Supporting Information

Excitation Wavelength Dependent Emission of Mn^{2+}/Sn^{2+} Co-doped Cs_3ZnI_5 for Optical Fluorescence Anti-counterfeiting Applications

Xiunan Li, [a] *Shuang Zhao,* [a] *Hailong Yu,* [a] *Jing Liu,* [a] *Bing Hu,* [a] *Qiuju Hu,* [b] *and Wenzhi Wu,* [a] ***

[a] School of Electronic Engineering, Heilongjiang University, Harbin, Heilongjiang 150080, China

[b] School of Arts and Sciences, Northeast Agricultural University, Harbin, Heilongjiang 150030, China

* Corresponding Author's E-mail: wuwenzhi@hlju.edu.cn

Contents list

1. Experiment and measurement

1.1 *Chemicals and reagents*

The following chemicals were purchased and used without further purification: cesium iodide (CsI, 99.9%), Zinc (II) iodide (ZnI_2, 99.99%), tin (II) iodide (SnI_2, 99.99%), manganese (II) acetate ((CH_3COO_2Mn), hypo phosphorous acid (H_3PO_2), hydroiodic acid (HI), isopropyl alcohol (C_3H_8O, AR,99.5%) and alcohol (C_2H_6O, 99.9%). All materials were purchased from Macklin.

1.2 *Synthesis of pure and doped Cs_3ZnI_5 SCs*

Here we used the gradient cooling crystallization method to prepared the single crystals of Mn^{2+}, Sn^{2+} co-doped Cs_3ZnI_5 SCs. For synthesizing Cs_3ZnI_5: Mn^{2+}/Sn^{2+} SCs. First, 8 mL HI and 2 mL H_3PO_2 solution were added to a 25 mL Teflon autoclave along with 6 mmol CsI, 1.57 mmol ZnI_2, 0.03 mmol SnI_2 and 0.4 mmol CH_3COO_2Mn. And the sealed Teflon autoclaves were transferred to a heating cabinet at 150 ℃ for 12 h, then the reaction temperature was lowered from 150 ℃ to room temperature with a rate of 10 ℃/h, after 7 h, homogeneous and smooth single crystals were obtained. After that, rinsed repeatedly with isopropanol or alcohol. Finally, the rinsed SCs were dried for time at 60 ℃ in a vacuum-heated oven. For synthesizing Cs_3ZnI_5: Sn^{2+} and Cs_3ZnI_5: Mn^{2+} SCs were also prepared according to the standard feed ratio using this synthesized method.

1.3 *Optical and structural characterization*

The phase purity and structural type are measured by the X-ray diffraction spectrometer (XRD-6100, Shimadzu) with Cu-Kα (λ=0.15 nm) radiation over the range of 10-60° (2θ). The data were obtained using an ESCAlab250 X-ray photoelectron Spectrometer (XPS) for surface analysis, the excitation source was Al-Kα ray (*hv*=1486.6 eV). The 405 nm continuous-wave (CW) laser (UV-FN-405-20mW, CNI) was used as an excitation light source for steady-state excitation. The steady-state PL spectra were collected using a spectrometer (HR4000CG-UV-NIR, Ocean Optics). The PLE spectra were measured by a HITACHI F-4600. In order to achieve higher time resolution, TRPL dynamics is also carried out by a time correlated single photon counting (TCSPC) systems from Boston Electronics. It consists of a monochromator

equipped with a detector (SPCM-01-20, Holita), single photon counting electronics module (FLA-130, Holita) accounting for data acquisition. Raman spectroscopy was performed at both room temperature and variable temperatures using a 532 nm laser for excitation. The temperature-dependent PL and Raman measurements were performed using a vacuum liquid nitrogen cryostat (Cryo-77, Oriental Koji) with a temperature range from 80 K to 480 K. Photoluminescence quantum yield (PLQY) measurements of samples in powder form was measured on a Hamamatsu C13534-11 absolute quantum yield measurement system (Hamamatsu Photonics) with a 150 W xenon monochromatic light source and 3.3 inch integrating sphere. The PLQY value of each peak was calculated by the formula 'Photoluminescence quantum yield (PLQY) =number of emitted photons/number of absorbed photons'. Where the number of emitted photons is the integral area of the peak, each peak has its own number of photons emitted (given by the test instrument). The number of absorbed photons is the total number of photons absorbed in the whole test process.[1, 2] Thermogravimetric analysis (TGA) of the title compounds were performed on a computer-controlled TG 550 (TA Instrument). Pure powder samples were loaded into platinum pans and heated with a ramp rate of 10 °C/min from room temperature to 550 °C.

