

## Supporting Information

### **Using single ammonium acidic salt towards simple green co-precipitation synthesis for Mn<sup>4+</sup>-activated fluorides**

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### Synthesis of Cs<sub>2</sub>MnF<sub>6</sub> precursor

Here, novel Cs<sub>2</sub>MnF<sub>6</sub> was particularly prepared as precursor via co-precipitation reaction on K<sub>2</sub>MnF<sub>6</sub> and CsF. Specifically, 5 mmol K<sub>2</sub>MnF<sub>6</sub> (followed Bode's method)<sup>1</sup> was dissolved in 10 mL of HF solution with continuous stirring, then 50 mmol CsF was slow added into above solution following with bright yellow precipitate of Cs<sub>2</sub>MnF<sub>6</sub> formed. The product was filtrated, washed with ethanol several times, and dried at 70 °C for 6 h. The X-ray powder diffraction measurement demonstrates the phase purity of Cs<sub>2</sub>MnF<sub>6</sub> (Fig. S1a). Under blue light excitation, it presents red line emission as those of Mn<sup>4+</sup>-activated fluorides (Fig. S1b). Notice that protection suit was needed during experimental process for human-security; meanwhile, centrifugal tubes were used as reactor to reduce the volatilization of HF.

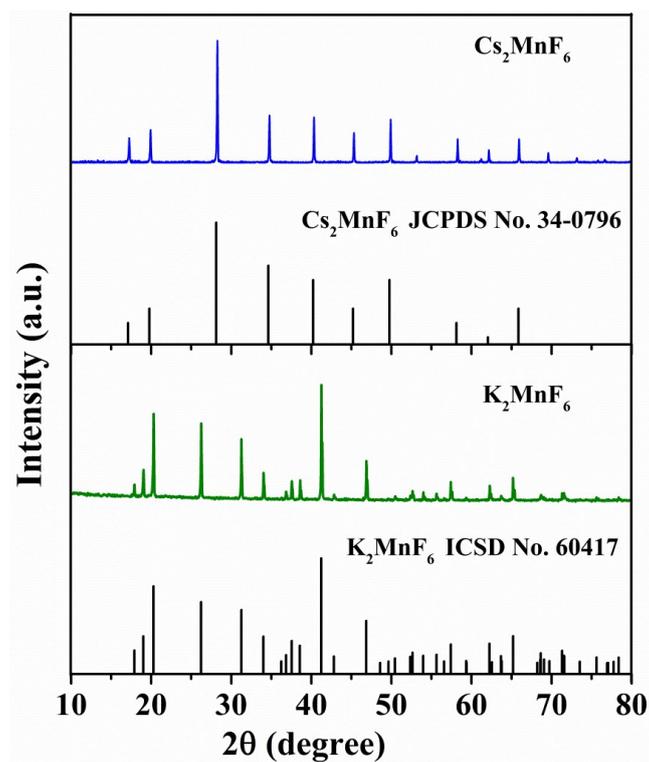
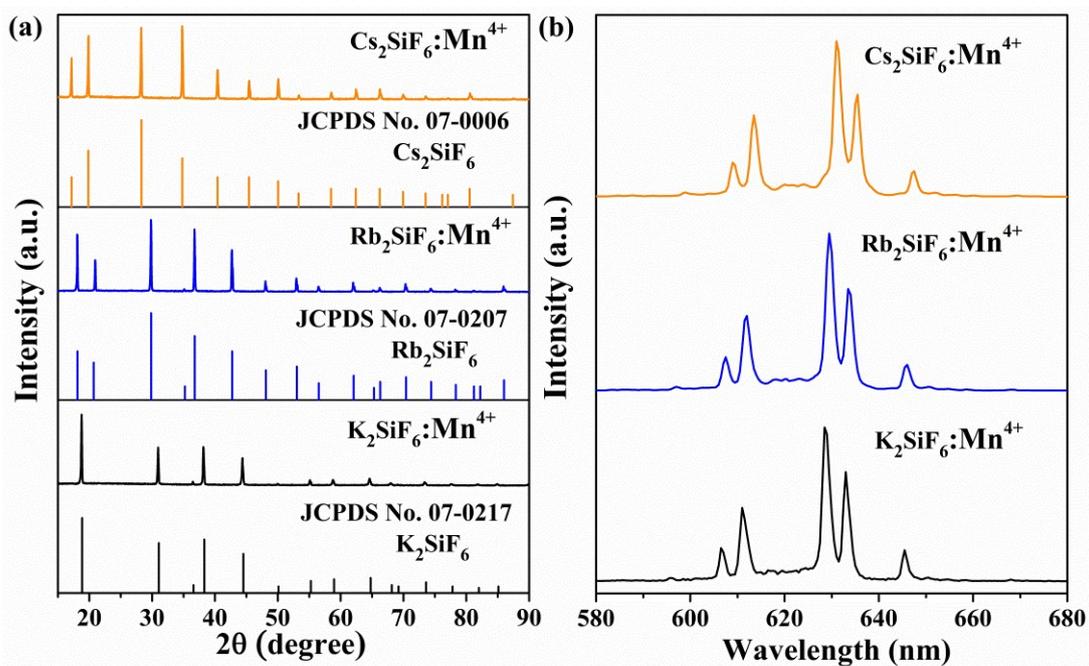
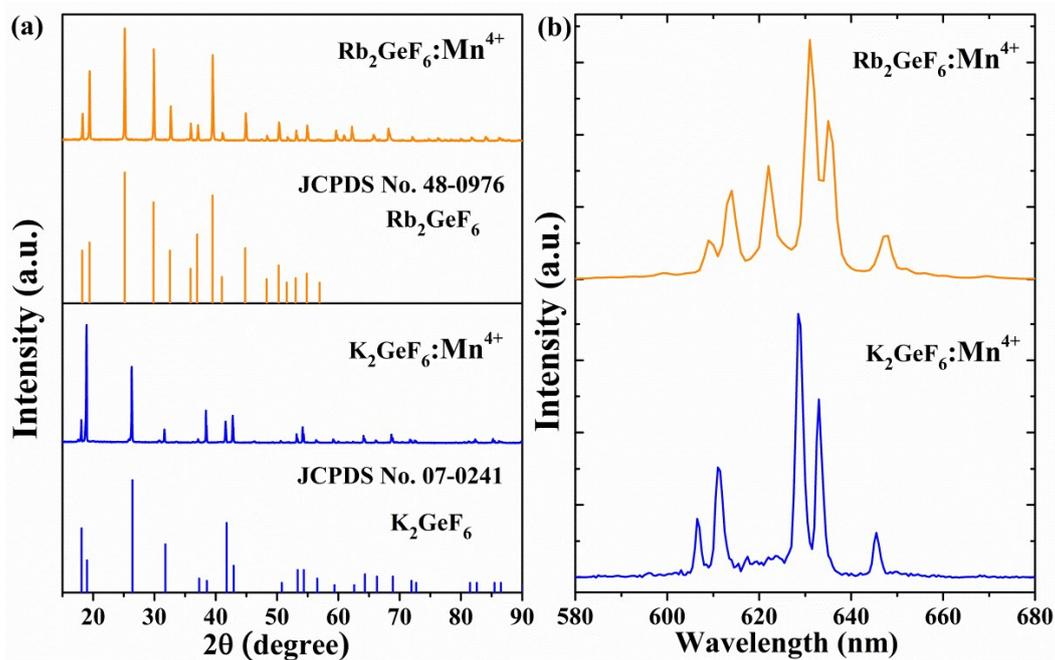


