Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Stable narrowband red phosphor $K_3GaF_6:Mn^{4+}$ derived from hydrous $K_2GaF_5(H_2O)$ and K_2MnF_6

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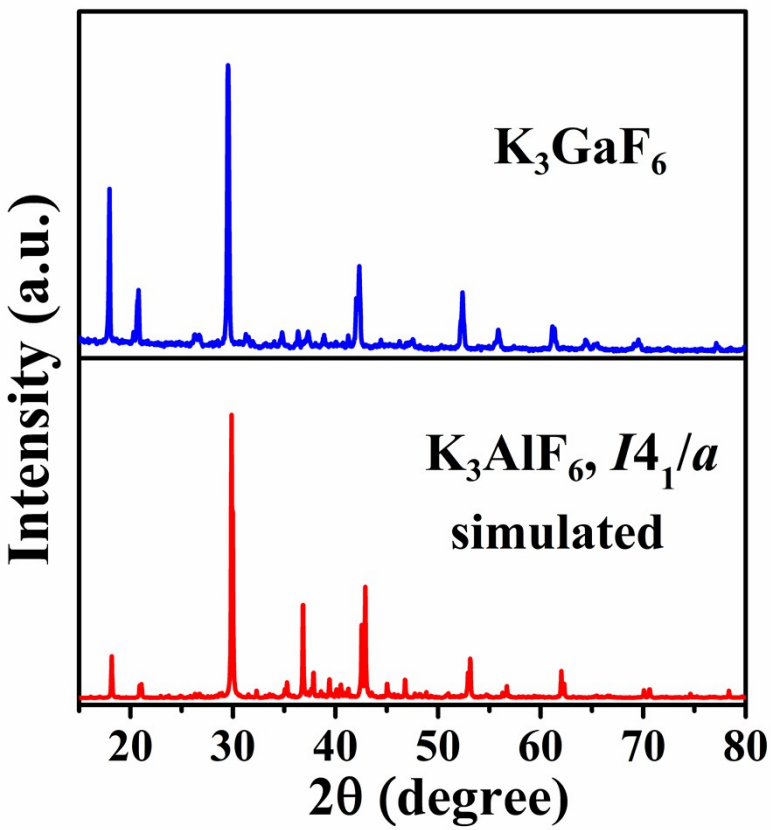

Fig. S1 XRD patterns of K_3AlF_6 and K_3GaF_6 in $I4_1/a$ space group.

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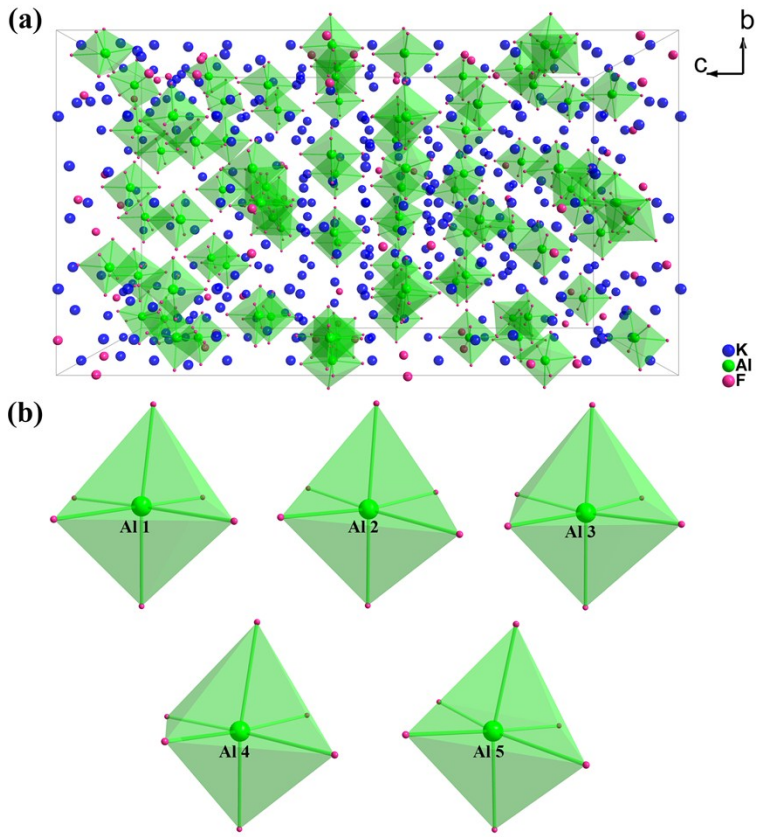

Fig. S2 Crystal structure of K_3AlF_6 in $I4_1/a$ space group: (a) the unit cell and (b) five types of distorted $[AlF_6]^{3-}$ octahedrons.