1.4 *Calculation formula*

The lifetime decay curve of Cs_3ZnI_5: 40%Mn^{2+} under 405 nm laser excitation can be fitted with a single exponential decay,[3]

$$I(t) = I_0 + A\exp(-t / \tau) \quad (1)$$

where $I(t)$ and I_0 denote the fluorescence intensity and the background intensity, A is emission intensity factor, and τ is decay times of exponential component.

The exciton binding energy (E_b) can be calculated as,[4, 5]

$$I(T)=I_0 / (1 + Be^{-E_b/k_BT}) \quad (2)$$

where I_0 is the estimative integrated fluorescence intensity at T=0 K; E_b is the exciton activation energy; k_B is the Boltzmann constant; B is a relative contribution of different activation energies.

2. Supplementary figures

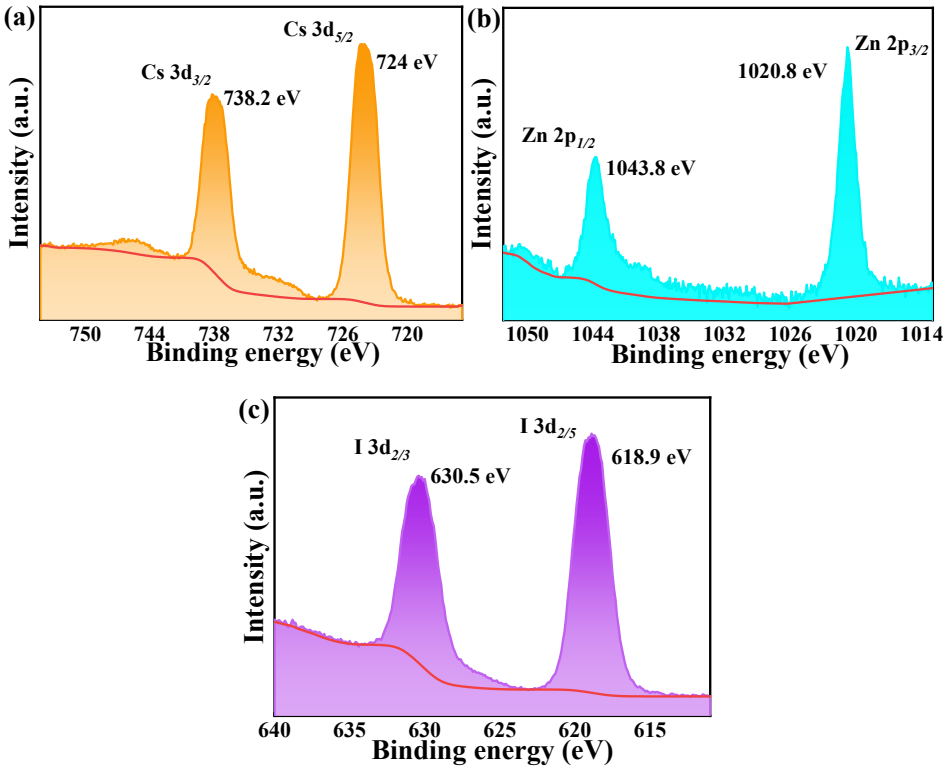

Fig S1 (a) High-resolution XPS spectra of Cs 3d, (b) Zn 2p and (c) I 3d, respectively.

