

# Efficient near-infrared luminescence based on double perovskite Cs<sub>2</sub>SnCl<sub>6</sub>

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## Experimental Section

**Chemicals and materials:** Cs<sub>2</sub>CO<sub>3</sub> (99.9%), SnCl<sub>4</sub> (99.99%), TeO<sub>2</sub> (99.99%) and ErCl<sub>3</sub>·6H<sub>2</sub>O (99.9%) were purchased from Aladdin (Shanghai, China). Ethanol and hydrochloric acid (HCl) were analytical grade and purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). All chemicals were used as received without further purification.

**Synthesis of Te<sup>4+</sup> and Er<sup>3+</sup> doped Cs<sub>2</sub>SnCl<sub>6</sub> microcrystals (MCs):** Te<sup>4+</sup> and Er<sup>3+</sup> singly-doped and Te<sup>4+</sup>/Er<sup>3+</sup> co-doped Cs<sub>2</sub>SnCl<sub>6</sub> MCs were synthesized via a co-precipitation method. In a typical 1.4% Te<sup>4+</sup>/10% Er<sup>3+</sup> MCs (nominal concentrations in mole ratio) synthesis, SnCl<sub>4</sub> (0.986 mmol), TeO<sub>2</sub> (0.014 mmol) and ErCl<sub>3</sub>·6H<sub>2</sub>O (0.1 mmol) were mixed with 15 mL of HCl and 5 mL of ethanol in a 20 mL glass bottle. The mixture was heated to 80 °C with vigorous stirring for 30 min until all the precursors were dissolved. Thereafter, 1 mmol Cs<sub>2</sub>CO<sub>3</sub> (dissolved in 2 mL of HCl) was added into the reaction mixture, and the MCs were immediately precipitated. The solution was then kept at 80 °C under vigorous stirring for another 0.5 h to ensure the complete reaction. The products were collected by centrifugation, washed with ethanol three times, and finally dried in an oven at 70 °C for 24 h.

For synthesizing singly-doped  $\text{Cs}_2\text{SnCl}_6$  MCs with different  $\text{Te}^{4+}$  concentrations ( $x\%$   $\text{Te}^{4+}$ ),  $x\%$  mmol of  $\text{TeO}_2$  and  $(1-x\%)$  mmol of  $\text{SnCl}_4$  were used under identical conditions. For synthesizing co-doped  $\text{Cs}_2\text{SnCl}_6$  MCs with different  $\text{Er}^{3+}$  concentrations ( $1.4\%$   $\text{Te}^{4+}/x\%$   $\text{Er}^{3+}$ ), 0.986 mmol of  $\text{SnCl}_4$ , 0.014 mmol of  $\text{TeO}_2$ , and  $x\%$  mmol of  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$  were used under identical conditions. For synthesizing  $\text{Cs}_2\text{SnCl}_6$  MCs with different  $\text{Te}^{4+}$  concentrations ( $x\%$   $\text{Te}^{4+}/10\%$   $\text{Er}^{3+}$ ),  $(1-x\%)$  mmol of  $\text{SnCl}_4$ ,  $x\%$  mmol of  $\text{TeO}_2$ , and 0.1 mmol of  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$  were used under identical conditions.

**Characterization:** Powder XRD patterns were collected with an X-ray diffractometer (TD-3700) using Cu  $\text{K}\alpha 1$  radiation ( $\lambda=0.154187$  nm). Inductively coupled plasma-mass spectroscopy (ICP-MS) analyses were conducted on an ICP-MS spectrometer (Agilent 8800). The scanning electron microscopy (SEM) measurements were performed on the Tescan Mira3 equipped with energy-dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher Scientific K-Alpha using Al  $\text{K}\alpha$  (1486.8 eV). UV-vis absorption spectra were measured on a Shimadzu UV-2600 spectrometer. Photoluminescence (PL) excitation and emission spectra were recorded on the HORIBA FluoroMax spectrometer. PL decay curves were measured on the FLS980 spectrometer (Edinburgh) equipped with both continuous (450 W) and pulsed xenon lamps. The PLQYs were obtained using an FLS1000 spectrometer (Edinburgh). The photographs of the samples were taken using a HongMi K40 cell phone without using any filter.