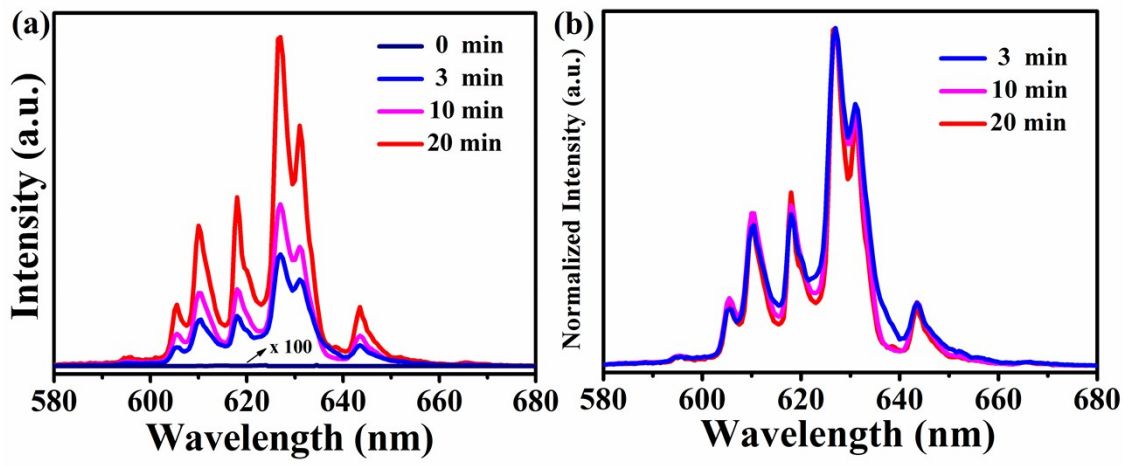

Fig. S3 The emission spectrum (a) and normalized emission spectrum (b) of time-dependent products from reaction of $K_3GaF_6:Mn^{4+}$: 0, 3, 10, and 20 min, respectively.

