

Supporting Information

High-performance and moisture-resistant red-emitting $\text{Cs}_2\text{SiF}_6:\text{Mn}^{4+}$ for high-brightness LED backlighting

Yong Liu,^a Zhi Zhou,^{*b} Lin Huang,^a Mikhail G. Brik,^{c,d,e} Shuaichen Si,^a Litian Lin,^a Tongtong Xuan,^a Hongbin Liang,^a Jianbei Qiu^{*f,g} and Jing Wang^{*a}

^a Ministry of Education Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry, Sun Yat-Sen University, Guangzhou, 510275, P. R. China

^b College of Science, Hunan Optical Agriculture Engineering Technology Research Center, Hunan Agricultural University, Hunan, 410128, P. R. China

^c College of Science, Chongqing University of Posts and Telecommunications, Chongqing, 400065, P. R. China

^d Institute of Physics, University of Tartu, W. Ostwald Str 1, Tartu, 50411, Estonia

^e Institute of Physics, Jan Długosz University, Armii Krajowej 13/15, PL-42200 Częstochowa, Poland

^f Faculty of Material Science and Engineering, Kunming University of Science and Technology, Kunming, 650093, P. R. China

^g Key Laboratory of Advanced Materials of Yunnan Province, Kunming, 650093, P. R. China

* E-mail: ceswj@mail.sysu.edu.cn (J. wang), zhoushi@hunau.edu.cn (Z. zhou), qiu@kmust.edu.cn (J. B. Qiu).

Synthesis of K_2MnF_6

The K_2MnF_6 precursor was prepared as follow: 9 g KHF_2 and 0.45 g KMnO_4 were fully dissolved in HF (40 wt%) solution. After 30 min of stirring, 0.3 ml H_2O_2 (30 wt%) was slowly added to precipitate K_2MnF_6 yellow powders. The obtained precipitate was filtered and washed with by acetone and oven-dried at 80 °C for 2.0 h.

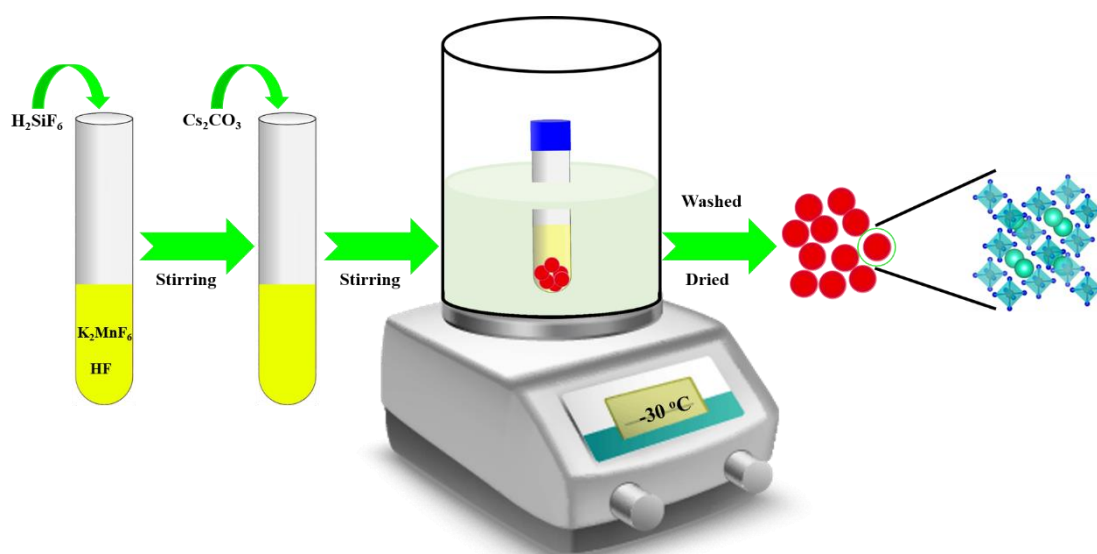


Fig. S1 Schematic diagram of the synthetic process of $\text{Cs}_2\text{SiF}_6:\text{Mn}^{4+}$ by a low-temperature co-precipitation method.

