Modulation of the Near-Infrared-I and -II luminescence of Thulium-Incorporated Lead-free Double Perovskite

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Experimental section

***1. Materials*:**

NaCl (99.99%), CsCl (99.99%), $InCl_3$ (99.99%), $SbCl_3$ (99.9%), TeO_2 (99.99%), and $TmCl_3 \cdot 6H_2O$ (99.99%) were purchased from Aladdin Reagent. Hydrochloric acid (HCl, analytical reagent grade) was purchased from Guangzhou Chemical Reagent Factory. All chemicals were used as received without any further purification.

2. Preparation of samples and LEDs:

2.1 Preparation of Sb^{3+}/Tm^{3+}-Codoped $Cs_2NaInCl_6$

Sb^{3+}/Tm^{3+}-codoped $Cs_2NaInCl_6$ was synthesized by the hydrothermal method. First, 2 mmol of CsCl, 1 mmol of NaCl, 0.05 of mmol $SbCl_3$, a variable ratio of $TmCl_3 \cdot 6H_2O$ to $InCl_3$ while keep the total amount of $TmCl_3 \cdot 6H_2O$ and $InCl_3$ 1 mmol, and 10 mL of HCl solution were added to a 25 ml stainless-steel autoclave. The sealed stainless steel reactor was heated at 180°C for 2 h, and kept for 12 h. The reactor was cooled to 50°C within 55 h, and finally cooled to room temperature (within 2 h). The single crystal was filtered, washed with isopropanol, and then dried at 60°C in an oven overnight.

2.2 Preparation of Te^{4+}/Tm^{3+}-Codoped $Cs_2NaInCl_6$

Te^{4+}/Tm^{3+}-codoped $Cs_2NaInCl_6$ was synthesized by the hydrothermal method. First, 2 mmol of CsCl, 1 mmol of NaCl, 0.01 of mmol TeO_2, a variable ratio of $TmCl_3 \cdot 6H_2O$ to $InCl_3$ while keep the total amount of $TmCl_3 \cdot 6H_2O$ and $InCl_3$ 1 mmol, and 10 mL of

HCl solution were added to a 25 ml stainless-steel autoclave. The rest remains consistent.

2.3 Fabrication of NIR LEDs

2 g of the $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ or $Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ powder was dispersed into 1.5 g of organic silicone, and then the gel mixture obtained was fixed on the surface of multiple LED chips (Zhongke Haoye (Dongguan) Material Technology Co., Ltd.) with emission wavelengths of 310 nm and 410 nm. Finally, the LEDs obtained by this method were dried at 80°C for 24 h in a vacuum drying chamber.

3. Characterization:

The PXRD measurements of samples were performed on a powder D2 diffractometer (Bruker) operating at 30 kV and 15 mA with monochromatized Cu-Kα radiation (λ = 1.5418 Å). ICP-MS was performed with an ICP-MS spectrometer (Agilent 7700). The optical UV−vis absorption spectra were collected by a UV-2600i Plus spectrophotometer at room temperature, in which $BaSO_4$ was used as the reference standard. The PL, PLE, and microsecond level lifetime spectra were performed using an FS5 spectrophotometer (Edinburgh Instruments Ltd., U. K.) with different detectors (Visible PMT and InGaAs 1650). The PLQY spectra were performed using an FS5 fluorescence spectrometer equipped with relevant accessories. The photoluminescence quantum yield (PLQY) of NIR emission was measured according to the method reported by Zhang et al.[1] The PL spectra of NIR LEDs were recorded on fiber spectrophotometer. NIR photographs were taken by a computer equipped with a domestic USB NIR camera.

