Supporting Information

Highly Efficient Blue Emission from Self-Trapped Excitons in Stable Sb³⁺-Doped Cs₂NaInCl₆ Double Perovskites

Ruosheng Zeng,^{†,‡} Leilei Zhang,[†] Yang Xue,[‡] Bao Ke,[†] Zhuang Zhao,[#] Dan Huang,^{‡,*} Qilin Wei,[‡] Weichang Zhou,^{#,§,*} Bingsuo Zou^{‡,*}

[†] School of Materials Science and Engineering, School of Life and Environmental Sciences, Guilin University of Electronic Technology, Guilin, 541004, People's Republic of China

[‡] School of Physical Science and Technology, Key Laboratory of New Processing Technology for Non-ferrous Metals and Materials (Ministry of Education), Guangxi Key Laboratory of Processing for Non-ferrous Metals and Featured Materials, Nanning 530004, People's Republic of China

[#] School of Physics and Electronics, Key Laboratory of Low-dimensional Quantum Structures and Quantum Control of Ministry of Education, Hunan Normal University, Changsha 410081, People's Republic of China

§ Key Laboratory for Matter Microstructure and Function of Hunan Province, Synergetic Innovation Center for Quantum Effects and Application, Hunan Normal University, Changsha 410081, People's Republic of China

* Corresponding Author: E-mail: danhuang@gxu.edu.cn (D. H.), wchangzhou@hunnu.edu.cn (W. Z.), zoubs@gxu.edu.cn (B. Z.)

Experimental Method and Characterization

Chemicals

Cesium chloride (CsCl, Alfa Aesar, 99.99%), antimony chloride (SbCl₃, Alfa Aesar, 99.999%) and indium chloride (InCl₃, Alfa Aesar, 99.99%) were purchased from Beijing Inno-chem Technology Company. Sodium chloride (NaCl, Alfa Aesar, 99.99%), hydrochloric acid (HCl, 37 wt% in water) and isopropanol ((CH₃)₂CHOH) were purchased from Sinopharm Chemical agent Company. All of these chemical agents were used without further purification.

Synthesis of Sb³⁺:Cs₂NaInCl₆ with different doping concentration (Sb/(Sb+In)= 0%, 5%, 10%, 15%, 30%, 60% and 100%)

Sb-doped Cs₂NaInCl₆ were synthesized by hydrothermal method. 1 mmol CsCl, 0.5 mmol NaCl, variable ratio of SbCl₃ to InCl₃ while keep the whole amount of SbCl₃ and InCl₃ to be 0.5 mmol, and 6 mL of HCl solution were added in the 25 ml stainless steel autoclave. The mixture solution was heated at 180 °C for 2 h, and then cooled slowly to room temperature over 10 h. The precipitated Sb³⁺:Cs₂NaInCl₆ were washed with isopropanol alcohol, and then was dried at 60 °C for 12 h.

Material characterization

The crystallographic phase structure was determined by X-ray diffraction (XRD, Bruker D8 Discover). The chemical state and element content were identified by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, ESCALAB 250Xi). The morphology and lattice structure were examined by transmission electron microscope (TEM) and high resolution TEM (HRTEM, JEOL, JEM-2100F). The chemical composition was analyzed by energy-dispersive spectrometry (EDS, Oxford X-max20 attached on the TEM). The absorption spectrum was measured using ultraviolet-visible spectrophotometer (PerkinElmer Instruments, Lambda 750). The photoluminescence (PL) and PL excitation (PLE) spectrum were carried out with the Hitachi F-4600 spectrophotometer. The PL quantum yields (QYs) were obtained by using the Fluromax-4P spectrometer (Horiba Jobin Yvon) with a QY accessory. The temperature-dependent PL spectra were measured by high resolution Raman spectrometer (Horiba Jobin Yvon, LabRAM HR Evolution) using the continuous wave (CW) laser with wavelength of 355 nm as the excitation light source. Linkam THMS600 and liquid nitrogen were used to cool or heat the samples in the range of 80-520 K. The PL decay profiles were measured with the Horiba Jobin Yvon Fluorolog-3 spectrometer. The DXR Raman Microscope (Thermo Fisher Scientific) was used to measure the Raman spectra.