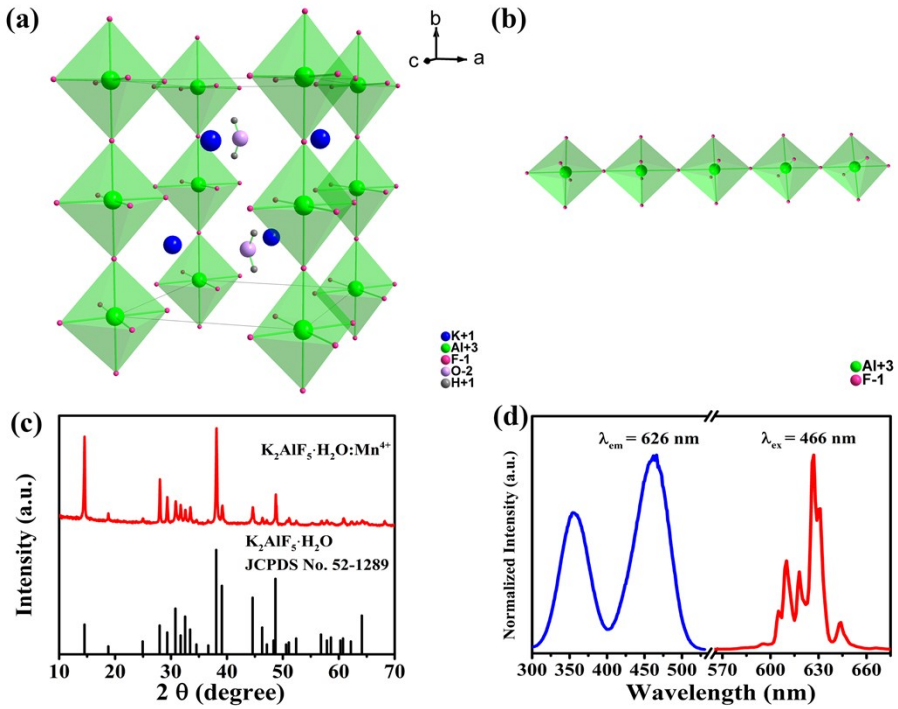

Fig. S4 The crystal structure of $K_2AlF_5·H_2O$ in $P2_1/m$ space group: the unit cell (a) and Al-F chain composed of corner-sharing [AlF_6] octahedrons (b). XRD pattern (c) and excitation, emission spectrum (d) of $K_2AlF_5·H_2O:Mn^{4+}$.

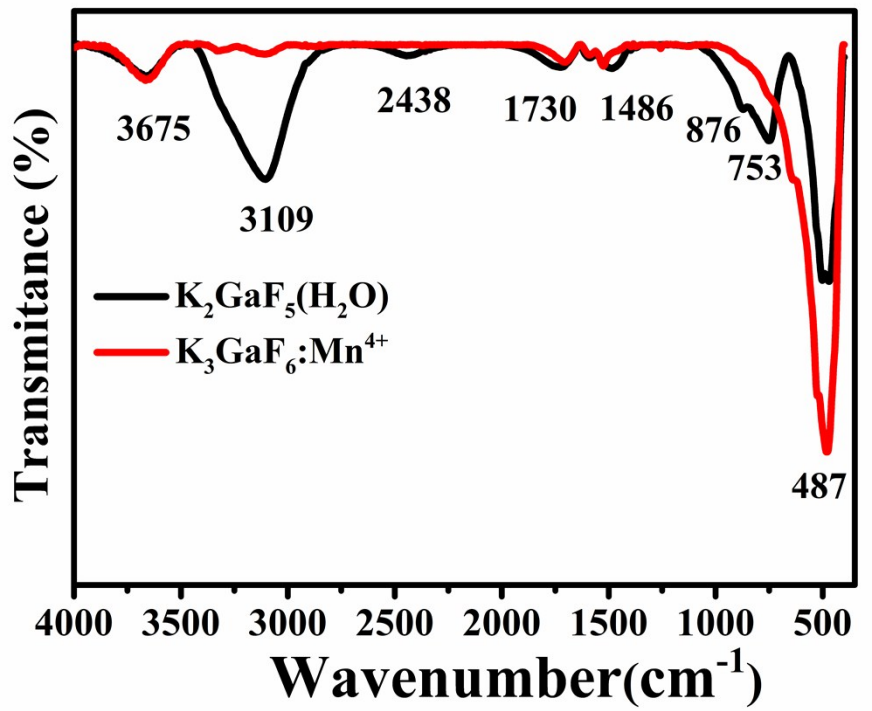

Fig. S5 IR spectra of $K_2GaF_5(H_2O)$ and $K_3GaF_6:Mn^{4+}$.