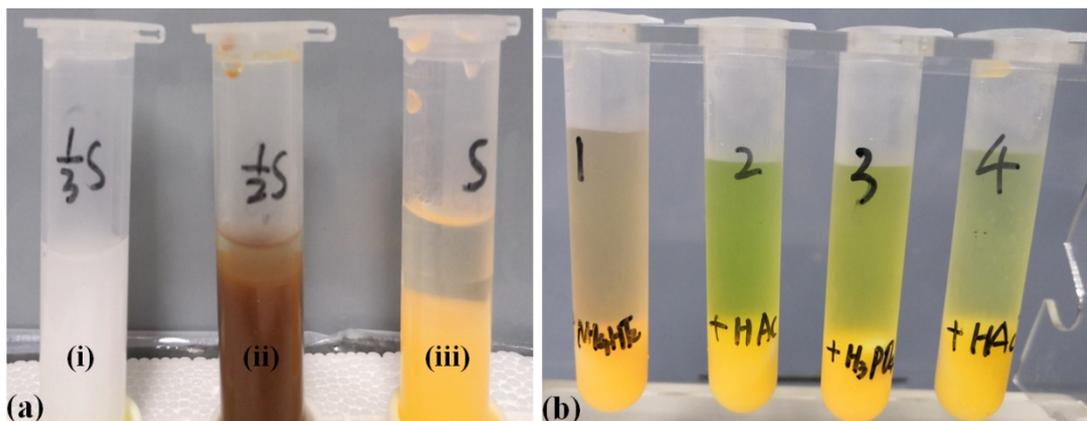
Fig. S1 XRD patterns of K<sub>2</sub>MnF<sub>6</sub> and Cs<sub>2</sub>MnF<sub>6</sub>.



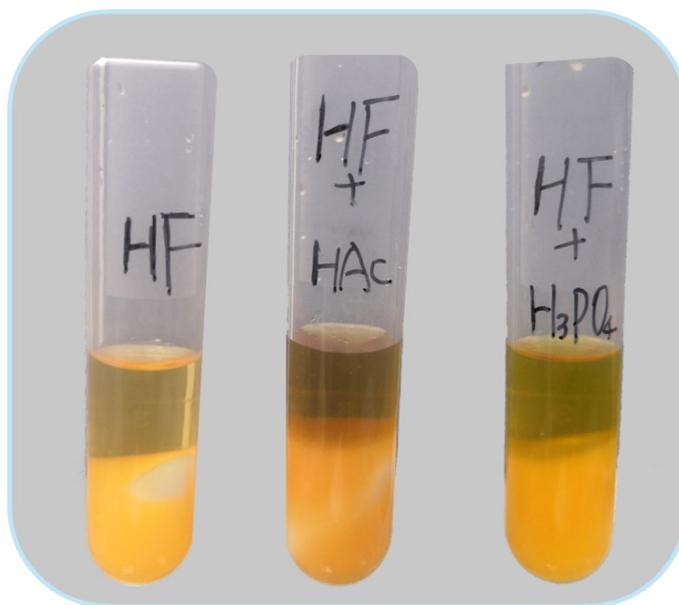
**Fig. S2** (a) XRD patterns and (b) emission spectra of  $A_2SiF_6:Mn^{4+}$  ( $A = K, Rb, Cs$ ) samples prepared under near-saturated  $NH_4HF_2$  solution.



**Fig. S3** (a) XRD patterns and (b) emission spectra of  $A_2GeF_6:Mn^{4+}$  ( $A = K, Rb, Cs$ ) samples prepared under  $NH_4HF_2$  solution.



**Fig. S4** (a) (i)  $GeO_2$  disperses in the  $0.946 \text{ g} \cdot \text{mol}^{-1}$   $NH_4HF_2$  solution;  $Cs_2GeF_6:Mn^{4+}$  was prepared in (ii)  $1.420 \text{ g} \cdot \text{mol}^{-1}$  and (iii)  $2.839 \text{ g} \cdot \text{mol}^{-1}$   $NH_4HF_2$  solution, respectively; (b) digital images of  $Cs_2GeF_6:Mn^{4+}$  reaction solutions using different synthetic strategies.