PLQYs testing and calculation**:** To test the NIR PLQY of $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ and $Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ samples, two detectors (Visible PMT and InGaAs 1650) were used interchangeably. Taking $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ sample as an example. First, the visible (360~700 nm) PLQY of $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ sample was measured using a PMT detector and found to be 41.41%. Then, we used this detector to measure the PL spectrum from 360 nm to 850 nm. Subsequently, an InGaAs 1650 detector was selected to test the NIR spectrum from 800 nm to 1500 nm. After measuring both spectra, the PL spectrum from 800 nm to 850 nm measured by the PMT detector was normalized with the PL spectrum from 800 nm to 850 nm measured by the InGaAs 1650 detector (Formula S1). After normalization, the ratio of the spectral area in the visible range (360~700 nm) to that in the NIR range (NIR-I: 700~1000 nm and NIR-II: 1000-1400 nm) was determined to be S1:S2:S3 = 1:0.22:1.18 (Formula S2). Therefore, the NIR PLQY is estimated to be approximately 58% (Formula S3). And the PLQY of NIR emission from $Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ sample has also undergone similar characterization tests. The specific calculations about $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ sample are as follows:

$$\frac{\int_{800\,nm}^{850\,nm} I_{PMT}(\lambda)d\lambda}{\int_{800\,nm}^{850\,nm} I_{InGaAs}(\lambda)d\lambda} = 1 \#(S1)$$

$$S1{:}S2{:}S3 = \int_{360\ nm}^{700\ nm} I_{PMT}(\lambda)d\lambda : \int_{800\ nm}^{1000\ nm} I_{InGaAs}(\lambda)d\lambda : \int_{1000\ nm}^{1400\ nm} I_{InGaAs}(\lambda)d\lambda = 1{:}0.22{:}1.18 \#(S2)$$

$$\frac{PLQY_{Vis}}{PLQY_{NIR}} = \frac{S1}{S2+S3} \rightarrow PLQY_{NIR} = PLQY_{Vis} \times \frac{S2+S3}{S1} = 58\% \#(S3)$$

***First principles calculations*:** The first-principles calculations were performed using the Vienna ab initio simulation package (VASP)[2,3]. A 1 × 1 × 2 supercell structure (80 atoms) was set up for the $Cs_2NaInCl_6$ system. Five systems were calculated: the undoped $Cs_2NaInCl_6$ system, the $Cs_2NaInCl_6{:}Sb^{3+}$ system (substituting one In^{3+} ion with a Sb^{3+} ion), the $Cs_2NaInCl_6{:}Te^{4+}$ system (substituting one In^{3+} ion with a Te^{4+} ion), the $Cs_2NaInCl_6{:}Sb^{3+}/Tm^{3+}$ system (substituting two In^{3+} ions with a Sb^{3+} ion and a Tm^{3+} ion), and the $Cs_2NaInCl_6{:}Te^{4+}/Tm^{3+}$ system (substituting two In^{3+} ions with a Te^{4+} ion and a Tm^{3+} ion). The Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) was applied[4,5]. The convergence tolerances were set to 2×10^{-5} eV per atom for the energy, the energy cutoff was set to 450.0 eV and a 1 × 1 × 1 Monkhorst–Pack k-point mesh was used for the calculations.

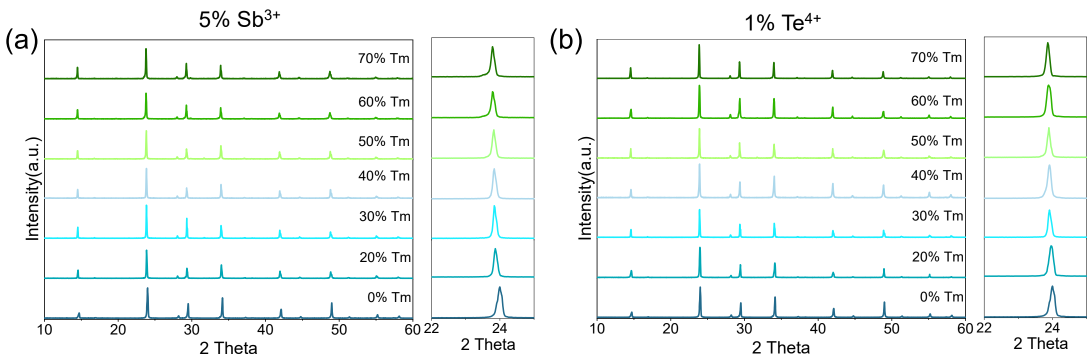

Figure S1. (a) XRD patterns of $Cs_2NaInCl_6$:Sb^{3+}/Tm^{3+} with different Tm^{3+}-doping concentrations. (b) XRD patterns of $Cs_2NaInCl_6$:Te^{4+}/Tm^{3+} with different Tm^{3+}-doping concentrations.