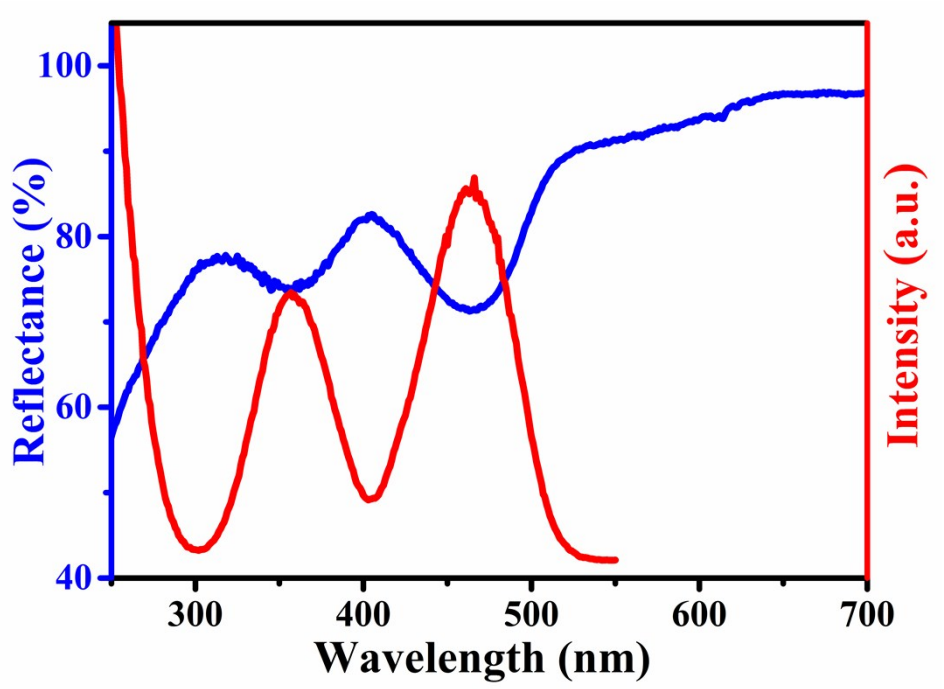

Fig. S6 The excitation spectra and diffuse reflection spectrum of $K_3GaF_6:Mn^{4+}$.

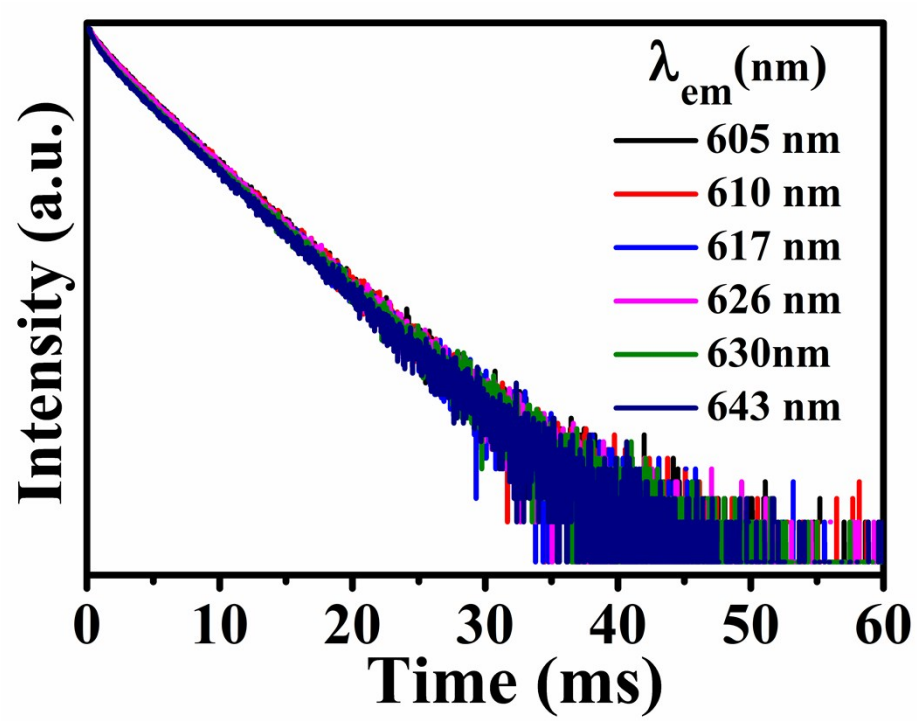

Fig. S7 Luminescence decay curves of different emission peaks in $K_3GaF_6:Mn^{4+}$ (2.27 at%) upon 467 nm excitation.