**Table S1.** Elemental analyses of the as-synthesized Cs<sub>2</sub>SnCl<sub>6</sub>: 1.4%Te<sup>4+</sup>/10%Er<sup>3+</sup> MCs by EDS.

| Sample   | Cs : Sn : Te : Er : Cl (molar ratio[%]) |
|--|---|
| Cs <sub>2</sub> SnCl <sub>6</sub> :1.4% Te <sup>4+</sup> /10% Er <sup>3+</sup> | 22.73 : 11.76 : 0.13 : 0.24 : 65.14     |

**Table S2** Nominal and actual Te<sup>4+</sup>/Er<sup>3+</sup> co-doping concentrations in Cs<sub>2</sub>SnCl<sub>6</sub> (1): 1.4% Te<sup>4+</sup>/10% Er<sup>3+</sup> MCs. The nominal Er<sup>3+</sup> doping concentration was defined by the molar ratio of Er to (Sn+Te) in the precursor solution, the nominal Te<sup>4+</sup> doping concentration was defined by the molar ratio of Te to (Sn+Te) in the precursor solution, and the actual Te<sup>4+</sup>/Er<sup>3+</sup> doping concentrations were identified by ICP-MS.

| Sample | Nominal                |                        | Actual                 |                        |
|--------|------------------------|------------------------|------------------------|------------------------|
|        | Te <sup>4+</sup> /mol% | Er <sup>3+</sup> /mol% | Te <sup>4+</sup> /mol% | Er <sup>3+</sup> /mol% |
| 1      | 1.4                    | 10                     | 1.6                    | 2.0                    |

**Table S3** The calculated lattice parameters of undoped, Er<sup>3+</sup> singly-doped, Te<sup>4+</sup> singly-doped and Te<sup>4+</sup>/Er<sup>3+</sup> co-doped Cs<sub>2</sub>SnCl<sub>6</sub> microcrystals via XRD peaks.

**Note:** a: cell lattice parameters, V: cell volume,  $R_{wp}$ : weighted profile factor,  $R_p$ : the reliability factor of the profile,  $\chi^2$ : goodness of fit.

| Samples        | a (Å)   | V (Å <sup>3</sup> ) | $R_{wp}$ (%) | $R_p$ (%) | $\chi^2$ |
|----------------|---------|---------------------|--------------|-----------|----------|
| Undoped        | 10.3853 | 1120.101            | 10.07        | 6.83      | 5.530    |
| 10% Er         | 10.3870 | 1120.662            | 10.02        | 6.86      | 5.750    |
| 1.4% Te        | 10.3882 | 1121.050            | 9.53         | 6.64      | 4.680    |
| 10% Er-1.4% Te | 10.3894 | 1121.422            | 10.50        | 7.02      | 5.812    |

**Table S4** Average PL lifetimes of Cs<sub>2</sub>SnCl<sub>6</sub>: 1.4% Te<sup>4+</sup>/x% Er<sup>3+</sup> MCs with different Er<sup>3+</sup> concentrations (x% Er<sup>3+</sup>) by monitoring the Te<sup>4+</sup> emissions at 577 nm. All samples show double-exponential decay behavior as the following formula:

$$I(t) = I_0 + A_1 e^{-\frac{t}{\tau_1}} + A_2 e^{-\frac{t}{\tau_2}}$$

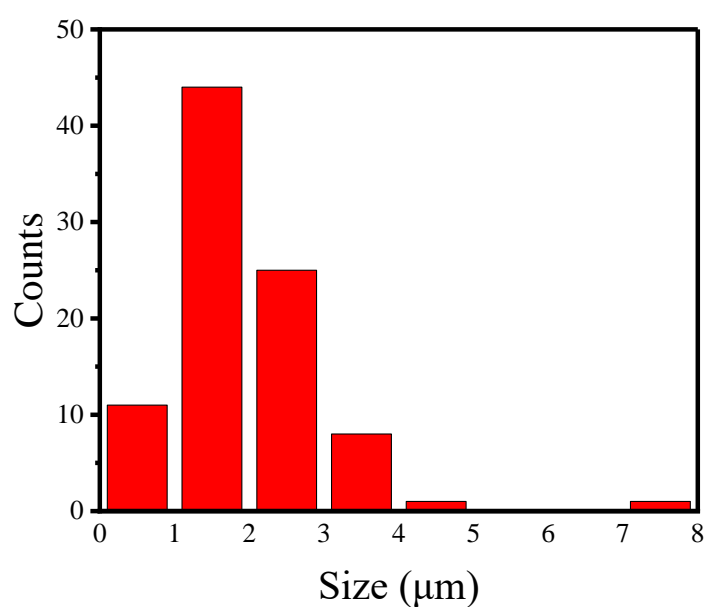
The average lifetime  $\tau_{avg}$  of the fluorescence energy level can be measured by the following formula:

$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

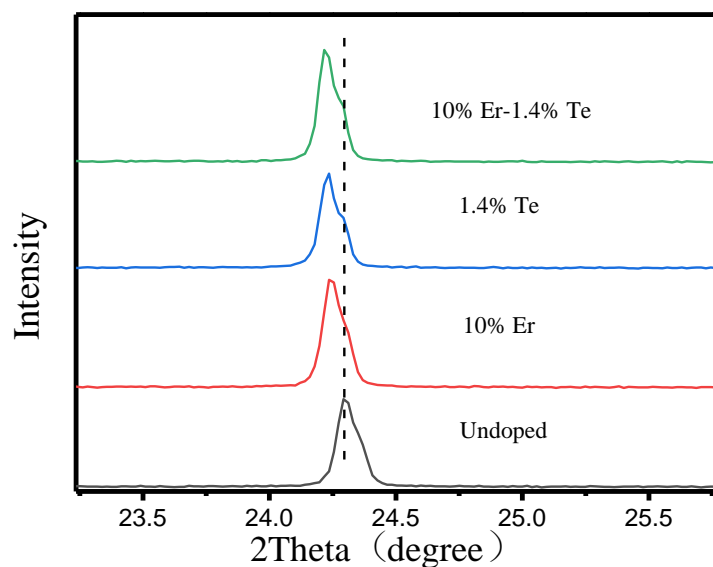
| x mol% Er | $\tau/\mu\text{s}$ |
|-----------|--------------------|
| 0         | 4.18               |
| 1         | 4.14               |
| 4         | 4.08               |
| 7         | 3.95               |
| 10        | 3.84               |
| 13        | 3.53               |
| 16        | 3.39               |

**Table S5** Temperature-dependent PL decay curves of Cs<sub>2</sub>SnCl<sub>6</sub>: 1.4%Te<sup>4+</sup>/10%Er<sup>3+</sup> MCs were obtained by monitoring the Er<sup>3+</sup> emission at 1540 nm. The PL lifetime of Er<sup>3+</sup> remained essentially unchanged (4.0 ms) with the temperature rise

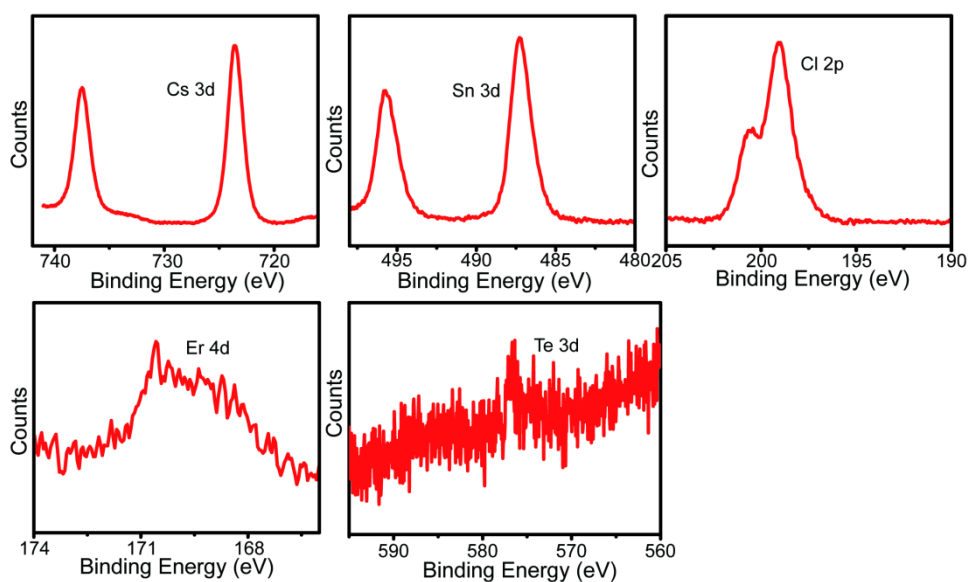
| Temperature (K) | Lifetime (ms) |
|-----------------|---------------|
| 80              | 4.1           |
| 140             | 4.2           |
| 200             | 4.0           |
| 260             | 3.9           |
| 320             | 3.8           |



