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$K_2NaAlF_6:Mn^{4+}$ red phosphor: Room-temperature synthesis and electronic/vibronic structures

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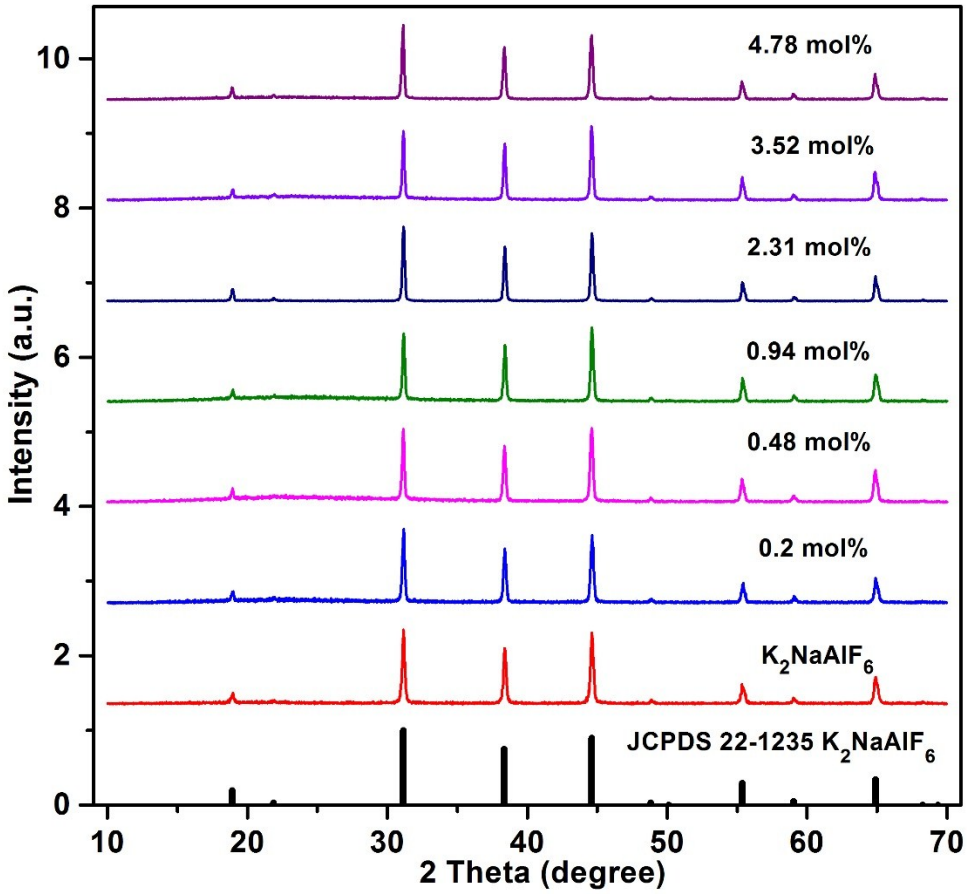

Figure S1 X-ray diffraction patterns of synthesized pure K_2NaAlF_6 crystal and K_2NaAlF_6:Mn^{4+} crystals with various Mn^{4+} doping concentrations of 0.20, 0.48, 0.94, 2.31, 3.52 and 4.78 at.%, respectively. All the patterns match well with the standard pattern of tetragonal-phase K_2NaAlF_6 crystal (JCPDS No. 22-1235) with the space group of $Fm\bar{3}m$.

