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Supporting Information

Moisture-resistant and highly efficient narrow-band red-emitting fluoride phosphor $K_2NaGaF_6:Mn^{4+}$ for warm white LED application

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Table S1 Selected bond lengths (Å) for K_2NaGaF_6.[a]

Atoms	Distances	Atoms	Distances
Ga(1)-F(1)#1	1.885(3)	K(1)-F(1)#17	2.90755(19)
Ga(1)-F(1)#2	1.885(3)	K(1)-F(1)#8	2.90755(19)
Ga(1)-F(1)	1.885(3)	K(1)-F(1)#9	2.90755(19)
Ga(1)-F(1)#3	1.885(3)	K(1)-Na(1)#13	3.55508(13)
Ga(1)-F(1)#4	1.885(3)	Na(1)-F(1)#18	2.220(3)
Ga(1)-F(1)#5	1.885(3)	Na(1)-F(1)#17	2.220(3)
Ga(1)-K(1)#5	3.55508(13)	Na(1)-F(1)	2.220(3)
Ga(1)-K(1)#6	3.55508(13)	Na(1)-F(1)#15	2.220(3)
Ga(1)-K(1)#7	3.55508(13)	Na(1)-F(1)#19	2.220(3)
Ga(1)-K(1)#8	3.55508(13)	Na(1)-F(1)#20	2.220(3)
Ga(1)-K(1)#9	3.55508(13)	Na(1)-K(1)#21	3.55508(13)
Ga(1)-K(1)#10	3.55508(13)	Na(1)-K(1)#22	3.55508(13)
K(1)-F(1)#1	2.90755(19)	Na(1)-K(1)#23	3.55508(13)
K(1)-F(1)#4	2.90755(19)	Na(1)-K(1)#8	3.55508(13)
K(1)-F(1)#11	2.90755(18)	Na(1)-K(1)#20	3.55508(13)
K(1)-F(1)#12	2.90755(19)	Na(1)-K(1)#24	3.55508(13)
K(1)-F(1)#13	2.90755(19)	F(1)-K(1)#21	2.90755(18)
K(1)-F(1)#14	2.90755(18)	F(1)-K(1)#9	2.90755(18)
K(1)-F(1)#15	2.90755(18)	F(1)-K(1)#8	2.90755(18)
K(1)-F(1)#16	2.90755(19)		

[a] Symmetry transformations used to generate equivalent atoms: (#1) *y*-1/2, *z*, *x*+1/2; (#2) -*y*+1/2, -*z*+1, -*x*+1/2; (#3) -*z*+1/2, -*x*+1/2, -*y*+1; (#4) *z*-1/2, *x*+1/2, *y*; (#5) -*x*, -*y*+1, -*z*+1; (#6) *x*, *y*-1/2, *z*-1/2 (#7) -*x*+1/2, -*y*+1, -*z*+3/2; (#8) -*x*+1/2, -*y*+3/2, -*z*+1; (#9) -*x*, -*y*+3/2, -*z*+3/2 (#10) *x*-1/2, *y*-1/2, *z*; (#11) *y*-1/2, *z*+1/2, *x*+1; (#12) *z*, *x*+1, *y*; (#13) *x*+1/2, *y*, *z*+1/2; (#14) -*y*+1, -*z*+1, -*x*+1; (#15) -*z*+1/2, -*x*+1, -*y*+3/2; (#16) -*z*+1, -*x*+1/2, -*y*+3/2; (#17) -*y*+1, -*z*+3/2, -*x*+1/2; (#18) *y*-1, *z*+1/2, *x*+1/2; (#19) *z*-1/2, *x*+1, *y*-1/2; (#20) -*x*, -*y*+2, -*z*+1; (#21) *x*-1/2, *y*, *z*-1/2; (#22) -*x*+1/2, -*y*+2, -*z*+3/2; (#23) *x*, *y*+1/2, *z*-1/2; (#24) *x*-1/2, *y*+1/2, *z*.

