

Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Excitation-Dependent Emission and Highly Efficient Near-Infrared luminescence in Cs₂NaScCl₆ Double Perovskite via Sb³⁺-Yb³⁺ Alloying for Multifunctional Photoelectric Applications

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EXPERIMENTAL SECTION

Materials and synthesis

The raw materials cesium chloride (CsCl, 99.99%), sodium chloride (NaCl, 99.99%), antimony oxide (Sb₂O₃, 99.99%), scandium oxide (Sc₂O₃, 99.99%), Ytterbium oxide (Yb₂O₃, 99.99%), were purchased from Macklin. Hydrochloric acid (HCl, 36 wt% in water) and ethanol (CH₃CH₂OH, 99.7%) were purchased from Chengdu Chron Chemicals. All of these materials were used as received without any further purification. Cs₂NaSc_{0.9-x}SbYb_xCl₆ (x=0, 1%, 3%, 5%, 10%, 15%) samples were synthesized via a hydrothermal method. In a typical synthesis, 6 mmol CsCl, 3 mmol NaCl, 1.5 mmol (Sc₂O₃+Sb₂O₃+Yb₂O₃) were taken in a high-pressure reactor with 12 mL HCl. Then kept it at 180 °C for 24 h, and slowly cooled it to room temperature at a rate of 3°C/h.

Characterization

The X-ray diffraction spectrum of the powder was collected on the TD-3500 X-ray diffractometer. The Cu-K α (1.54 Å) radiation source was used, the tube voltage of 30 kV and the tube current of 20 mA. The morphologies and energy dispersive X-ray spectroscopy (EDS) were obtained using a field emission scanning electron microscopy (FE-SEM). The photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra were recorded by using an FLS920 spectrofluorometer (Edinburgh) with a 450 W Xe lamp as the excitation light source, and the infrared emission was measured on a liquid nitrogen-cooled NIR photomultiplier tube (PMT) detector (Hamamatsu P9289P and R5509). Fluorescence decay curve was measured by FLS 980 spectrometer (Edinburgh, UK). The temperature-dependent luminescence properties were investigated using an intensified multichannel spectrometer (MCPD-7000, Otsuka Electronics, Japan). The pc-NIR LEDs were fabricated by mixing a transparent silicone resin containing the corresponding phosphors and InGaN blue chips. The mass ratio of phosphor to silicon resin was fixed at 1:1. The photoelectric properties of the fabricated LED, including electroluminescence spectroscopy, etc, were measured through the integrating sphere (HSP6000 spectroscopic analysis system, Hangzhou, China).

Results and Discussion

X-ray photoelectron spectroscopy (XPS) analyses of the exemplary $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ DPs reveal the presence of Cs 3d, Na 1s, Sc 2p, Cl 2p, Sb 3d and Yb 4d orbitals in the samples, respectively (Fig. S1,S2). In addition, the Sb, Sc and Yb elements are proved to be +3 valence, peaks located at 536.0 and 531.3 eV are attributed to $3d_{3/2}$ and $3d_{5/2}$ orbits of Sb^{3+} ions, and the peak at 402.6 eV is assigned to 2p orbit of Sc^{3+} and the peak at 186.3 eV is assigned to 4d orbit of Yb^{3+} ions. These results indicate the successful realization of the $\text{Sb}^{3+}/\text{Yb}^{3+}$ alloying in $\text{Cs}_2\text{NaScCl}_6$ crystal.

