Supporting Information

Dual-Response Photoluminescence of Rare Earth-Based Halide Double Perovskite

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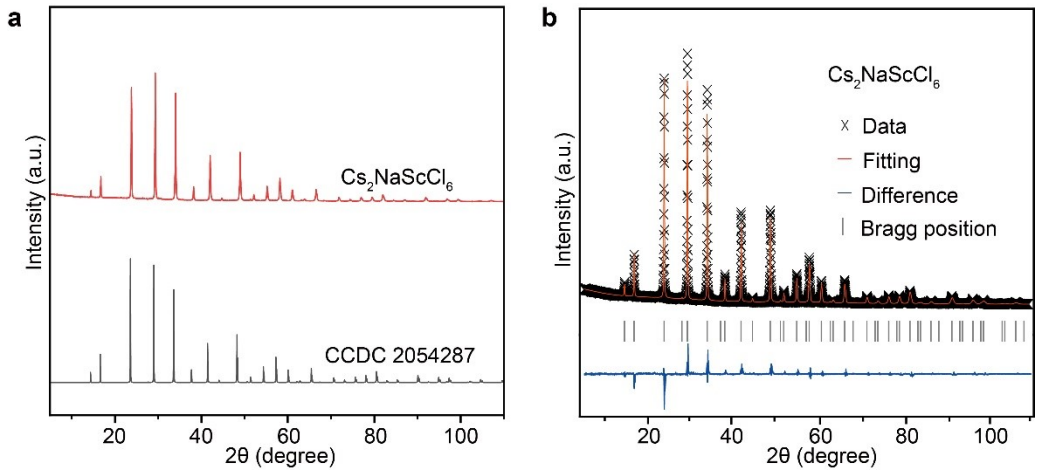

Figure S1. (a) XRD pattern and (b) corresponding XRD Rietveld refinement of as-prepared $Cs_2NaScCl_6$. The pattern at the bottom of (b) is the literature reference for the cubic $Cs_2NaScCl_6$ crystal. Rietveld refinement was conducted using the GSAS II package.[1]

Table S1. Crystallographic parameters obtained from XRD Rietveld refinements for $Cs_2NaScCl_6$ and $Cs_2NaScCl_6$: 1%Sb.

Parameter	$Cs_2NaScCl_6$	$Cs_2NaScCl_6$: 1%Sb	CCDC 2054287[a]
Crystal phase	cubic	cubic	cubic
Space group	*Fm-3m*	*Fm-3m*	*Fm-3m*
a = b = c	*10.4852(9) Å*	*10.4828(3) Å*	*10.4904 Å*
α = β = γ	*90°*	*90°*	*90°*
volume	*1152.7(6) Å³*	*1151.9(5) Å³*	*1154.4528 Å³*
z	*4*	*4*	*4*
Radiation	Cu Kα	Cu Kα	-
R_p	6.65%	4.84%	-
wR_p	9.45%	6.49%	-
Gof	1.86	1.90	-

[a] Literature reference.

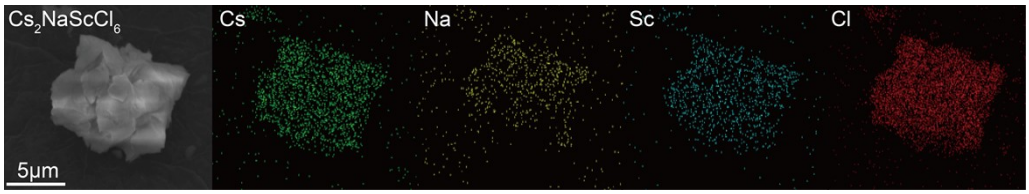

Figure S2. SEM image (left panel) and corresponding elemental mapping of as-prepared $Cs_2NaScCl_6$.

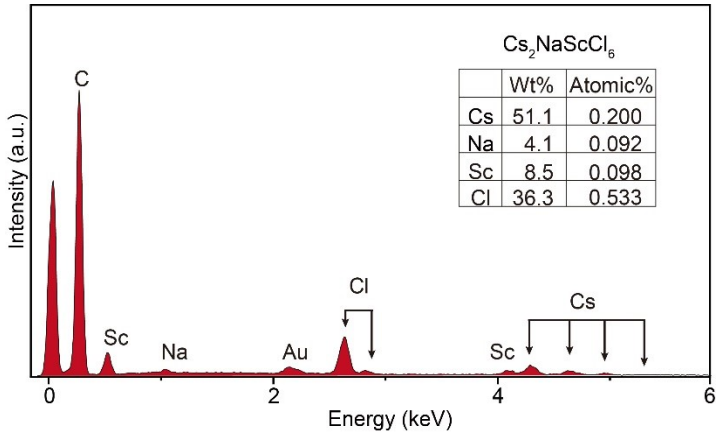

Figure S3. EDS spectrum of as-prepared $Cs_2NaScCl_6$.

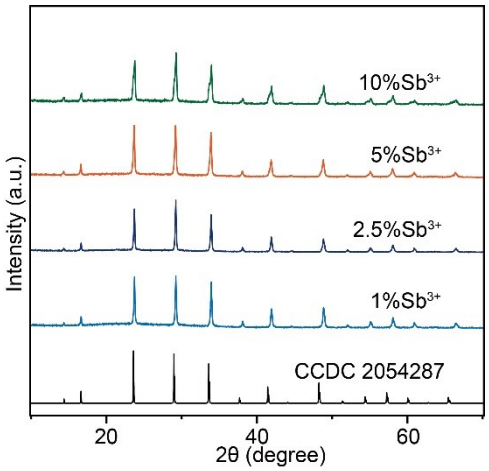

Figure S4. XRD patterns of $Cs_2NaScCl_6$: Sb with different doping concentrations of Sb^{3+}. The pattern at the bottom is the literature reference for the cubic $Cs_2NaScCl_6$ crystal.

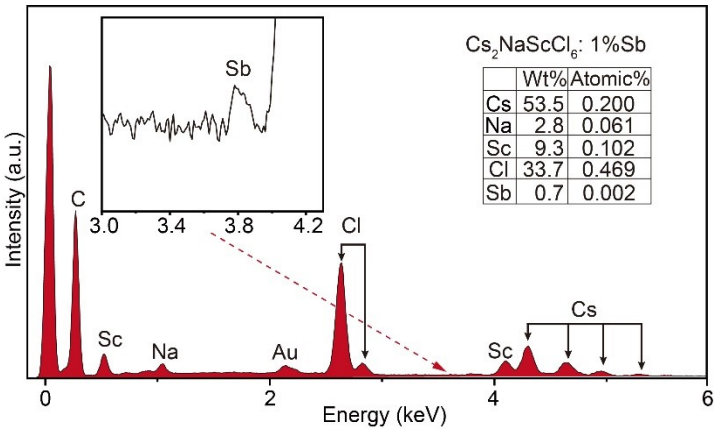

Figure S5. EDS spectrum of as-prepared $Cs_2NaScCl_6$: 1%Sb.

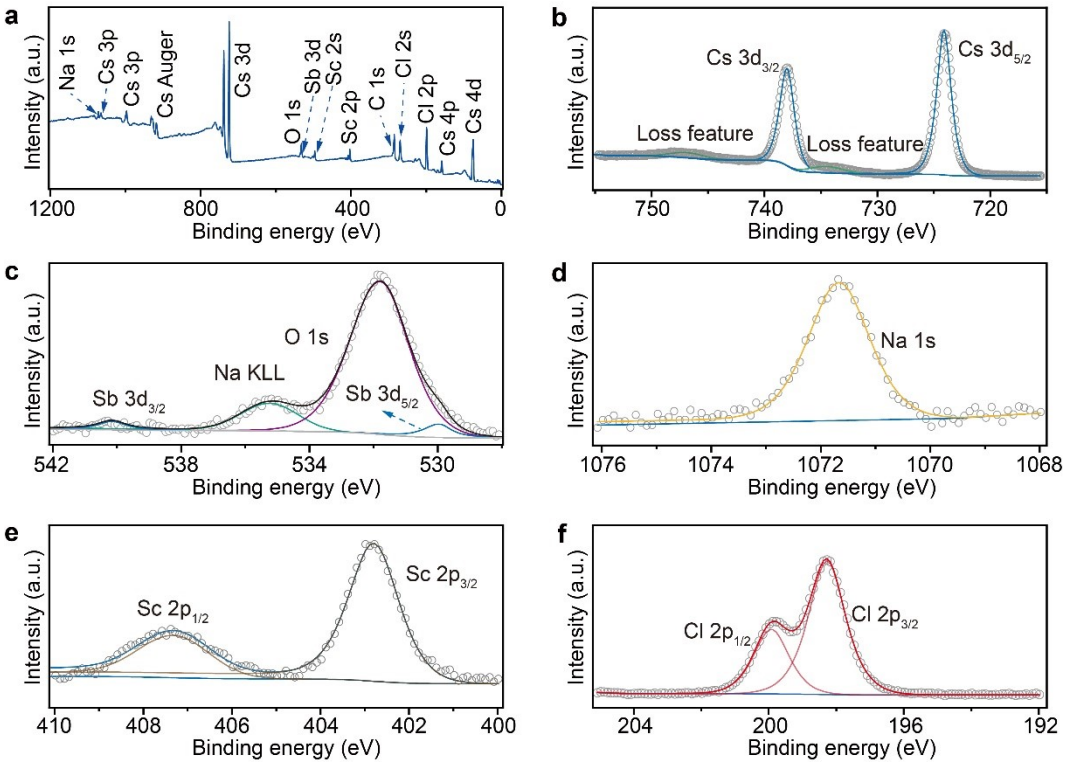

Figure S6. (a) Survey XPS spectrum of $Cs_2NaScCl_6$: 1%Sb and corresponding high-resolution XPS spectra of (b) Cs 3d, (c) Sb 3d, (d) Na 1s, (e) Sc 2p, and (f) Cl 2p. Colored lines in (b–f) are fitting curves.

