Supporting Information

Novel Mn^{4+}-activated Fluoride Red Phosphor $Cs_{30}(Nb_2O_2F_9)_9(OH)_3·H_2O:Mn^{4+}$ With Good Waterproof Stability for WLEDs

Yingyuan Chen,[a] Feilong Liu,[a] Ziwang Zhang,[a] Junyu Hong,[a] Maxim S. Molokeev,[bcd] Ivan A. Bobrikov,[e] Jianxin Shi,[a] Jianbang Zhou*[af] and Mingmei Wu*[a]

a. *MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry/School of Marine Sciences, Sun Yat-Sen University, Guangzhou 510275/Zhuhai 519082, P. R. China. Email: ceswmm@mail.sysu.edu.cn*

b. *Laboratory of Crystal Physics, Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk 660036, Russia*

c. *Siberian Federal University, Krasnoyarsk 660041, Russia*

d. *Department of Physics, Far Eastern State Transport University, Khabarovsk 680021, Russia*

e. *Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna 141980, Russia*

f. *Institute of Resources Utilization and Rare Earth Development, Guangdong Academy of Sciences, Guangzhou 510650, PR China. Email: zhoujb4079@foxmail.com*

* Email: ceswmm@mail.sysu.edu.cn (M. M. Wu), zhoujb4079@foxmail.com (J. B. Zhou)

Table S1 Main parameters of processing and refinement of the samples

Chemical formula	$Cs_{30}(Nb_2O_2F_9)_9 \cdot 4(H_2O,OH,O)$			
Sp.Gr.	*P*-3*m*1			
Cell parameters (Å, º)	*a* = 21.3475 (6) *c* = 8.5095 (3)			
Volume (Å^3), *Z*	*V* = 3358.4 (2), 1			
Data	X-ray	T.O.F.1	T.O.F.2	T.O.F.3
2θ-interval (°)	6.5-140	–	–	–
T.O.F. interval (μs)	–	6041-46297	17792-80000	7408-40000
d-interval (Å)	0.820-13.587	1.473-11.291	1.229-5.519	0.714-3.857
No. of reflections	108	428	707	3431
R_{wp} (%)	2.44	3.78	2.09	0.72
R_p (%)	2.42	2.650	2.46	0.65
R_B (%)	3.84	3.25	0.61	2.61

Table S2 Fractional atomic coordinates and isotropic displacement parameters (Å^2)

	x	*y*	*z*	B_{iso}	Occ.
Cs1	0.1919 (2)	0.09595 (12)	0.2713 (8)	0.7 (2)	1
Cs2	0.3357 (3)	0	0	0.8 (3)	1
Cs3	0.3307 (3)	0	0.5	0.8 (3)	1
Cs4	0.5084 (2)	0.25422 (11)	0.7550 (6)	0.6 (2)	1
Cs5	0.57850 (14)	0.42150 (14)	0.2799 (7)	0.7 (2)	1
Nb1	0.4041 (2)	0.20203 (12)	0.2952 (6)	1.1 (3)	1
O1	0.4731 (5)	0.2365 (2)	0.1627 (12)	0.85 (18)	1
F1	0.3312 (4)	0.1656 (2)	0.5052 (11)	0.85 (18)	1
F2	0.4556 (6)	0.2897 (4)	0.4271 (9)	0.85 (18)	1
F3	0.3441 (5)	0.1055 (4)	0.2304 (12)	0.85 (18)	1
Nb2	0.2789 (3)	0.13947 (12)	0.7340 (6)	1.2 (3)	1
O2	0.2567 (4)	0.1283 (2)	0.9106 (7)	0.85 (18)	1
F4	0.3534 (2)	0.1153 (3)	0.7664 (8)	0.85 (18)	1
F5	0.2223 (4)	0.0555 (4)	0.6495 (7)	0.85 (18)	1
Nb3	0.53592 (13)	0.0719 (3)	0.8048 (6)	1.0 (2)	1
O3	0.5620 (2)	0.1240 (4)	0.6658 (8)	0.85 (18)	1
F6	0.5	0	1	0.85 (18)	1
F7	0.4979 (3)	0.1158 (3)	0.9303 (7)	0.85 (18)	1
F8	0.4412 (3)	0.0062 (4)	0.7422 (8)	0.85 (18)	1
O1W	1/3	2/3	0.707 (3)	0.85 (18)	1
O2W	0	0	0.5	0.85 (18)	1
O3W	0	0	0	0.85 (18)	1

