Supporting Information

Enhancement of Self-Trapped Exciton and Near-Infrared Emission in Bi³⁺/Er³⁺ Co-Doped Cs₂Ag_{0.4}Na_{0.6}InCl₆ Double Perovskite

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1. Experimental sections

1.1 Chemical and materials: The following reagents were used in the synthesis process. CsCl (99.9%) and ErCl₃.6H₂O (99.9%) were purchased from Sigma–Aldrich. AgCl (99.9%), InCl₃ (99.9%), and BiCl₃ (99.9%) were purchased from Alfa Aeaser. HCl (37%) was purchased from Merck. Anhydrous ethanol (99.9%) was purchased from ECHO.

1.2 Synthesis of Cs₂AgInCl₆:Er: An acid-based precipitation method was used to synthesize Cs₂AgInCl₆:Er mentioned in a previous report, with some modifications.¹⁹ For the reaction, 0.75 mmol of AgCl, 0.75 mmol of InCl₃, and 1.5 mmol of ErCl₃.6H₂O were mixed into the 3 mL of HCl and stirred at 70°C–80°C for 20 min. Afterward, 1.5 mmol of CsCl was added to the reaction, which was continued until a white precipitate was formed. The reaction was further cooled down to room temperature. The precipitate was washed with ethanol and centrifuged five times at 5000 rpm for 6 min. The washed sediment was further dried at 60°C for 24 h.

1.3 Synthesis of Cs₂AgIn_{0.92}Bi_{0.08}Cl₆:Er: For the reaction, 0.75 mmol of AgCl, 0.69 mmol of InCl₃, 0.06 mmol of BiCl₃, and 1.5 mmol of ErCl₃.6H₂O were mixed into 3 mL of HCl and stirred at 70°C–80°C for 20 min. Afterward, 1.5 mmol of CsCl was added to the reaction, which was continued until a white precipitate was formed. The remaining process is as same as that used for synthesizing Cs₂AgInCl₆:Er.

1.4. Synthesis of $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er: For the reaction, 0.3 mmol of AgCl, 0.45 mmol of NaCl, 0.69 mmol of InCl₃, 0.06 mmol of BiCl₃, and 1.5 mmol of ErCl₃.6H₂O were mixed into 3 mL of HCl and stirred at 70°C–80°C for 20 min. Afterward, 1.5 mmol of CsCl was added to the reaction, which was continued until a white precipitate was formed. The remaining process is as same as that used for synthesizing Cs₂AgInCl₆:Er.

1.5. Characterizations: Powder Synchrotron X-ray diffraction was used to study the crystal structure from the 01C2 beamline at 0.829657 nm wavelength and TOPAS for refinement of all the samples. Photoluminescence between 400 and 1700 nm was measured using a fluorometer (Edinburg) with a 1.5 nm slit with excitation and 2 nm of emission slit width in Fig. 3c. Scanning electron microscope image collected from the ZEISS. The photoluminescence spectra (PL) were measured using the Flouromax 4P spectrofluorometer between 450–800 nm. Absorption (ABS) and photoluminescence excitation (PLE) spectra were recorded using a Quantaurus-QY spectrometer (Hamamatsu) with an integrating sphere. Photocurrent excitation (PC) spectra were acquired from pelleted samples with gold electrodes produced by the magnetron sputtering process using the NanoPVD-S10A vacuum deposition system (Moorfield Nanotechnology). The PC spectra were acquired using a setup consisting of a B2987A electrometer (Keysight) with an internal voltage source, 150 W Xe light source coupled with Omni- λ 150 mm monochromator (LOT Oriel). The measurements were carried out under 50 V in a vacuum. The optical excitation was modulated using an optical chopper, and the output PC signal was demodulated using an SR7270 lock-in amplifier (AMETEK). The temperature and pressure-dependent PL spectra were recorded using a Shamrock SR750 grating spectrometer with an iDus 420 CCD detector (Andor Technology). Raman spectra were recorded at room temperature and ambient pressure on a Horiba Jobin Yvon Lab Ram Aramis spectrometer with a He-Ne laser providing excitation light at 633 nm with 1200 l/mm grating. For temperature-dependent measurements, the samples were held in the THMS600 cooling and heating stage (Linkam Scientific). Luminescence kinetic measurements were carried out using a 2501S grating spectrometer (Bruker Optics) combined with a C4334-01 streak camera