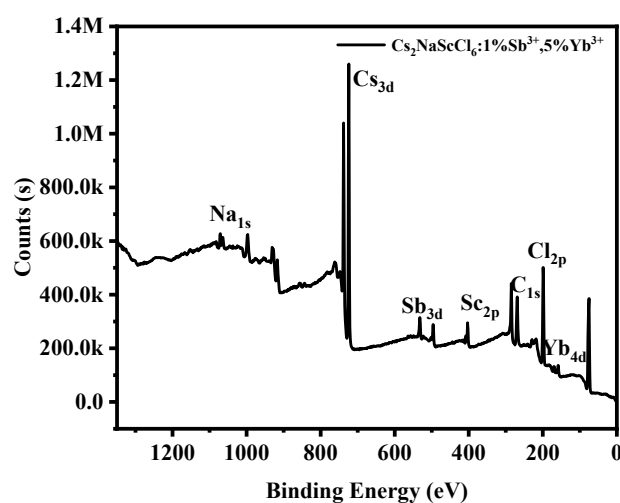


Fig. S1 XPS spectra for a survey scan

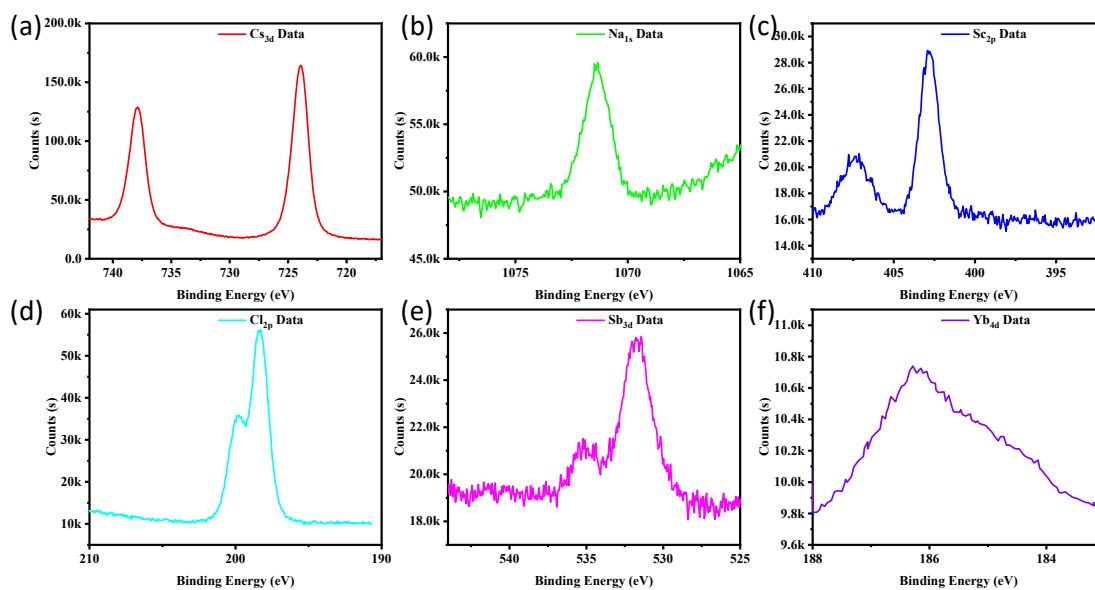


Fig. S2 High-resolution XPS spectra for Cs, Na, Sc, Cl, Sb and Yb elements

To confirm optimal Sb^{3+} doping concentration, Sb^{3+} -doped $\text{Cs}_2\text{NaScCl}_6$ crystal are prepared. The X-ray powder diffraction (XRD) patterns of the $\text{Cs}_2\text{NaScCl}_6: x\% \text{Sb}$ ($x = 0, 0.5, 1, 3, 5$) are shown in Fig. S3a. The results show that the Sb^{3+} -doped $\text{Cs}_2\text{NaScCl}_6$ crystals match well with the standard values without impurity phase. Fig. S3b shows that the PL emission intensity first increases to 1% Sb^{3+} doping concentration, then decrease.

