

Supporting Information

Multicolor Luminescence and Afterglow from Cs₂NaScCl₆: Sb³⁺, Mn²⁺ Crystals

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Experimental Section:

Materials:

All reagents were used as received without any further purification: cesium chloride (CsCl, 99.9%), sodium chloride (NaCl, 99.9%), scandium oxide (Sc₂O₃, 99.9%), antimony chloride (SbCl₃, 99.9%) and manganese chloride (MnCl₂, 99.9%) were purchased from Shanghai Macklin Biochemical Co., Ltd., China; hydrochloric acid (HCl, 12 M) and isopropyl alcohol (C₃H₈O) were purchased from Yantai Far East Fine Chemical Co., Ltd., China.

Synthesis of Cs₂NaScCl₆:1%Sb³⁺, 5%Mn²⁺ Single Crystals:

The Cs₂NaScCl₆:1%Sb³⁺, 5%Mn²⁺ single crystals were grown in a hydrothermal vessel.¹ Typically, 6 mmol CsCl, 3 mmol NaCl, 3 mmol Sc₂O₃, 0.03 mmol SbCl₃ and 0.15 mmol MnCl₂ were weighed and loaded into a 25-mL Teflon vessel. Then, 12 mL HCl was added and stirred vigorously. At room temperature, the precursors did not dissolve completely. Then the Teflon vessel was sealed and put into a muffle furnace before heating to 180 °C. The temperature was maintained for 12 h, and then slowly lowered to room temperature at a cooling rate of ~3°C/h. Single crystals were collected at the bottom of vessel and washed with a small amount of isopropyl alcohol. The crystals were dried at 60 °C and placed in capped vials for further characterization.

The Fabrication of Anti-Counterfeiting Patterns:

Firstly, the single crystals were thoroughly ground in an agate mortar for 5 min to obtain a fine powder. The afterglow slurry was obtained by mixing the powder (0.1 g) with epoxy resin (7 mL) with stirring. The afterglow slurry of varied luminescence was poured into a petri-dish and allowed to solidify at 60 °C for 3 h. The resulted film was cut into designed shapes to form the anti-counterfeiting patterns.

X-ray Diffraction:

X-ray diffraction patterns were collected using an X-ray diffractometer (BRUKER AXS GMBH D8 FOCUS) coupled with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$), with a scanning rate at 5

°/min and a step size of 0.04°.

Steady-State Photoluminescence (PL) Spectra and PL QY Measurement:

The $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}, x\text{Mn}^{2+}$ single crystals were transferred to a quartz cuvette for steady-state PL spectra and PL QY measurement. A spectrometer (FS5, Edinburgh Instruments) equipped with a Teflon integrating sphere was used to record the PL spectra and PL QY. The excitation wavelength was set at 340 nm, and PL spectra and PL QY were recorded with step size of 1 nm and dwell time of 0.1 s. The reference phosphor was Cs_4PbBr_6 powders, which was alike the sample in terms of morphology and excitation wavelength. In addition, the reference phosphor has a steady PL QY of 90% under 340 nm excitation. The temperature-dependent PL spectra were collected by a fiber optic spectrometer (Aurora 4000, GE-UV-NIR, Changchun New Industries Optoelectronics Tech. Co., Ltd).

Radioluminescence (RL) Spectra and Afterglow Decay Measurement:

The $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}, x\text{Mn}^{2+}$ single crystals were transferred to a quartz cuvette for RL spectra and afterglow decay measurement. A spectrometer (FS5, Edinburgh Instruments) coupled with an X-ray tube (Tungsten target, Moxtex) was used to record the RL spectra. Similarly, the RL spectra were recorded with step size of 1 nm and dwell time of 0.1 s. The afterglow decay was recorded by using a spectrometer (FS5, Edinburgh Instruments) coupled with an X-ray tube. Typically, the afterglow decay was recorded after the crystal being irradiated under the X-ray source for 1 min, and afterglow signal at 450 nm or 620 nm were collected against time. The X-ray outlet was set to 1 cm away from sample for all spectral measurement. The X-ray dose rate was controlled by input current (0 – 100 μA) while voltage of X-ray tube was fixed at 50 kV.