(Hamamatsu). The pulsed excitation of tunable wavelength was provided by PL2251A picosecond YAG: Nd laser coupled with PG 401/SH Optical Parametric Generator (EKSPLA). Two types of investigations were used: electron paramagnetic resonance (EPR) spectroscopy and superconducting quantum interference device (SQUID) magnetometry. These techniques are, to some extent, complementary to each other. The EPR technique reports the contribution of paramagnetic ions, while the SQUID magnetic susceptibility technique determines the contribution of all magnetic units to the magnetic properties of the entire sample volume. EPR spectra were recorded at 3 K–300 K using a conventional Bruker X-band ELEXSYS E500 CW spectrometer operating at 9.458 GHz and 0.63 mW microwave power. The magnetic induction was up to 1.4 T. The first derivative of the absorption spectrum as a function of applied magnetic induction was recorded. The EPR/NMR program was used to identify the spin Hamiltonian parameters.

The parameters of the spin Hamiltonian (SH) were determined using the following form and EPR/NMR program:

$$H = H_{Zeeman} + H_{ZFS} + H_{HI}$$
$$H = \mu_B B \cdot g \cdot S + D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + E\left(S_x^2 - S_y^2\right)$$

where µB refers to Bohr magneton; B indicates the induction of magnetic field; g refers to the spectroscopic splitting factor; S is electron spin; and D and E are axial and rhombic distortions of octahedral, respectively. It consists of Zeeman interactions, zero-field splitting components, and hyperfine interactions. For the first erbium center with a spin of S = 3/2 and I = 7/2 (blue EPR line in **Fig. S3**), the above parameters are $g_x = 4.06$ (5), $g_y = 4.02$ (5), $g_z = 3.70$ (5), D = 0.006 cm⁻¹, E = 0 cm⁻¹, and A = 15.9 mT. The SH values indicate an axial symmetry surrounding Er³⁺ ions with small axial distortion. Only the Zeeman part of the spin Hamiltonian was used to simulate the second Er³⁺ center with a fictitious spin of S = $\frac{1}{2}$. The following values were obtained: $g_x = 9.41$ (2), $g_y = 5.36$ (2), and $g_z = 3.70$ (5), indicating low symmetry of the Er³⁺ ions (purple EPR line in **Fig.S3**). An average value, $g_{av} = (g_x+g_y+g_z)/3 \sim 6.2$, indicates that the signal originates from the F6 state.

The third paramagnetic center originates from electrons trapped by point defects in the $Cs_2AgInCl_6$ crystal lattice, as indicated by the Lorentzian EPR signal at g_{eff} = 2.005 (brown EPR line in Fig.S3). The results of the fitting of SH parameters by the least square method are clearly shown in **Fig.S3**. The values of SH parameters for Er^{3+} ions $S_{eff} = 1/2$ are similar (in the range of measurement error) as well as the position of EPR line g_{eff} = 2.005 originating from trapped electrons in the crystal lattice for all three systems. Also, for the EPR line coming from Er^{3+} ions (S = 3/2, I = 7/2) the SH parameters do not undergo any change. Significant evolutions can be observed in the integrated intensity of the EPR signal. Namely, the integrated intensity of the EPR signal from Er^{3+} ions with a spin of $S_{eff} = 1/2$ increases just after the addition of Bi^{3+} and Na⁺ dopants. The opposite situation occurs for the EPR signal coming from Er³⁺ ions with a spin of S = 3/2 and I = 7/2. It should be noted that, with a significant amplitude of the signal, the integrated intensity of the EPR signal is much lower than that for the signal coming from Er^{3+} ions with a spin of $S_{eff} = 1/2$ (3.4% of the total integrated intensity of the EPR signal from Cs₂AgInCl₆). No significant changes in the integrated EPR intensity originating from crystal lattice defects were observed.