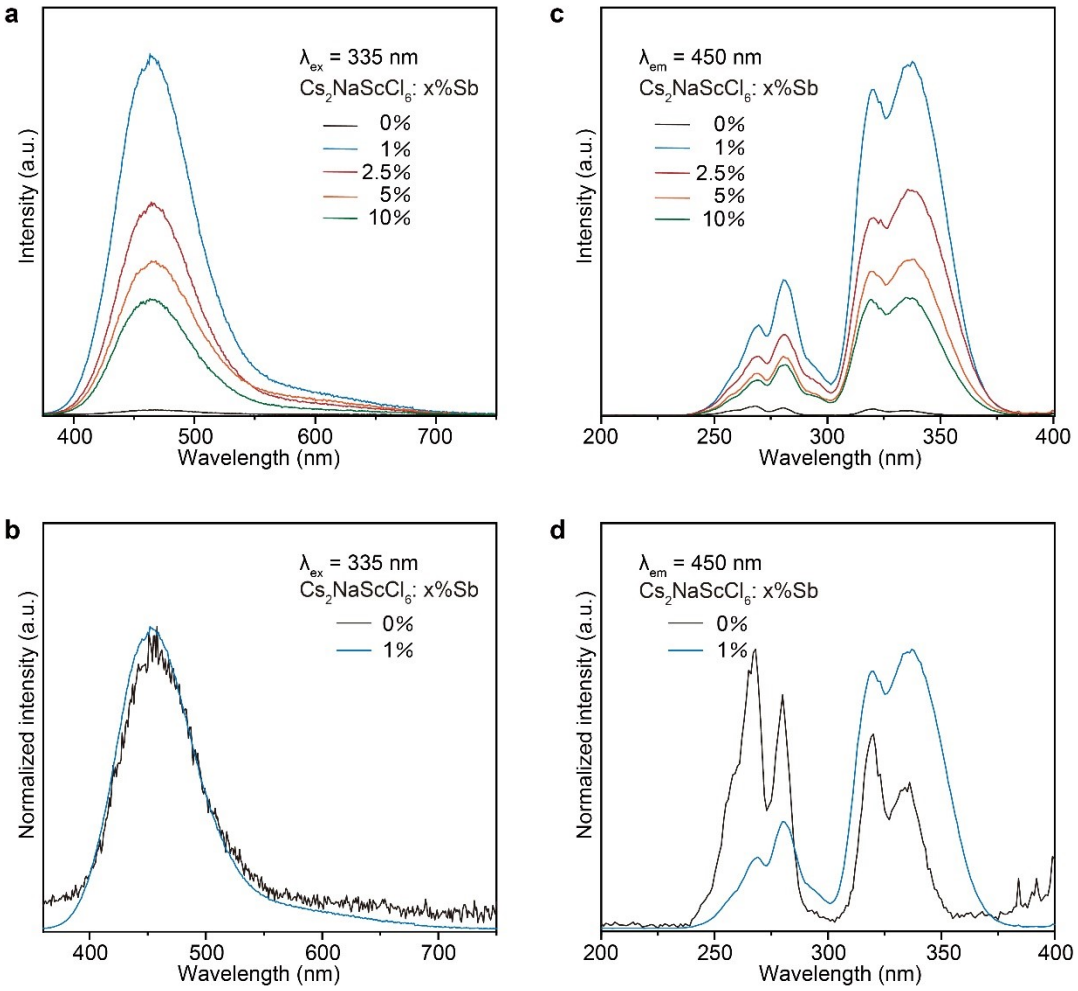

Figure S7. (a) Luminescence spectra of $Cs_2NaScCl_6$ doped with different concentrations of Sb^{3+}. (b) Normalized luminescence spectra of undoped $Cs_2NaScCl_6$ and $Cs_2NaScCl_6$: 1%Sb. (c) Excitation spectra of $Cs_2NaScCl_6$ doped with different concentrations of Sb^{3+} monitored at 450 nm. (d) Normalized excitation spectra of undoped $Cs_2NaScCl_6$ and $Cs_2NaScCl_6$: 1%Sb monitored at 450 nm.

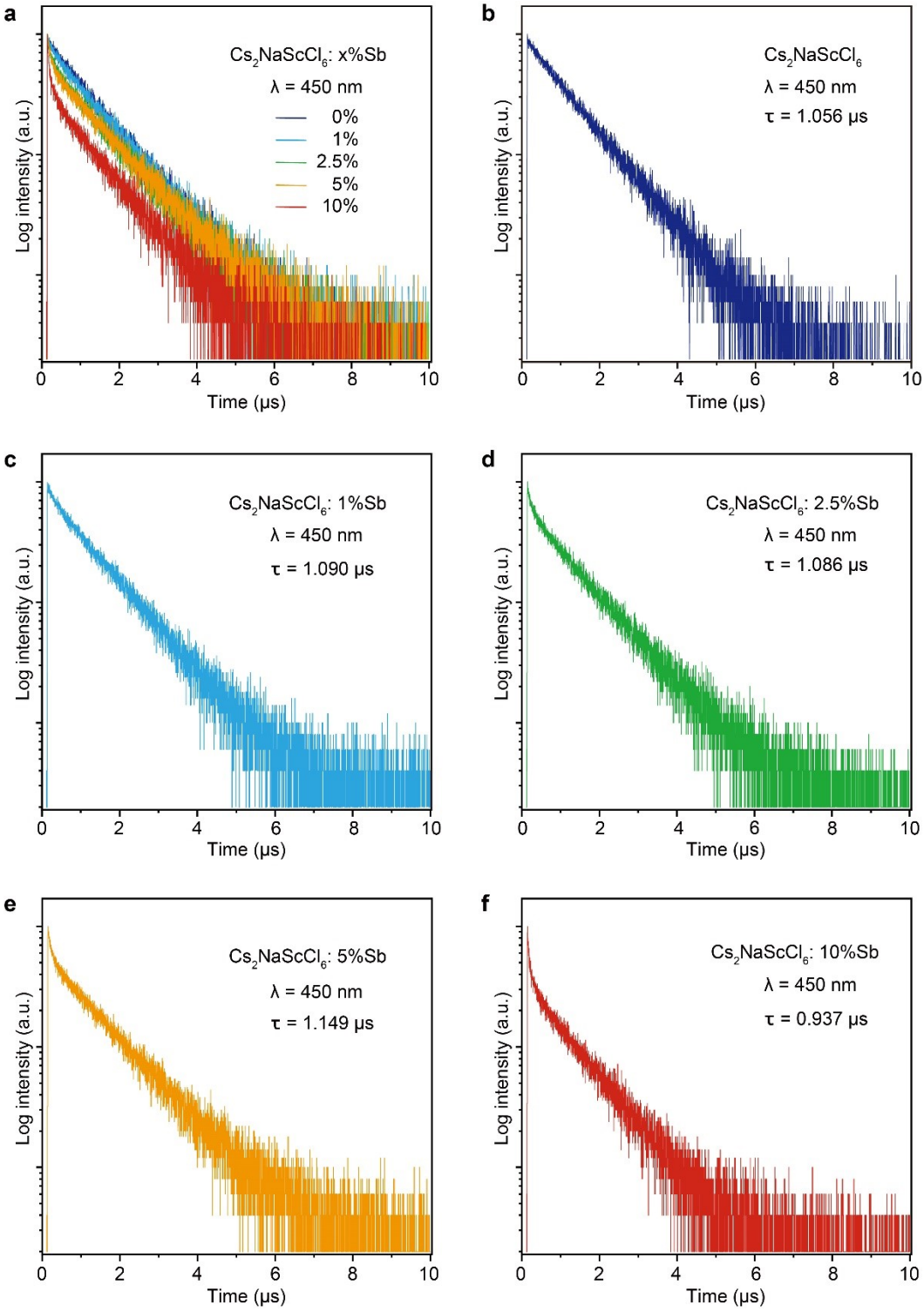
a
$Cs_2NaScCl_6$: x%Sb
λ = 450 nm
0%
1%
2.5%
5%
10%
Log intensity (a.u.)
Time (μs)
b
$Cs_2NaScCl_6$
λ = 450 nm
τ = 1.056 μs
Log intensity (a.u.)
Time (μs)
c
$Cs_2NaScCl_6$: 1%Sb
λ = 450 nm
τ = 1.090 μs
Log intensity (a.u.)
Time (μs)
d
$Cs_2NaScCl_6$: 2.5%Sb
λ = 450 nm
τ = 1.086 μs
Log intensity (a.u.)
Time (μs)
e
$Cs_2NaScCl_6$: 5%Sb
λ = 450 nm
τ = 1.149 μs
Log intensity (a.u.)
Time (μs)
f
$Cs_2NaScCl_6$: 10%Sb
λ = 450 nm
τ = 0.937 μs
Log intensity (a.u.)
Time (μs)

Figure S8. Luminescence decay curves of $Cs_2NaScCl_6$ doped different concentrations of Sb^{3+} at 450 nm. (a) Overlay curves, (b) 0%Sb, (c) 1%Sb, (d) 2.5%Sb, (e) 5%Sb, and (f) 10%Sb. The excitation source is a 260 nm pulsed light emitting diode.

Table S2. Fitting results of decay curves of Sb^{3+}-doped $Cs_2NaScCl_6$.[a]

Sb^{3+} content (%)	τ_1 (ns)	Rel. (%)	τ_2 (ns)	Rel. (%)	Lifetime (ns)
0	1056.76	100	-	-	1056.76
1	145.66	2.84	1118.21	97.16	1090.76
2.5	111.81	5.27	1140.55	94.73	1086.37
5	89.03	5.63	1212.93	94.37	1149.69
10	59.69	8.22	1016.01	91.73	937.41

[a] Decay curves were fitted using a single exponential function (S1) or double exponential function (S2) as follows:

$$I_t = I_0 exp\left(-\frac{t}{\tau}\right) \#(S1)$$

$$I_t = A_1 exp\left(-\frac{t}{\tau_1}\right) + A_2 exp\left(-\frac{t}{\tau_2}\right) \#(S2)$$

where I_0 is the maximum fluorescence intensity, t is time, I_t is the fluorescence intensity at time t, τ is lifetime, and A is the amplitude of a lifetime component.