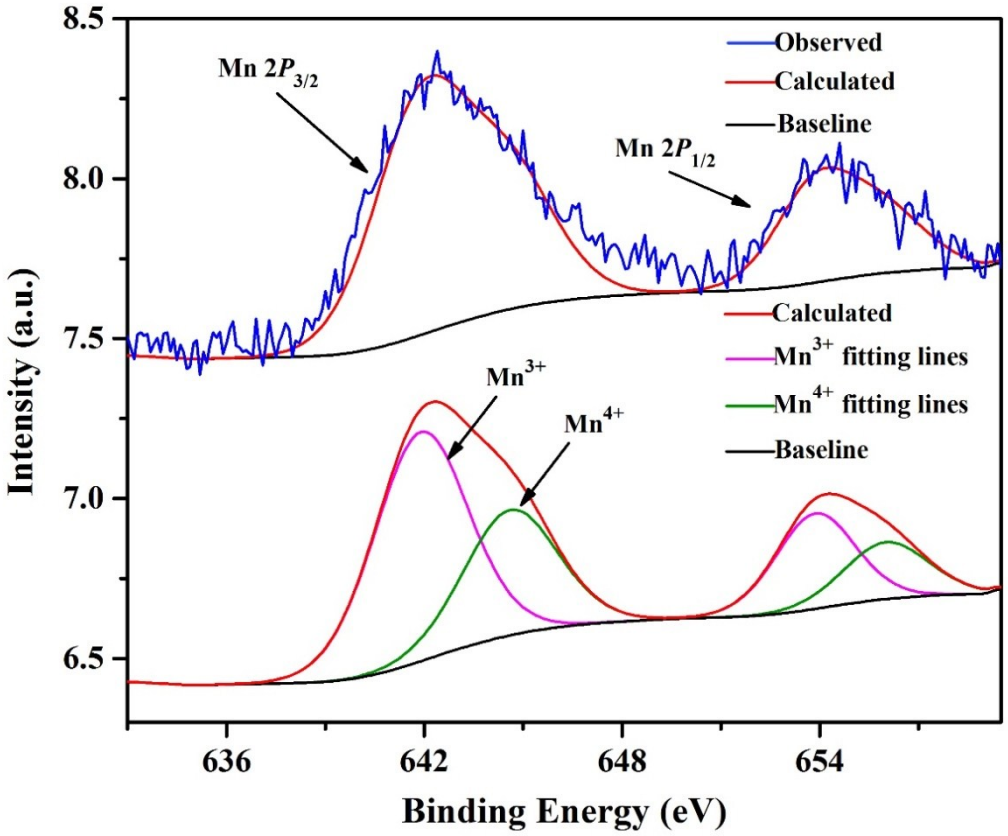

Figure S2 Mn-2p core-level X-ray photoelectron spectra (XPS) for $2p_{1/2}$ and $2p_{3/2}$ of Mn^{3+} and Mn^{4+} ions in the K_2NaAlF_6:Mn^{4+} (2.31 at.%) sample. The smooth solid lines represent the fitted lines. The results show that both Mn^{3+} and Mn^{4+} ions exist in the K_2NaAlF_6 host.