**Fig. S5** Digital images of  $Cs_2GeF_6:Mn^{4+}$  reaction solutions under  $HF$  solution coexisting with  $HAc$  or  $H_3PO_4$  addition.

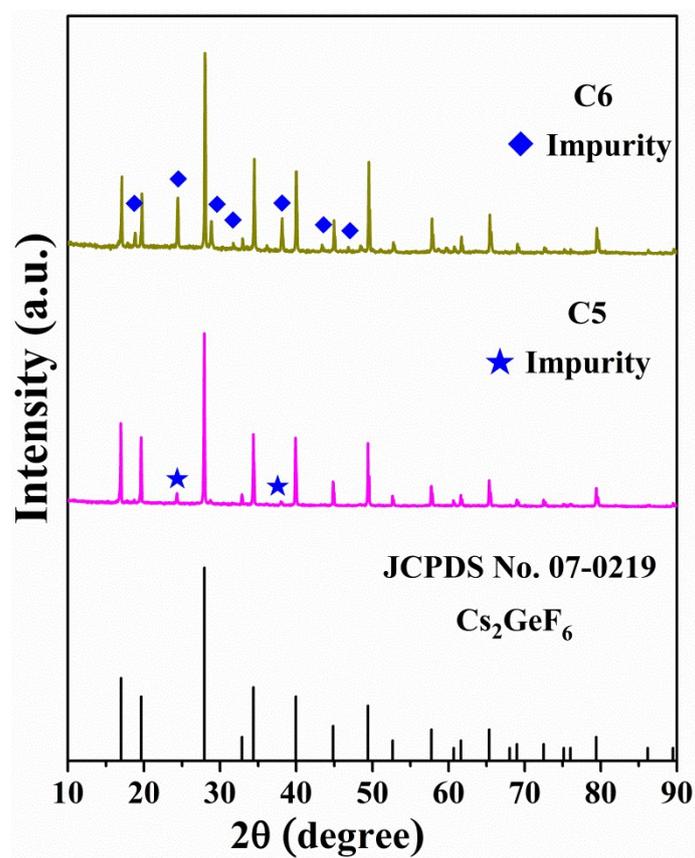


Fig. S6 XRD patterns of  $\text{Cs}_2\text{GeF}_6:\text{Mn}^{4+}$  samples synthesized using strategies C5-C6.