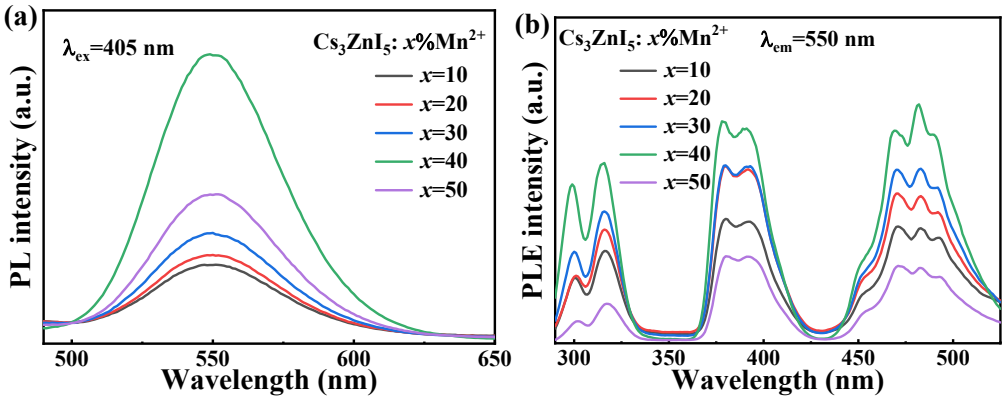

Fig. S2 PL and PLE spectra at different concentrations for Cs_3ZnI_5: $x\%Mn^{2+}$.

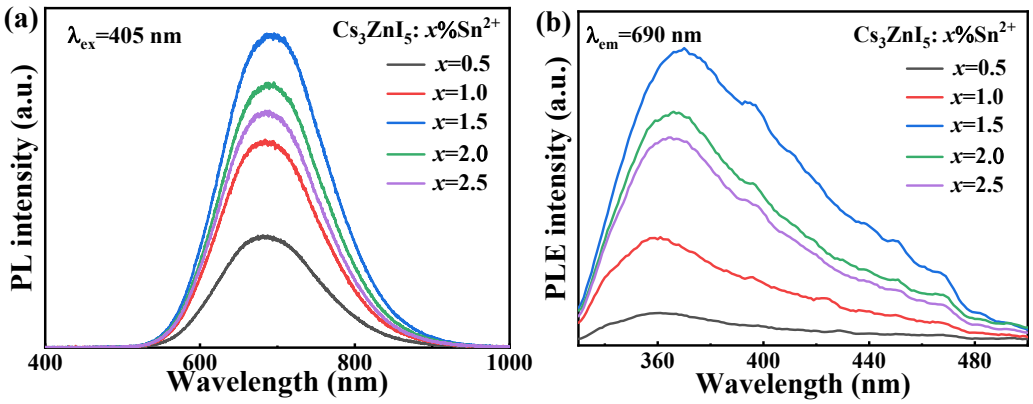

Fig. S3 PL and PLE spectra at different concentrations for Cs_3ZnI_5: $x\%Sn^{2+}$.