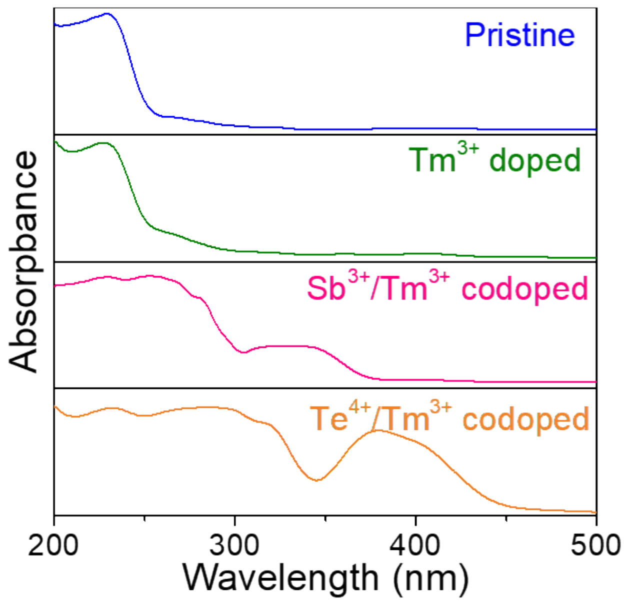

Figure S2. Absorption spectra of pure, Tm^{3+}-doped, Sb^{3+}/Tm^{3+}-codoped, and Te^{4+}/Tm^{3+}-codoped $Cs_2NaInCl_6$.

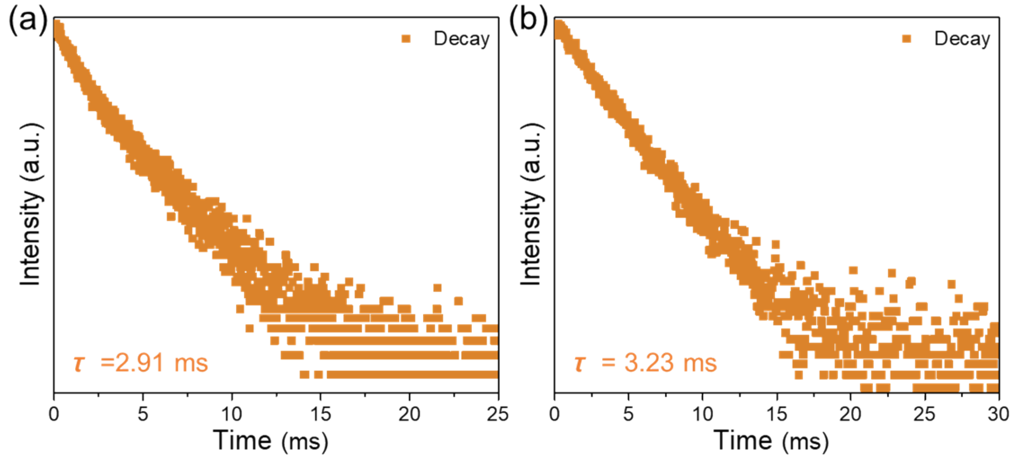

Figure S3. PL decay curves of (a) $Cs_2NaInCl_6$:Sb^{3+}/Tm^{3+} (λ_{ex} = 320 nm, λ_{em} = 808 nm), (b) $Cs_2NaInCl_6$:Te^{4+}/Tm^{3+} (λ_{ex} = 440 nm, λ_{em} = 808 nm).