For decay curves fitted by the double exponential function, lifetime was calculated using the following formula:

$$\tau = \tau_1 * Rel_1 + \tau_2 * Rel_2 \#(S3)$$

where Rel_1 and Rel_2 are the proportion of τ_1 and τ_2 component and can be calculated by:

$$Rel_1 = \frac{A_1\tau_1}{A_1\tau_1 + A_2\tau_2} * 100 \#(S4)$$

$$Rel_2 = \frac{A_2\tau_2}{A_1\tau_1 + A_2\tau_2} * 100 \#(S5)$$

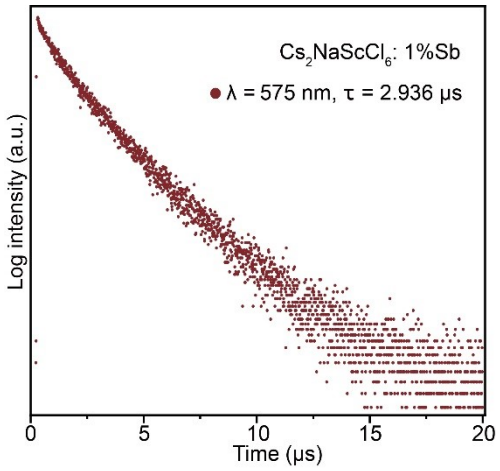

Figure S9. Luminescence decay curve of $Cs_2NaScCl_6$: 1%Sb at 575 nm. The excitation source is a 310 nm pulsed light emitting diode.

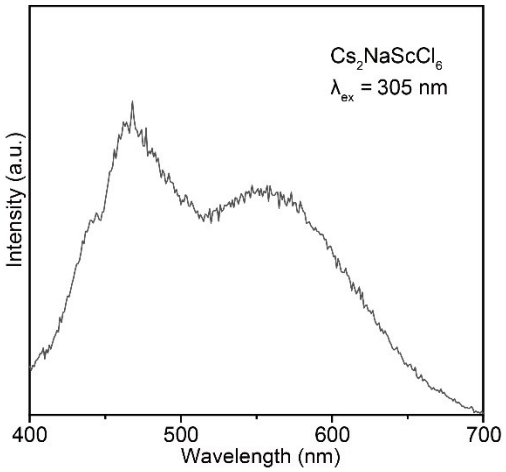

Figure S10. Luminescence spectrum of $Cs_2NaScCl_6$ under 305 nm excitation.

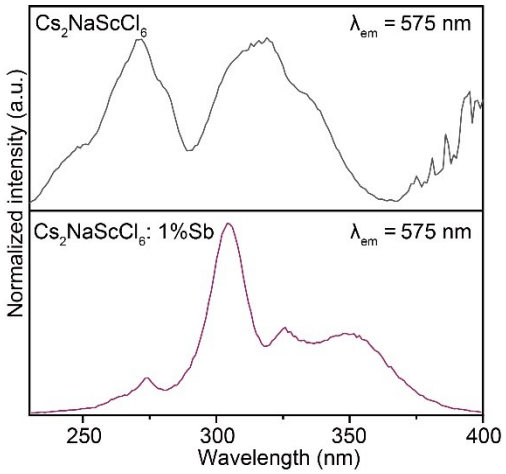

Figure S11. Normalized excitation spectra of $Cs_2NaScCl_6$ and $Cs_2NaScCl_6$: 1%Sb monitored at 575 nm.

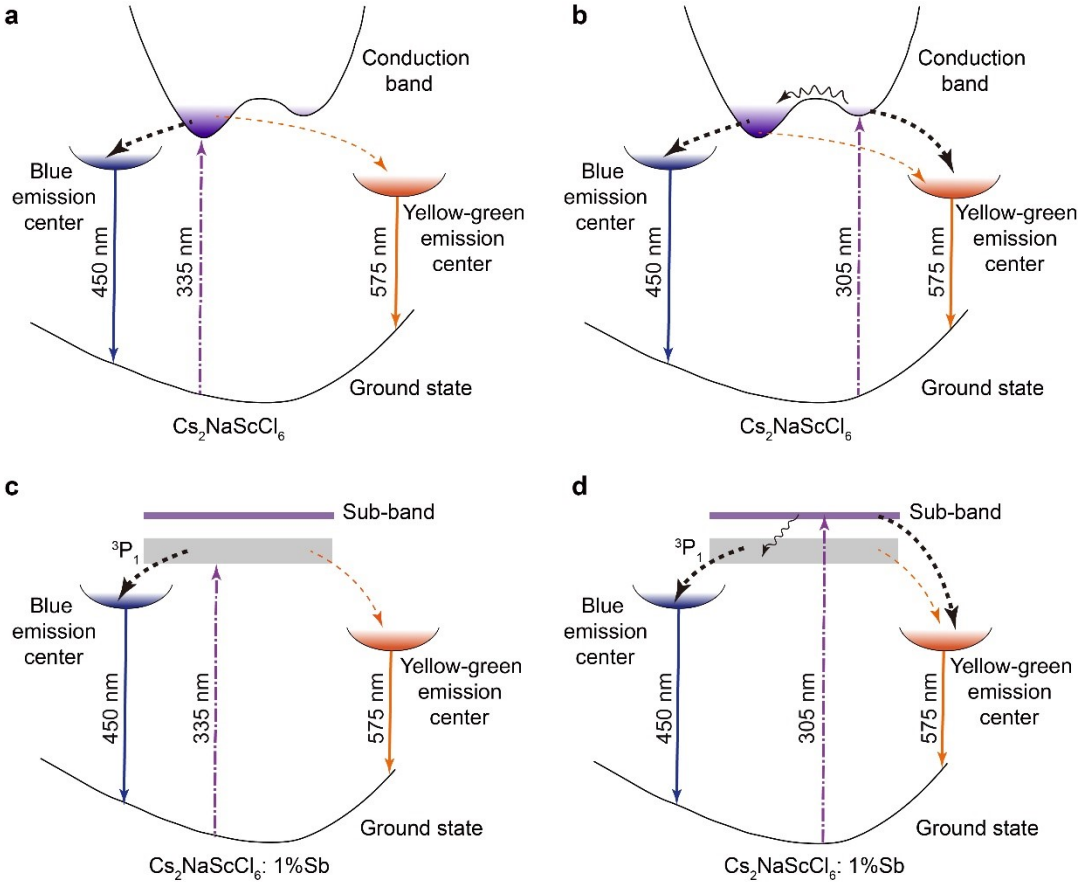

Figure S12. Schematic illustration of the proposed luminescence process of (a) $Cs_2NaScCl_6$ under 335 nm excitation, (b) $Cs_2NaScCl_6$ under 305 nm excitation, (c) $Cs_2NaScCl_6$: 1%Sb under 335 nm excitation, and (d) $Cs_2NaScCl_6$: 1%Sb under 305 nm excitation at room temperature. The dashed-dotted, solid, and wavy arrows represent excitation, emission, and relaxation processes, respectively. The dashed arrows indicate the STE formation in (a), (b) and energy transfer in (c), (d). The orange dashed line indicates a relatively weak process.

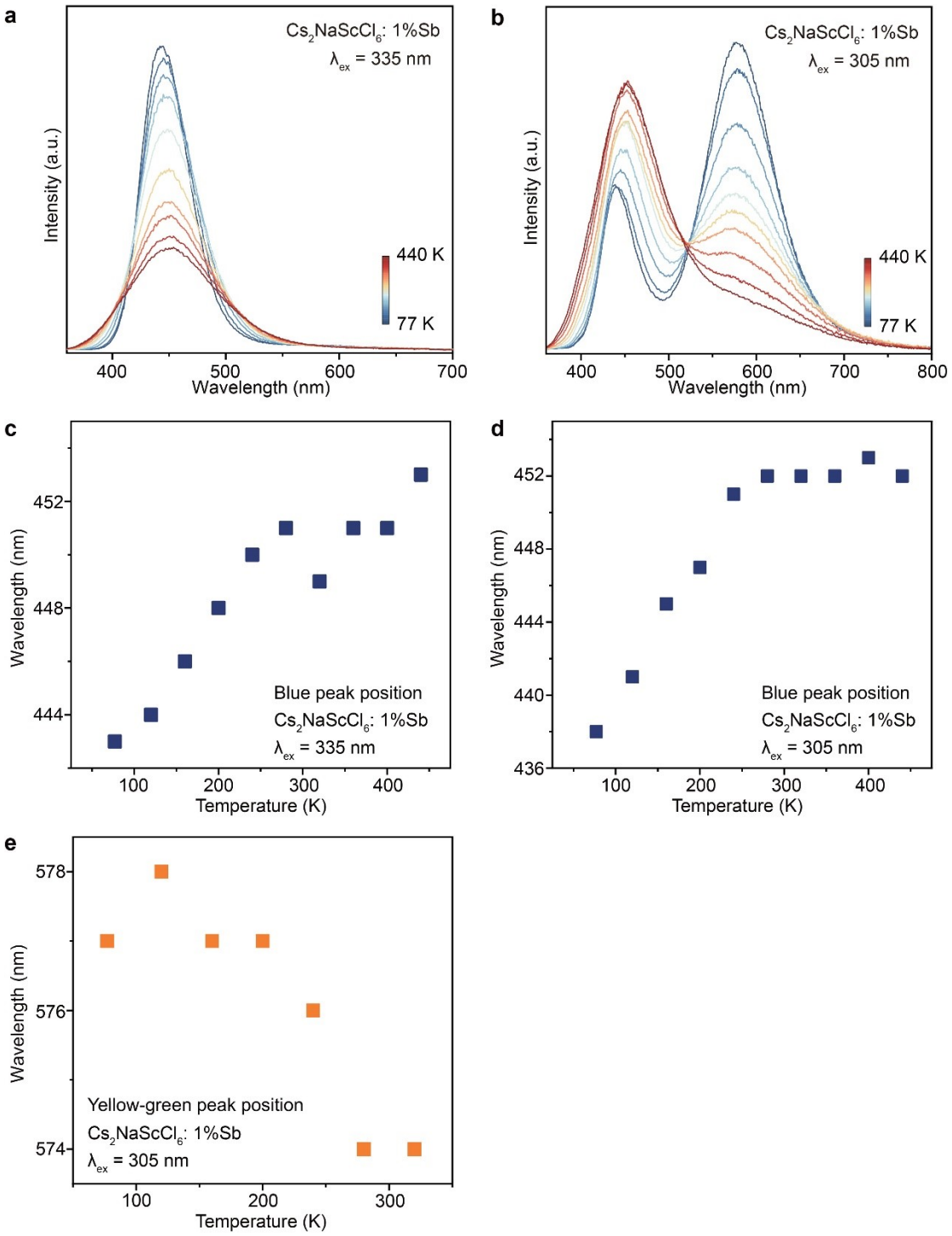

Figure S13. Temperature-dependent luminescence spectra of $Cs_2NaScCl_6$: 1%Sb under a) 335 nm and b) 305 nm excitation. c–e) The corresponding variation of emission peak positions under **c** 335 and d, e) 305 nm excitation.