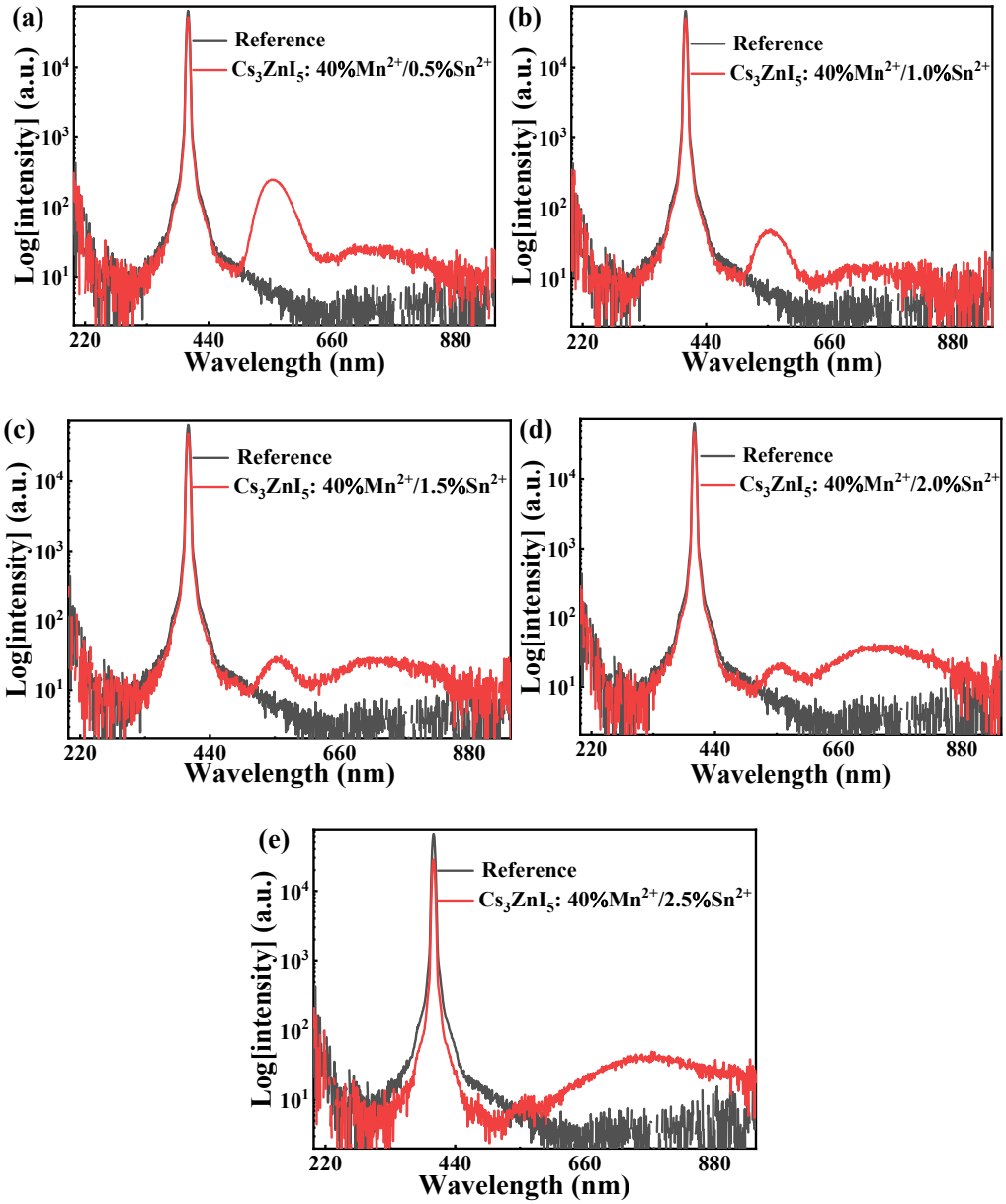

Fig. S4 PL spectra monitored at different Sn^{2+} feed rate for Cs_3ZnI_5: 40%Mn^{2+}/*y*%Sn^{2+} under 405 nm laser excitation.

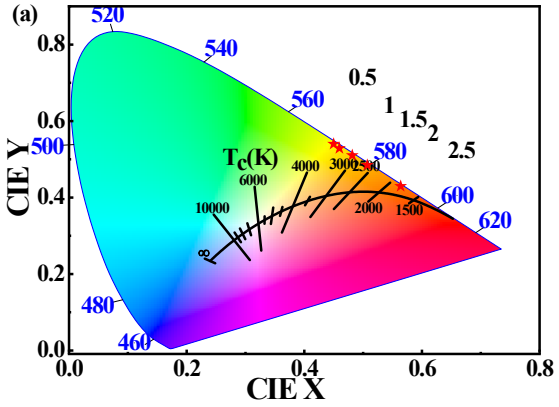

Fig. S5 CIE color coordinate for Cs_3ZnI_5: 40%Mn^{2+}/*y*%Sn^{2+} (*y*=0.5, 1.0, 1.5, 2.0, 2.5).

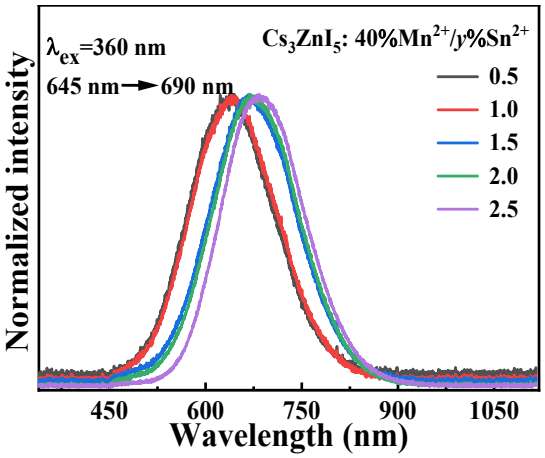

Fig. S6 PL spectra for Cs_3ZnI_5: 40%Mn^{2+}/*y*%Sn^{2+} (*y*=0.5, 1.0, 1.5, 2.0, 2.5) under 360 nm laser excitation.