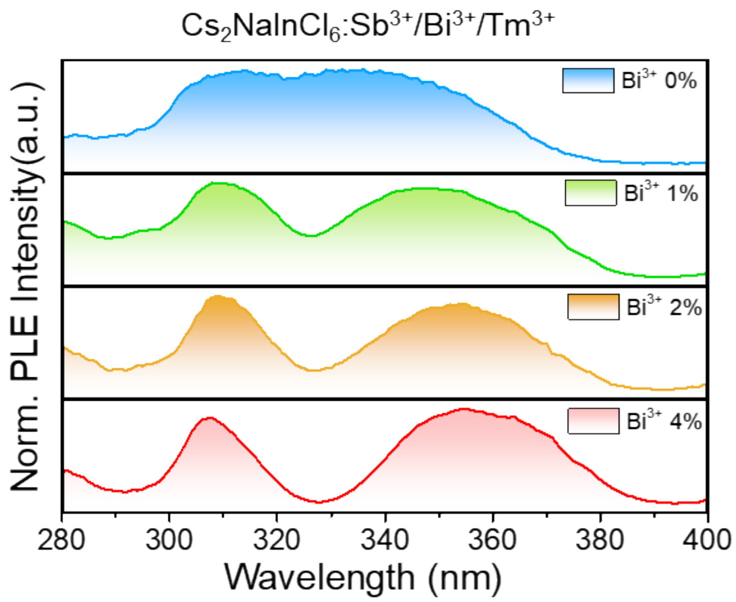

Figure S4. PLE spectra for $Cs_2NaInCl_6$:Sb^{3+}/Bi^{3+}/Tm^{3+} at emission wavelengths of 450 nm.

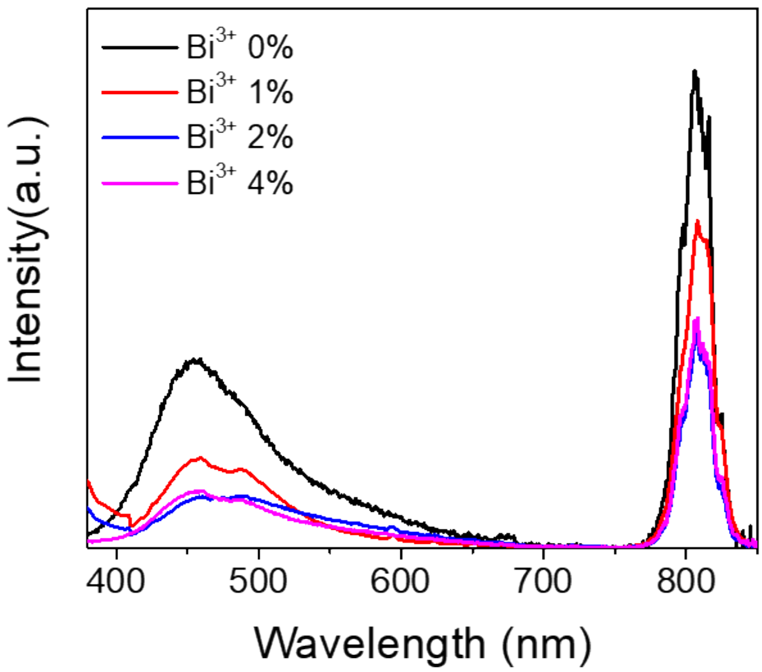

Figure S5. PL spectra for $Cs_2NaInCl_6$:Sb^{3+}/Bi^{3+}/Tm^{3+} under different Bi^{3+} ions concentration.

