K₂LiScF₆:Cr³⁺/Mn⁴⁺ Fluoride Phosphor with Enhanced Broadband Emission for NIR pc-LEDs

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Experimental section

Materials

KF (99.9%), Li(OH) $\mathbf{\Phi}$ H₂O (99.98%), KHF₂ (99.0%), Sc₂O₃ (99.9%), NH₄HF₂ (98%) and CrF₃ (AR) were purchased from Aladdin Co., Ltd. KMnO₄ (99.5%), Hydrofluoric acid (HF, 40 wt%) and hydrogen peroxide solution (H₂O₂, 30 wt%) were purchased from Guangzhou Chemical Reagent Factory.

The $(NH)_4ScF_6$, $(NH)_4CrF_6$ and K_2MnF_6 precursors was prepared by a coprecipitation method according to Ref. 1 and 2, respectively.

Synthesis procedure

A series of K₂LiScF₆:xCr³⁺ (x = 0, 0.01, 0.05, 0.10, 0.15, 0.20) samples were synthesized by a hydrothermal method. In a typical procedure, 1.9 mmol (NH)₄ScF₆ and 0.1 mmol (NH)₄CrF₆ were dissolved in 25 ml H₂O under stirring. Then 10 mmol KF and 2 mmol Li(OH)**\Phi**H₂O were added into the above solution and stirred for 20 min. The mixture was further transferred to a 50 mL Teflon bottle autoclave and maintained at 200 °C for 10 h. After cooling down to room temperature, the precipitates were collected by centrifugation and washed three times with deionized water and ethanol. Finally, the products were obtained by drying at 75 °C for 3 h.

A series of K₂LiScF₆: xMn^{4+} (x = 0.0005, 0.001, 0.003, 0.005, 0.007, 0.009) samples were prepared by a cation exchange approach.^{3, 4} Typically, 0.0099 g of K₂MnF₆ powders were first dissolved in 1 ml of HF solution. Then, 0.9763 g of as-prepared K₂LiScF₆ powders were added into the above solution and stirred for 20 min. After centrifugation and washing three times with ethanol, the final K₂LiScF₆: xMn^{4+} products were obtained by drying at 75 °C for 3 h. The K₂LiScF₆:Cr³⁺,0.001Mn⁴⁺ samples were synthesized in a similar procedure by using K₂LiScF₆:Cr³⁺ to replace K₂LiScF₆.

Characterization

The X-ray diffraction (XRD) patterns of the as-prepared samples were collected by a Bruker D8 ADVANCE diffractometer with a Cu-K α ($\lambda = 1.5405$ Å) at 40 kV and 40 mA. Rietveld refinement was performed using TOPAS-Academic V5. The thermogravimetric curve was measured by a simultaneous thermal analyzer (Netzsch STA449 F5). The room-temperature (RT) and temperature-dependent photoluminescence (PL) spectra, as well as the PL decay curves were recorded with a FLS1000 spectrometer (Edinburgh Instruments) equipped with a thermo-electronic cooled (-22 °C) R928P photomultiplier (PMT) from Hamamatsu and a MercuryiTC temperature controller from Oxford. The excitation source of the luminescence spectra was a 450 W Xe900 continuous xenon lamp. The quantum yield was examined with a Hamamatsu C9920-03G absolute quantum yield measurement system. SEM images were collected on an electron microscope (FEI Quanta 400). Compositional analyses were verified by inductively coupled plasma atomic emission spectrometry (ICP).

The band structure and electronic structures were calculated according to the density functional theory implemented in the Vienna ab initio simulation package. The exchange correlation potential was approximated by generalized gradient approximation with the PBE functional.⁵ The cutoff energy E_{cut} and k-point mesh were set as 544.20 eV and the 5 × 5 × 5 Monkhorst-Pack grid, respectively. The convergence criterion for the electronic energy was 10⁻⁶ eV, whereas the structures were relaxed until the Hellmann–Feynman forces were smaller than 0.03 eV Å⁻¹.

The NIR LED device was fabricated by coating the $K_2LiScF_6:0.10Cr^{3+}$ phosphor and epoxy resin, with a mass ratio of 1:1, on a blue InGaN chip (450 - 460 nm, 1 W). The current-dependent electroluminescence and output power were measured using an ATA-1000 photoelectric measuring system (EVERFINE, China).

	Wyck.	Site	X	у	Z
Κ	8c	-43m	1/4	1/4	1/4
Sc	4a	m-3m	0	0	0
F	24e	4m.m	0.2466(1)	0	0
Li	4b	m-3m	1/2	1/2	1/2

Table S1 Crystallographic information and fractional atomic coordinates of K2LiScF6.

Table S2 The actual Cr^{3+} content and IQE of K₂LiScF₆: xCr^{3+} (x = 0.01, 0.05, 0.10, 0.15, 0.20).