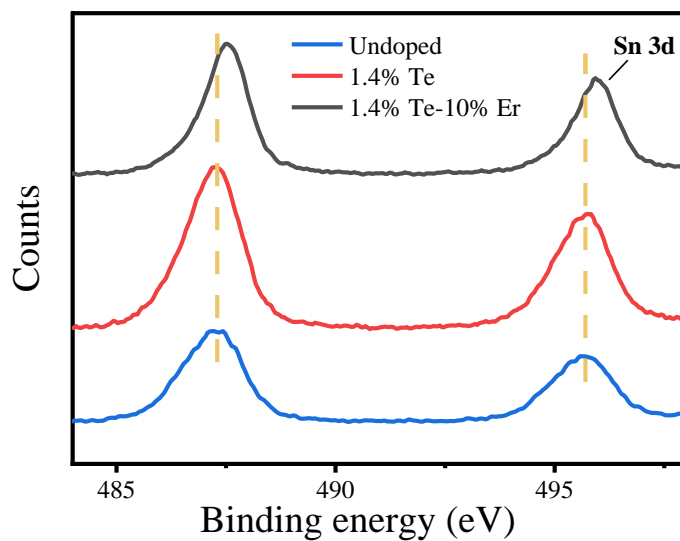
**Figure S1.** Particle size statistics of Te<sup>4+</sup>/Er<sup>3+</sup> co-doped Cs<sub>2</sub>SnCl<sub>6</sub> microcrystals.



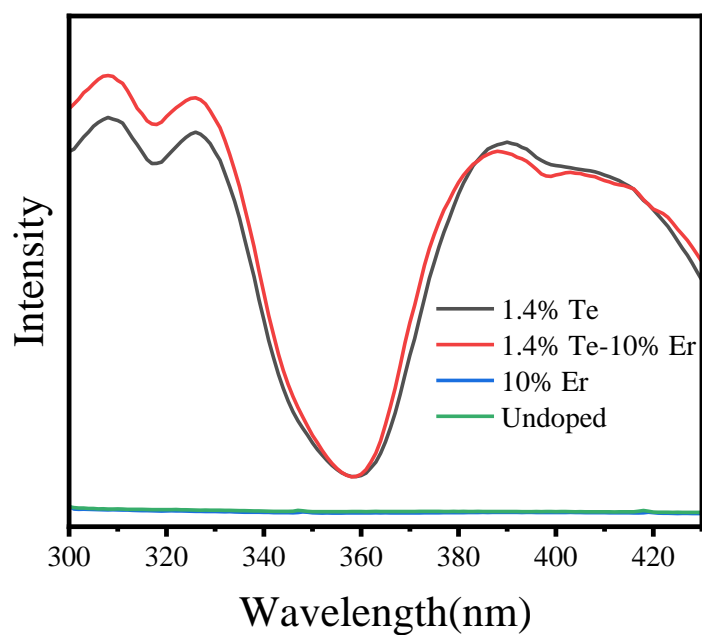
**Figure S2.** Enlarged shifts of (220) peak of the undoped,  $\text{Te}^{4+}$  singly-doped,  $\text{Er}^{3+}$  singly-doped and  $\text{Te}^{4+}/\text{Er}^{3+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$  MCs.



**Figure S3.** XPS spectra of  $\text{Te}^{4+}/\text{Er}^{3+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$  microcrystals.

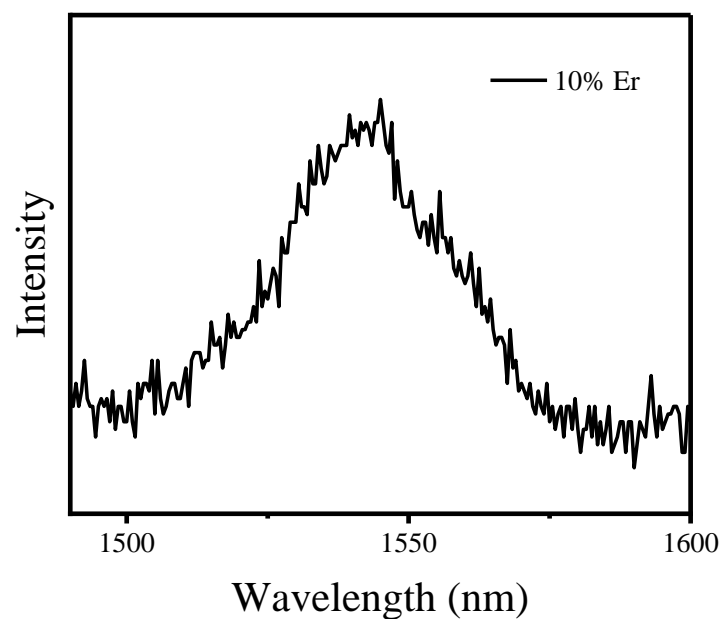


**Figure S4.** Representative XPS spectra of Sn 3d in the undoped,  $\text{Te}^{4+}$  singly-doped and  $\text{Te}^{4+}/\text{Er}^{3+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$  MCs.