Table S3 Main bond lengths (Å)

	Bond lengths (Å)		Bond lengths (Å)
Cs1—F1	3.256 (9)	Cs5—F7^{viii}	3.327 (8)
Cs1—F3	3.172 (8)	Cs5—F8^{ix}	3.299 (7)
Cs1—O2^{i}	3.294 (9)	Cs5—O1W^{x}	3.262 (3)
Cs1—F5^{ii}	3.076 (7)	Nb1—O1	1.703 (9)
Cs2—F3^{iii}	2.922 (9)	Nb1—F1	2.237 (9)
Cs2—F4^{ii}	3.037 (6)	Nb1—F2	1.978 (9)
Cs2—F7^{ii}	3.145 (6)	Nb1—F2^{v}	1.978 (9)
Cs2—F8^{ii}	3.099 (7)	Nb1—F3	1.885 (8)
Cs3—F2^{iv}	3.254 (9)	Nb1—F3^{v}	1.885 (8)
Cs3—F3^{ii}	3.125 (9)	Nb2—O2	1.558 (8)
Cs3—F4^{ii}	3.199 (6)	Nb2—F4	1.920 (6)
Cs3—F5^{ii}	3.333 (7)	Nb2—F5	1.740 (7)
Cs3—F8^{ii}	3.086 (7)	Nb3—O3^{xi}	1.525 (8)
Cs4—F2	3.238 (9)	Nb3—F6^{xii}	2.127 (5)
Cs4—F4	3.154 (5)	Nb3—F7^{xi}	1.855 (6)
Cs4—F7	3.217 (6)	Nb3—F7	1.855 (6)
Cs4—F7^{v}	3.217 (6)	Nb3—F8^{xi}	1.871 (7)
Cs5—F2^{vi}	2.998 (9)	Nb3—F8	1.871 (7)
Cs5—O3^{vii}	3.340 (9)		

Symmetry codes for $Cs_{30}(Nb_2O_2F_9)_9\cdot 4H_2O$: (i) *x*, *y*, *z*-1; (ii) *x*-*y*, -*y*, -*z*+1; (iii) *x*-*y*, -*y*, -*z*; (iv) *y*, -*x*+*y*, -*z*+1; (v) *x*, *x*-*y*, *z*; (vi) -*y*+1, -*x*+1, *z*; (vii) -*x*+*y*+1, -*x*+1, *z*; (viii) -*x*+*y*+1, -*x*+1, *z*-1; (ix) -*x*+1, -*x*+*y*+1, -*z*+1; (x) -*x*+1, -*x*+*y*, -*z*+1; (xi) -*x*+*y*+1, *y*, *z*; (xii) -*x*+1, -*y*, -*z*+2.

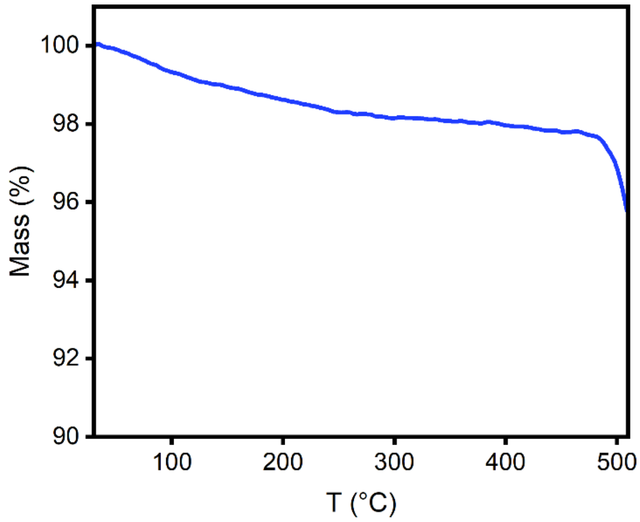

Fig. S1 TGA of CNOF sample.

