

## Electronic Supporting Information

### **Design of Cr<sup>3+</sup>-activated broadband NIR phosphors with tunable and abnormal thermal quenching behavior for NIR pc-LEDs**

Qijian Zhu, †<sup>ab</sup> Jiansheng Huo, †<sup>a</sup> Quwei Ni,<sup>ab</sup> Qihong Zhang,<sup>a</sup> Junhao Li,<sup>a</sup> Haiyong Ni<sup>a</sup> and Jianbang Zhou\*<sup>a</sup>

<sup>a</sup> Guangdong Provincial Key Laboratory of Rare Earth Development and Application, Institute of Resources Utilization and Rare Earth Development, Guangdong Academy of Sciences, Guangzhou 510651, P.R. China.

<sup>b</sup> School of Chemistry, Guangzhou Key Laboratory of Analytical Chemistry for Biomedicine, South China Normal University, Guangzhou 510006, P.R. China.

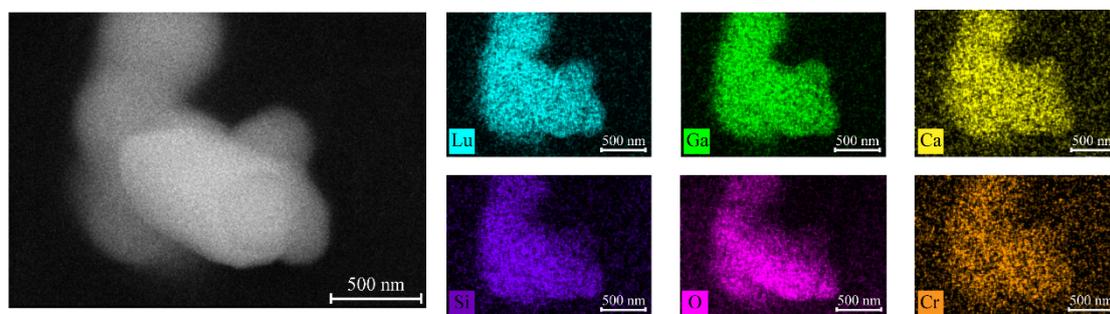
† Q.J. Zhu and J.S. Huo contributed equally to this work.

