials at the same time. The five vials were at the same temperature and stir speed. After the color change from white to green at approximately 5 min, the as-synthesized nanocrystals were collected via centrifugation at 6000 rpm for 5 min, followed by dispersion in 2 mL of hexane for further characterizations.

Non-emissive Cs4PbBr6 nanocrystals: First, 36.7 mg of PbBr₂ were dissolved in 5 mL of ODE, 0.2 mL of OA, and 1.5 mL of OAm in a 25 mL round bottom flask on hotplate at approximately 100°C. After PbBr₂ was dissolved, the temperature was set to 80°C. Then, 0.17 mL of Cs-OA precursor and 0.58 mL of OA were mixed and heated to 150°C, and the mixture was injected in the flask. After stirring for approximately 5 min, the flask was quickly cooled with a cold water bath. The non-emissive Cs₄PbBr₆ nanocrystals were collected via centrifugation at 6000 rpm for 5 min, followed by dispersion in 2 mL of toluene for further characterization.

Green-emissive CsPbBr₃ nanocrystals: First, 25 μ L of Cs-oleate precursor, 10 mL of n-hexane, and 5 mL of OA were loaded in a 20 mL vial. Subsequently, a mixture of 0.107 mL of PbBr₂ (0.3 M, DMF), 0.9 mL of DMF, 0.1 mL of OA, 0.05 mL of OAm, and 2 μ L of HBr(48%) was injected into the vials. After the color changed from white to green at approximately 5 min, the assynthesized CsPbBr₃ nanocrystals were collected via centrifugation at 6000 rpm for 5 min, followed by dispersion in 2 mL of hexane for further characterization.

X-ray diffraction measurements. Powder X-ray diffraction was performed using a Bruker AXS D8 diffractometer with Cu-K α radiation ($\lambda = 1.5406$ Å). The samples were prepared by drop-casting the nanocrystal suspension onto a clean glass slide, followed by drying at room temperature.

Steady-state photoluminescence and absorption measurements. The as-prepared Cs₄PbBr₆ nanocrystals were diluted in n-hexane for steady-state photoluminescence and absorption measurements. A Cary 5000 UV-vis spectrometer (Agilent Technologies) was used for absorption measurements in the range from 200 nm to 800 nm. A FluoroMax-4 spectrofluorometer (Horiba Scientific; a slit width of 0.24 mm and a scan rate of 500 nm/min) was used to record the photoluminescence spectra. The excitation wavelength used for nanocrystals was set at 375 nm. The photoluminescence quantum yield were measured using an Edinburgh Instruments FLS920 Spectrofluorometer, with 375 nm excitation wavelength.

The temperature-dependent photoluminescence spectra were characterized using a Horiba JY LabRAM Aramis spectrometer with an Olympus 50x lens in a Linkam THMS600 stage. A 473nm laser was used as the excitation source. The exciton binding energies of CsPbBr₃ NCs and Cs₄PbBr₆ NCs were obtained by fitting the integrated temperature-dependent photoluminescence intensities using the Arrhenius formula: $I = I_0/[1 + aexp(-E_b/kT)]$, where E_b is the exciton binding energy, k is the Boltzmann constant, I_0 is the zero-temperature PL intensity and a represents the strength of the quenching process.

Time-correlated single photon counting (TCSPC) measurements. The Cs₄PbBr₆ nanocrystals sample was excited by a pulsed laser diode (400 nm) that was purchased from HORIBA Jobin Yvon, model (DD-405L, IRF \approx 65 ps). The repetition rate of the pulsed laser ranged from a few kHz to MHz by a DDC1 picosecond controller also purchased from HORIBA. The laser light was tightly focused on the sample using an objective lens from Olympus Ltd., (Plan N, 10x/0.25). The maximized emission was collected from the same excited area by the objective lens after passing through a reflective beam splitter (R 488) from Thorlabs. The collected emission was focused on a commercial Avalanche photodiode that is controlled and by a Hydra Harp 400 multichannel picosecond event timer unit from PicoQuant to detect the emission in a single photon fashion, *i.e.*, one per laser pulse at max. Then, the collected emission intensity versus time was analyzed and fitted using multi-exponential decay equations.

Transmission electron microscopy (TEM) measurements. TEM images were acquired using a Tecnai transmission electron microscope with an acceleration voltage of 120 keV. HRTEM images were acquired using the same instrument. Note that the nanocrystals were not stable under irradiation with electron beams and tended to decompose within a short period of time (< 5s).