There is a continuing and slow weight loss slop with the temperature increasing up to 470 °C, indicating the presence of water molecules and OH^-.

0% 2.85% 4.16% 6.66% 9.68% 11.4%

Fig. S2 Photos of CNOFM with different Mn^{4+} contents under daylight.

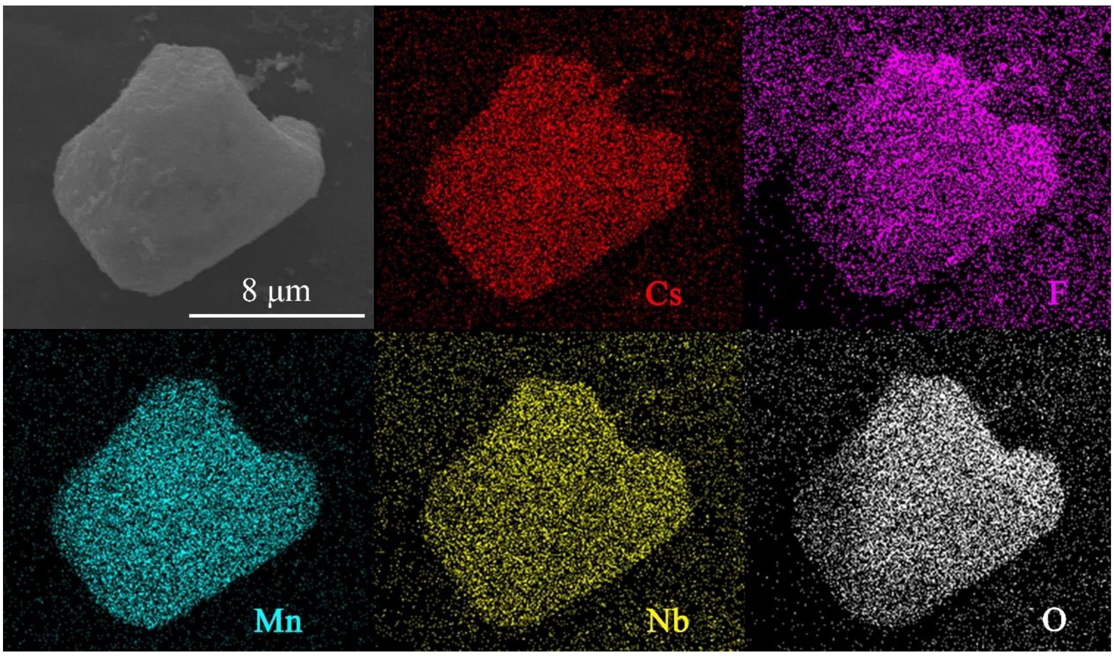

Fig. S3 SEM image and elemental mapping of the CNOF:Mn^{4+}.

Table S4 Actual Mn^{4+} content, lifetime, internal PL quantum yields (IQE), adsorption efficiency (AE) and external PL quantum yields (EQE) of CNOFM phosphors.