Nominal concentration of Cr^{3+} (at.%)	1.00	5.00	10.00	15.00	20.00
Cr ³⁺ content (at.%, ICP)	1.24	5.22	9.82	14.93	19.15
IQE (%)	/	61.0	77.6	51.0	34.4

Table S3 Lifetime ($\lambda_{ex} = 432 \text{ nm}, \lambda_{em} = 770 \text{ nm}$) of K₂LiScF₆:*x*Cr³⁺ (*x* = 0.01, 0.05,

0.10,	0.15,	0.20).
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Cr ³⁺ content	0.01	0.05	0.10	0.15	0.20
Lifetime (ms)	0.38	0.35	0.34	0.31	0.28
R ²	0.999	0.999	0.999	0.999	0.999

Table S4 Lifetime of Mn⁴⁺ and the energy transfer efficiency from Mn⁴⁺ to Cr³⁺ (η_{ET}) of K₂LiScF₆:0.001Mn⁴⁺,*x*Cr³⁺ (x = 0, 0.01, 0.05, 0.10).

Cr ³⁺ content	0	0.01	0.05	0.10
Lifetime of Mn ⁴⁺ (ms)	5.63	2.66	1.12	0.51
η_{ET} (%)	0	52.75	80.11	90.94



Fig. S1 Thermogravimetric curve of K₂LiScF₆ from room temperature to 1000 °C.



Fig. S2 Elemental mapping of $K_2LiScF_6:Cr^{3+}$.



Fig. S3 PLE spectra ($\lambda_{em} = 770 \text{ nm}$) of K₂LiScF₆:xCr³⁺ (x = 0.01, 0.05, 0.10, 0.15, 0.20).



Fig. S4 (a) PL spectra ($\lambda_{ex} = 432 \text{ nm}$) and (b) concentration-dependent PL intensity of K₂LiScF₆:*x*Cr³⁺ (*x* = 0.07, 0.09, 0.10, 0.11, 0.13).



Fig. S5 Decay time ($\lambda_{ex} = 432 \text{ nm}$, $\lambda_{em} = 770 \text{ nm}$) of K₂LiScF₆:*x*Cr³⁺ (*x* = 0.01, 0.05, 0.10, 0.15, 0.20).



Fig. S6 XRD patterns of $K_2LiScF_6:xMn^{4+}$ (x = 0.0005, 0.001, 0.003, 0.005, 0.007, 0.009).



Fig. S7 (a) PL and (b) PLE spectra of K₂LiScF₆:*x*Mn⁴⁺ (*x* = 0.0005, 0.001, 0.003, 0.005, 0.007, 0.009).



Fig. S8 PL spectra of $K_2LiScF_6:0.01Cr^{3+}, 0.001Mn^{4+}$ and $K_2LiScF_6:0.01Cr^{3+}$ under excitation of 340 nm.



Fig. S9 Decay curves of K_2LiScF_6 :0.001Mn⁴⁺, xCr^{3+} (x = 0, 0.01, 0.05, 0.10).

To evaluate the energy transfer efficiency from Mn^{4+} to Cr^{3+} in K₂LiScF₆, the decay curves ($\lambda_{ex} = 462 \text{ nm}$, $\lambda_{em} = 633 \text{ nm}$) of K₂LiScF₆: 0.001Mn⁴⁺,*x*Cr³⁺ are measured (Fig. S9). The decay curves can be fitted well with a second-order exponential decay equation:

$$I(t) = I_0 + A_1 exp(-t/t_1) + A_2 exp(-t/t_2)$$
 S1

where I_0 is the initial emission intensity, A_1 and A_2 are constants, and τ_1 and τ_2 are decay times. The average lifetime can be obtained using the following equation:

$$\tau_{ave} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$
 S2

The calculated results (Table S4) show that the lifetime of Mn^{4+} decreases with increasing Cr^{3+} concentration due to energy transfer from Mn^{4+} to Cr^{3+} . Furthermore, the energy transfer efficiency from Mn^{4+} to Cr^{3+} can be obtained with the decay time using the following equation:

$$\eta_{\rm ET} = 1 - \tau/\tau_0$$
 S3

where τ and τ_0 represent the lifetime of Mn⁴⁺ with and without Cr³⁺. The results indicate that the efficiency increases with increasing Cr³⁺ content until it reaches a maximum of 90.94% at x = 0.10 (Table S4).



Fig. S10 Temperature-dependent PL spectra of $K_2LiScF_6:0.10Cr^{3+}$ (298 – 423 K).



Fig. S11 Integrated emission intensity of $K_2LiScF_6:0.10Cr^{3+}, 0.001Mn^{4+}$ and $K_2LiScF_6:0.10Cr^{3+}$ as a function of temperature (298 – 423 K).



Fig. S12 Schematic configurational coordinate diagram of K_2LiScF_6 : Cr³⁺.

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