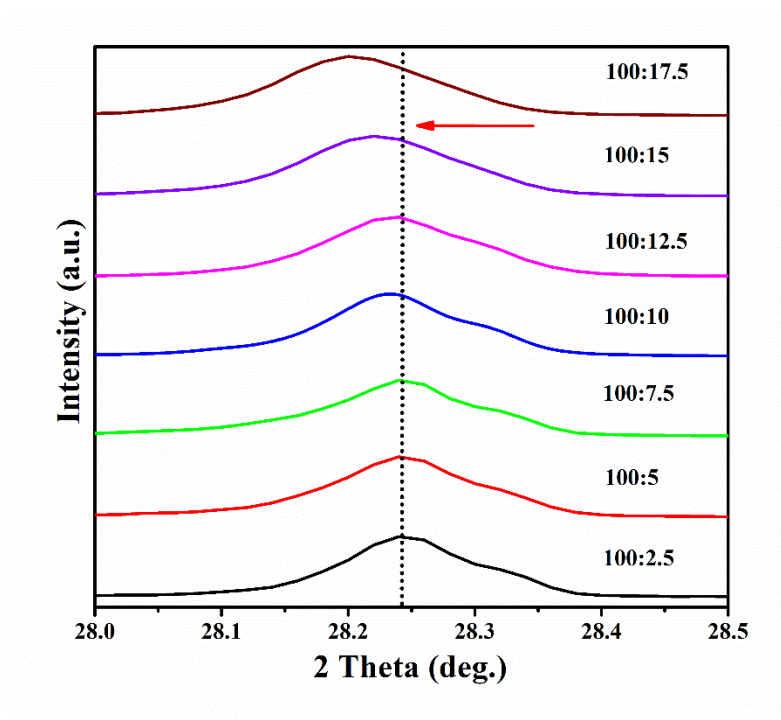


Fig. S2 Enlargements of XRD patterns of $\text{Cs}_2\text{SiF}_6\text{:Mn}^{4+}$ samples synthesized with different molar ratios of H_2SiF_6 to K_2MnF_6 over a range of $28\text{--}28.5^\circ$.

Table S1 ICP-AES results of CSFM phosphors prepared with different molar ratios of H_2SiF_6 to K_2MnF_6 . The molar ratio of Cs_2CO_3 to H_2SiF_6 is fixed at 1:1.

samples	nominal molar ratios of	actual Mn^{4+} concentration (mol%)
	H_2SiF_6 to K_2MnF_6	
a	100:2.5	2.94
b	100: 5	5.91
c	100:7.5	8.24
d	100:10	10.34
e	100:12.5	12.29
f	100:15	15.47
g	100:17.5	18.51
h	100:20	20.03

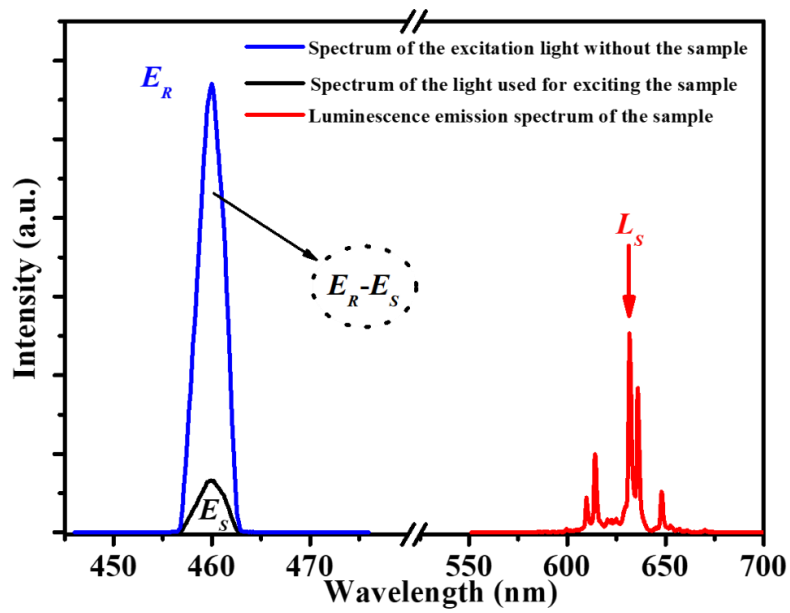


Fig. S3 Spectrum of the excitation light without the p-CSFM sample (E_R), spectrum of the light used for exciting the p-CSFM sample (E_S), luminescence emission spectrum of the p-CSFM sample (L_S).