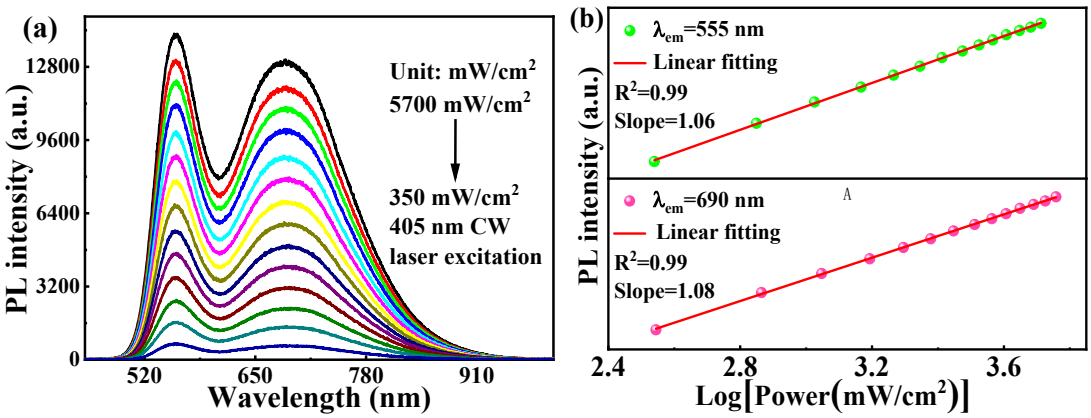

Fig. S7 (a) PL spectra of Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+} with different pump fluences under 405 nm laser excitation, (b) The linear fitting between PL intensity and pump fluence.

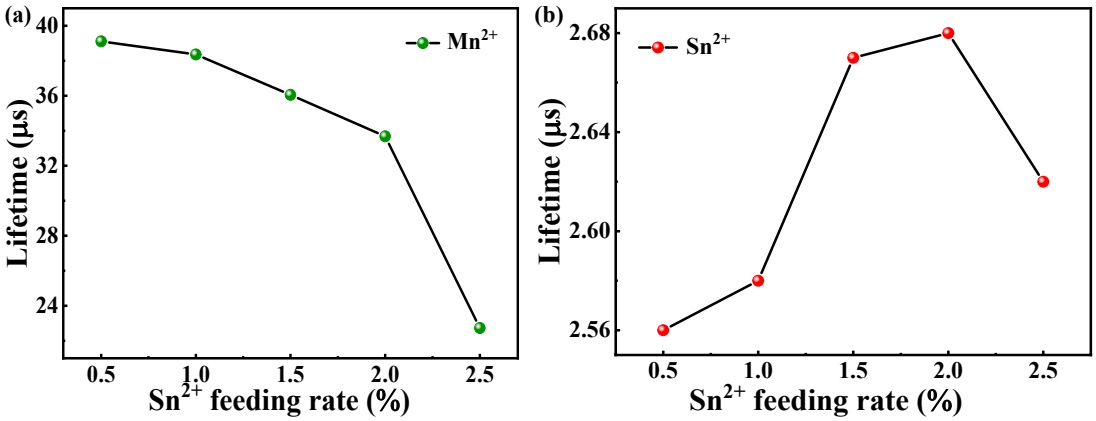

Fig. S8 (a) Lifetime value of Mn^{2+} in Cs_3ZnI_5: 40%Mn^{2+}/*y*%Sn^{2+} (*x*=0.5, 1.0, 1.5, 2.0, 2.5) (405 nm excitation, 555 nm emission), and (b) Sn^{2+} (405 nm excitation, 690 nm emission).