Photoluminescence Lifetime Measurement:

The lifetime of single crystal was obtained with a time-resolved spectrometer (Delta-flex, Horiba Scientific). A pulsed 355-nm LED lamp was used as the excitation source for millisecond temporal resolution.

Thermoluminescence (TL) Measurement:

The single crystals were charged with an X-ray tube (dose rate: 7.4 mGy/s) for 1 min before transferring into a heating chamber (HCS421VXY, Instec Inc). After a short standby of 1 min, the TL spectra were recorded using a sensitive power meter (1936-R, Newport) as increasing temperature (2.5 K/s) by a controlling module.

Optical Photographs of Single Crystals:

Optical photographs of single crystals were taken by a Canon 90D camera. The afterglow images required a long exposure time (2 s) and a high ISO (25600) value. In contrast, the exposure time and ISO of the luminescence photographs under 365-nm and X-ray tube (Dose rate: 7.4 mGy/s) excitation were quite short, down to 1/4 s and 1600, respectively.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) Measurement.

Inductively coupled plasma optical emission spectrometry measurement was collected by the ICP-OES instrument (Agilent 720ES) and approximately 50-mg sample powder was acid-dissolved prior to testing.

Table S1. Actual molar ratio of Cs₂NaScCl₆:1%Sb³⁺, xMn²⁺ crystals by ICP-OES.

sample	Actual conc. of Sb ³⁺ (%)	Actual conc. of Mn ²⁺ (%)
1%Sb ³⁺	0.3	0
1%Sb ³⁺ , 5%Mn ²⁺	0.38	0.23
1%Sb ³⁺ , 20%Mn ²⁺	0.36	2.11

Table S2. Fitting results of PL decay curves of Mn-doped crystals.

Doping conc.	τ_x /ms	W_{ET} (10 ⁴ s ⁻¹)	η_{ET}
0%	2.35	N.A.	N.A.
5%	1.55	21.97	34.0%
10%	1.40	28.88	40.4%
20%	1.32	33.21	43.8%
40%	1.20	40.78	48.9%
60%	1.17	42.92	50.2%

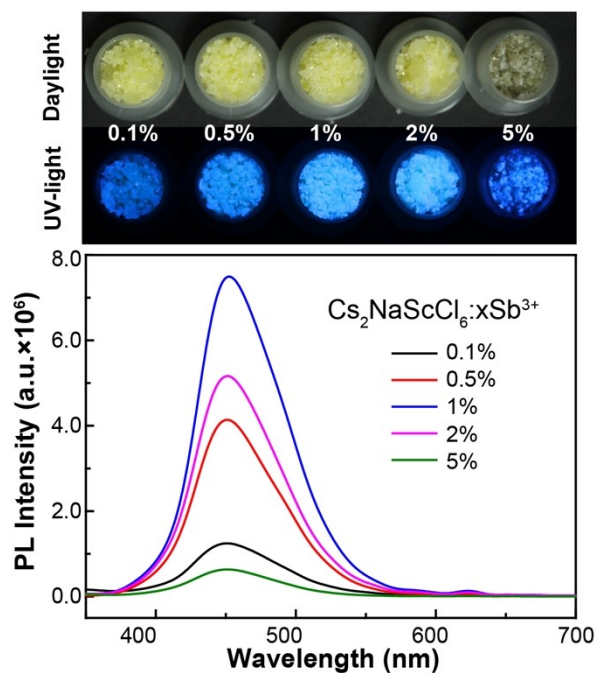


Figure S1. Steady-state PL spectra under 254-nm excitation of $\text{Cs}_2\text{NaScCl}_6$ crystals with varied Sb^{3+} -doping concentrations. Insets showed photographs of the crystals under UV and day light, respectively.

To optimize the doping concentration, we have conducted a series of crystal synthesis and measured the PL intensity of samples. As shown in Figure S3, PL spectra of $\text{Cs}_2\text{NaScCl}_6$ single crystals suggested an optimal doping concentration of 1%, which is similar to the conclusion in the reference.²