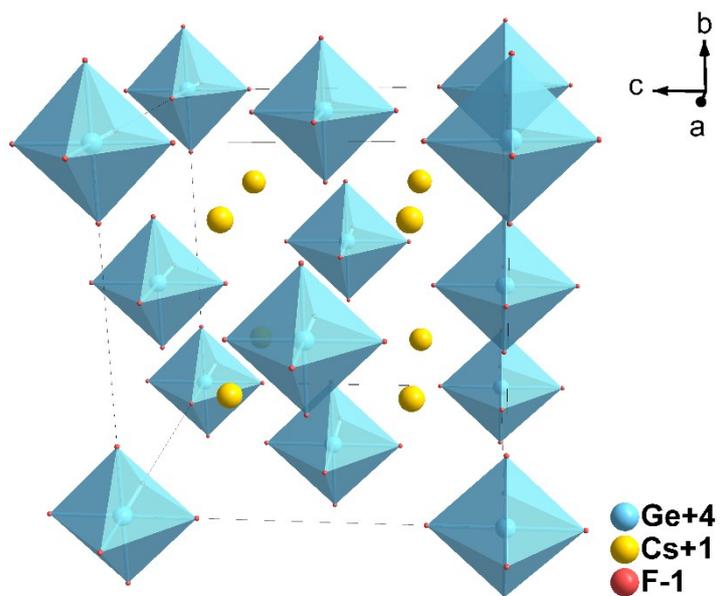
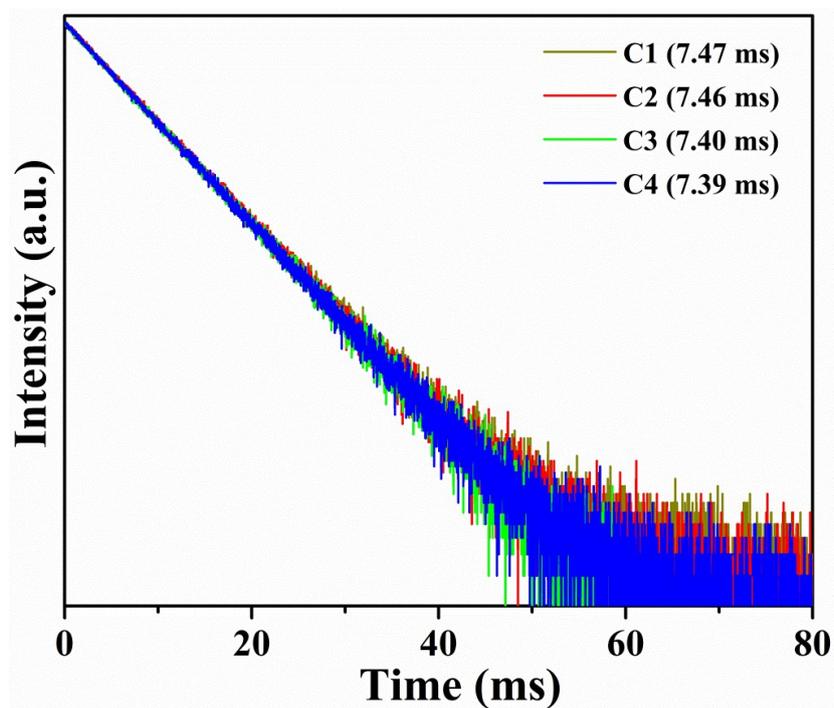
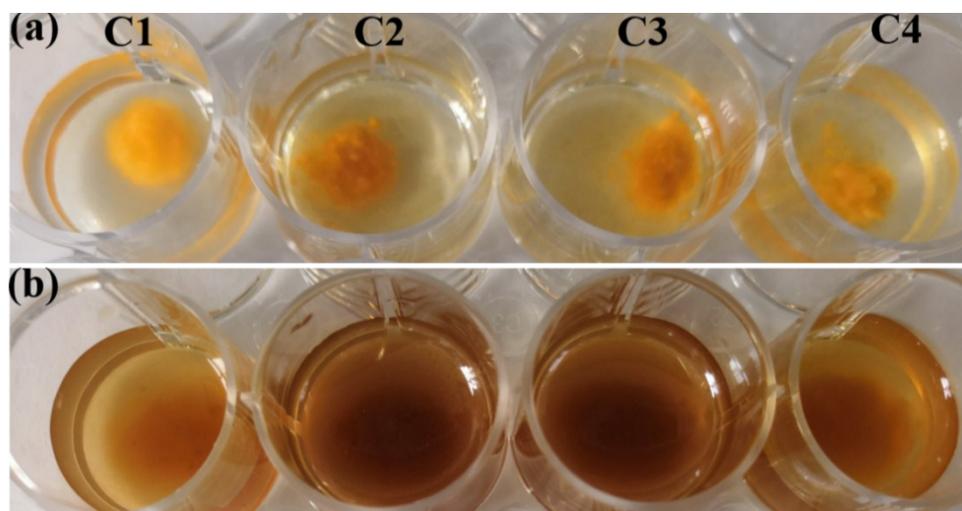


Fig. S7 The crystal structure of  $\text{Cs}_2\text{GeF}_6$  from ICSD 35547.



**Fig. S8** The luminescence decay curves of  $\text{Cs}_2\text{GeF}_6:\text{Mn}^{4+}$  phosphors synthesized using strategies C1-C4.



