Electronic Supplementary Information

Formation mechanism, improved photoluminescence and LED applications of red phosphor K$_2$SiF$_6$:Mn$^{4+}$

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(a) Cubic  (b) Hexagonal

Figure S1. The structure projection of K$_2$SiF$_6$ with (a) cubic and (b) hexagonal structures plotted by software Diomand 3.0.
Figure S2. XRD and images of samples (a-c) prepared from (a) 0.505 g KNO₃, 4.45 g (NH₄)₂SiF₆, 0.1975 g KMnO₄, 20 mL HF and 20 mL H₂O, (b) 0.29 g KF, 4.45 g (NH₄)₂SiF₆, 0.1975 g KMnO₄ and 40 mL 20% HF, (c) 0.29 g KF, 4.45 g (NH₄)₂SiF₆, 0.1975 g KMnO₄, 0.6 mL H₂O₂ and 40 mL H₂O at room temperature. The three samples show no luminescence under UV lamp.
Figure S3. (a) XRD pattern and (b) SEM image of the brown solid sample synthesized from KMnO₄ (10.1 mol/L) and HF (wt.10%) in hydrothermal reaction at 120 °C for 12 h.

Figure S4 Thermogravimetrics (TG) and different scanning calorimeter (DSC) graphs of as synthesized K₂SiF₆:Mn⁴⁺ under N₂ atmosphere. The thermal stability of the red phosphor K₂SiF₆:Mn⁴⁺ is investigated by thermogravimetrics analysis and different scanning calorimeter (DSC; Netzsch STA 449 C, at a heating rate of 10K/min).
**Figure S5.** Raman spectra of phosphor (a) undoped K$_2$SiF$_6$ and (b) K$_2$SiF$_6$:Mn$^{4+}$.

Raman spectra were performed on a JY-T64000 Raman spectroscopy at room temperature with a laser excitation at 632.8 nm (1.96 eV, 3 mW).

**Figure S6.** Infrared spectra of phosphors K$_2$SiF$_6$:Mn$^{4+}$ named (a) KSFM-1, (b) KSFM-2, (c) KSFM-3, and (d) KSFM-4.

The infrared spectra were performed on Perkin-Elmer 580 B infrared
spectrophotometer using the KBr pellet technique.

**Figure S7.** Excitation spectra of red phosphor $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ monitored at (a) 628 nm, (b) 612 nm, and (c) 646 nm; (d) curve is normalized electro-luminescence spectrum of InGaN LED chip.

**Figure S8.** Emission spectra of red phosphor $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ excited at (a) 450 nm, (b)
355 nm, and (c) 250 nm.

**Figure S9.** Excitation (a, b: monitored at 629 nm) and emission (c, d: excited at 467 nm) spectra of as-prepared red phosphor K$_2$SiF$_6$:Mn$^{4+}$ named KSFM-2 and KSFM-4.

**Figure S10.** CIE (X, Y) coordinate diagram showing chromaticity point (marked by symbol of star) of WLED fabricated with yellow phosphor YAG:Ce and our as-prepared red phosphor K$_2$SiF$_6$:Mn$^{4+}$ on GaN chip.