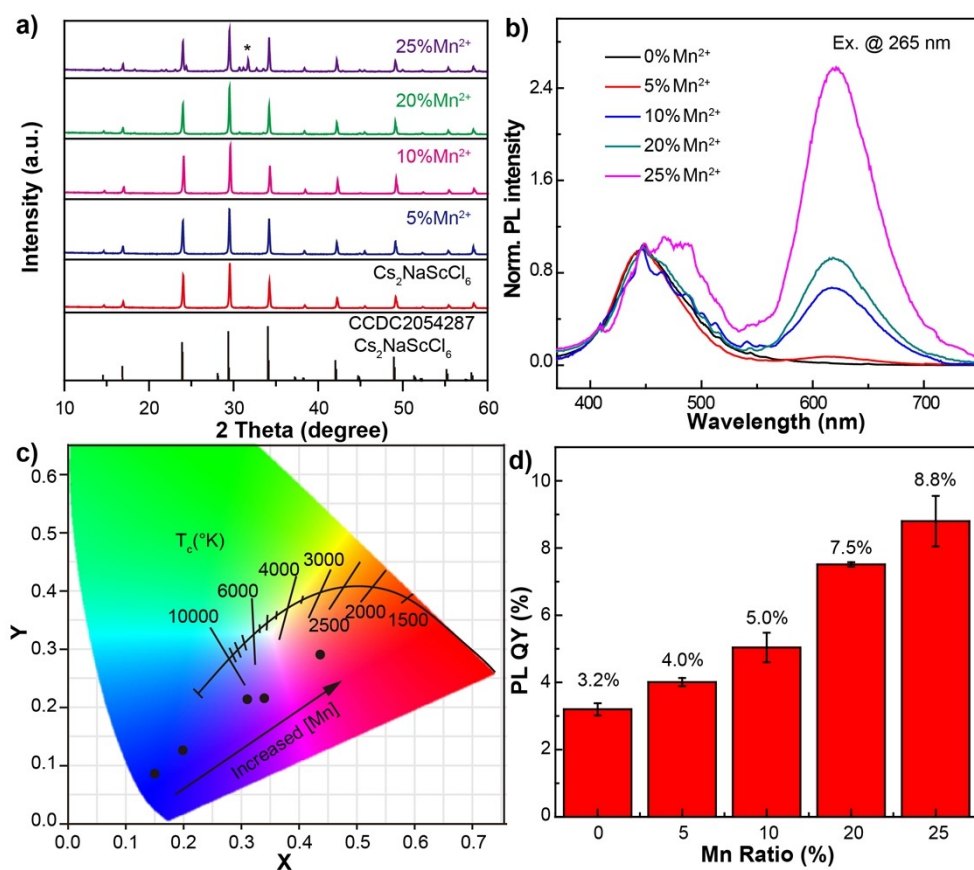


Figure S2. Photophysical Properties of $\text{Cs}_2\text{NaScCl}_6:\text{xMn}^{2+}$ Crystals. (a) X-ray diffraction (XRD) patterns of the $\text{Cs}_2\text{NaScCl}_6:\text{xMn}^{2+}$. The asterisk marked an impurity phase of NaCl. (b) Steady-state PL spectra of crystals with varied Mn^{2+} -doping concentrations, which were normalized at 450 nm. (c) CIE chroma coordinates of samples under 254 nm-UV irradiations, showing the color tuning from blue to red. (d) PL QYs for a series of the Mn^{2+} doped crystals.

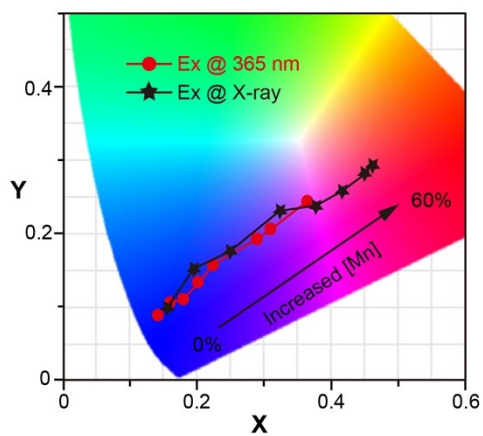


Figure S3. CIE chroma coordinates of $\text{Cs}_2\text{NaScCl}_6:x\text{Mn}^{2+}:1\%\text{Sb}^{3+}$ crystal samples under X-ray and UV irradiation, showing the fine-tuning ability of colors from blue to red.