*Corresponding Author.*

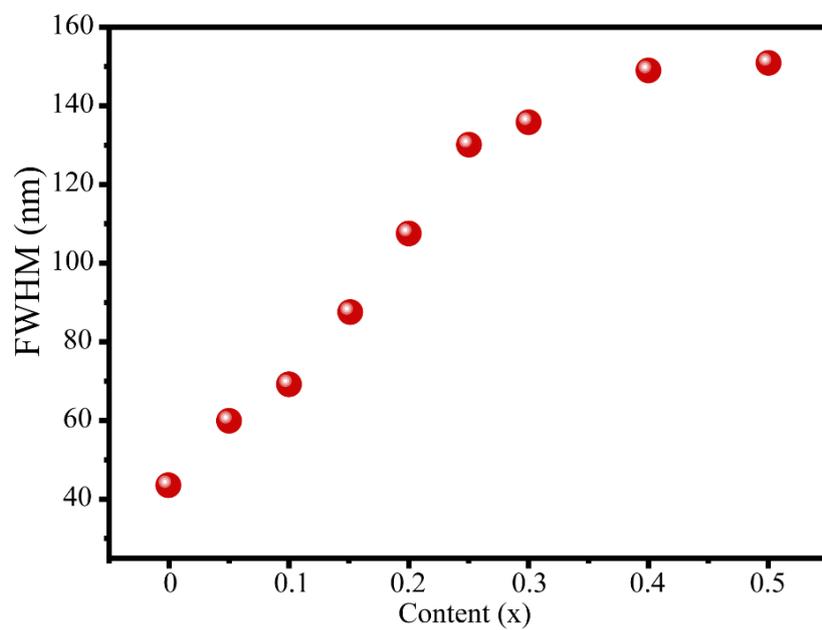
\* *E-mail:* zhoujb4079@foxmail.com

**Table S1** Main parameters of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}$  refinement.

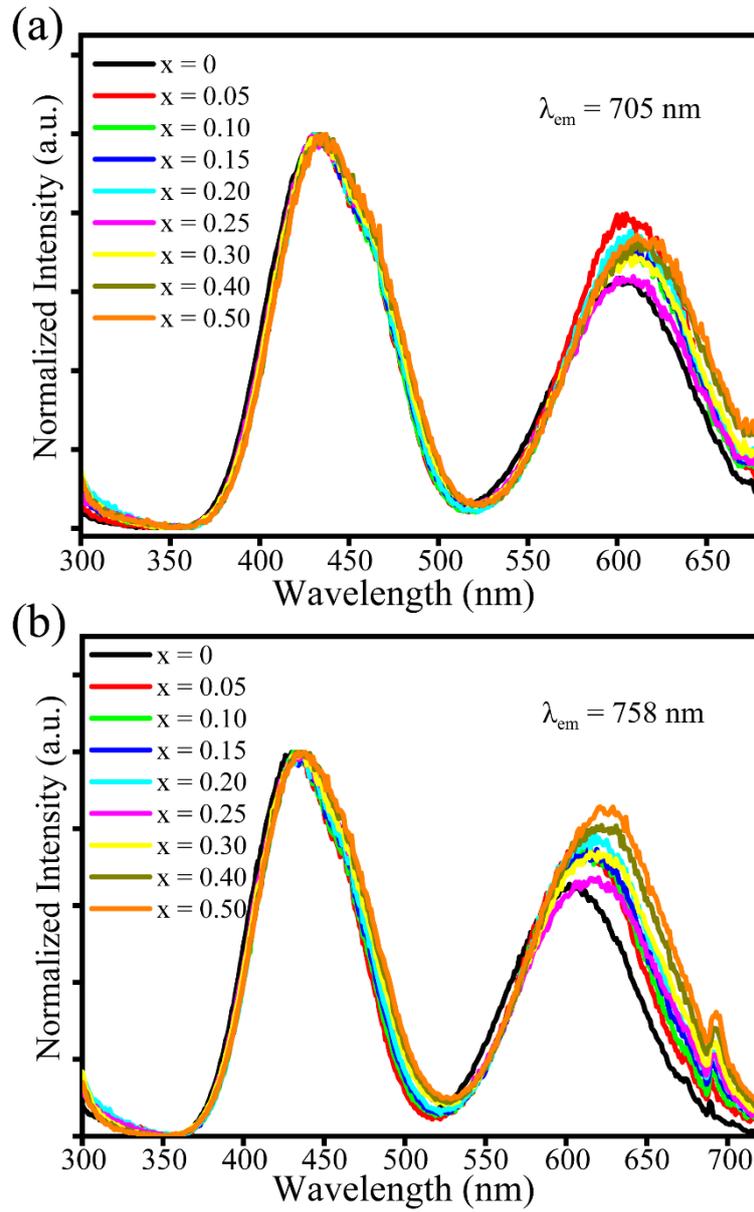
Chemical formula	Space group	Cell parameters	Volume ( $\text{\AA}^3$ )	$R_p\%$	$R_{wp}\%$
$\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}$	$Ia\bar{3}d$	$a = b = c = 12.18 \text{ (\AA)}$ $\alpha = \beta = \gamma = 90 \text{ (}^\circ\text{)}$	1807.42	6.00	10.23



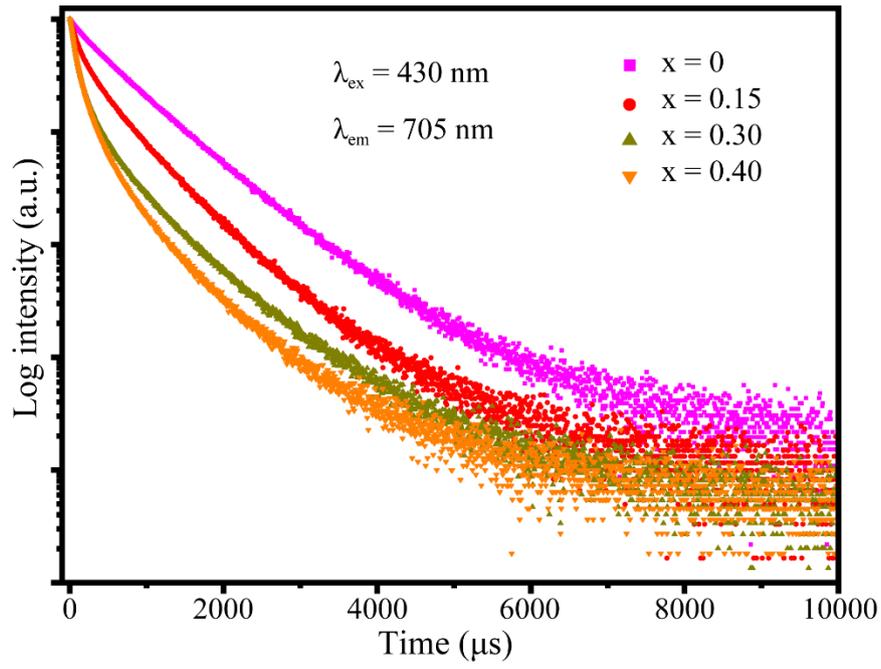
**Fig. S1.** SEM and elemental mapping images of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  phosphor.