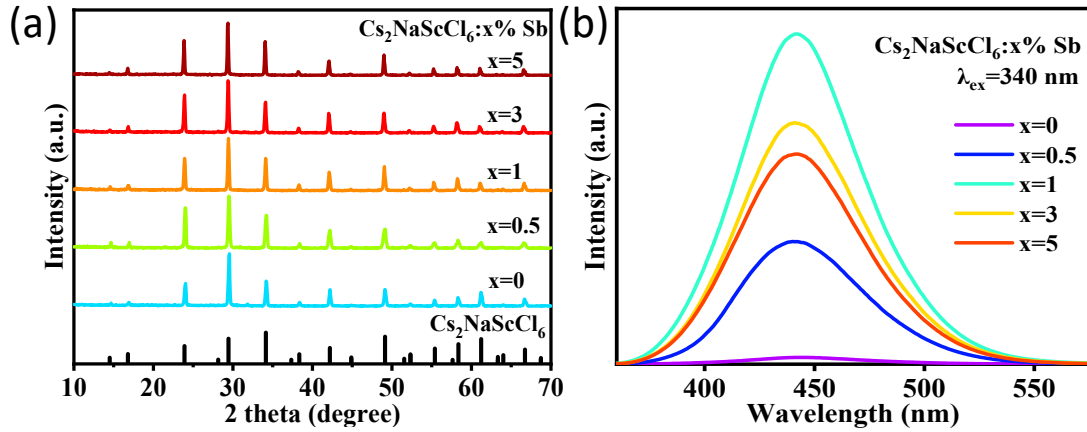


Fig. S3 The XRD patterns (a) and PL (b) spectra of $\text{Cs}_2\text{NaScCl}_6: x\% \text{Sb}^{3+}$ ($x=0-5$).

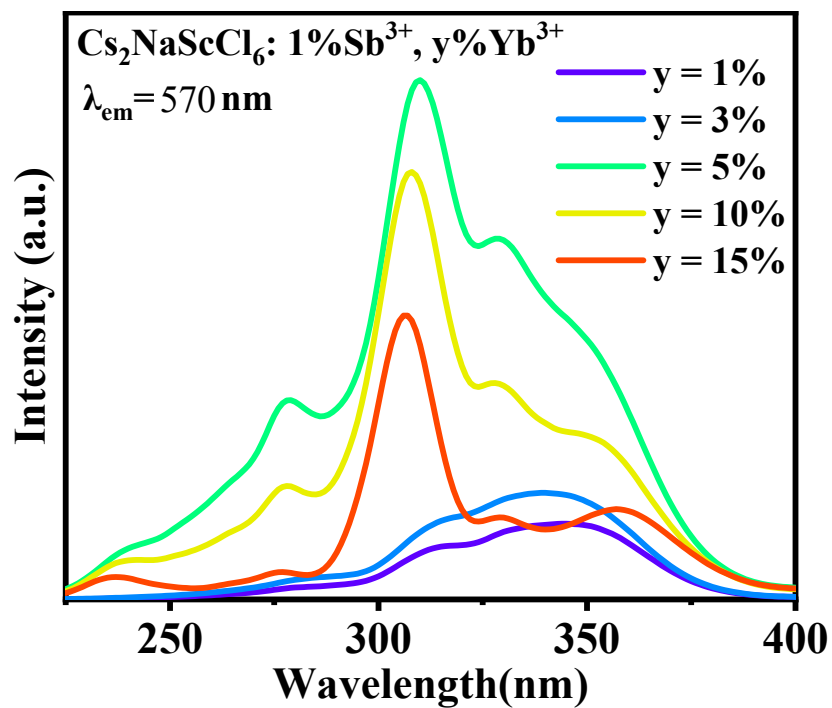


Fig. S4 Excitation spectra of $\text{Cs}_2\text{NaScCl}_6:\text{Sb}^{3+}, \text{Yb}^{3+}$ DPs under monitored at 570 nm.