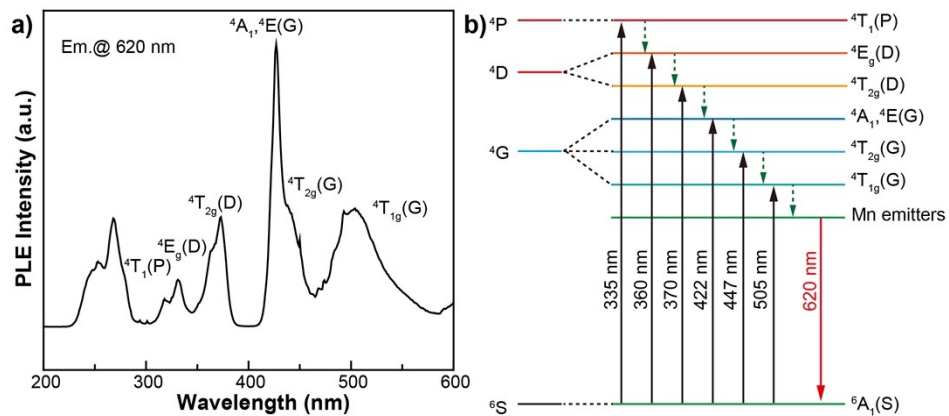


Figure S4. (a) PLE spectrum of $\text{Cs}_2\text{NaScCl}_6: 20\%\text{Mn}^{2+}$ crystal at 620 nm were monitored. (b) Characteristic energy level structure and excited transition diagram of Mn^{2+} ion.

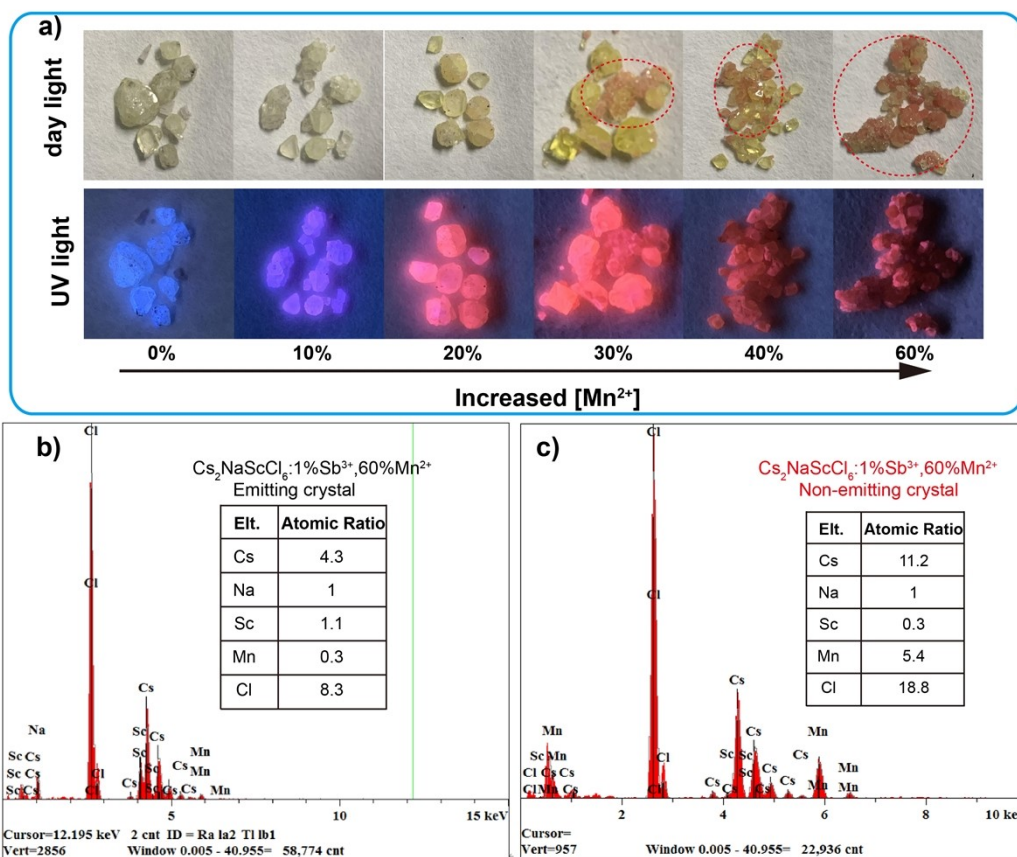


Figure S5. (a) Photographs of $Cs_2NaScCl_6:1\%Sb^{3+}, xMn^{2+}$ crystals under daylight and 365-nm UV light. EDS spectra of yellow (b) and red (c) crystals in $Cs_2NaScCl_6:1\%Sb^{3+}, 60\% Mn^{2+}$ single crystals.