Magnetic measurements were performed using a SQUID magnetometer (Quantum Design MPMS-XL-7). The magnetic susceptibility data were obtained in zero-field-cooled and field-cooled modes. Measurements were recorded for temperatures up to 300 K and magnetic fields H = 100 Oe and H= 1 kOe. The magnetic susceptibility was analyzed using the Curie–Weiss law at temperatures above the Curie temperature and for a weak magnetic field to satisfy the condition $H/kT \ll 1$. The susceptibility data were corrected due to the diamagnetism of a sample holder and the constituent atoms by Pascal's constants.



Fig. S1. Rietveld refinements of (a) $Cs_2AgInCl_6$:Er, (b) $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and (c) $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er. (d) Crystal structure of $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.

| x | Cs_AgInCl ₆ : Er | Cs ₂ AgIn _{0.92} Bi _{0.08} Cl ₆ : Er | Cs_Ag_Na_InBi_CI_6 : Er |
|-----------------------------------------|-----------------------------|------------------------------------------------------------------------------|-------------------------|
| a (Å) | 10.480020(85) | 10.50381(10) | 10.53972(11) |
| V (Å ³) | 1151.029(28) | 1158.887(33) | 1170.812(37) |
| Cs ₂ AgInCl ₆ (%) | 99.28 | 99.03 | 98.81 |
| AgCI (%) | 0.72 | 0.97 | 1.19 |
| 2 | 1.31 | 1.22 | 1.16 |
| R _{wp} (%) | 6.80 | 6.25 | 5.87 |
| R _p (%) | 5.37 | 4.86 | 4.72 |

Tab. S1. Refinement results derived from Rietveld refinement of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.

Tab. S2. Atomic positions derived from Rietveld refinement of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.

| Cs ₂ AgInCl ₆ : Er | | | | | | | | | |
|----------------------------------------------------------------------------------------------------------------|-------------|------|------|------------|-----------------------|--|--|--|--|
| Site | Х | у | Z | Occ | Beq (Å ²) | | | | |
| Cs1 | 0.25 | 0.25 | 0.25 | 1 | 1.649(35) | | | | |
| Ag1 | 0 | 0 | 0 | 1 | 1.649(76) | | | | |
| In1 | 0.50 | 0.50 | 0.50 | 0.909(11) | 1.231(72) | | | | |
| Er1 | 0.50 | 0.50 | 0.50 | 0.091(11) | 1.231(72) | | | | |
| CI1 | 0.26013(49) | 0 | 0 | 1 | 2.189(58) | | | | |
| | | | | | | | | | |
| Cs2AgIn0.92Bi0.08Cl6 : Er | | | | | | | | | |
| Site | х | У | Z | Occ | Beq(Å ²) | | | | |
| Cs1 | 0.25 | 0.25 | 0.25 | 1 | 2.082(37) | | | | |
| Ag1 | 0 | 0 | 0 | 1 | 1.785(75) | | | | |
| In1 | 0.50 | 0.50 | 0.50 | 0.886(17) | 0.92(23) | | | | |
| Bi1 | 0.50 | 0.50 | 0.50 | 0.075(99) | 0.92(23) | | | | |
| Er1 | 0.50 | 0.50 | 0.50 | 0.038(14) | 0.92(23) | | | | |
| CI1 | 0.25940(48) | 0 | 0 | 1 | 2.234(54) | | | | |
| | . , | | | | · · · | | | | |
| Cs ₂ Ag _{0.4} Na _{0.6} In _{0.92} Bi _{0.08} Cl ₆ : Er | | | | | | | | | |
| Site | Х | У | Z | Occ | Beq(A ²) | | | | |
| Cs1 | 0.25 | 0.25 | 0.25 | 1 | 1.932(37) | | | | |
| Ag1 | 0 | 0 | 0 | 0.3457(50) | 1.715(96) | | | | |
| Na1 | 0 | 0 | 0 | 0.6543(50) | 1.715(96) | | | | |
| In1 | 0.50 | 0.50 | 0.50 | 0.80(38) | 1.365(44) | | | | |
| Bi1 | 0.50 | 0.50 | 0.50 | 0.08(22) | 1.365(44) | | | | |
| Er1 | 0.50 | 0.50 | 0.50 | 0.12(31) | 1.365(44) | | | | |
| Cl1 | 0.26180(28) | 0 | 0 | 1 | 2.141(51) | | | | |
| | | | | | | | | | |