**Fig. S9** Digital images of samples C1-C4 soaked in water with the same mass concentration after (a) 2 min and (b) 10 min. (dry samples were conserved for six months)

**Table S1** The maximum solubility of some reagents in near-saturated  $\text{NH}_4\text{HF}_2$  (S) solution.

Reagent	Amount/g	Volume of S/mL	Saturation concentration / $\text{mol}\cdot\text{L}^{-1}$
$\text{H}_2\text{SiO}_3$	3.121		0.400
$\text{GeO}_2$	5.588		0.534
$\text{TeO}_2$	7.983		0.500
$(\text{NH}_4)_2\text{SiF}_6$	12.825	100	0.720
$(\text{NH}_4)_2\text{TiF}_6$	10.926		0.552
$(\text{NH}_4)_2\text{ZrF}_6$	4.825		0.200
$\text{K}_2\text{TiF}_6$	6.020		0.250

**Table S2** The near-saturated solutions by using various acidic salts.

strategy	acidic salt	dose of acidic salt (mmol)	dose of $\text{H}_2\text{O}$ (mL)	pH
R1	$\text{NaHF}_2$	15		2.5~3.0
R2	$\text{KHF}_2$	15		2.5~3.0
R3	$\text{NH}_4\text{H}_2\text{PO}_4$	25	30	5.0~5.4
R4	$\text{KH}_2\text{PO}_4$	25		5.0~5.4

**Table S3** QEs of  $\text{Cs}_2\text{GeF}_6:\text{Mn}^{4+}$  phosphors synthesized under different strategies.

Sample	IQE	EQE
C1	93.3	71.1
C2	84.2	56.4
C3	79.6	48.1
C4	70.1	41.7

**Table S4** ICP results of Mn<sup>4+</sup> actual doped concentration of Cs<sub>2</sub>GeF<sub>6</sub>:Mn<sup>4+</sup> phosphors.

Mole ratio of Cs <sub>2</sub> MnF <sub>6</sub> to GeO <sub>2</sub>	Mn <sup>4+</sup> concentration (at%)
2:100	1.53
4:100	3.65
6:100	5.34
8:100	7.86
10:100	9.25
12:100	10.42

## Parameters

### Color purity

The color purity is an important parameter to evaluate the color-quality of narrow-band luminescent materials, which can be calculated by using the expression as follow: [2]

$$\text{color purity} = \frac{\sqrt{(x - x_i)^2 + (y - y_i)^2}}{\sqrt{(x_d - x_i)^2 + (y_d - y_i)^2}} \times 100\% \quad (1)$$

where  $(x, y)$ ,  $(x_i, y_i)$  and  $(x_d, y_d)$  are color coordinates of present phosphor, equal-energy illuminant and the dominant wavelength of light source, respectively.

### Chromaticity shift ( $\Delta E$ )

The chromaticity shift ( $\Delta E$ ) is a specific parameter to describe the color fluctuations of luminescent materials aroused by increasing temperature. It can be calculated according to the equation below: [3]

$$\Delta E = \sqrt{(u'_t - u'_0)^2 + (v'_t - v'_0)^2 + (w'_t - w'_0)^2} \quad (2)$$

where  $u' = 4x/(3 - 2x + 12y)$ ,  $v' = 9y/(3 - 2x + 12y)$ , and  $w' = 1 - u' - v'$ .  $x$  and  $y$  are the chromaticity coordinates in CIE 1931,  $u'$  and  $v'$  are the chromaticity coordinates in  $u'v'$

uniform color space, and  $\theta$  and  $t$  are the chromaticity shift at 25 °C and a given temperature, respectively.

### **References**

1. H. Bode, H. Jøsssen, F. Bandte, *Angew. Chem.*, 1953 65, 304-304.
2. E. F. Schubert, *Light emitting diodes*, Cambridge University Press, 2nd edn, 2006.
3. C. C. Tsai, W. C. Cheng, J. K. Chang, L. Y. Chen, J. H. Chen, Y. C. Hsu, W. H. Cheng, *IEEE J. Disp. Technol.*, 2013, 9, 427-432.