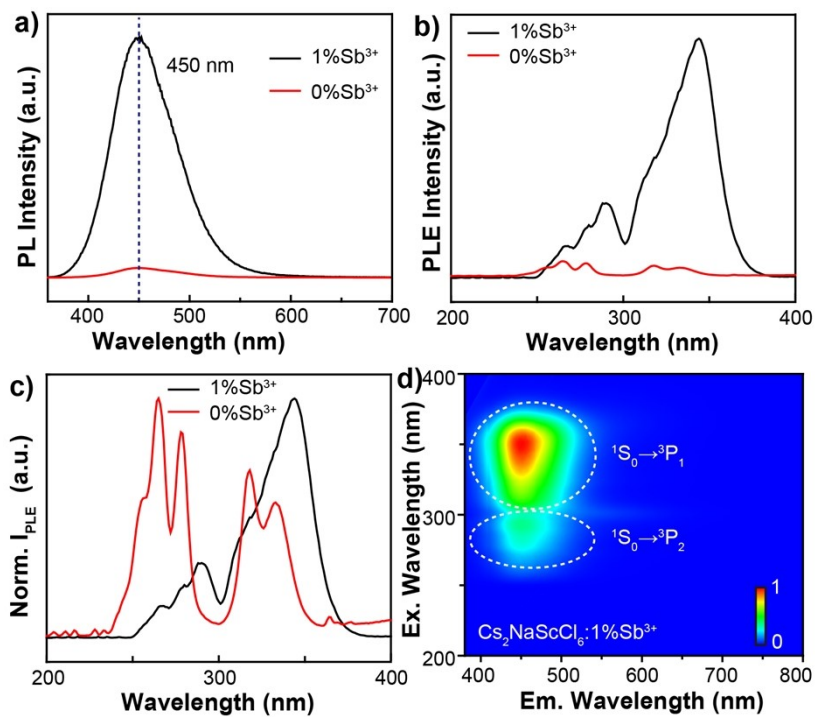


Figure S6. PL (a) and PLE (b) spectra of Sb-doped crystals and undoped crystals. (c) Normalized PLE spectra of Sb-doped crystals and undoped crystals. (d) Excitation-emission mapping of the $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}$ crystals.

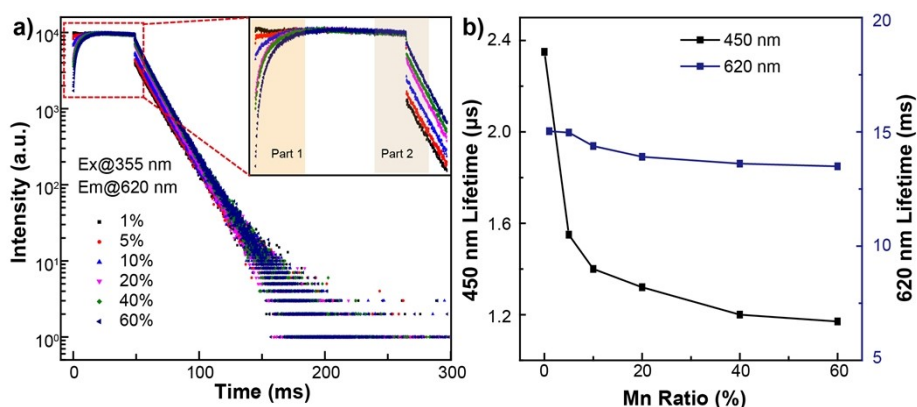


Figure S7. (a) Photoluminescence decay curves for the Mn^{2+} emission (620 nm) of $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}, x\text{Mn}^{2+}$ crystal. Part 1 represented the rising stage, where the direct excitation of Mn^{2+} leads to the steep rise. Instead, the energy transfer from STE to Mn^{2+} resulted a slow rise. As Mn^{2+} content increased, the slow-rise portion increased, indicating more Mn^{2+} emission was indirectly excited by energy transfer. Part 2 represented a rapid decline, which is the STE overlapping portion of Mn^{2+} . This portion decreased with increasing Mn^{2+} content. (b) The fitting results of the average lifetime of STE (Figure 2d) and Mn^{2+} (Figure S9a) emission.