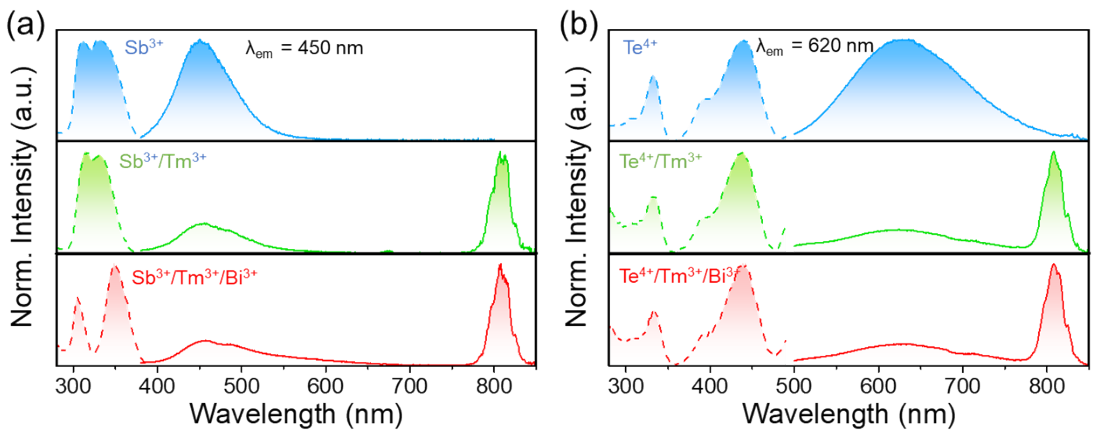

Figure S6. (a) The PLE and PL spectra of Sb^{3+}, Sb^{3+}/Tm^{3+} and Sb^{3+}/Tm^{3+}/Bi^{3+} doped $Cs_2NaInCl_6$. (b) The PLE and PL spectra of Te^{4+}, Te^{4+}/Tm^{3+} and Te^{4+}/Tm^{3+}/Bi^{3+} doped $Cs_2NaInCl_6$.

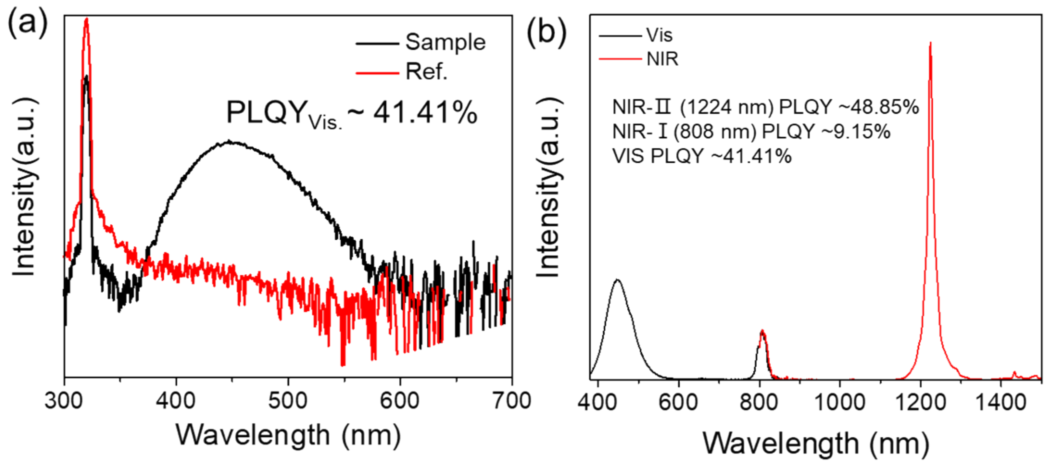

Figure S7. (a) PLQY measurement of $Cs_2NaInCl_6$:5%Sb^{3+}/60%Tm^{3+} in the visible region. (b) PL spectra of $Cs_2NaInCl_6$:5%Sb^{3+}/60%Tm^{3+} in whole range of 400-1500 nm, and the integrated intensity of NIR and visible emission.

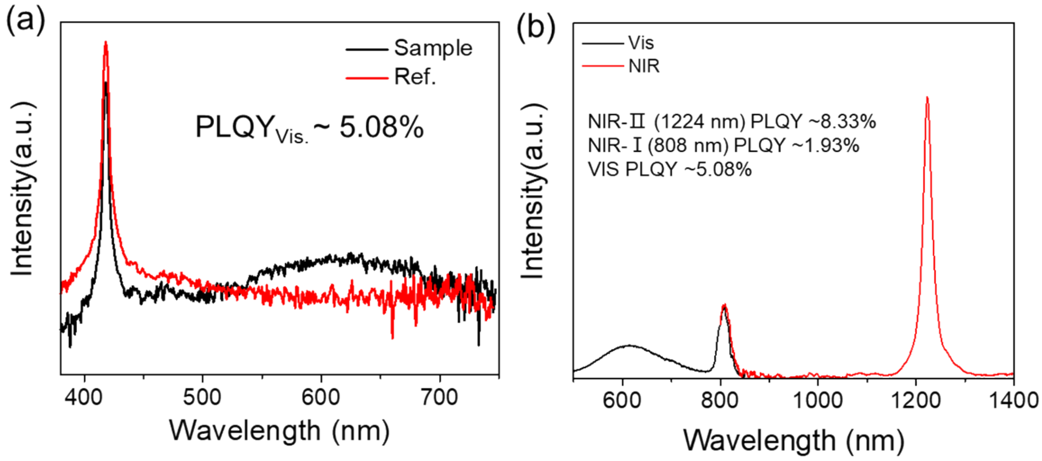

Figure S8. (a) PLQY measurement of $Cs_2NaInCl_6$:1%Te^{4+}/50%Tm^{3+} in the visible region. (b) PL spectra of $Cs_2NaInCl_6$:1%Te^{4+}/50%Tm^{3+} in whole range of 500-1400 nm, and the integrated intensity of NIR and visible emission.