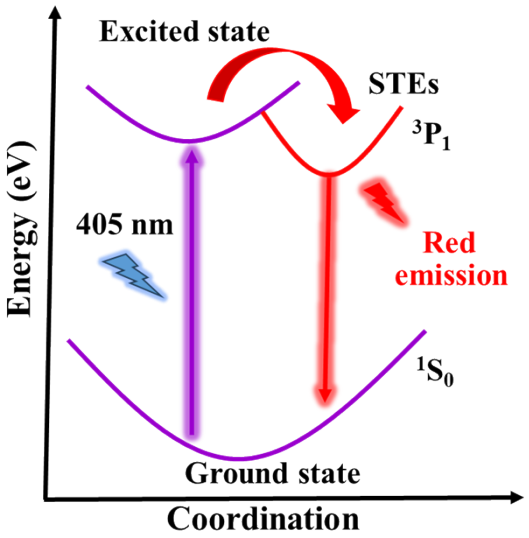

Fig. S9 The mechanisms of the red emission in Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+}.

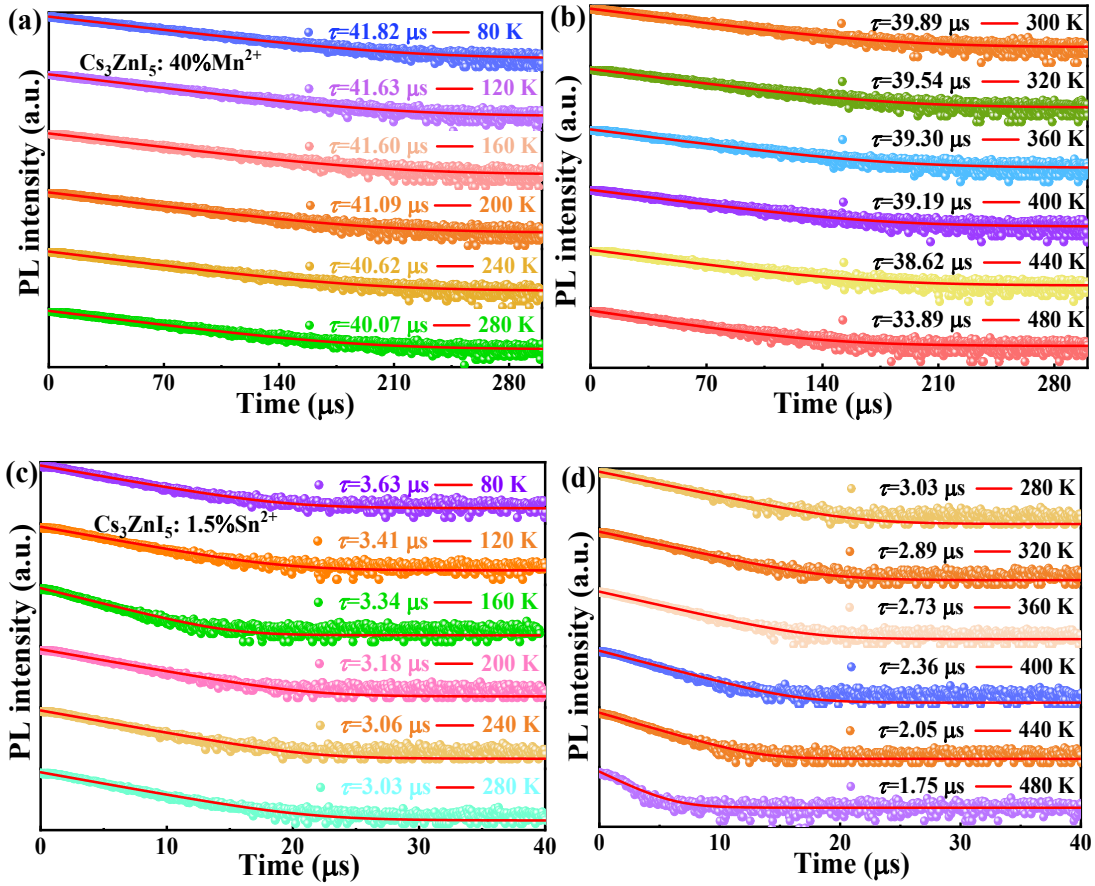

Fig. S10 (a, b) Lifetime curves spectra of Mn^{2+} in Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+} at different temperatures (405 nm excitation, 555 nm emission), (c, d) Sn^{2+} (405 nm excitation, 690 nm emission).