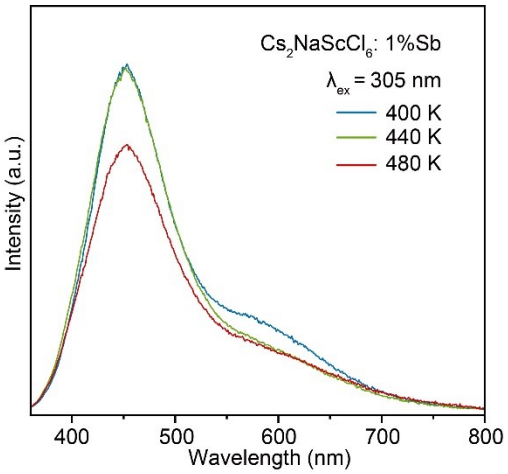

Figure S14. Luminescence spectra of $Cs_2NaScCl_6$: 1%Sb under 305 nm excitation at 400, 440, and 480 K.

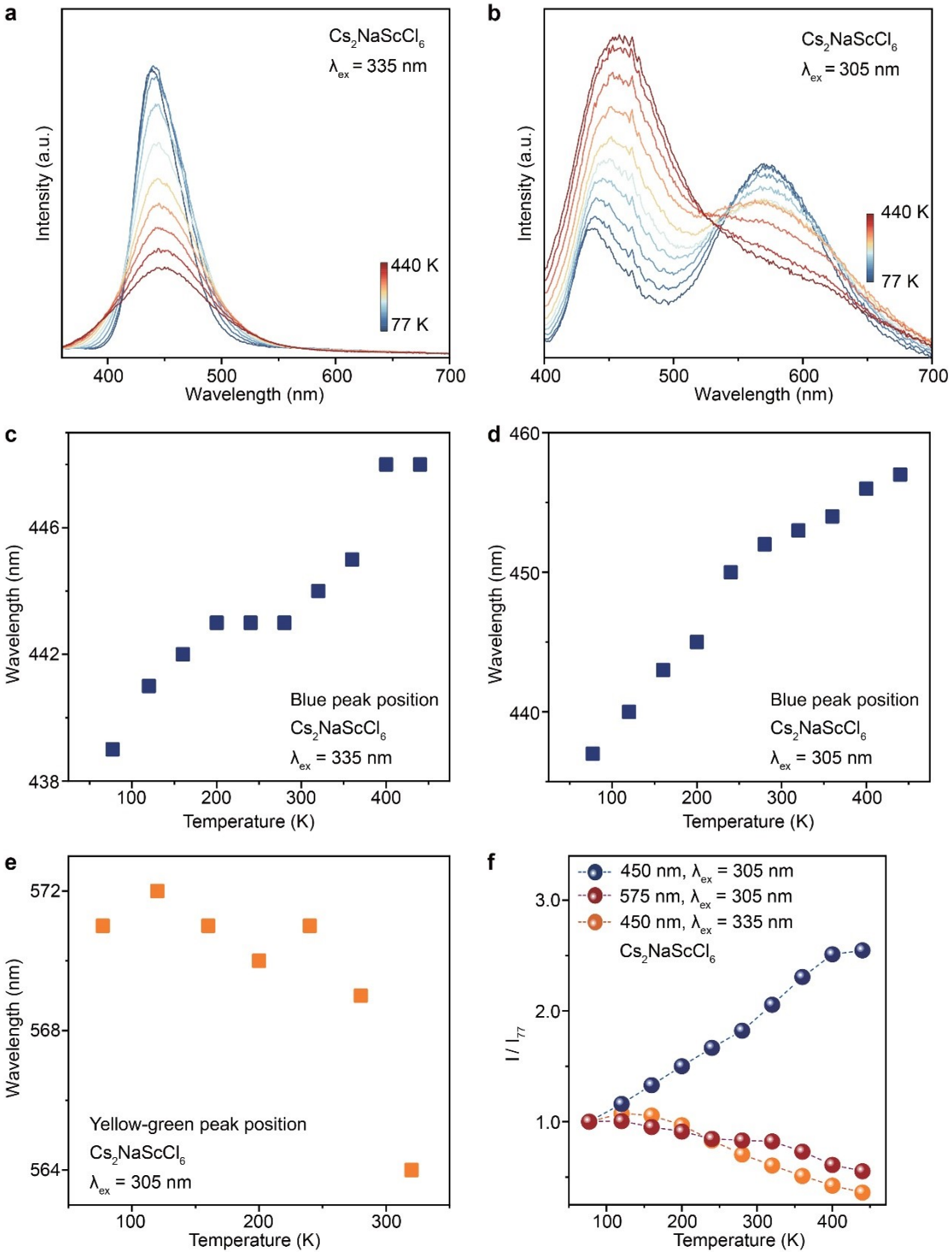

Figure S15. Temperature-dependent luminescence spectra of $Cs_2NaScCl_6$ under (a) 335 nm and (b) 305 nm excitation. (c−e) The corresponding variation of emission peak positions under (c) 335 and (d, e) 305 nm excitation. (f) Temperature-dependent emission intensity ratio (I_x / I_{77}) of the

emission of $Cs_2NaScCl_6$ at 450 and 575 nm under 305 and 335 nm excitation. I_X and I_{77} denote the emission intensity at X and 77 K, respectively.

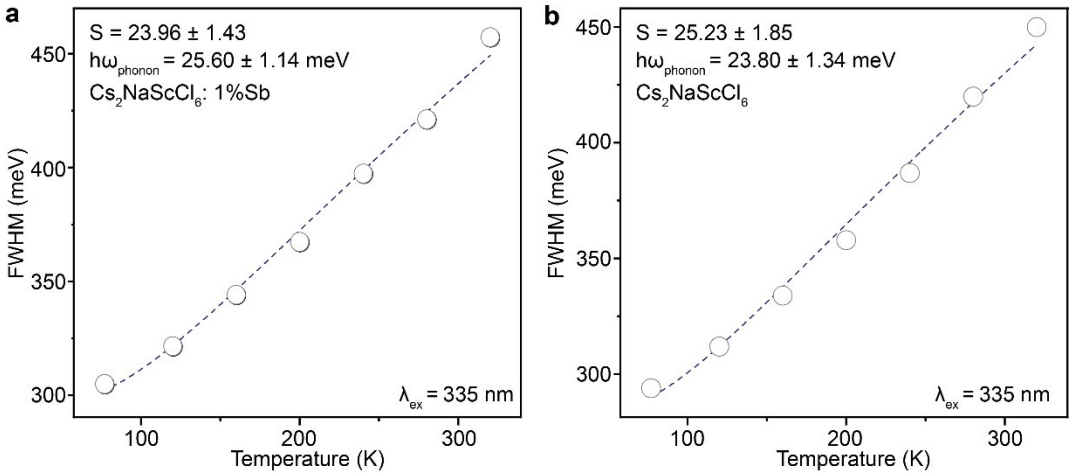

Figure S16. Full width at half maxima (FWHM) of the blue emission of (a) $Cs_2NaScCl_6$: 1%Sb and (b) $Cs_2NaScCl_6$ as a function of temperature under 335 nm excitation and the corresponding fitting (dashed lines) to extract the Huang-Rhys factor (S).

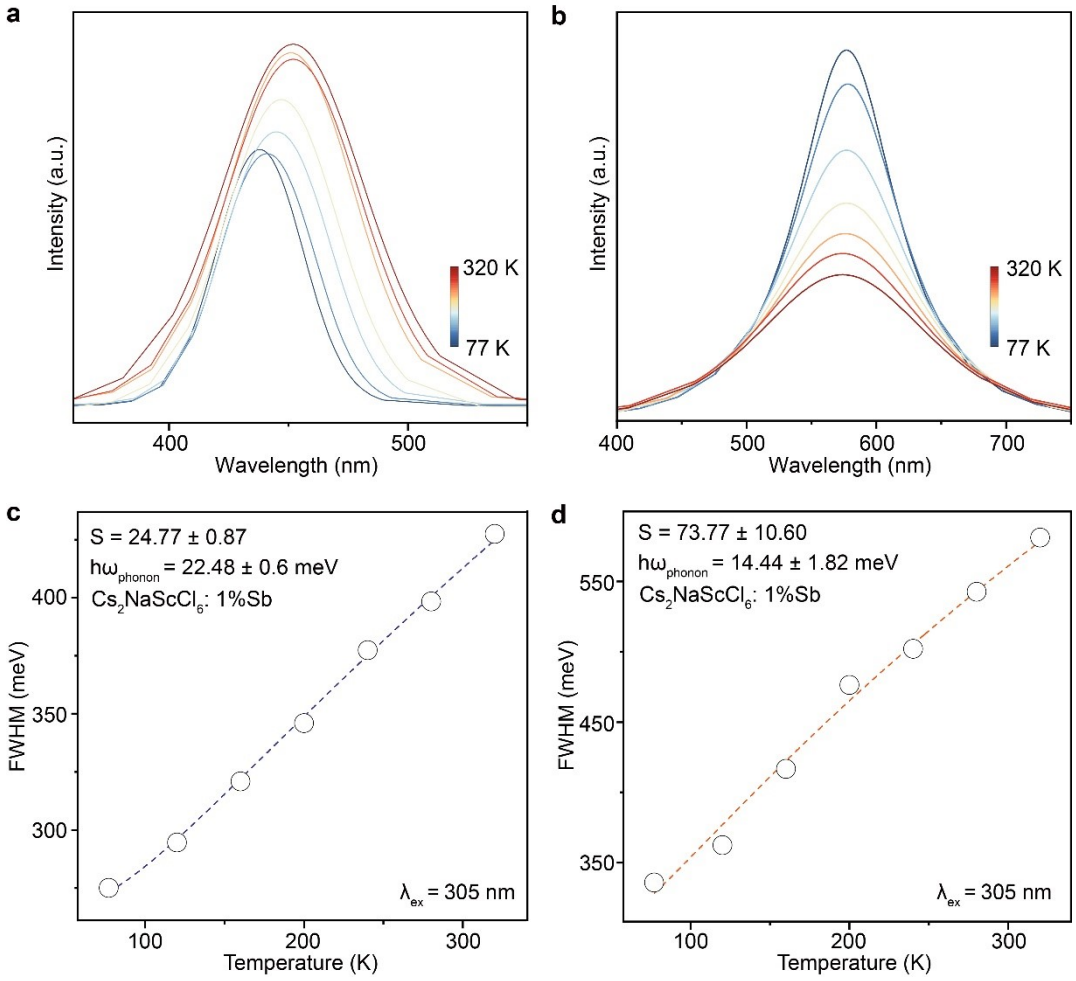

Figure S17. Fitted (a) blue and (b) yellow-green emission of the temperature-dependent luminescence spectra of $Cs_2NaScCl_6$: 1%Sb under 305 nm excitation. Full width at half maxima (FWHM) of the (c) blue and (d) yellow-green emission as a function of temperature under 305 nm excitation and the corresponding fitting (dashed lines) to extract the Huang-Rhys factor (*S*).