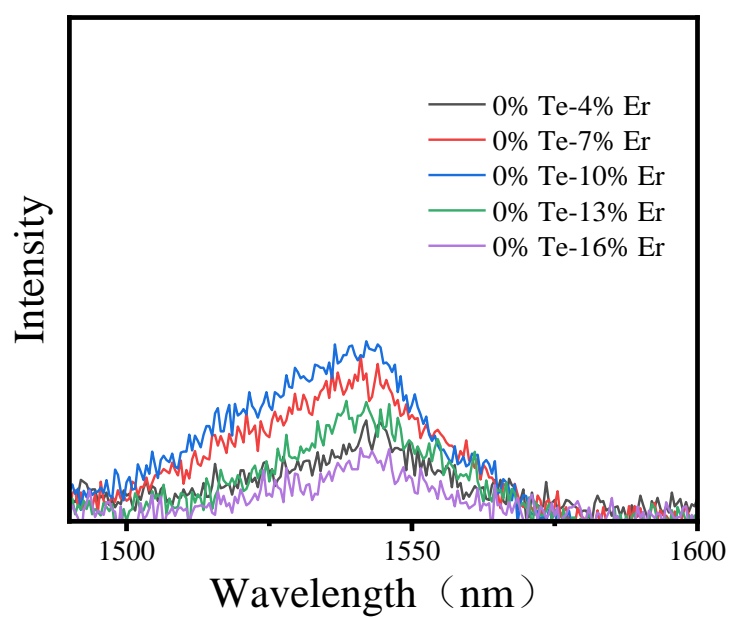


**Figure S5.** PLE spectra ( $\lambda_{\text{em}}=577$  nm) of undoped,  $\text{Er}^{3+}$  doped,  $\text{Te}^{4+}$  doped and  $\text{Te}^{4+}/\text{Er}^{3+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$  microcrystals in the visible region.