Tab. S3. Inductively coupled plasma optical emission spectroscopy (ICP-OES) of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.The concentration of the elements was

 $Er(\%) = 100 * \frac{Er}{Er + Bi + In}$. All other elements were calculated using

the formulas
$$Bi(\%) = 100 * \frac{Bi}{Er + Bi + In}$$
 and $In(\%) = 100 * \frac{In}{Er + Bi + In}$

| Sample | Precursors | | | Precursors (ICP-OES) | | |
|----------------------------------------------------------------------------------------------------------------|------------|--------|--------|----------------------|--------|--------|
| | In (%) | Bi (%) | Er (%) | In (%) | Bi (%) | Er (%) |
| Cs ₂ AgInCl ₆ : Er | 100 | 0 | 200 | 92.6 | | 7.4 |
| Cs ₂ Ag In _{0.92} Bi _{0.08} Cl ₆ : Er | 92 | 8 | 200 | 82.9 | 13.9 | 3.2 |
| Cs ₂ Ag _{0.4} Na _{0.6} In _{0.92} Bi _{0.08} Cl ₆ : Er | 92 | 8 | 200 | 75.7 | 12.6 | 11.7 |



Fig. S2. Scanning electron microscopy (SEM) of Cs₂AgInCl₆:Er, Cs₂AgIn_{0.92}Bi_{0.08}Cl₆:Er, and Cs₂Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl₆:Er.



Fig. S3. Experimental EPR spectrum of $Cs_2AgInCl_6$:Er at T = 5.14 K. Simulated EPR spectra show a contribution from different paramagnetic centers.



Fig. S4. Normalized PLE and PL spectra of $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er at the emission wavelength of 1540 nm and excitation wavelength of 352 nm.



Fig. S5. Luminescence decay curve of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er at the emission wavelength of 1540 nm and excitation wavelength of 352 nm.



Fig. S6. Temperature-dependent emission spectra of (a) $Cs_2AgInCl_6$:Er and (b) $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er under the excitation wavelength of 375 and 315 nm on UV chip, respectively. Temperature-dependent PL emission intensity obtained by integrating PL spectra of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.



Fig. S7. Temperature dependence of luminescence decay curves of $Cs_2AgInCl_6$:Er and $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er measured at maximum luminescence. Temperature evolution of average decay times calculated for $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er (c) linear scale and (d) log scale.



Fig. S8. Streak image of $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er sample at 10 K in 100 µs time ranges showing two kinds of luminescence: (b) time-resolved emission spectra collected as ns (orange) and µs (blue) time intervals.



Fig. S9. Raman spectra of $Cs_2AgInCl_6$:Er, $Cs_2AgIn_{0.92}Bi_{0.08}Cl_6$:Er, and $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.



Fig. S10. (a) Pressure dependence of PL spectra (absolute values) up to 105 kbar. (b) Detailed view of the section marked by the blue rectangle in (a) for $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl_6$:Er.



Fig. S11. Pressure dependence of PL peak location (black points) and FWHM (red points) for Cs₂Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}Cl₆:Er.



Fig. S12. Pressure dependence of calculated average decay time before phase transition at 70 kbar (black points) and after phase transition for the two constituents observed in the PL spectrum at 410–430 (red points) and 500–600 (green points) nm for $Cs_2Ag_{0.4}Na_{0.6}In_{0.92}Bi_{0.08}CI_6$:Er.