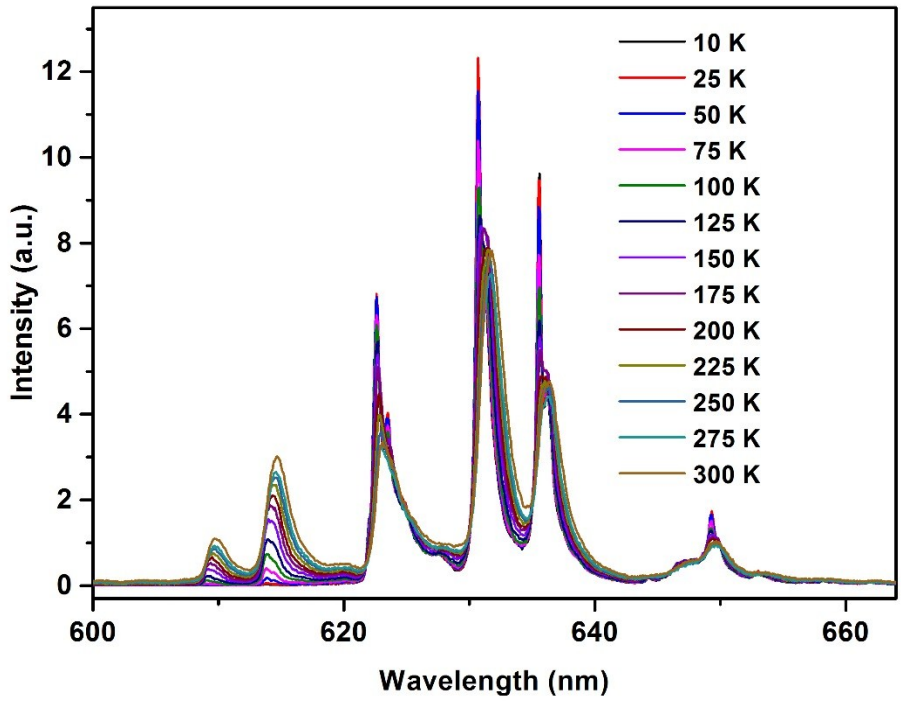

Figure S3 Temperature-dependent PL spectra at 10-300 K for the $K_2NaAlF_6:Mn^{4+}$ (2.31 at.%) sample.

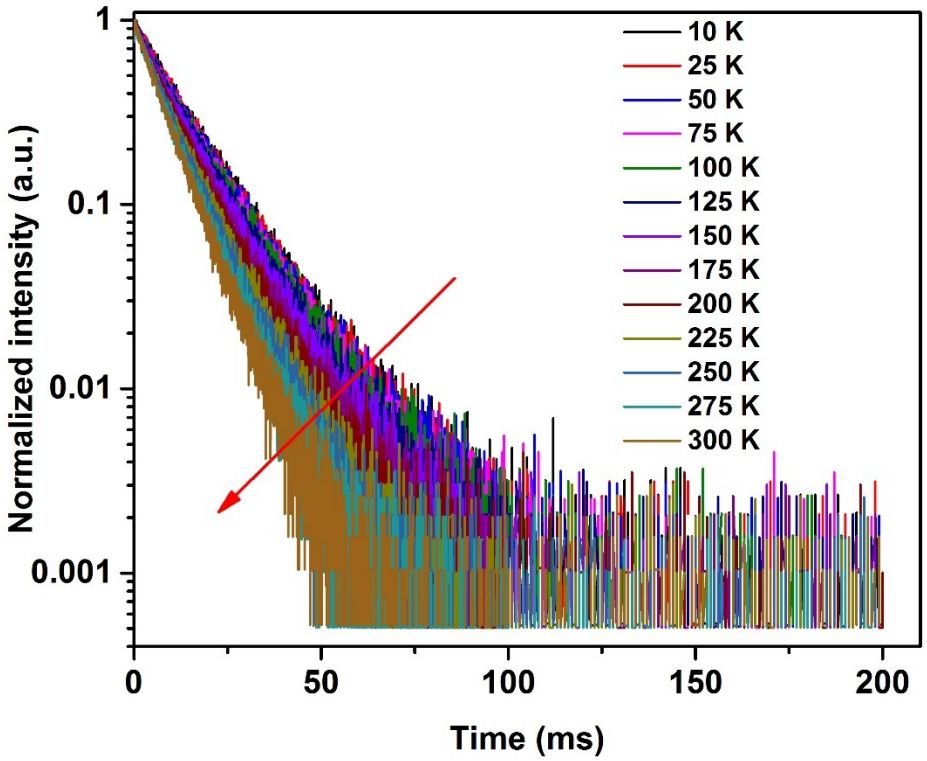

Figure S4 Temperature-dependent PL decays at 10-300 K from the ^2E state of the $K_2NaAlF_6:Mn^{4+}$ (2.31 at.%) sample.