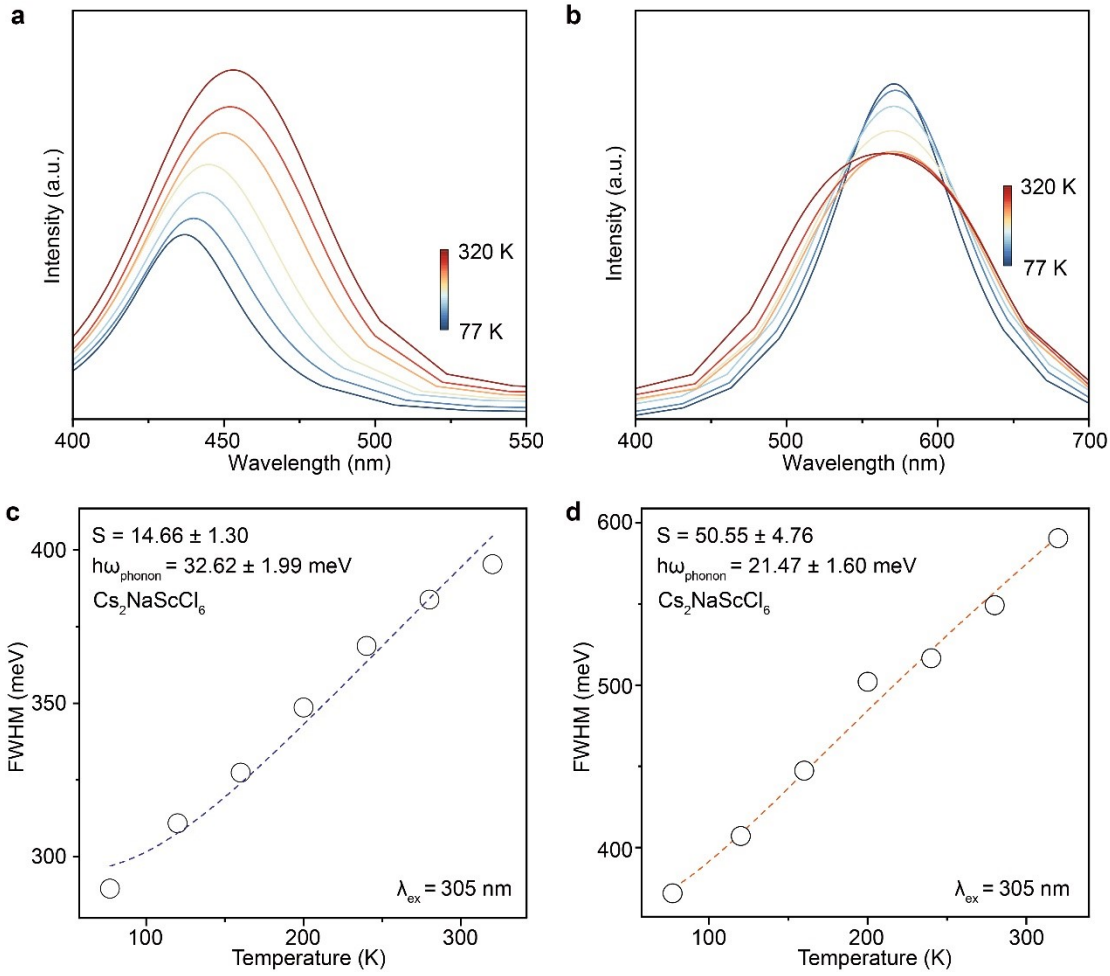

Figure S18. Fitted (a) blue and (b) yellow-green emission of the temperature-dependent luminescence spectra of $Cs_2NaScCl_6$ under 305 nm excitation. Full width at half maxima (FWHM) of the (c) blue and (d) yellow-green emission as a function of temperature under 305 nm excitation and the corresponding fitting (dashed lines) to extract the Huang-Rhys factor (*S*).

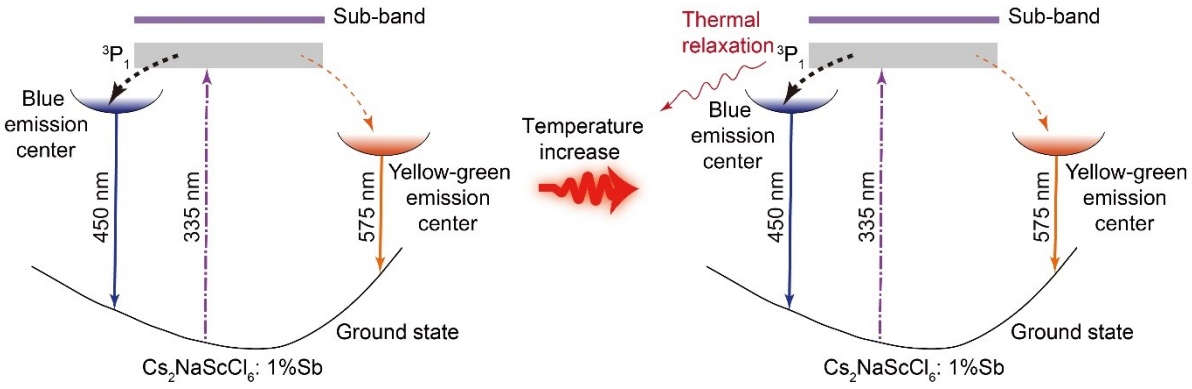

Figure S19. Schematic illustration of the proposed luminescence processes of $Cs_2NaScCl_6$: 1%Sb under 335 nm excitation. In the diagram, the dashed-dotted, solid, dashed, and wavy arrows represent excitation, emission, energy transfer, and relaxation processes, respectively. The orange dashed line indicates a relatively weak energy transfer process.

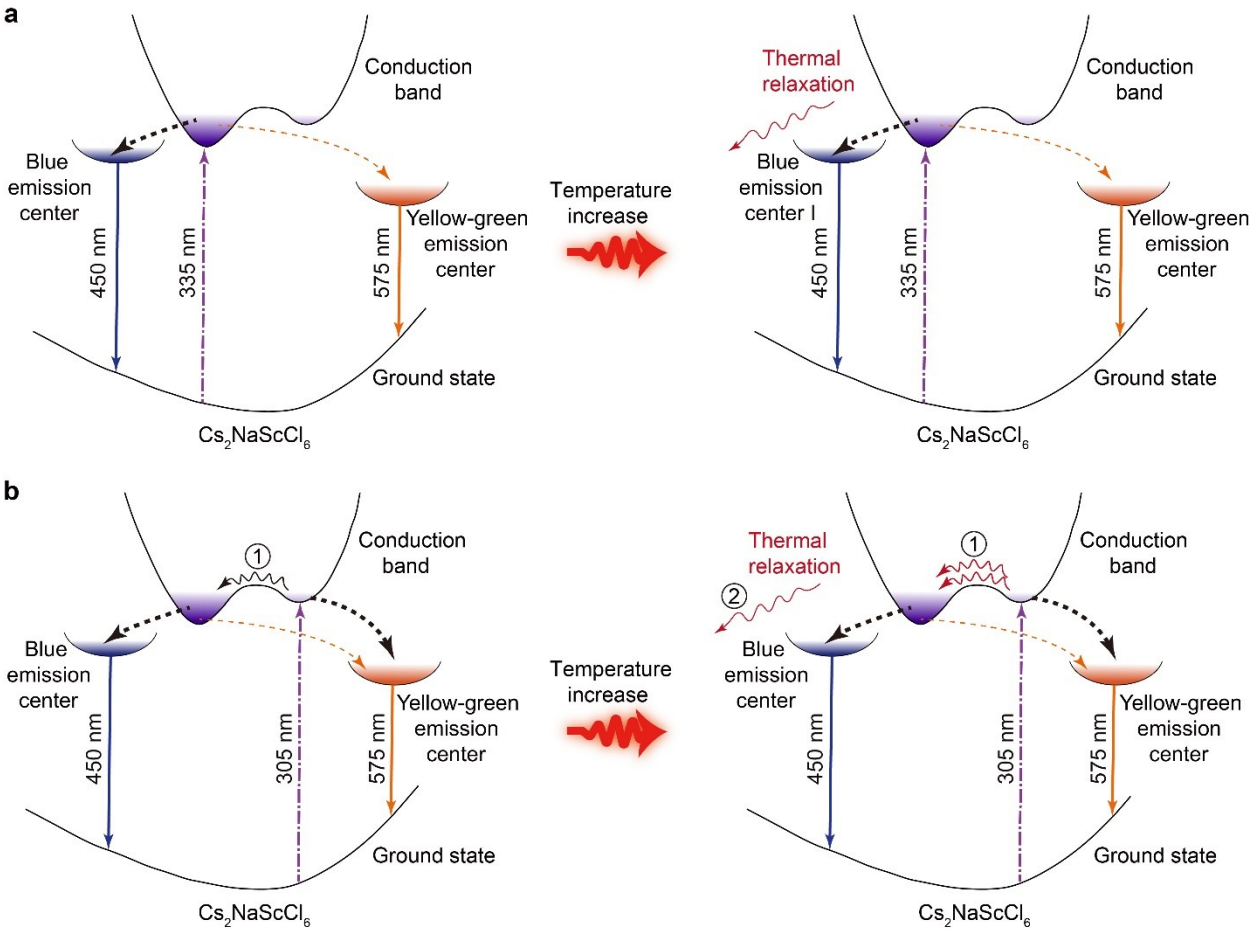

Figure S20. Schematic illustration of the proposed luminescence processes of $Cs_2NaScCl_6$ under (a) 335 and (b) 305 nm excitation. In the diagram, the dashed-dotted, solid, dashed, and wavy arrows represent excitation, emission, STE formation, and relaxation processes, respectively. The orange dashed line indicates a relatively weak energy transfer process.