Note: The values of absorption efficiency, internal and external quantum efficiency were calculated by the following equation:

$$IQE = \frac{I_{em}}{I_{abs}} = \frac{\int L_S}{\int E_R - \int E_S}$$

$$EQE = \frac{I_{em}}{I_{in}} = \frac{\int L_S}{\int E_R}$$

$$AE = \frac{I_{abs}}{I_{in}} = \frac{\int E_R - \int E_S}{\int E_R}$$

$$EQE = IQE \times AE$$

Where IQE , EQE and AE represent internal quantum efficiency, external quantum efficiency and absorption efficiency, respectively. I_{em} , I_{abs} and I_{in} represent the emitted photons, the absorbed photons, and the incident photons. L_S is the luminescence emission spectrum of the sample, E_R and E_S is the spectrum of the excitation light without and with the sample in the sphere.

Table S2 QE results of (a, b) original and passivated (c, d) $\text{Cs}_2\text{SiF}_6:\text{Mn}^{4+}$ with 400 μL H_2O_2 before and after under HTHH conditions for 28 days.

samples	IQE	EQE	AE (%)
a	96	85.32	88.88
b	16	14.29	89.31
c	98	85.07	86.80
d	64	56.69	88.57

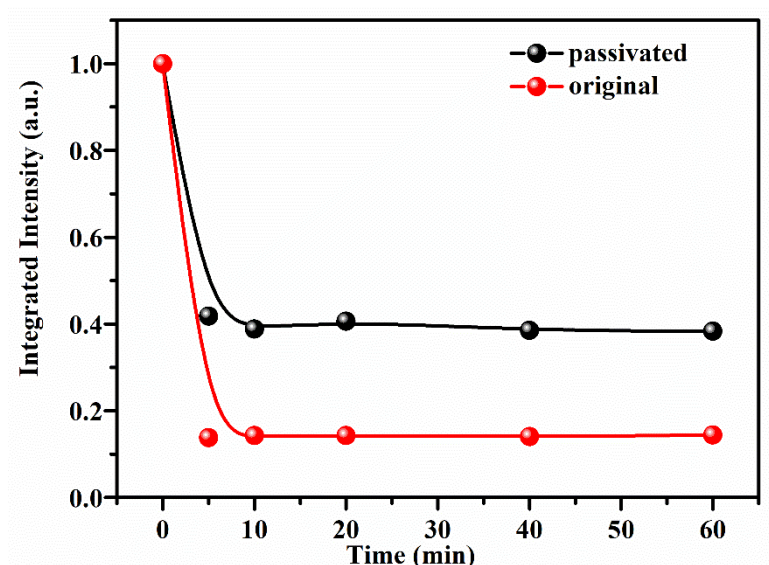


Fig. S4 The relative integrated emission intensity of original and passivated $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ phosphors as a function of time in deionized water.

We did water erosion experiments and compared the water-resistant properties of original and passivated $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ phosphors (Fig. S4). After being immersed in deionized water with a solid-to-liquid ratio of 1 g/10 mL for 5 min, the integrated emission intensity of original $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ declines significantly and retains only 13% of the initial intensity. It is comparatively seen that passivated $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ shows a more stable tendency in the water phase than original samples. After 5 min of immersion, the emission intensity of passivated $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ remains 41% of the original value. According to our previous study¹, this is mainly due to the fact that the solubility of the matrix in water (0.6 g/100 ml)² is so great that the passivation layer on the phosphor surface dissolves. This may need to be ameliorated by increasing in the thickness of the passivation layer on the phosphor.