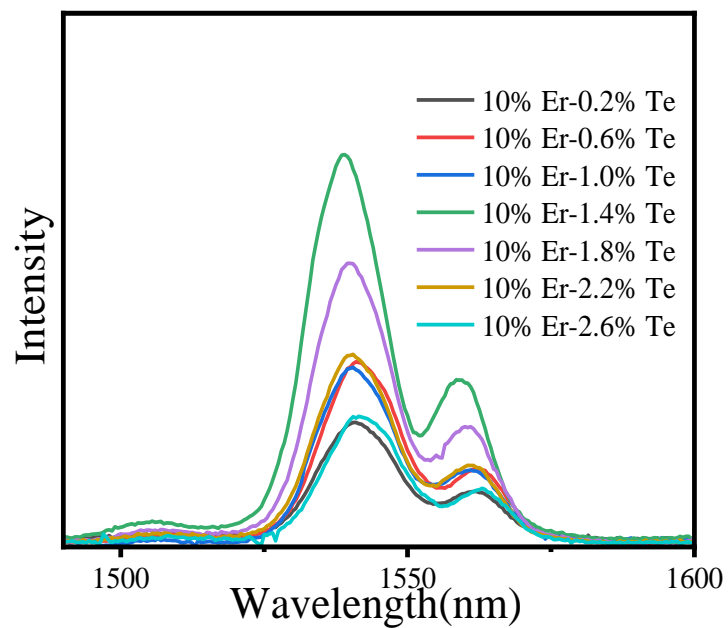




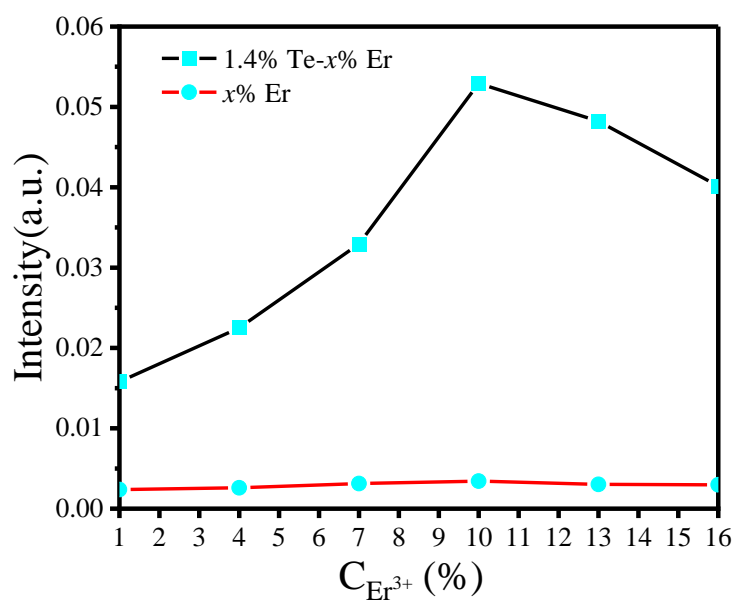
**Figure S6.** PL spectra ( $\lambda_{\text{ex}}=391$  nm) of 10% Er<sup>3+</sup> doped Cs<sub>2</sub>SnCl<sub>6</sub> microcrystals in the NIR region.



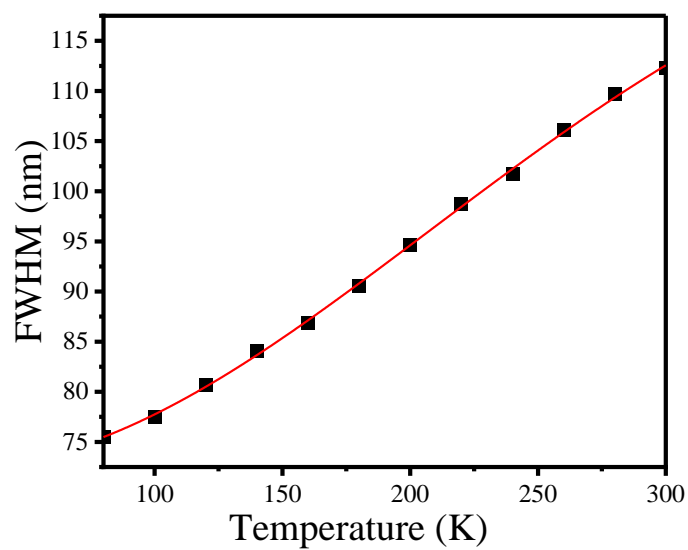
**Figure S7.** PL emission spectra ( $\lambda_{\text{ex}}=391$  nm) of  $x\%$  Er<sup>3+</sup> doped Cs<sub>2</sub>SnCl<sub>6</sub> microcrystals in the NIR region.



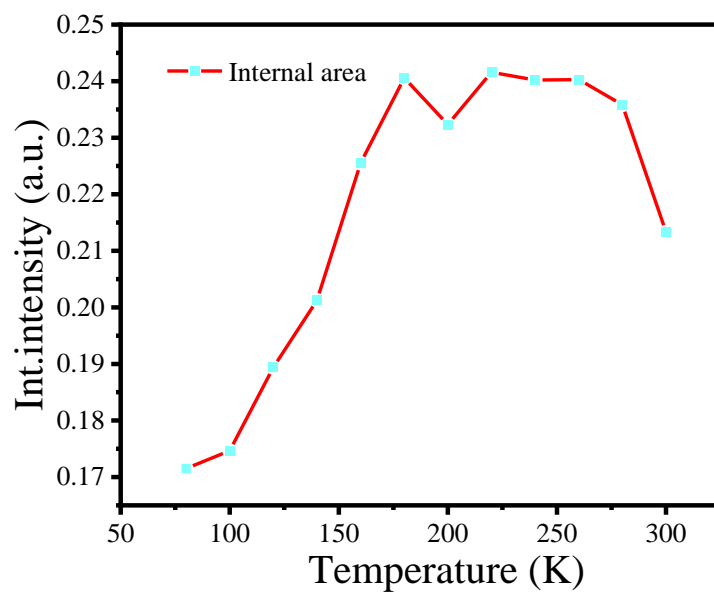
**Figure S8.** PL emission spectra ( $\lambda_{\text{ex}}=391$  nm) of  $x\%$   $\text{Te}^{4+}$ -10%  $\text{Er}^{3+}$  co-doped  $\text{Cs}_2\text{SnCl}_6$  microcrystals.