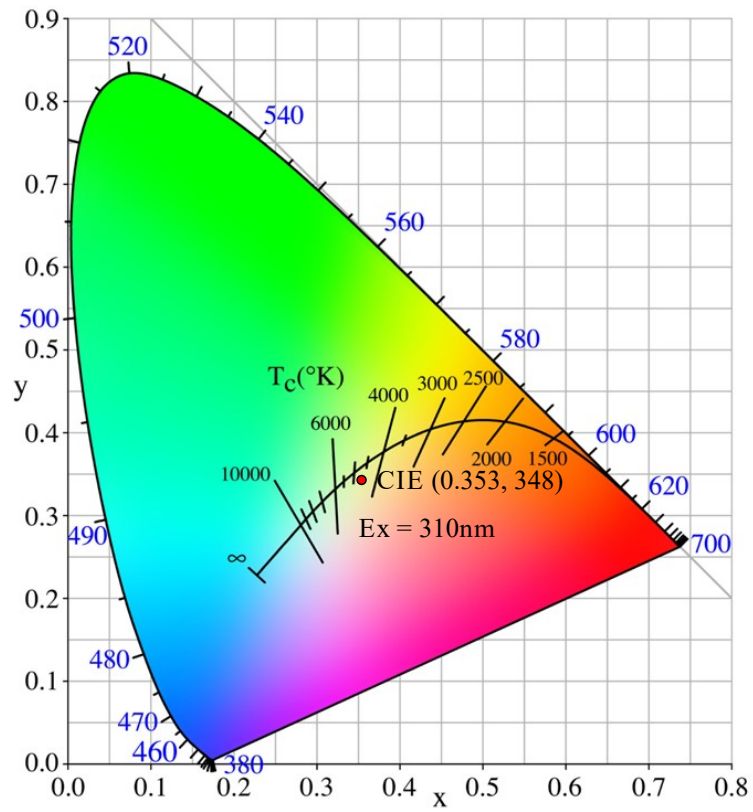


Fig. S5 CIE chromaticity coordinates of $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ sample.

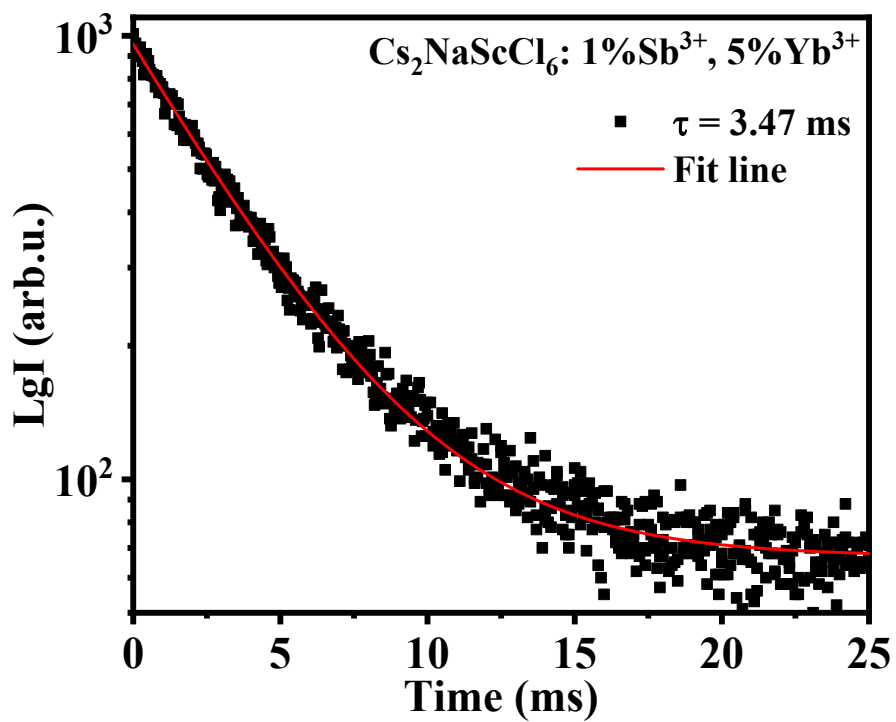


Fig. S6. NIR PL decay time of Cs₂NaScCl₆: 1%Sb, 5%Yb.

The visible emission intensity gradually decreases with increasing temperature from 300 to 500 K (Fig. 3d, S5). The decreased PL intensity agrees with the model that more phonons participation exacerbates the nonradiative recombination and strong electron-phonon coupling at high temperature. Fig. 3e shows the normalized integrated emission intensities of $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ samples. The results indicate that the integrated emission intensity of the $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ remains at about 86% of that at 298 K at temperature of 425 K, which indicates the excellent thermal stability of the samples. Moreover, the $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ exhibits excellent ambient stability. The XRD patterns (Fig. S6) show that the $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ structure can hold stable for 30 days with the visible, as well as the visible light and NIR emission intensity also remain the almost same intensity as the original value respectively under ambient conditions (Fig. 3f, S7).