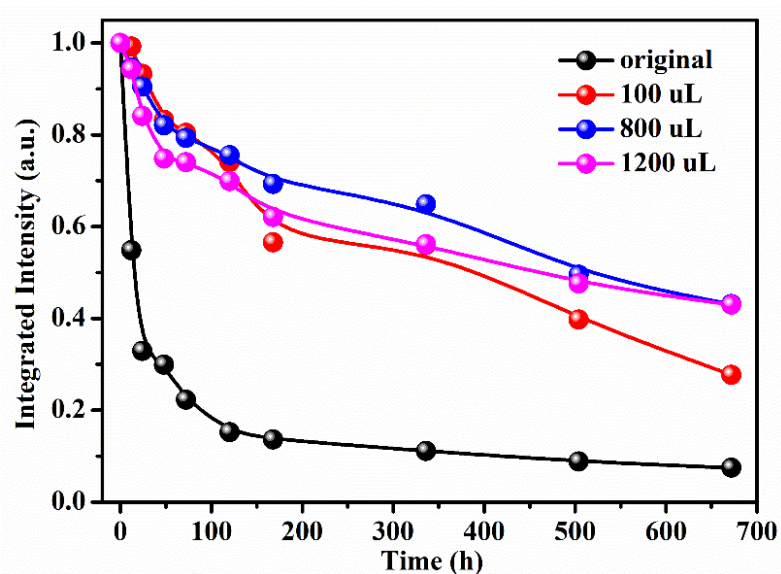


Fig. S5 The relative integrated emission intensity of original CSFM and passivated $\text{Cs}_2\text{SiF}_6: \text{Mn}^{4+}$ with different volume of H_2O_2 under HHHT at various times.

Table S3 IQY, EQY and absorption efficiency data of fluoride phosphors.

phosphors	synthesis	IQE/%	EQE/%	AE/%	Ref.
Cs ₂ SiF ₆ :Mn ⁴⁺	low temperature co-precipitation	98	85.07	86.8	this work
K ₂ TiF ₆ :Mn ⁴⁺	cation exchange	82.5	56.8	68.8	3
Rb ₂ GeF ₆ :Mn ⁴⁺	co-precipitation	72.9	57.2	78.4	4
K ₃ AlF ₆ :Mn ⁴⁺	co-precipitation	88	50.6	57.5	5
Cs ₂ SiF ₆ :Mn ⁴⁺	co-precipitation	89	71	79.7	6
K ₂ GeF ₆ :Mn ⁴⁺	crystallization	93	73	78	7
KNaSiF ₆ :Mn ⁴⁺	co-precipitation	90	41	45.5	8

References:

- (1) L. Huang, Y. Liu, J. Yu, Y. Zhu, F. Pan, T. Xuan, M. G. Brik, C. Wang and J. Wang, *ACS Appl Mater Inter*, 2018, **10**, 18082-18092.
- (2) D. R. Schink, *Radiochemistry of silicon*. National Academies, **1968**.
- (3) T. Han, T. C. Lang, J. Wang, M. J. Tu and L. L. Peng, *RSC Adv*, 2015, **5**, 100054-100059.
- (4) W. L. Wu, M. H. Fang, W. L. Zhou, T. Lesniewski, S. Mahlik, M. Grinberg, M. G. Brik, H. S. Sheu, B. M. Cheng, J. Wang and R. S. Liu, *Chemistry of Materials*, 2017, **29**, 935-939.
- (5) E. Song, J. Wang, J. Shi, T. Deng, S. Ye, M. Peng, J. Wang, L. Wondraczek and Q. Zhang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 8805-8812.
- (6) E. Song, Y. Zhou, X.-B. Yang, Z. Liao, W. Zhao, T. Deng, L. Wang, Y. Ma, S. Ye and Q. Zhang, *ACS Photonics*, 2017, **4**, 2556-2565.
- (7) W. Zhou, M.-H. Fang, S. Lian and R.-S. Liu, *ACS Appl Mater Inter*, 2018, **10**, 17508-17511.
- (8) Y. Jin, M. H. Fang, M. Grinberg, S. Mahlik, T. Lesniewski, M. G. Brik, G. Y. Luo, J. G. Lin and R. S. Liu, *ACS Appl Mater Interfaces*, 2016, **8**, 11194-11203.