Supplementary materials

Enhancement of water resistance thermal and stability of $Na_3HTiF_8:Mn^{4+}$ by co-doping with organic amine cation

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2 2 Experimental and methodology section

2.1 Reagent and apparatus

All chemicals were reagent-grade pure and purchased from the Sinopharm Chemical Reagent Co. Ltd., China. XRD was performed at a scanning rate of 5°/min from10° to 80° for 2θ at room temperature by using a Rigaku D/max2500 V diffractometer. It was equipped with a graphite monochromator by utilizing monochromatic CuKα radiation (λ = 0.154178 nm). The morphologies of the samples were examined by Hitachi S-3400 scanning electron microscopy (SEM) with an attached energy-dispersive X-ray spectrometer (EDS). The structure of the phosphor interior was measured by transmission electron microscope (TEM). Samples were mounted on an aluminum slice coated with Au. The photoluminescence excitation (PLE) and

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emission (PL) spectra were recorded at room temperature by a Shimadzu RF-53001 spectrophotometer equipped with a xenon lamp as the excitation source. The luminescence decay curve and the photoluminescence quantum yields were obtained from an Edinburgh FLS980 fluorescence spectrophotometer. The performance of WLEDs was measured using an auto temperatured LED opto-electronic analyzer (ATA-1000, Everfine). The results of the equations presented in the paper were obtained by using the programs compiled with VBA (Visual Basic for Applications) by ourselves.

2.2 Synthesis of samples

2.2.1 K_2MnF_6

4.5 g $KMnO_4$ and 45.0 g KHF_2 were dissolved in 150 ml HF (40%) solution, stirring for 30 min. Dropping 30% H_2O_2 into the above solution slowly, after filtering by ethanol and drying at 70 °C for 2 hours, the yellow powder of K_2MnF_6 was obtained

2.2.2 Na_2TiF_6:xMn^{4+}(NTFM, x = 0.02-0.10)

To synthesize the Na_2TiF_6 matrix, Na_2CO_3 was dripped into H_2TiF_6 and dried at 70 °C. Solution A was obtained by adding 1.2mmol K_2MnF_6 to 15 mL HF. After stirring for 15 minutes, 20 mmol Na_2TiF_6 was added to A and stirred for 30 minutes to obtain NTFM. Samples of Na_2TiF_6:xMn^{4+} (x = 0.02-0.10) were prepared by using the same processes.

2.2.3 Na_3HTiF_8:$y(C_2H_5OH)_3NH^+$ (NTF:$yTEOAH^+$, y = 0.01-0.30)

Firstly, 0.2-2 mmol $(C_2H_5OH)_3N$ was slowly added into 20 mmol H_2TiF_6 solutions with stirring, and then Na_2CO_3 was put into the mixture until the pH of the solution

reaches 7. Then, the precipitates were collected, suction filtered, and dried at 70 °C for 5 hours, and the powder of NHTF:yTEOAH$^+$ (y = 0.01-0.30) were obtained.

2.2.4 Na_3HTiF_8:0.06Mn^{4+},$yC_2H_5OH)_3NH^+$ (NHTFM:yTEAOH$^+$)

1.2 mmol (0.2966 g) K_2MnF_6 were dissolved in 15 ml HF (40%) to obtain yellow solution, 18.8 mmol NHTF:yTEOAH$^+$ (x = Mn/(Mn+Ti) = 0.06) were put into the solution and stirring for 30 minutes respectively. Then, the depositions were filtered, washed with acetone several times, and dried at 70 °C for 3 hours to obtain samples of NHTFM:yTEOAH$^+$ (y = 0.01-0.30).

3 The negative thermal quenching

The value of *Dq/B* can be described with Eqs. (S1−S4) [39-41].

$$Dq = \frac{E(^4A_{2g} - {}^4T_{2g})}{10} \tag{1}$$

$$x = \frac{E(^4A_2 - {}^4T_1) - E(^4A_2 - {}^4T_2)}{Dq} \tag{2}$$

$$\frac{Dq}{B} = \frac{15(x-8)}{x^2 - 10x} \tag{3}$$

$$B = \frac{(x^2 - 10x) * Dq}{15(x\ -18)} \tag{4}$$

Where B is Racah parameters, and Dq is crystal-field splitting parameter. E is the energy of different energy levels.

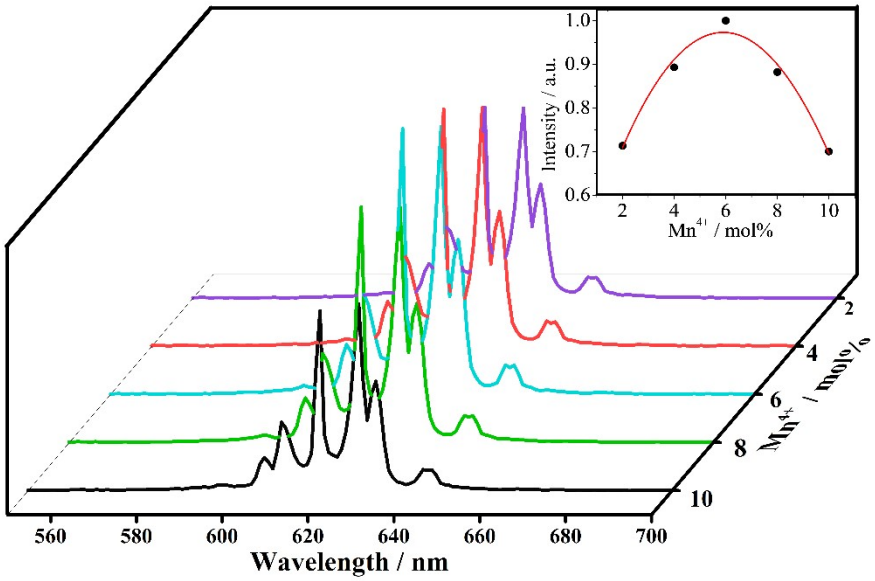

Fig. S1 PL spectra of NTF:xMn^{4+} (x = 0.02-0.1).