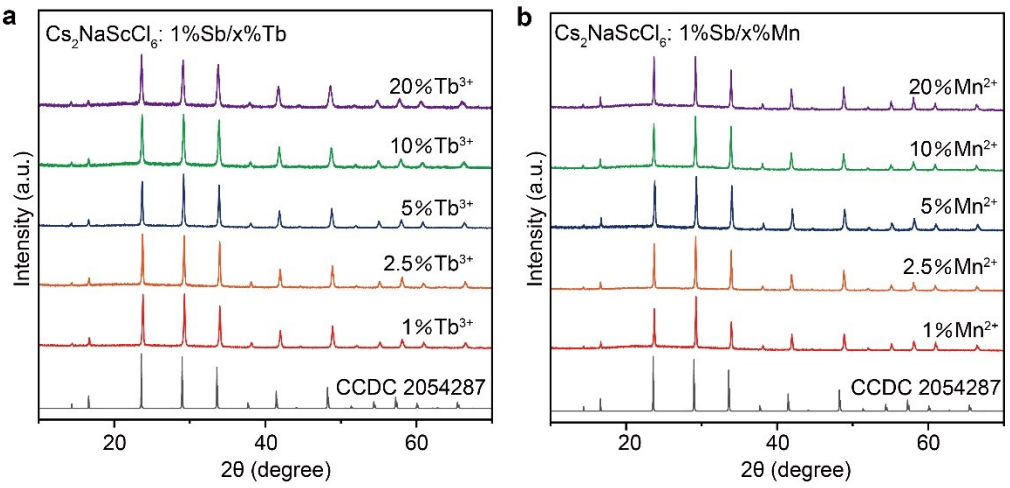

Figure S21. XRD patterns of (a) $Cs_2NaScCl_6$: 1%Sb/x%Tb and (b) $Cs_2NaScCl_6$: 1%Sb/x%Mn. The pattern at the bottom of (a, b) is the literature reference for the cubic $Cs_2NaScCl_6$ crystal.

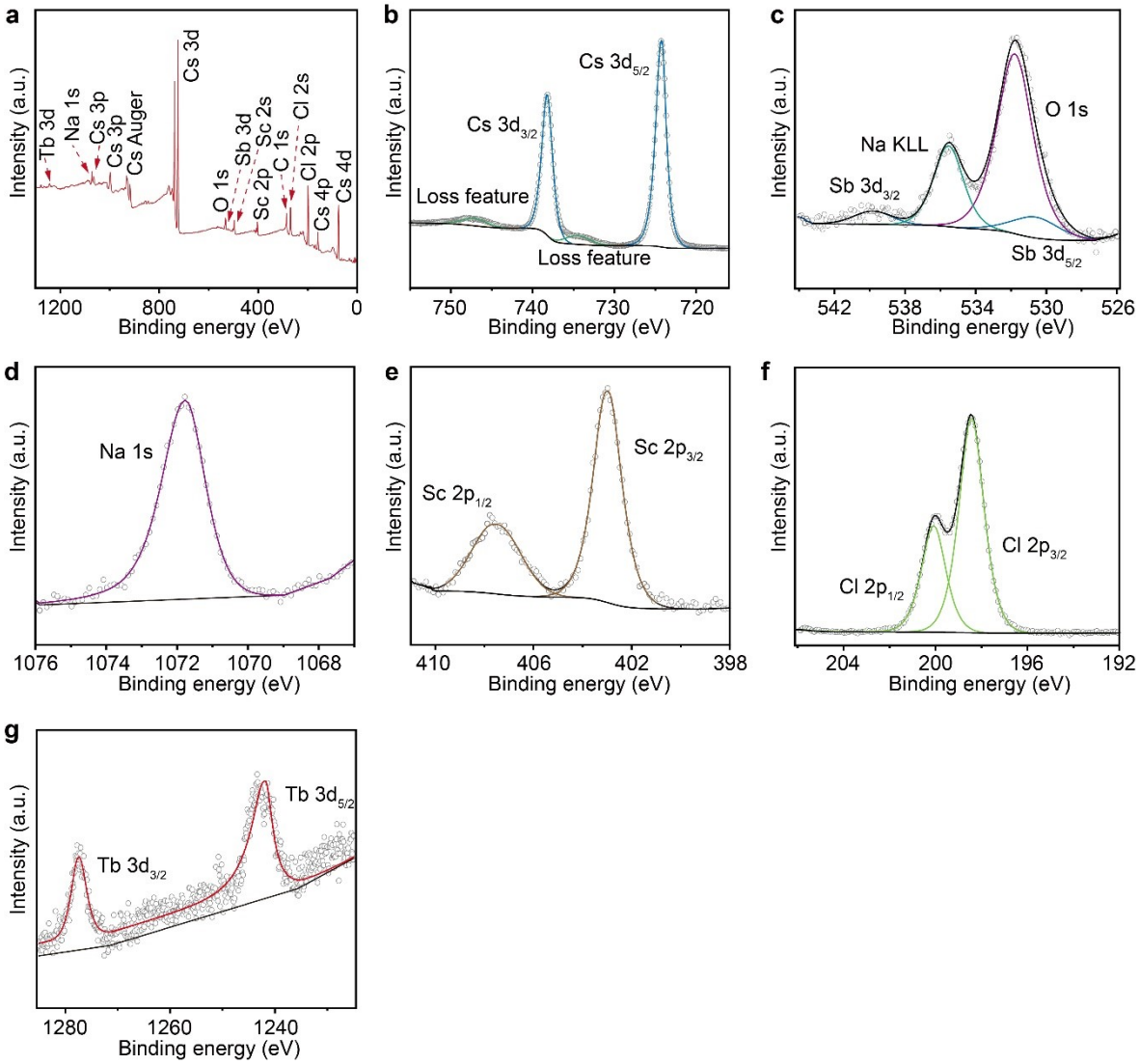

Figure S22. (a) Survey XPS spectrum of $Cs_2NaScCl_6$: 1%Sb/20%Tb and corresponding high-resolution XPS spectra of (b) Cs 3d, (c) Sb 3d, (d) Na 1s, (e) Sc 2p, (f) Cl 2p, and (g) Tb 3d. Colored lines in (b–g) are fitting curves.

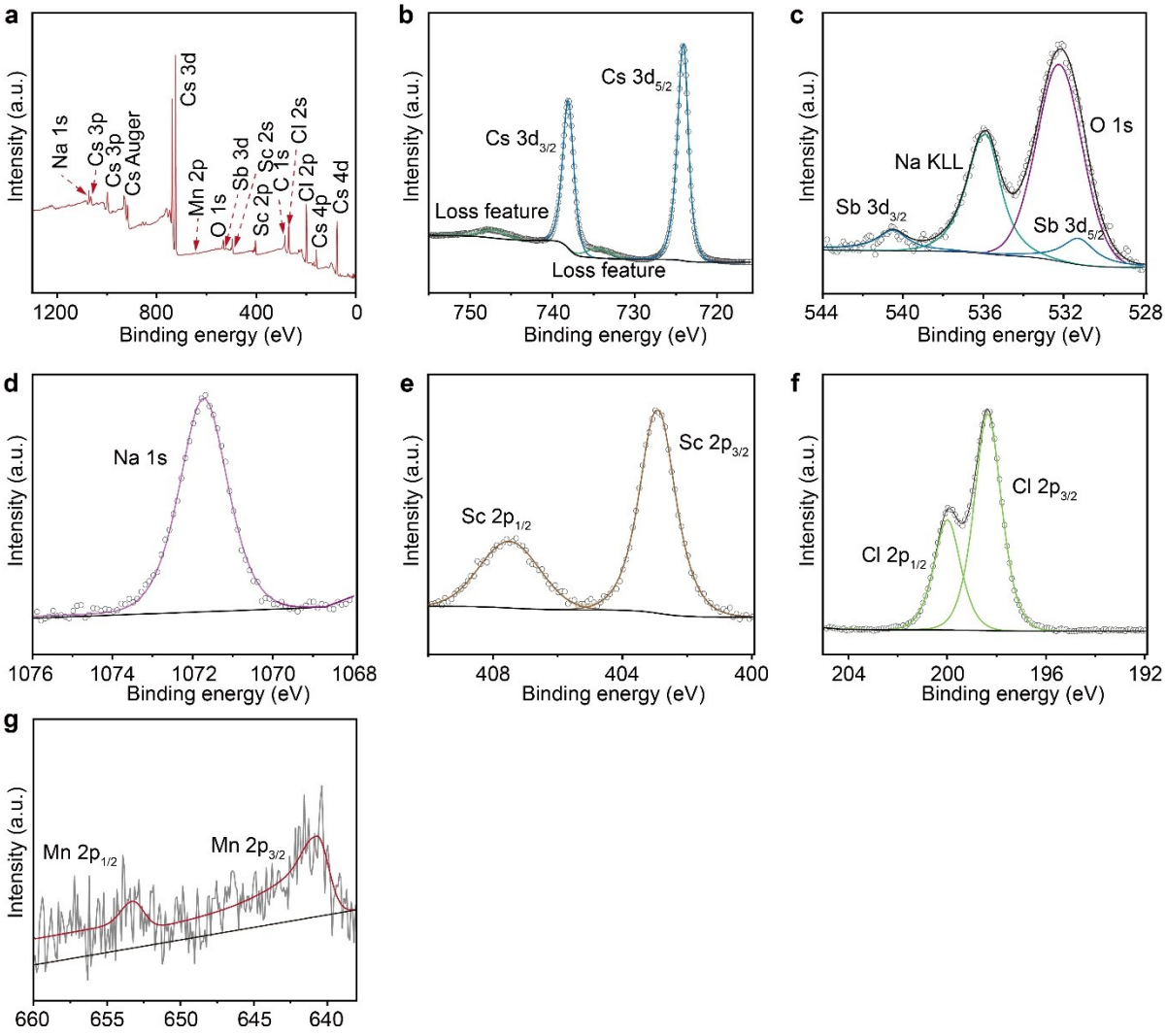

Figure S23. (a) Survey XPS spectrum of $Cs_2NaScCl_6$: 1%Sb/5%Mn and corresponding high-resolution XPS spectra of (b) Cs 3d, (c) Sb 3d, (d) Na 1s, (e) Sc 2p, (f) Cl 2p, and (g) Mn 2p. Colored lines in (b–g) are fitting curves.