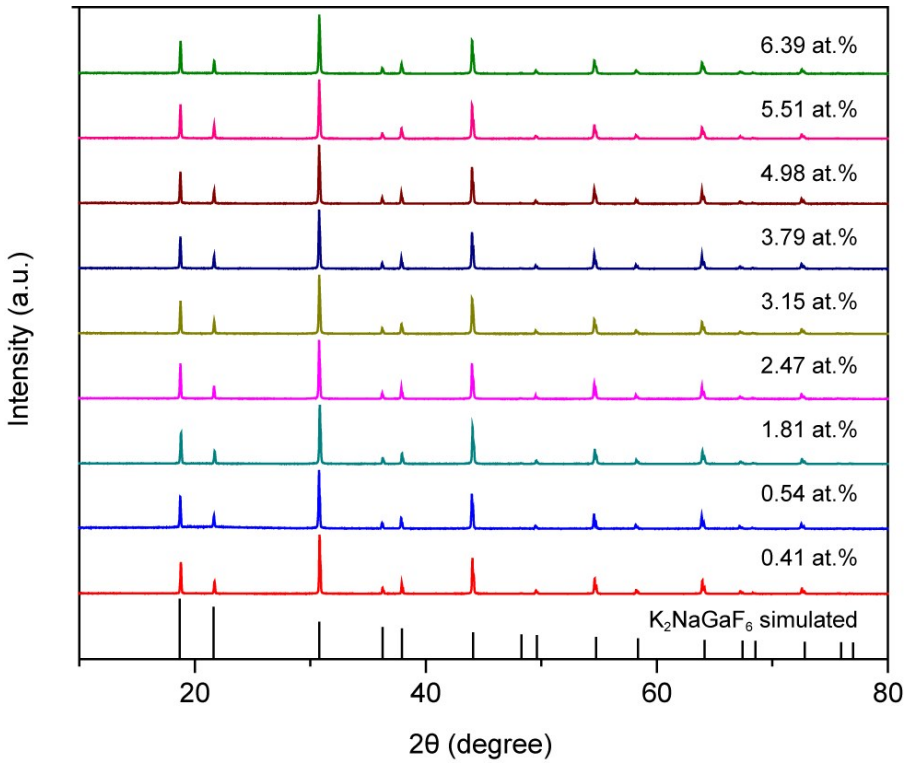

Figure S1 X-ray diffraction (XRD) patterns of K_2NaGaF_6:Mn^{4+} red phosphors with various Mn^{4+} concentrations. All the patterns match well with the simulated XRD pattern derived from single crystal diffraction data of K_2NaGaF_6 crystal.