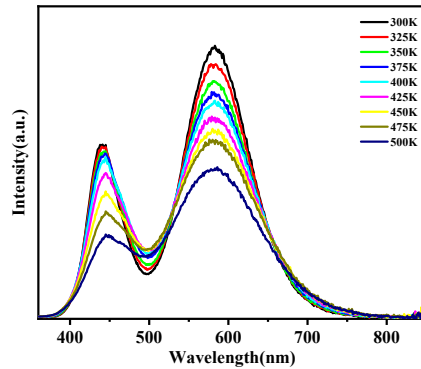


Fig. S7 Temperature-dependent photoluminescence spectra of $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb}^{3+},5\%\text{Yb}^{3+}$ from 298 to 450 K under excitation at 340 nm.

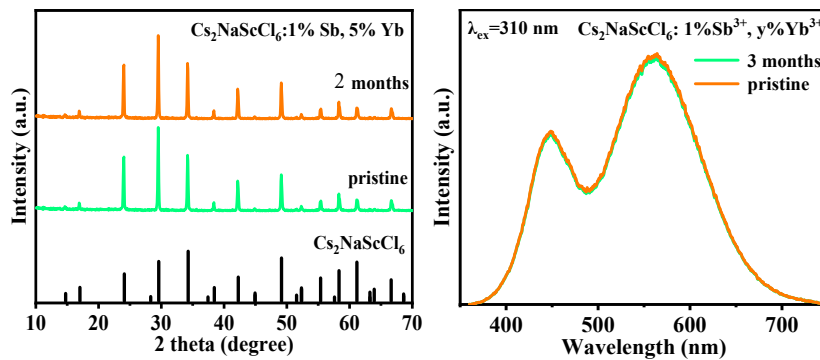


Fig. S8 XRD patterns and PL intensity of pristine $\text{Cs}_2\text{NaScCl}_6:1\%\text{Sb},5\%\text{Yb}$ and the same sample after exposing at ambient air for 60 days.

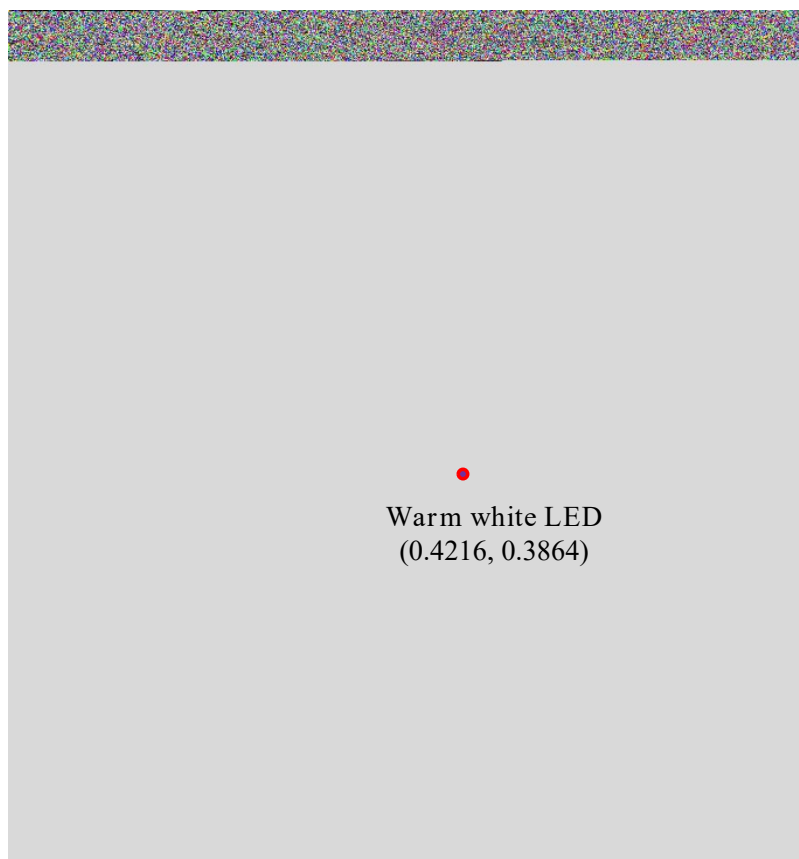


Fig. S9 The CIE chromaticity coordinates of the warm white-LED device.