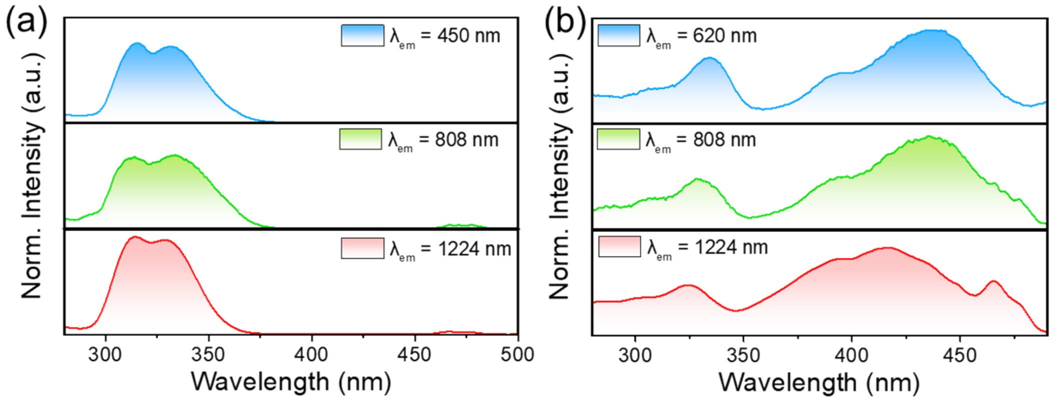

Figure S9. PLE spectra of (a) $Cs_2NaInCl_6$:5%Sb^{3+}/60%Tm^{3+}, (b) $Cs_2NaInCl_6$:1%Te^{4+}/50%Tm^{3+}.

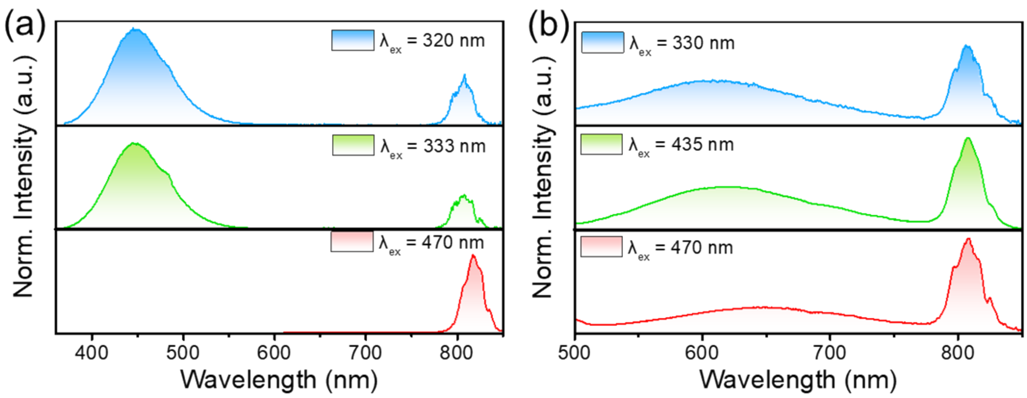

Figure S10. PL spectra of (a) $Cs_2NaInCl_6$:5%Sb^{3+}/60%Tm^{3+}, (b) $Cs_2NaInCl_6$:1%Te^{4+}/50%Tm^{3+} under different excitation wavelength.