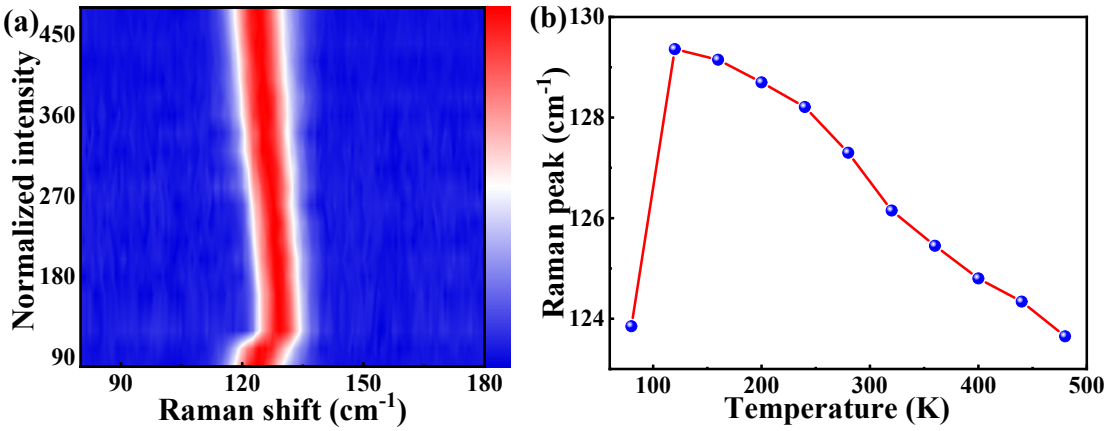

Fig. S11 (a) Raman Spectra of Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+} at different temperatures (80-480 K). (b) Variation of Raman peak position as temperatures (80-480 K).

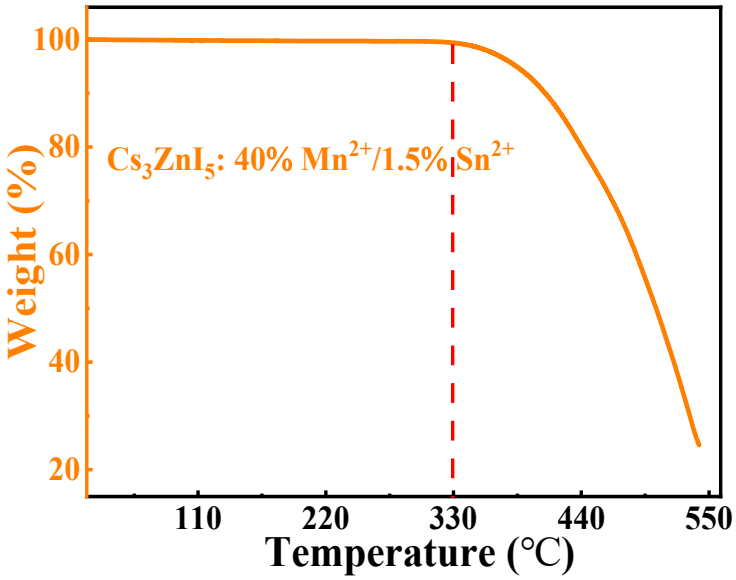

Fig. S12 Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+} of thermogravimetric analysis graphs.