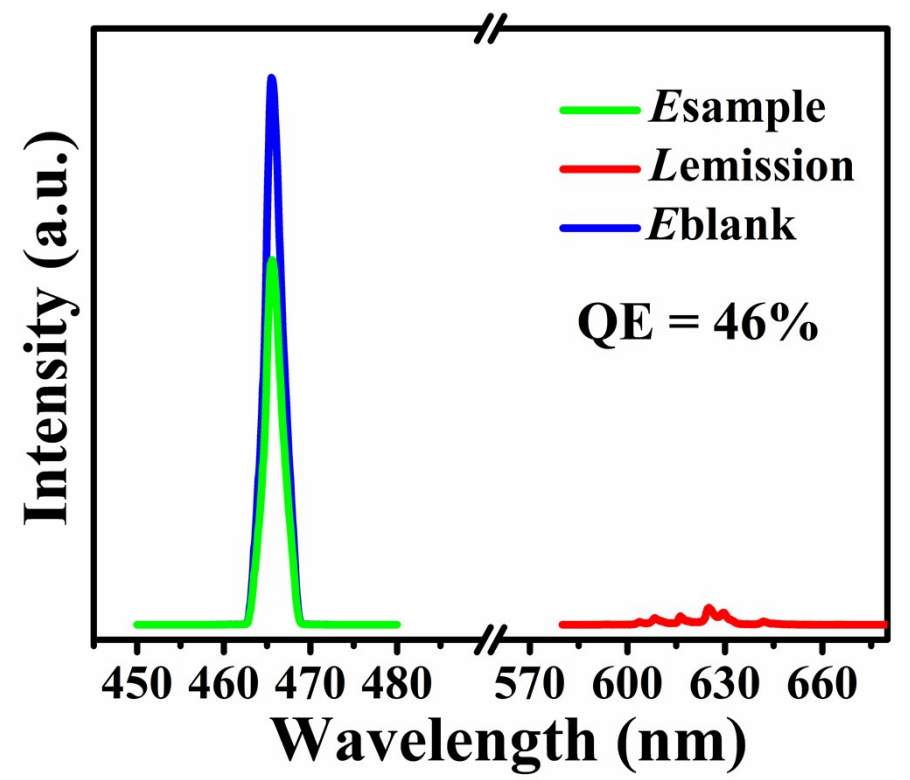

Fig. S8 Excitation line of blank ($BaSO_4$) (*E*blank) and excitation (*E*sample) and emission (*L*emission) spectra of $K_3GaF_6:Mn^{4+}$ (2.27 at%). The quantum efficiency (QE) can be calculated as follows:

$$QE = \frac{\int Lemission}{\int Eblank - \int Esample} \qquad (1)$$

where *L*emission and *E*sample are the emission and excitation spectra of objective samples; *E*blank is the spectrum of the excitation light without samples in integrating sphere. All of spectra were recorded by an optical integrating sphere coupled to the FLS920 fluorescence spectrophotometer at room temperature.

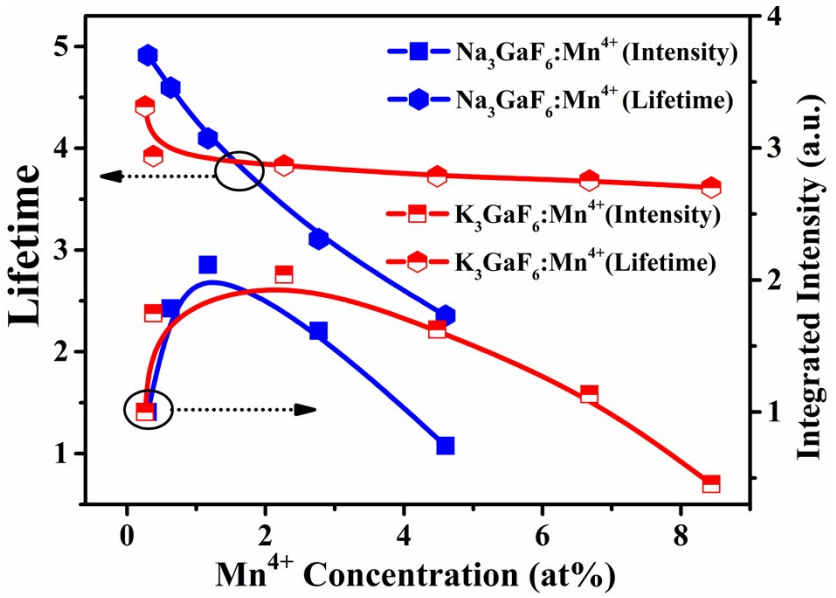

Fig. S9 Concentration dependent integrated intensities and decay lifetimes of $A_3GaF_6:Mn^{4+}$ (A = Na, K) with various Mn^{4+} contents.