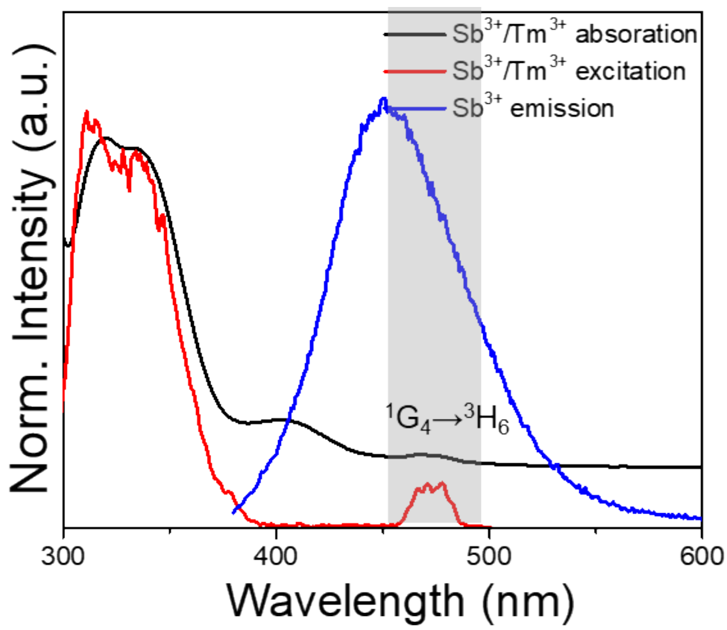

Figure S11. Absorption and excitation spectrum of Tm^{3+} ions and Sb^{3+} emission in $Cs_2NaInCl_6$.

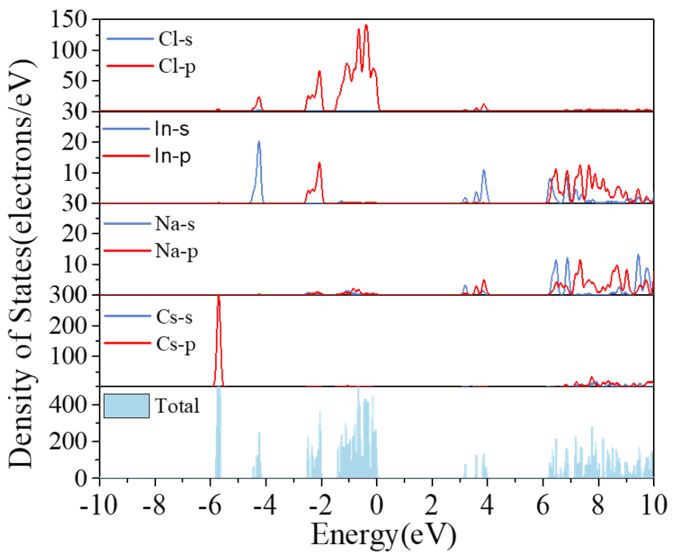

Figure S12. The density of states of $Cs_2NaInCl_6$.

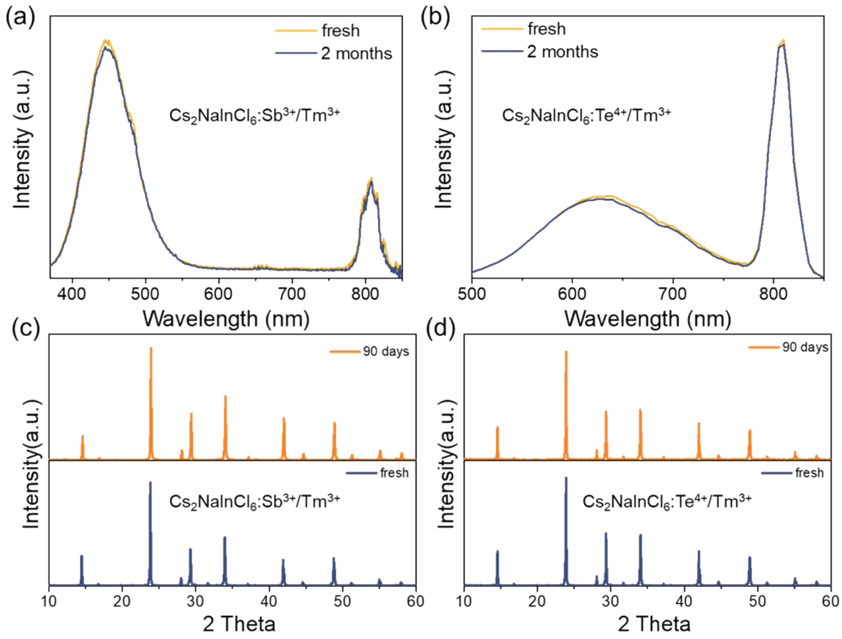

Figure S13. PL intensity of (a) $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ and (b) $Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ after exposing at ambient air for 2 months. PXRD patterns of (c) $Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ and (d) $Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ after 90 days of exposure to light and moisture conditions.