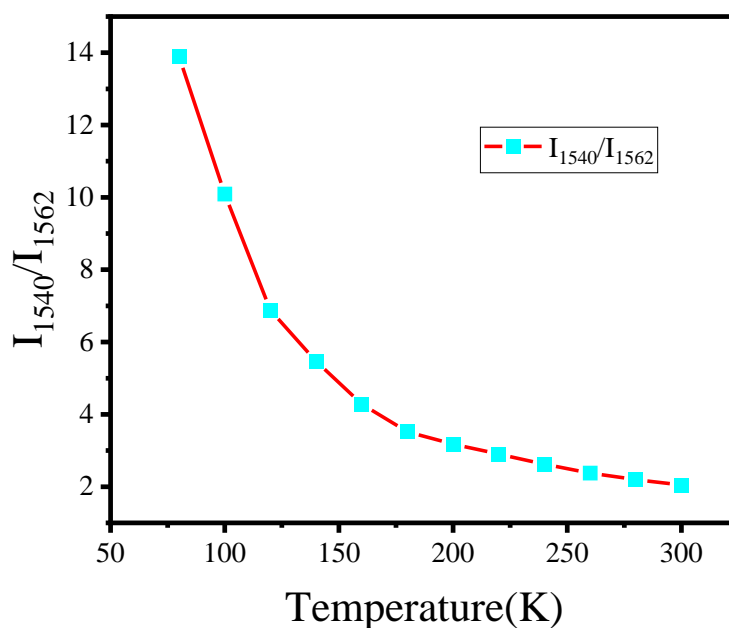
**Figure S9.** NIR intensity variations of  $\text{Er}^{3+}$  singly doped and 1.4%  $\text{Te}^{4+}$ - $\text{Er}^{3+}$  co-doped samples with different  $\text{Er}^{3+}$  concentrations ( $C_{\text{Er}^{3+}}$  (%)).



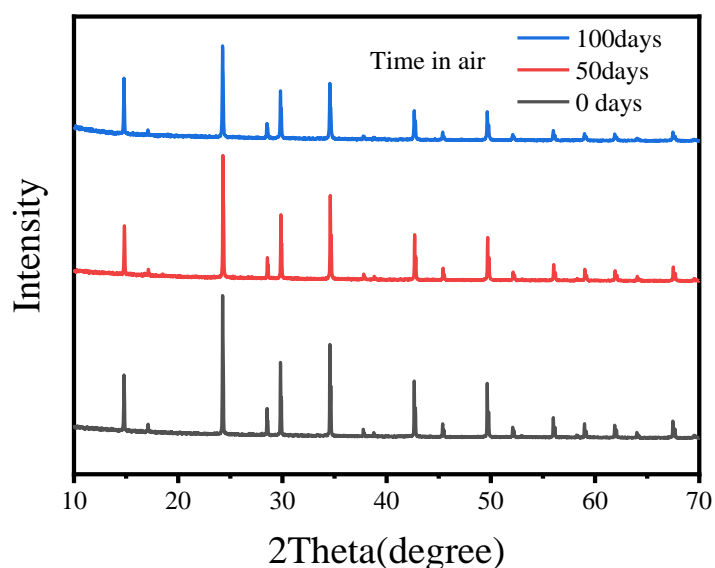
**Figure S10** Fitting results of the FWHM as a function of temperature.



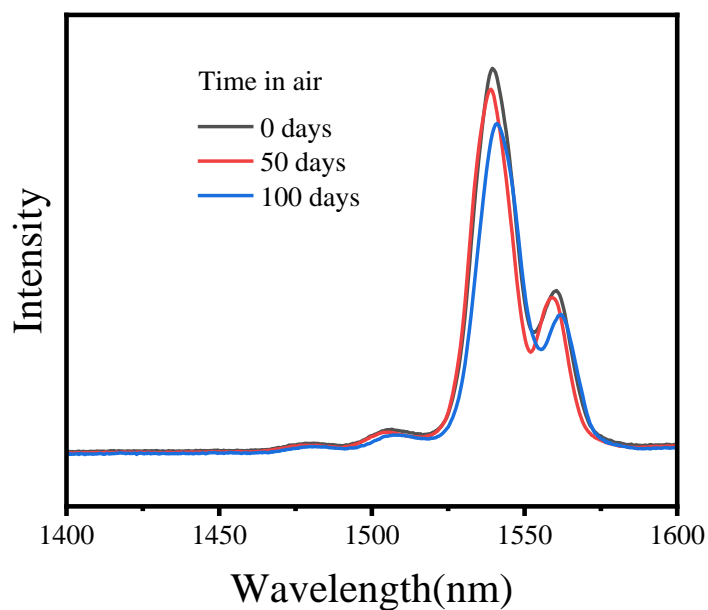
**Figure S11.** Integral intensity of NIR peak at different temperatures (80-300 K).