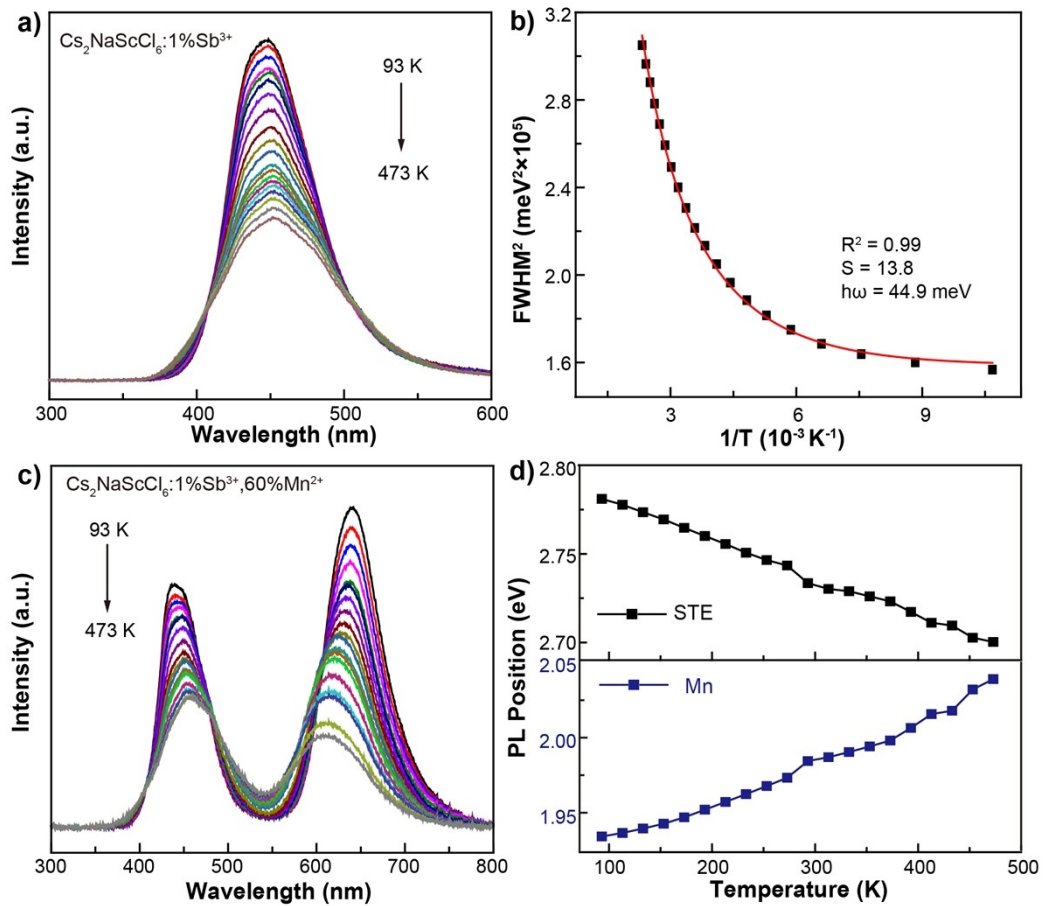


Figure S8. Temperature-dependent PL emission of $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}$ (a) and $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+}, 60\%\text{Mn}^{2+}$ crystal (c) under 275 nm lamp excitation. (b) FWHM was plotted as a function of temperature. (d) The PL position of STE and Mn^{2+} emission showed different trends with the increasing temperature.

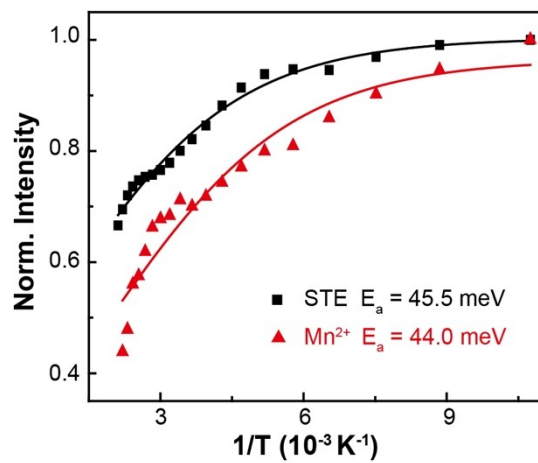


Figure S9. Integrated PL emission intensity of Cs₂NaScCl₆:1%Sb³⁺, 60%Mn²⁺ crystal was plotted as a function of temperature.