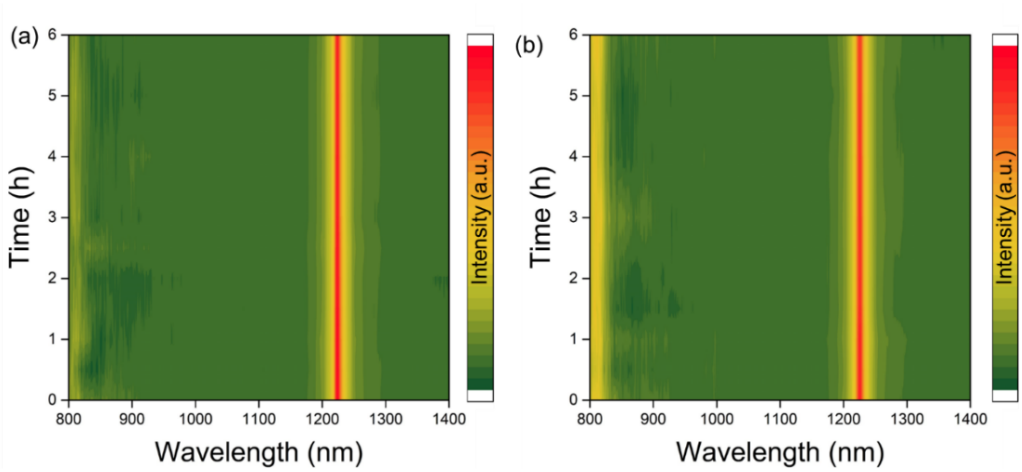

Figure S14. The PL-temperature correlation maps of (a) $Cs_2NaInCl_6:5\%Sb^{3+}/60\%Tm^{3+}$ and $Cs_2NaInCl_6:1\%Te^{4+}/50\%Tm^{3+}$ maintained at 400 K for 6 h.

Table S1. ICP elemental analysis of $Cs_2NaInCl_6$:Sb^{3+}/Tm^{3+}

Feeding ratio		Actual	
Sb^{3+}	Tm^{3+}	Sb^{3+}	Tm^{3+}
5%	20%	0.11%	0.51%
5%	30%	0.14%	0.73%
5%	50%	0.23%	1.31%
5%	60%	0.30%	2.98%
5%	70%	0.65%	7.26%

Table S2. ICP elemental analysis of $Cs_2NaInCl_6$:Te^{4+}/Tm^{3+}

Feeding ratio		Actual	
Te^{4+}	Tm^{3+}	Te^{4+}	Tm^{3+}
1%	20%	0.12%	0.18%
1%	30%	0.25%	0.41%
1%	50%	0.48%	1.79%
1%	60%	0.62%	2.32%
1%	70%	0.85%	5.36%

Table S3. The PL lifetimes of $Cs_2NaInCl_6$:Sb/Tm monitored at 450 nm.

Lifetime	450 nm (μs)	η_T (%)
$Cs_2NaInCl_6:Sb^{3+}$	1.80	--
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (10%)	1.79	0.56
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (20%)	1.69	6.11
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (30%)	1.65	8.33
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (40%)	1.59	11.67
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (50%)	1.38	23.33
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (60%)	1.26	30.00
$Cs_2NaInCl_6:Sb^{3+}/Tm^{3+}$ (70%)	0.79	56.11

Table S4. The PL lifetimes of $Cs_2NaInCl_6$:Te/Tm monitored at 620 nm.

Lifetime	620 nm (μs)	η_T (%)
$Cs_2NaInCl_6:Te^{4+}$	1.51	--
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (10%)	1.46	3.31
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (20%)	1.29	14.57
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (30%)	1.18	21.85
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (40%)	0.96	36.42
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (50%)	0.94	37.75
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (60%)	0.86	43.05
$Cs_2NaInCl_6:Te^{4+}/Tm^{3+}$ (70%)	0.85	43.71

References:

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