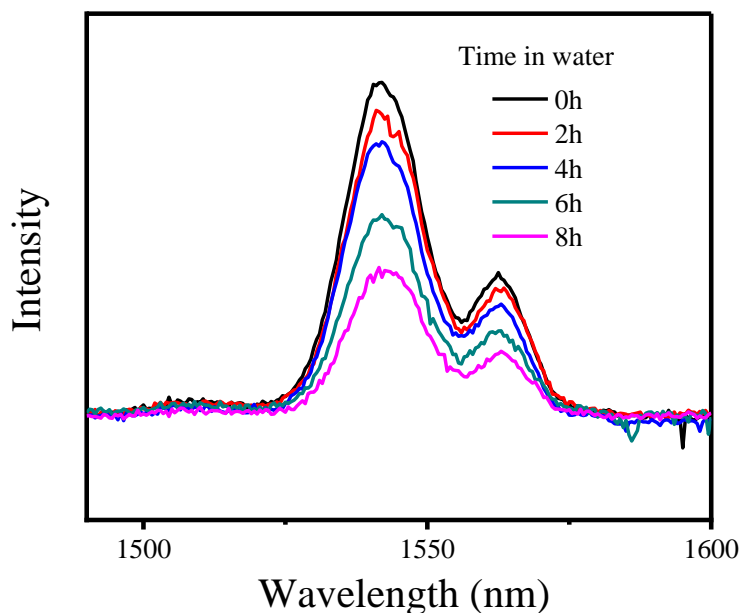
**Figure S12.** Peak intensity ratio of 1540 nm ( $I_{1540}$ )/1562 nm ( $I_{1562}$ ) emissions at different temperatures.



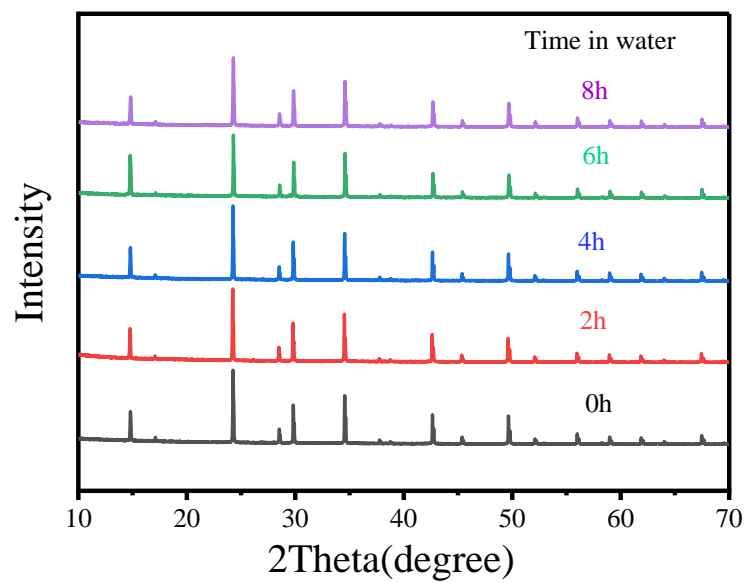
**Figure S13.** XRD patterns of  $\text{Cs}_2\text{SnCl}_6:1.4\% \text{Te}^{4+}/10\% \text{Er}^{3+}$  MCs before and after their exposure to ambient air for 50 and 100 days. The XRD patterns remain essentially unchanged, manifesting the excellent air stability of the MCs.



**Figure S14.** PL emission spectra ( $\lambda_{\text{ex}}=391$  nm) of  $\text{Cs}_2\text{SnCl}_6:1.4\% \text{Te}^{4+}/10\% \text{Er}^{3+}$  MCs before and after their exposure to ambient air for 50 and 100 days. The spectra curves of the MCs remained essentially unchanged after their storage in ambient air for 100 days, except for a slight decrease in the PL intensities, manifesting the striking air stability of the MCs.



**Figure S15.** PL emission spectra ( $\lambda_{\text{ex}}=391$  nm) of  $\text{Cs}_2\text{SnCl}_6: 1.4\% \text{Te}^{4+}/10\% \text{Er}^{3+}$  MCs before and after their soak in water for 2-8 h.



**Figure S16.** XRD patterns of Cs<sub>2</sub>SnCl<sub>6</sub>: 1.4% Te<sup>4+</sup>/10% Er<sup>3+</sup> MCs before and after their soak in water for 2-8 h.