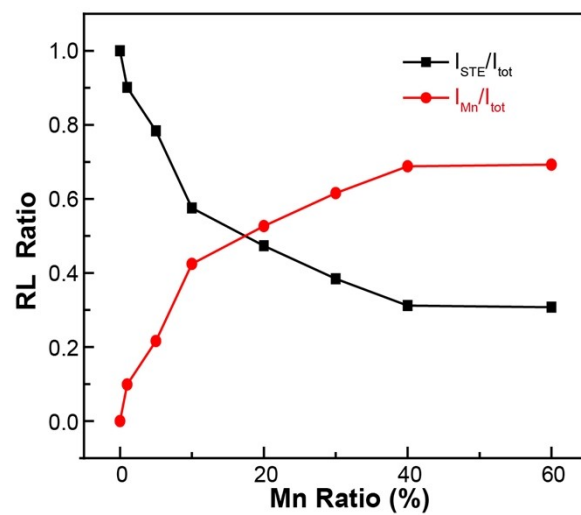


Figure S10. The RL spectra of Cs₂NaScCl₆:1%Sb³⁺, xMn²⁺ crystal showed a decrease in the STE portion and an increase Mn²⁺ portion.

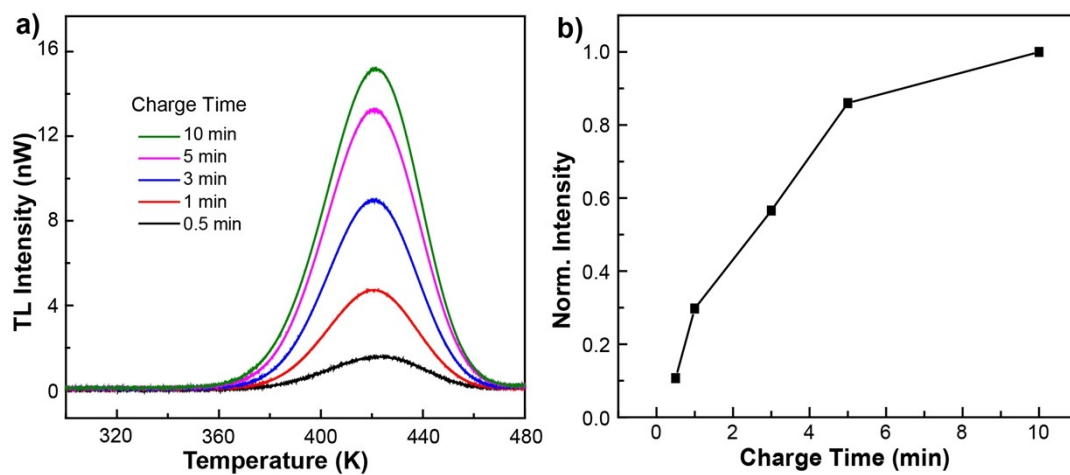


Figure S11. (a) TL curves were collected at different charging time (0.5 – 10 min) with a heating rate of 2.5 K s^{-1} . (b) TL intensity was plotted against charging time, showing a sign of saturation after 5 min.

References:

1. W. Zheng; X. Li; N. Liu; S. Yan; X. Wang; X. Zhang; Y. Liu; Y. Liang; Y. Zhang and H. Liu, Solution-Grown Chloride Perovskite Crystal of Red Afterglow, *Angew Chem Int Ed.*, 2021, **60**, 24450-24455.
2. X. Jiang; H. Ding; F. Yang; F. Luo; Z. Gan; Z. Fan; F. Gao; Z. Cheng; G. Luo and W. Zhou, Sb³⁺/Sm³⁺ Codoped Cs₂NaScCl₆ All-Inorganic Double Perovskite: Blue Emission of Self-Trapped Excitons and Red-Emission Via Energy Transfer, *Inorg. Chem.*, 2024, **63**, 10756-10766.