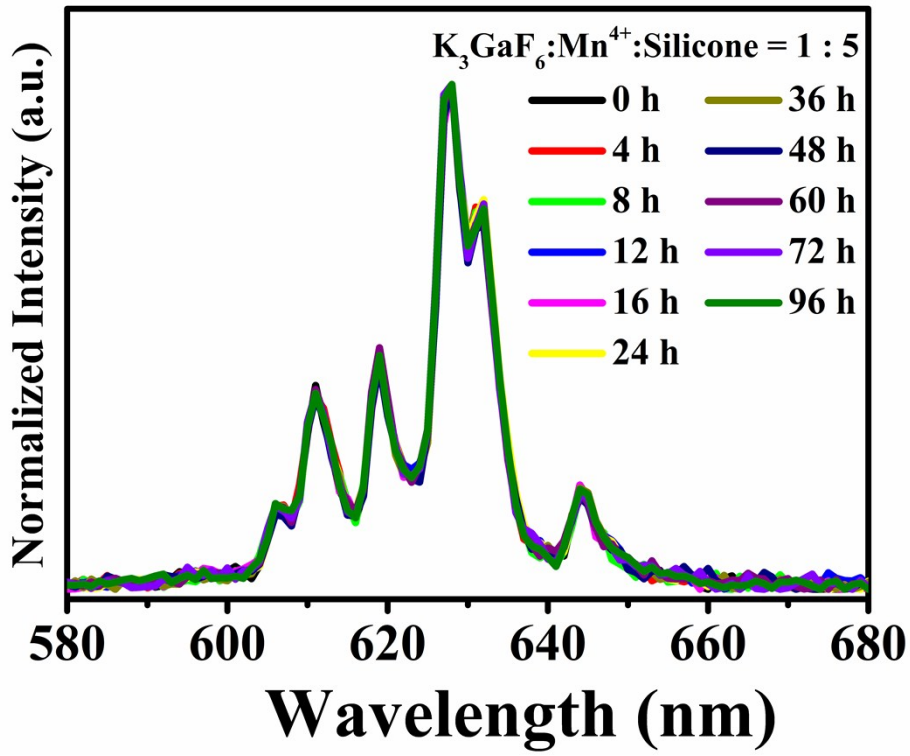

Fig. S10 (a) Time-dependent normalized luminescence spectra of $K_3GaF_6:Mn^{4+}$ (2.27 at%) loaded in the 85 % humidity and 85 °C environment.

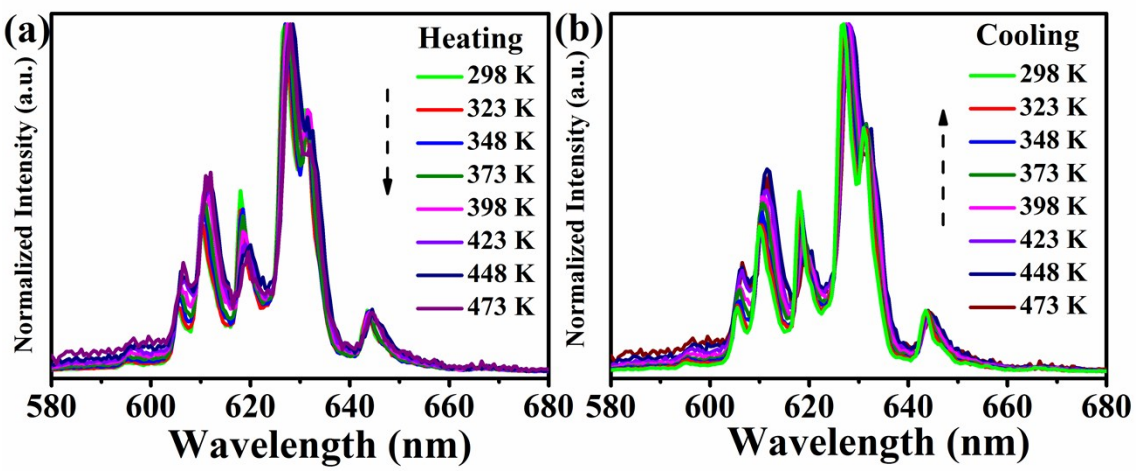

Fig. S11 Normalized temperature-dependent luminescence spectra of $K_3GaF_6:Mn^{4+}$ (2.27 at%) in the cyclic process of heating and cooling between 298 to 473 K.