Nominal content of [Mn] (at.%)	3	5	7	9	11
Actual [Mn] (at.%)	2.85	4.16	6.66	9.68	11.4
IQE (%)	21.0	24.2	29.6	23.6	22.2
AE (%)	23.5	28.5	33.7	39.2	40.2
EQE (%)	4.93	6.90	10.0	9.25	8.92
Lifetime (ms)	1.30	1.38	1.37	1.36	1.40

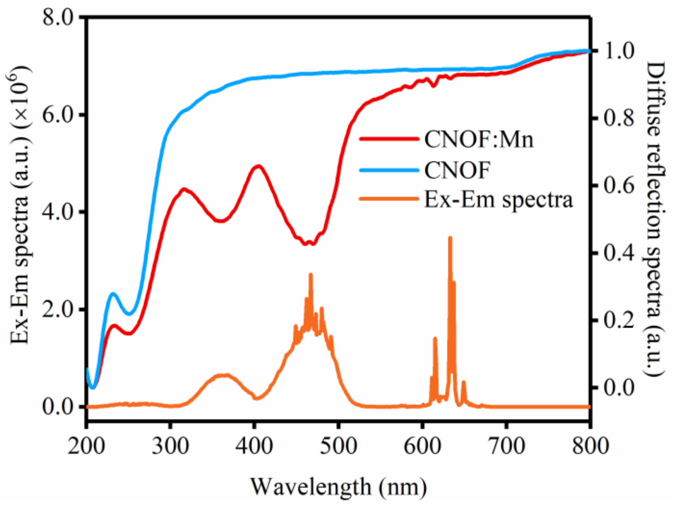

Fig. S4 Diffuse reflection spectra of CNOF and CNOFM, and the excitation (Ex)-emission (Em) spectra of CNOFM.

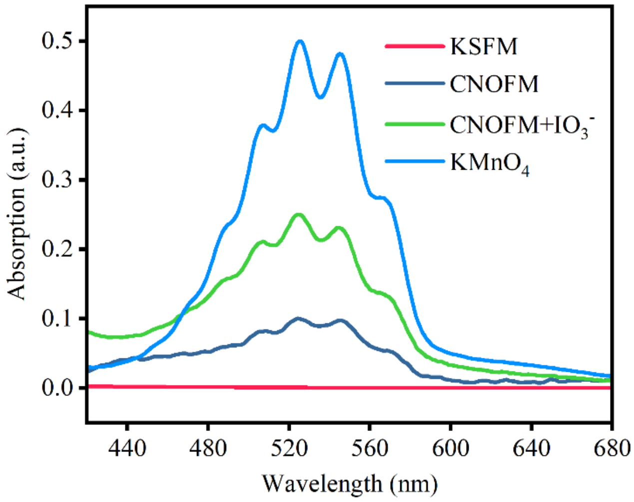

Fig. S5 Absorption spectra for the leachate of the immersed CNOFM and KSFM phosphors, as well as the $KMnO_4$ and another leachate of the immersed CNOFM treated with periodic acid.

The CNOFM phosphor evidently exhibits better waterproof properties, and this phenomenon is similar to $Cs_2NbOF_5:Mn^{4+}$ phosphor reported by J. Zhou and et cetera, which is another Mn^{4+}-activated phosphors centered at Nb(V).[1] J. Zhou propounded a kind of disproportionation reaction mechanism as follow for better understanding of the enhanced waterproof property of the Nb(V) centered fluoride phosphors.

$$5Mn^{4+} + 8H_2O \xrightarrow{Nb^{5+}} 2MnO_4^- + 3Mn^{2+} + 16H^+$$

The slightly solute Nb(V) catalyzed the disproportionation reaction of the dissolved Mn^{4+} ions and instantly generated the soluble Mn^{2+} and MnO_4^- ions (Fig.S4) rather than the dark Mn-oxides. Then a shell without Mn^{4+} can be formed on the surface of CNFOM and the hydrolysis of $[MnF_6]^{2-}$ groups will be prevented, and therefore, properly enhanced the water-resistant ability of the phosphors.[1]

Reference

1 J. Zhou, Y. Chen, C. Jiang, B. Milićević, M. S. Molokeev, M. G. Brik, I. A. Bobrikov, J. Yan, J. Li and M. Wu, *Chem. Eng. J.*, 2021, **405**, 126678.