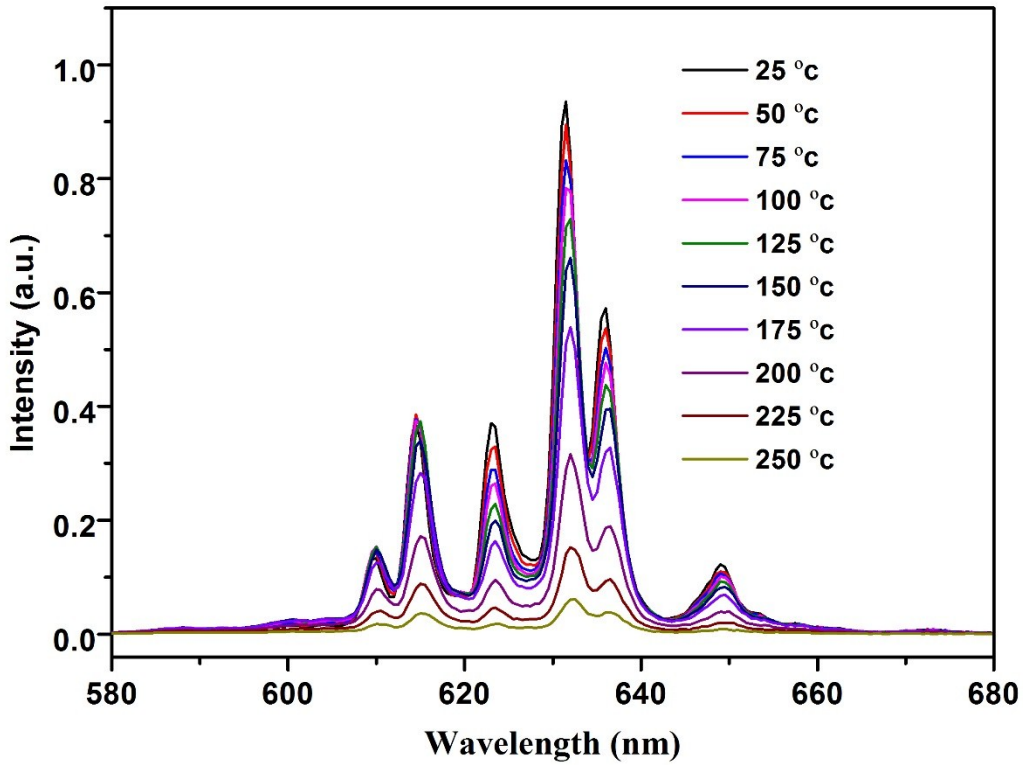

Figure S5 Temperature-dependent PL spectra at 25-150 °C for the $K_2NaAlF_6:Mn^{4+}$ (2.31 at.%) sample.

Supplementary Discussion.

Calculation of crystal field parameters of D_q, B, C. The values of D_q, B and C can be calculated based on experimentally determined energy levels using 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 ΔE represents the energy difference between $^4T_1$ and $^4T_2$. The energies of $^4T_1$, $^4T_2$ and ^2E were experimentally determined to be 28023 cm^{-1}, 21824 cm^{-1} and 16067 cm^{-1}, respectively. From equations (1)-(3), the value of D_q, B, C were calculated to be 2182 cm^{-1}, 573 cm^{-1} and 4088 cm^{-1}, respectively.

Calculation of energies of $^2T_1$ and $^2A_1$ states. Once the values of D_q, B and C have been determined, the energies of $^2T_1$ and $^2A_1$ states can be determined by the following equations:

$$E(^2T_1–^2E) = 66B^2/(10D_q), \quad (4)$$

$$E(^2A_1–^4A_2) = 10D_q + 4B + 3C, \quad (5)$$

The calculated values of energies of $^2T_1$ and $^2A_1$ are 17060 cm^{-1} and 36376 cm^{-1}, respectively.

Supplementary References

1. B. Henderson and G. F. Imbusch, *Optical spectroscopy of inorganic solids*, Oxford university Press, 1989.
2. M. J. Reisfeld, N. A. Matwiyoff and L. B. Asprey, *J. Mol. Spectrosc.*, 1971, **39**, 8-20.