Table S1 Synthesis strategies of $A_3GaF_6:Mn^{4+}$ (A = Na, K) by co-precipitation method.

Compound	Ga source	A source	Mn precursor	Molar ratio of Ga atom to A atom	Amount of HF solution (49 wt.%)/mL
$Na_3GaF_6:Mn^{4+}$	Ga_2O_3	NaF	K_2MnF_6	5:10	10
$K_3GaF_6:Mn^{4+}$	Ga_2O_3	K_2CO_3		5:16	8

Table S2 Selected bond lengths (Å) and bond valence sum (BVS) calculations for $K_2GaF_5(H_2O)$.[a]

Bond	Distance	BVS	BVS(Sum)
Ga(1)-F(1)	1.8681(19)	0.511	2.989
Ga(1)-F(1)#A	1.8681(19)	0.511	
Ga(1)-F(2)	1.8897(18)	0.482	
Ga(1)-F(2)#A	1.8897(18)	0.482	
Ga(1)-F(3)	1.876(3)	0.501	
Ga(1)-O(1)	1.986(4)	0.501	
K(1)-F(1)	2.696(2)	0.123	1.262
K(1)-F(1)#B	2.687(2)	0.152	
K(1)-F(1)#C	2.792(2)	0.114	
K(1)-F(2)#D	2.674(2)	0.157	
K(1)-F(2)	3.400(2)	0.058	
K(1)-F(2)#E	2.788(2)	0.116	
K(1)-F(3)	2.7805(11)	0.111	
K(1)-F(3)#A	2.7805(11)	0.111	
K(1)-F(3)#F	2.8040(12)	0.111	
K(1)-F(3) #D	2.8040(12)	0.111	
K(1)-O(1)#E	3.2454(13)	0.049	
K(1)-O(1)#C	3.2454(13)	0.049	
O(1)-Ga(1)	1.986(4)	0.501	0.598
O(1)-K(1) #C	3.2454(13)	0.049	
O(1)-K(1) #E	3.2454(13)	0.049	

[a]Symmetry codes for $K_2GaF_5(H_2O)$: (A) -x,y,-z+1/2; (B) -x+1/2,-y+1/2,-z; (C) -x+1/2,y-1/2,-z+1/2; (D) -x,-y+1,-z; (E) x-1/2,y-1/2,z; (F) x,-y+1,z+1/2.

Table S3 ICP results of $K_3GaF_6:Mn^{4+}$ phosphors prepared with different mole ratios of Ga_2O_3 to K_2MnF_6.

Samples	Experimental molar ratio of Ga_2O_3 to K_2MnF_6	Actual doping concentration of Mn^{4+} (mol%)
G1	100:0.5	100:0.26
G2	100:1	100:0.38
G3	100:3	100:2.27
G4	100:5	100:4.48
G5	100:7	100:6.68
G6	100:10	100:8.44

Table S4 Photoelectric parameters of the three fabricated warm WLEDs.

Device	Chromaticity coordinate (x, y)	CCT(K)	Ra	R9	Efficacy (lm/W)
LED 1	(0.3822, 0.3902)	4048	83.9	34.7	102.7
LED 2	(0.3979, 0.3939)	3691	87.2	50.2	92.1
LED 3	(0.4476, 0.4253)	2994	88.4	55.0	71.0

Table S5 Photoelectric parameters of warm WLEDs denoted as LED I and LED II by using $Na_3GaF_6:Mn^{4+}$ and $K_3GaF_6:Mn^{4+}$ as red light component, respectively.

No.	CIE coordinates	CCT (K)	Ra	R9	Efficacy (lmW^{-1})
LED I	(0.4434 0.4131)	2966	81	31	56.73
LED II	(0.4476, 0.4253)	2994	88.4	55.0	71.0