Low-Dose high-resolution transmission electron microscopy (HRTEM) measurements. Lowdose HRTEM images were acquired with a Gatan K2 Summit direct-detection electron-counting (DDEC) camera on a Cs-corrected Titan cubed G2 60-300 electron microscope at 300 kV. A stack of successive short-exposure frames (0.05 s/frame, and 120 frames) was recorded on each particles at extremely low doses (~30-40 e/A²). Drift between frames was corrected based on the methods reported in the literature⁴. **Table S1.** Space group and experimental lattice constants (the calculated values at the GGA/PBE level of theory are given in parentheses) of the related compounds, used to calculate the defect formation energies and charge transition energy levels.

Compounds	Space Group	Lattice Constant (Å)		
		a	b	С
Cs	Im3̄m	6.140 (6.140)	6.140 (6.140)	6.140 (6.140)
Pb	Fm3̄m	4.950 (5.057)	4.950 (5.057)	4.95 (5.057)
PbBr ₂	Pnma	8.020 (8.234)	4.715 (4.720)	9.485 (10.413)
CsBr	Pm3m	4.290 (4.390)	4.290 (4.390)	4.290 (4.390)
CsPbBr ₃ (cubic)	Pm3̄m	5.874 (6.004)	5.874 (6.004)	5.874 (6.004)
CsPbBr ₃ (orthorhombic)	Pnma	8.244 (8.508)	8.198 (8.255)	11.735 (11.940)
CsPb ₂ Br ₅	I4/mcm	8.601 (8.605)	8.601 (8.605)	16.127 (16.608)
Cs4PbBr ₆	R3c	13.732 (14.067)	13.732 (14.067)	17.324 (17.578)



Figure S1. Brillouin zone k-paths of (a) CsPbBr₃ (cubic); (b) CsPbBr₃ (orthorhombic); (c) CsPb₂Br₅; and (d) Cs₄PbBr₆, used to calculate the electronic band structures.



Figure S2. Stability regions of different compounds *vs.* Br and Pb chemical potentials of (a) CsPbBr₃ (cubic); (b) CsPbBr₃ (orthorhombic); (c) CsPb₂Br₅; and (d) Cs₄PbBr₆. The shaded region indicates the equilibrium chemical potential region. The representative points (A: Pb-rich/Br-poor, B: moderate, C: Br-rich/Pb-poor conditions) are chosen for the defect formation energy calculations.



Figure S3. (a) Illustrations of antisite Pb_{Cs} , Pb_{Br} , and Cs_{Br} in Cs_4PbBr_6 ; (b) calculated neutral defect formation energies for Pb_{Cs} , Pb_{Br} , and Cs_{Br} in $CsPbBr_3$ (orthorhombic), $CsPb_2Br_5$ and Cs_4PbBr_6 at Pb-rich/Br-poor, moderate, and Br-rich/Pb-poor conditions.

Table S2. Comparisons of calculated neutral defect formation energies (in eV) between cubic- and orthorhombic-phase CsPbBr₃ at Pb-rich/moderate/Br-rich conditions.



Defects	Orthorhombic (3×3×2 supercell)	Cubic (3×3×3 supercell)	
V _{Br}	2.69/1.94/1.20	1.85/1.11/0.36	
V _{Pb}	0.98/2.17/3.37	3.11/4.32/5.51	
V _{Cs}	0.44/1.48/2.52	0.10/1.14/2.18	
Pb _{Cs}	2.60/2.44/2.29	3.73/3.58/3.42	
Pb _{Br}	6.14/4.19/2.25	5.59/3.65/1.70	
Cs _{Br}	6.20/4.41/2.62	5.55/3.76/1.97	



Figure S4. TEM images of green-emissive Cs₄PbBr₆ under Br-poor, Br-slightly poor, moderate, Br-slightly rich, and Br-rich growth conditions.



Figure S5. Energy-dispersive X-ray (EDX) spectra of Cs_4PbBr_6 under (a) moderate and (b) Brpoor conditions.



Figure S6. Steady-state absorption spectra of green-emissive Cs₄PbBr₆ NCs under Br-poor, Brslightly poor, moderate, Br-slightly rich, and Br-rich growth conditions in n-hexane solution. The dashed black line is the photoluminescence excitation (PLE) of Cs₄PbBr₆ NCs under moderate condition.



Figure S7. (a) XRD spectra; (b) steady-state absorption (solid black line), photoluminescence excitation (dashed black line) and photoluminescence spectra (solid red line), excitation wavelength = 375 nm; and (c) time-resolved photoluminescence spectra of CsPbBr₃ NCs in n-hexane solution.



Figure S8. Temperature dependent steady-state photoluminescence spectra of (a) CsPbBr₃ and (b) Br-poor Cs₄PbBr₆ nanocrystals.



Figure S9. Drift-corrected HRTEM image of green-emissive Cs₄PbBr₆ NCs. The fast Fourier transform (FFT) patterns are shown as insets.

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