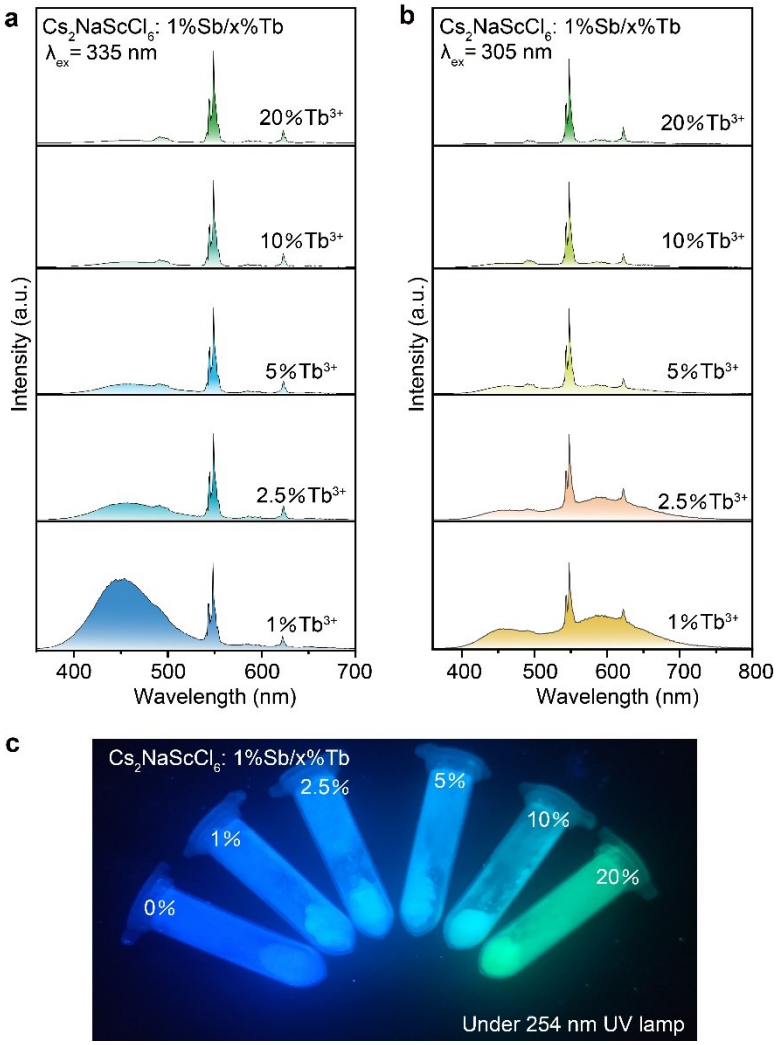

Figure S24. Luminescence spectra of $Cs_2NaScCl_6$: 1%Sb/x%Tb (x = 1, 2.5, 5, 10, and 20) under (a) 335 and (b) 305 nm excitation, respectively. (c) Photos of $Cs_2NaScCl_6$: 1%Sb/x%Tb (x = 0, 1, 2.5, 5, 10, and 20) samples under 254 nm light irradiation.

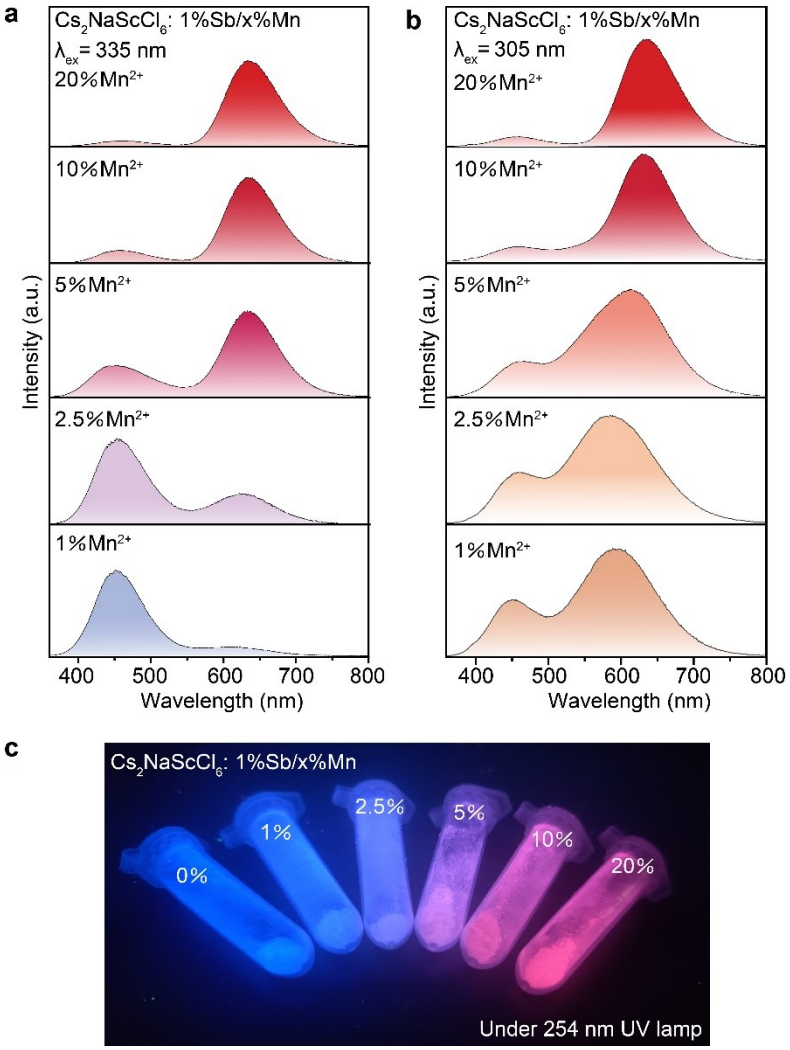

Figure S25. Luminescence spectra of $Cs_2NaScCl_6$: 1%Sb/x%Mn (x = 1, 2.5, 5, 10, and 20) under (a) 335 and (b) 305 nm excitation, respectively. (c) Photos of $Cs_2NaScCl_6$: 1%Sb/x%Mn (x = 0, 1, 2.5, 5, 10, and 20) samples under 254 nm light irradiation.

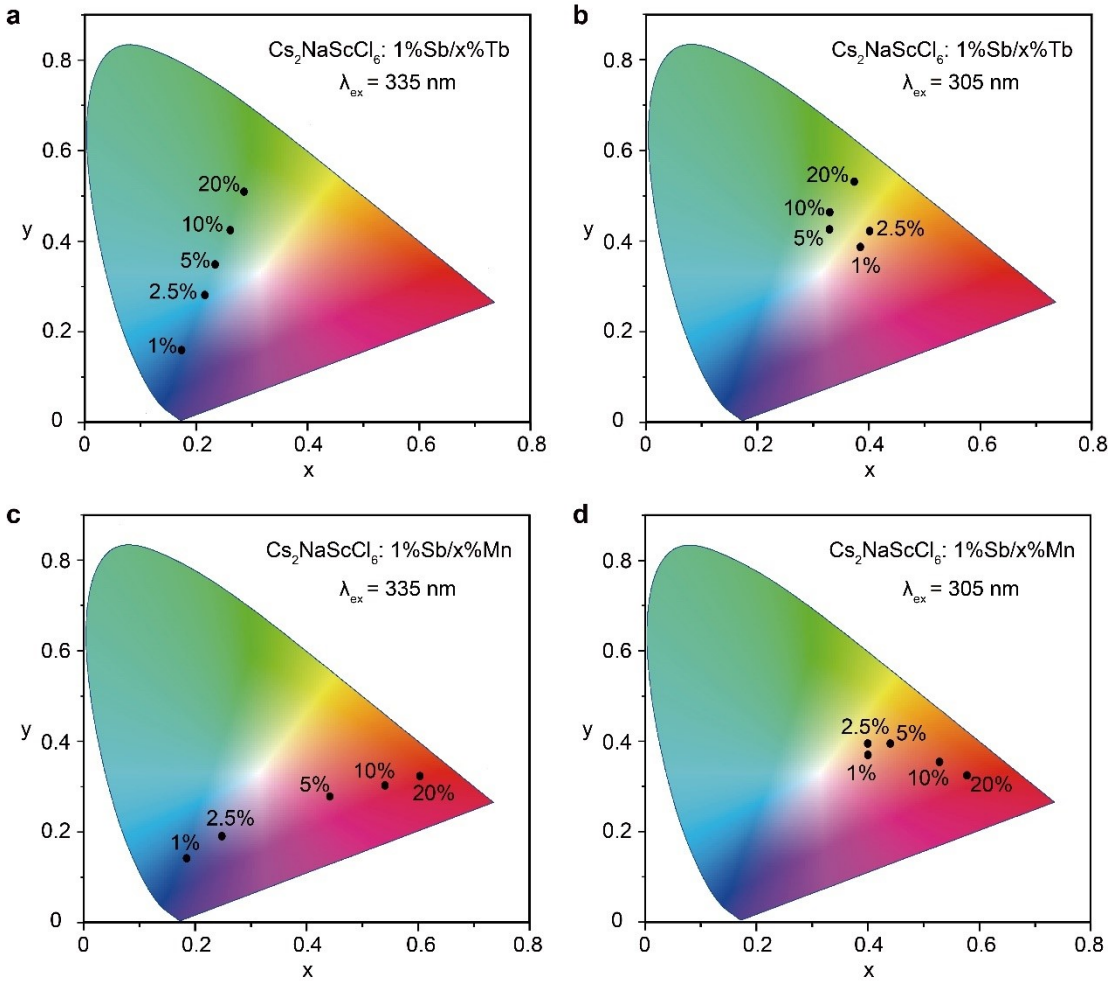

Figure S26. CIE chromaticity diagrams of $Cs_2NaScCl_6$: 1%Sb co-doped with different concentrations of (a), (b) Tb^{3+} and (c), (d) Mn^{2+} under (a), (c) 335 and (b), (d) 305 nm excitation, respectively.