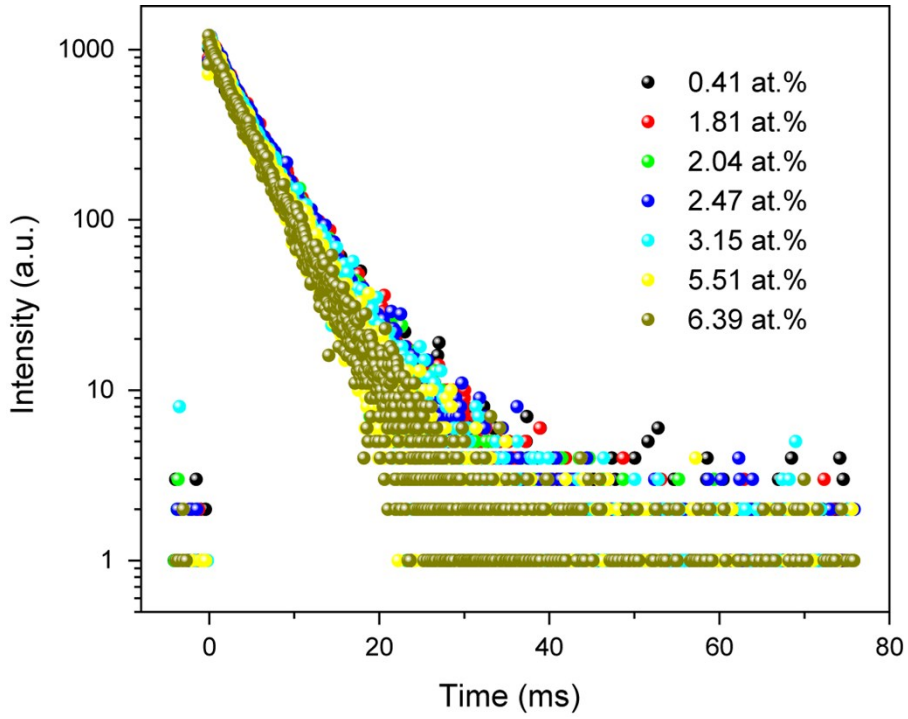

Figure S2 Photoluminescence (PL) decay curves from ^2E energy state of Mn^{4+} ions in $K_2NaGaF_6:Mn^{4+}$ samples with various Mn^{4+} concentrations by monitoring 631 nm emission at room temperature (RT).

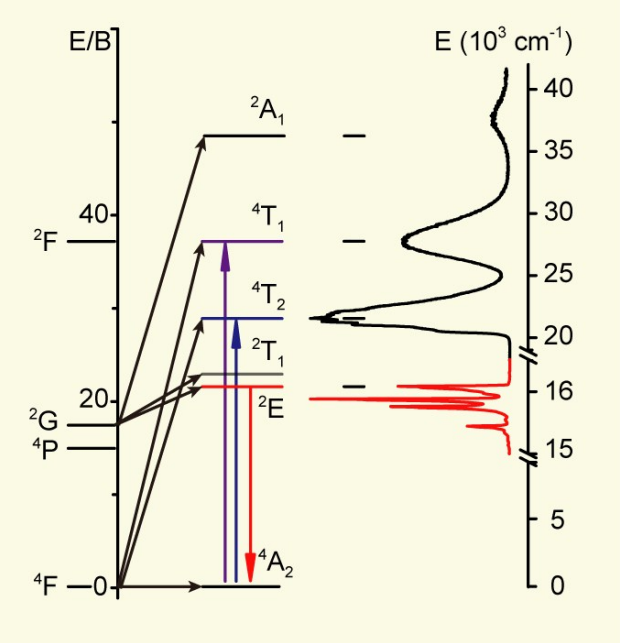

Figure S3 Excitation and emission spectra of the $K_2NaGaF_6:Mn^{4+}$ (0.54 at.%) sample measured at 10 K.

Supplementary Discussion

The values of D_q, B and C can be calculated based on experimentally measured excitation and emission spectra, according to the following equations[1-2]:

$$E(^4T_2 - {}^4A_2) = 10D_q \quad (1)$$

$$\frac{B}{D_q} = \frac{(\Delta E/D_q)^2 - 10(\Delta E/D_q)}{15(\Delta E/D_q - 8)} \quad (2)$$

$$E(^2E - {}^4A_2) = 9B + 3C - 90B^2/(10D_q) \quad (3)$$

Where $\Delta E = E(^4T_1(^4F)) - E(^4T_2)$.

The energies of $^4T_1$, $^4T_2$ and ^2E were experimentally determined to be 27778 cm^{-1}, 21580 cm^{-1} and 16088 cm^{-1}, respectively. From equations (1)-(3), the value of D_q, B, and C were calculated to be 2158 cm^{-1}, 574 cm^{-1} and 4099 cm^{-1}, respectively.

$$E(^2T_1 - {}^2E) = 66B^2/(10D_q) = 1008\ cm^{-1} \quad (4)$$

$$E(^2A_1 - {}^4A_2) = 10D_q + 4B + 3C = 36173\ cm^{-1} \quad (5)$$

From equations (4)-(5), the value of $^2T_1$, $^2A_1$ were calculated to be 17096 cm^{-1}, and 36173 cm^{-1}, respectively.

Supplementary References

1 B. Henderson and G. F. Imbusch, Optical spectroscopy of inorganic solids, Oxford University Press, Great Clarendon Street, Oxford, 2006.
2 M. J. Reisfeld, N. A. Matwiyoff and L. B. Asprey, J. Mol. Spectrosc., 1971, 39, 8-20.