Calculation details

Our first-principles calculations are performed by the VASP¹ package in the framework of density functional theory (DFT). The generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE)² is used to describe the exchange-correlation functional. Based on previous studies³⁻⁶, the spin-orbit coupling (SOC) has a strong

effect on the ABX₃ compounds. Therefore, we have considered SOC effect in all calculations. The cut-off energy for the plane wave basis is set to 500 eV and a r-centered $3\times3\times3$ Monkhorst-pack mesh is employed. Our calculated lattice constants are a = b = c = 10.36 Å and $\alpha = \beta = \gamma = 90^{\circ}$ with the space group of Fm³ m(No. 225).

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Figure S1. Crystal structure of Sb³⁺-doped Cs₂NaInCl₆ double perovskites.



Figure S2. (a) XPS spectra of In and Sb in 10%Sb³⁺:Cs₂NaInCl₆. (b) The survey spectrum of 10%Sb³⁺:Cs₂NaInCl₆.

Table S1. Elements content of $Cs_2NaInCl_6$, 5%Sb³⁺:Cs_2NaInCl_6, 10%Sb³⁺:Cs_2NaInCl_6and 15%Sb³⁺:Cs_2NaInCl_6 from the quantitative analysis of XPS data.

	Cs	Na	In	Cl	Sb
Cs ₂ NaInCl ₆	22.65	11.32	8.84	57.19	N/A
5%Sb ³⁺ :Cs ₂ NaInCl ₆	23.06	12.5	8.19	55.14	1.11
10%Sb ³⁺ :Cs ₂ NaInCl ₆	22.25	11.53	7.65	56.32	2.25
15%Sb ³⁺ :Cs ₂ NaInCl ₆	23.25	8.42	7.89	57.73	2.72



Figure S3. SEM image of 10%Sb³⁺:Cs₂NaInCl₆ and corresponding EDS mappings of Cs, Na, In, Cl, Sb elements.



Figure S4. HRTEM image and corresponding FFT (inset) of 10%Sb³⁺:Cs₂NaInCl₆.



Figure S5. Absorption spectra of $Sb^{3+}:Cs_2NaInCl_6$ with Sb/(In+Sb) feed ratios of 0%, 10%, 30%, 100%.



Figure S6. PL spectra of Cs₂NaInCl₆.



Figure S7. PL spectra of Sb³⁺:Cs₂NaInCl₆ with more fine Sb/(In+Sb) feed ratios of 0%,



2%, 4%, 5%, 10%, 12%, 15%.

Figure S8. The PLQY measurement cross-sectional view of 10%Sb³⁺:Cs₂NaInCl₆ sample (the yellow curve) shows that the PLQY is as high as 75.89%. The excitation wavelength was 315 nm. The cyan blue curve is the reference cross-sectional view of BaSO₄ sample.



Figure S9. Raman spectra of Sb³⁺:Cs₂NaInCl₆ with Sb/(In+Sb) feed ratios of 0%, 5%,

10%, 15%, 30%, 60%, 100%.



Scheme S1. Schematic diagram of proposed energy transfer model of STEs.



Figure S10. Fitting results of the FWHM (meV) as a function of temperature via the

formula of $FWHM = 2.36\sqrt{S}\hbar\omega_{phonon}\sqrt{\coth\frac{\hbar\omega_{phonon}}{2K_BT}}$ to obtain the Huang–Rhys factor

(S), where \mathcal{O}_{phonon} is the frequency of longitudinal optical (LO) phonon.



Figure S11. Dependence of the PL peak position (nm) and FWHM (nm) of 10%Sb³⁺:Cs₂NaInCl₆ with temperature.



Figure S12. Fitting results of the FWHM (meV) as a function of reciprocal temperature via the formula of $\Gamma(T) = \Gamma_0 + \Gamma_{op} / (e^{\hbar \omega_{op}/K_BT} - 1)$ to obtain the phonon coupling energy, where Γ_0 is the intrinsic line width at absolute temperature 0 K, Γ_{op} is the electron–optical phonon coupling energy, $\hbar \omega_{op}$ is the longitudinal optical phonon energy, and K_B is the Boltzmann constant.



Figure S13. Time-resolved PL decay of Sb:Cs₂NaInCl₆ with Sb/(In+Sb) feed ratios of 0%, 5%, 10%, 15%, 30%, 60%.



Figure S14. Thermogravimetric analysis (TGA) of 10%Sb³⁺:Cs₂NaInCl₆.