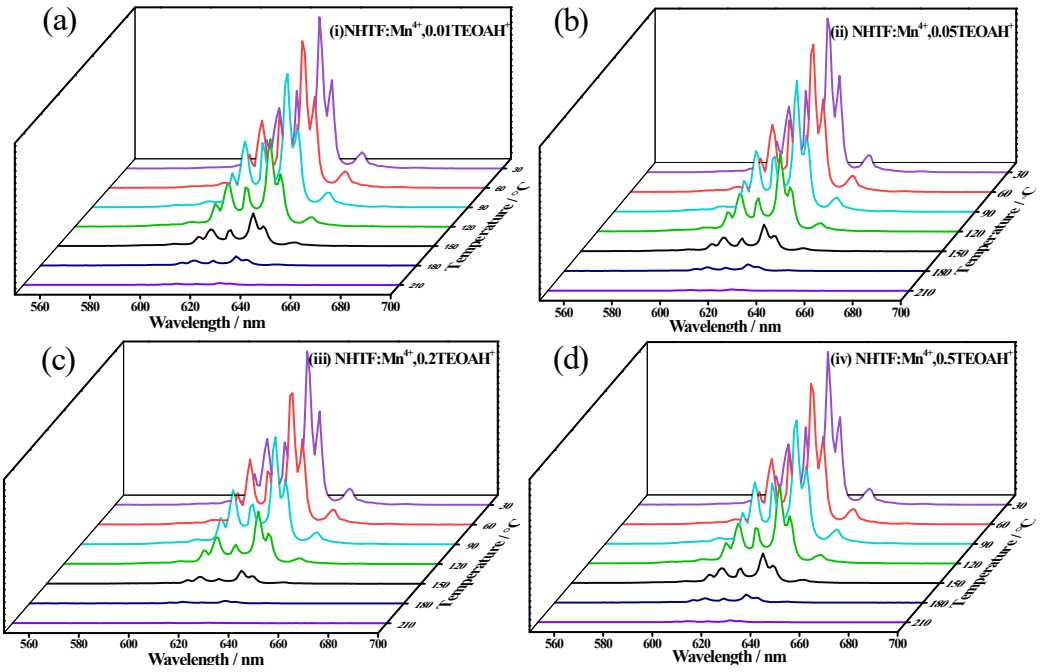

Fig. S2 PL spectra of samples: (a) NHTFM:0.01TEOAH$^+$, (b) NHTFM:0.05TEOAH$^+$, (c) NHTFM:0.20TEOAH$^+$, (d) NHTFM:0.30TEOAH$^+$.

Table S1. XRD refined lattice parameters of the samples

No.	a / Å	b / Å	c / Å	α = β = γ/ °	V / Å³
(i)	7.1874	13.850	6.5479	90	651.55
(ii)	7.1676	13.854	6.5456	90	649.99
(iii)	7.1282	13.730	6.5054	90	636.67
(iv)	7.2051	13.872	6.5512	90	654.76
(v)	7.2146	13.871	6.5524	90	655.72
Na_3HTiF_8(PDF)	7.1820	13.860	6.5380	90	650.80

(i-v) NHTFM:y$TEOAH^+$ (y_{i-v} = 0.01, 0.05, 0.15, 0.20, 0.30)

Table S2. Rietveld refinement of X-ray powder diffraction data of NTFM.

	x/a	y/b	z/c	Mult	U_{ISO}
F2	0.23741(28)	0.76259(28)	0.7698(9)	6	0.025
F1	0.10254(28)	0.89746(28)	0.2017(7)	6	0.0388(16)
F3	0.4238(5)	0.5762(5)	0.2240(12)	6	0.0939(16)
Ti1	0.0	0.0	0.0	1	0.0304
Ti2	0.3333	0.6667	0.5445(8)	2	0.02874
Na1	0.3570(4)	0.0	0.0	6	0.0751(18)

Table S3. Rietveld refinement of X-ray powder diffraction data of NHTFM:0.01$TEOAH^+$.

Atom	x/a	y/b	z/c	Mult	U_{ISO}
F2	0.1848(6)	0.23598(29)	0.25	8	0.0393(9)
F1	0.18035	0.05397	0.25	8	0.0393(9)
F3	0.0	0.15173(32)	-0.0413(7)	8	0.0327
Na1	0.0	0.67772(35)	0.25	4	0.0291(8)
Na2	0.2452(5)	0.39702(24)	0.25	8	0.0291(8)
Ti1	0.0	0.14447(18)	0.25	4	0.02398
F4	0.0	0.41807(30)	0.0307(6)	8	0.0393(9)
H	0.0	0.5	0	4	0.15452