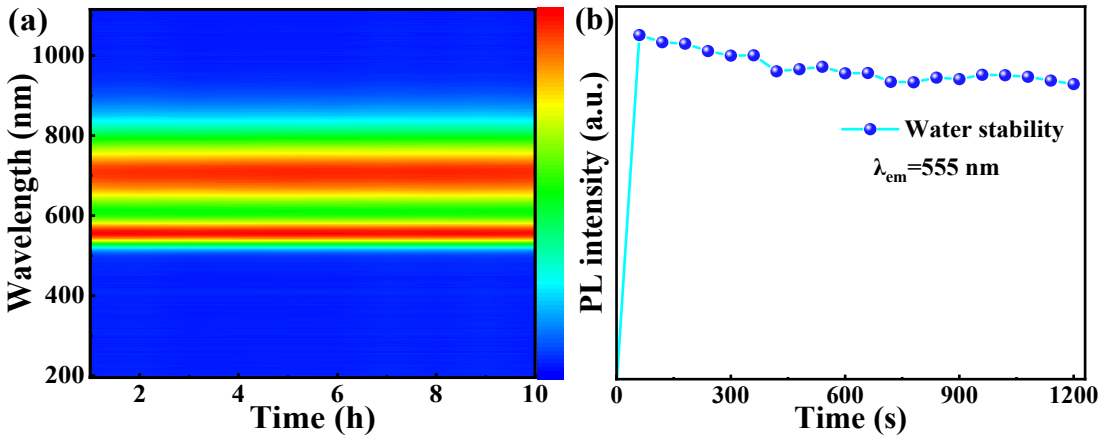

Fig. S13 (a) Cs_3ZnI_5: 40%Mn^{2+}/1.5%Sn^{2+} of fluorescence stability measured in air, and (b) water stability measured in air without any encapsulation.

3. Supplementary table

Table S1. PLQY values for Cs_3ZnI_5: x%Mn^{2+}, Cs_3ZnI_5: x%Sn^{2+} and Cs_3ZnI_5: 40%Mn^{2+}/y%Sn^{2+} samples.

Cs_3ZnI_5: Mn^{2+}		Cs_3ZnI_5: Sn^{2+}		Cs_3ZnI_5: 40%Mn^{2+}/Sn^{2+}		
Dopant Mn (%)	PLQY (%)	Dopant Sn (%)	PLQY (%)	Dopant Sn (%)	PLQY 555 nm (%)	PLQY 690 nm (%)
10	22	0.5	6.7	0.5	13.2	0.5
20	23	1	17.3	1	7.6	1.8
30	24.5	1.5	21.2	1.5	6.7	2
40	25	2	18.8	2	5	4.2
50	24.3	2.5	18.3	2.5	1.11	25.7

References

1. Yu.Y.; Zou.C.; Shen.W.; Zheng.X.; Tian.Q.; Yu.Y.; Chen.C.; Zhao.B.; Wang.Z.; Di.D.; Bakr.O.; Liao.L., Efficient Near-Infrared Electroluminescence from Lanthanide-Doped Perovskite Quantum Cutters. *Angewandte Chemie International Edition*, **2023,** *62* (22), e202302005-e202302013.
2. Shen.X.; Wang.Z.; Tang.C.; Zhang.X.; Lee.B.; Li.X.; Li.D.; Zhang.Y.; Hu.J.; Zhao.D.; Zhang.F.; Yu.W.; Dong.B.; Bai.X., Near-Infrared LEDs Based on Quantum Cutting-Activated Electroluminescence of Ytterbium Ions. *Nano Lett.*, **2022,** *23* (1), 82-90.
3. Zhao, S.; Zou, J.; Xu, H.; Hu, Q.; Han, Q.; Wu, W., Luminescent Enhancement and Multi-mode Optical Thermometry of Erbium Doped Halide Cs_2(Na/Ag)$BiCl_6$ Microcrystals. *J. Rare Earths*, **2024**. In press
4. Gao, M.; Pan, Y.; Peng, C.; Ding, Y.; Lian, H.; Li, L.; Lin, J., White Light Emission from Single-Component $Cs_7Cd_3Br_{13}$: Pb^{2+}, Mn^{2+} Crystals with High Quantum Efficiency and Enhanced Thermodynamic Stability. *Chem. Mat.*, **2023,** *35* (2), 773-782.
5. Gong, Z.; Zheng, W.; Huang, P.; Cheng, X.; Zhang, W.; Zhang, M.; Han, S.; Chen, X., Highly Efficient Sb^{3+} Emitters in 0D Cesium Indium Chloride Nanocrystals with Switchable Photoluminescence Through Water-triggered Structural transformation. *Nano Today*, **2022,** *44*, 101460-101468.