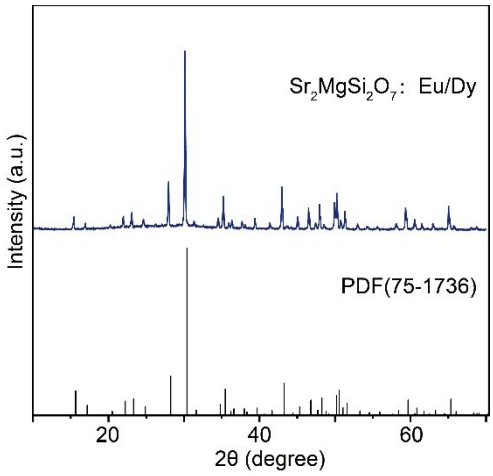

Figure S27. XRD patterns of $Sr_2MgSi_2O_7$: Eu/Dy.

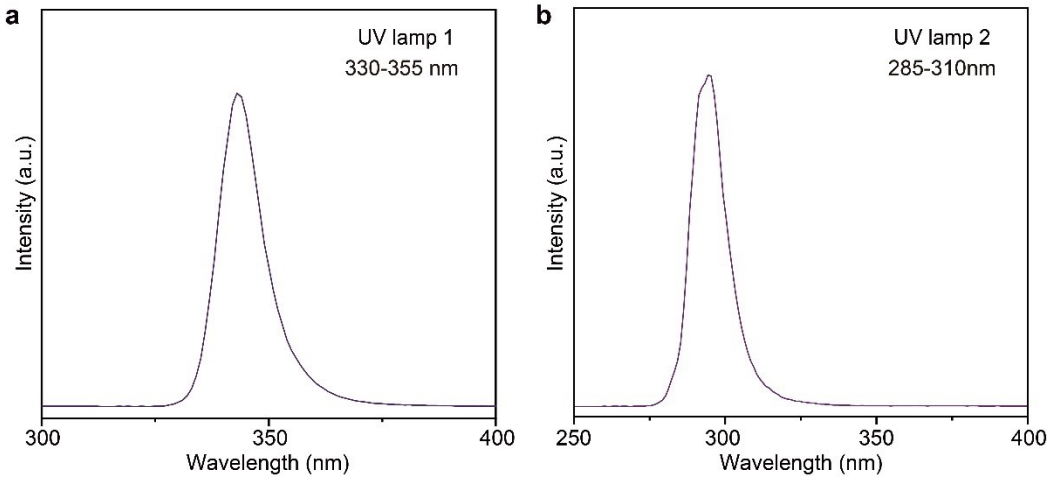

Figure S28. Luminescence spectra of different UV lamp centered at about 335 nm and 300 nm.

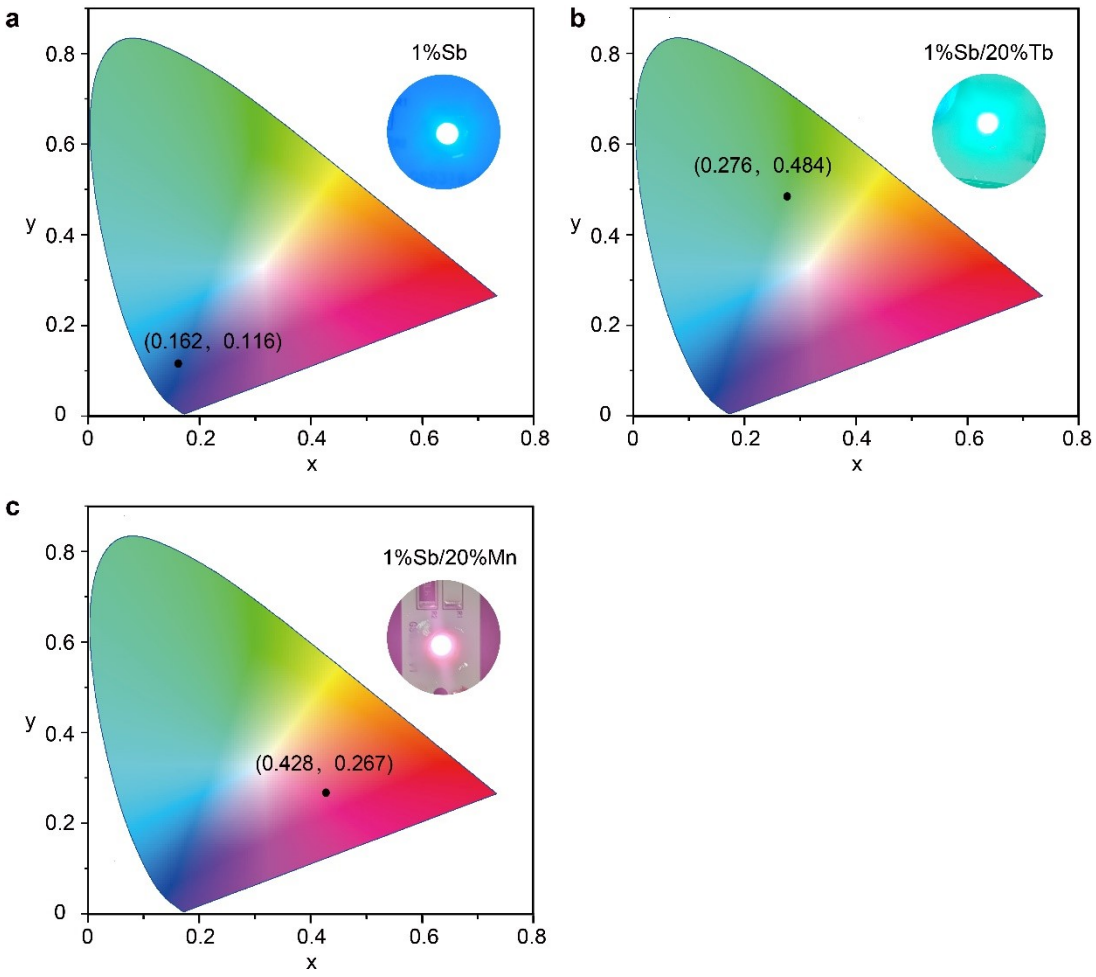

Figure S29. CIE chromaticity diagrams of fabricated LEDs using (a) $Cs_2NaScCl_6$: 1%Sb, (b) $Cs_2NaScCl_6$: 1%Sb/20%Tb, and (c) $Cs_2NaScCl_6$: 1%Sb/20%Mn, respectively. Insets are photos of the corresponding LED.

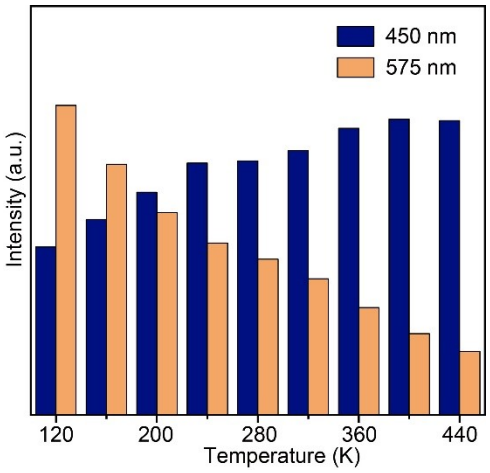

Figure S30. Histogram of the emission intensity at 450 and 575 nm of $Cs_2NaScCl_6$: 1%Sb under 305 nm excitation at different temperatures.

The relationship between temperature and luminescence intensity ratio (LIR) can be fitted using the following equation.

$$LIR = \frac{I_{575}}{I_{450}} = A\exp(B/T) + C\#(S6)$$

where A, B, and C are constant parameters, T is the absolute temperature, I_{575} is the luminescence intensity at 575 nm, and I_{450} is the luminescence intensity at 450 nm. The absolute sensitivity (S_a) and relative sensitivity (S_r) at different temperatures were then calculated using the following equations.

$$S_a = \left|\frac{\sigma LIR}{\sigma T}\right| = A\exp(B/T) \times \frac{B}{T^2}\#(S7)$$

$$S_r = 100\% \times \left|\frac{1}{LIR}\frac{\sigma LIR}{\sigma T}\right| = 100\% \times \frac{A\exp(B/T)}{A\exp(B/T) + C} \times \frac{B}{T^2}\#(S8)$$

Table S3. Maximum absolute sensitivity ($S_{a(max)}$) and maximum relative sensitivity ($S_{r(max)}$) of some recently reported lead-free halide double perovskite-based thermometers.

Material	$S_{a(max)}$ (K^{-1})	$S_{r(max)}$ (K^{-1})	Temperature range (K)	Reference
$Cs_2NaBiCl_6$: Er	0.0094	1.27	313-537	2
$Cs_2AgInCl_6$: Yb/Er	0.0130	-	100-600	3
Cs_2NaYCl_6: Sb/Tb/Ho	0.3511	1.59	160-360	4
$Cs_2NaInCl_6$: Sb/Sm	0.00173	0.75	140-280	5
$Cs_2AgInCl_6$: Bi/Tb	0.0215	2.25	303-423	6
$Cs_2NaScCl_6$: Sb	0.019	1.05	120-440	This work

References

1. B. H. Toby and R. B. Von Dreele, *J. Appl. Crystallogr.*, 2013, **46**, 544-549.
2. K. Zhu, Z. Wang, H. Xu and Z. Fu, *Adv. Opt. Mater.*, 2022, **10**, 2201182.
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