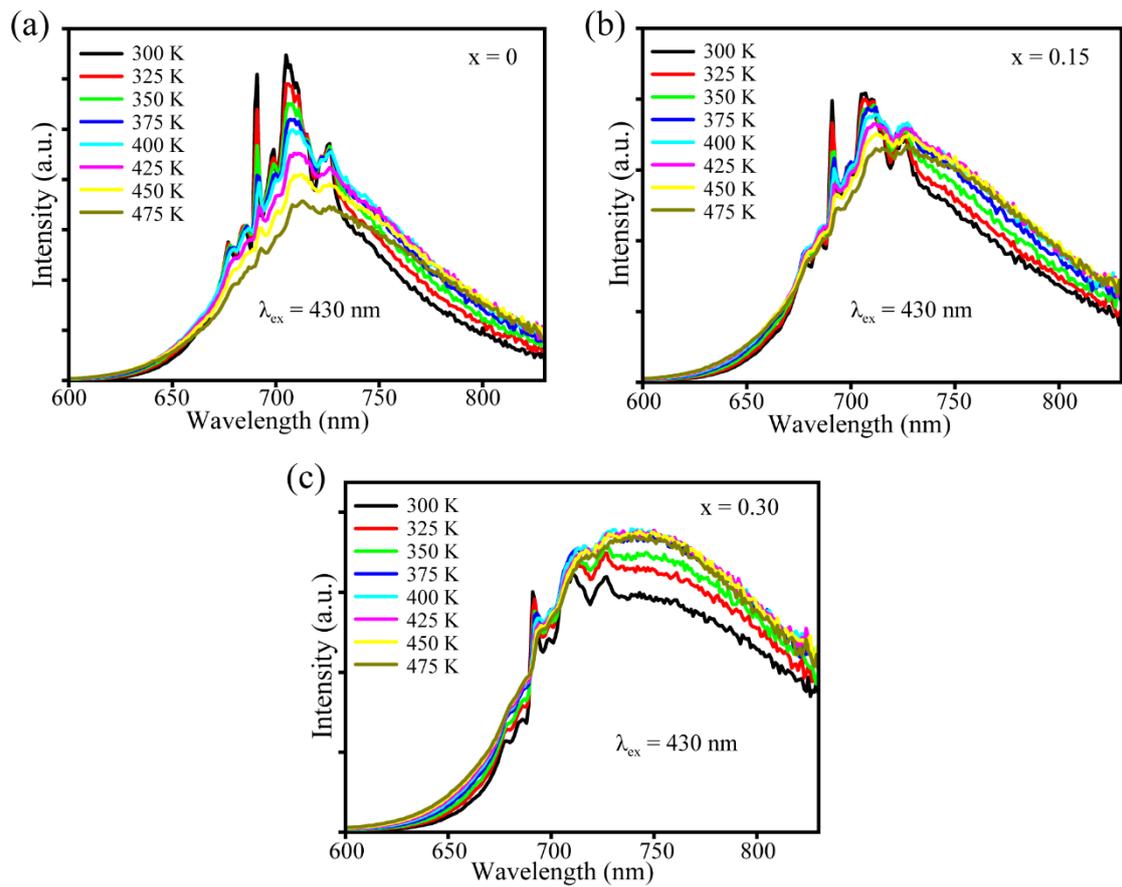
**Fig. S2.** FWHM of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.5$ ).



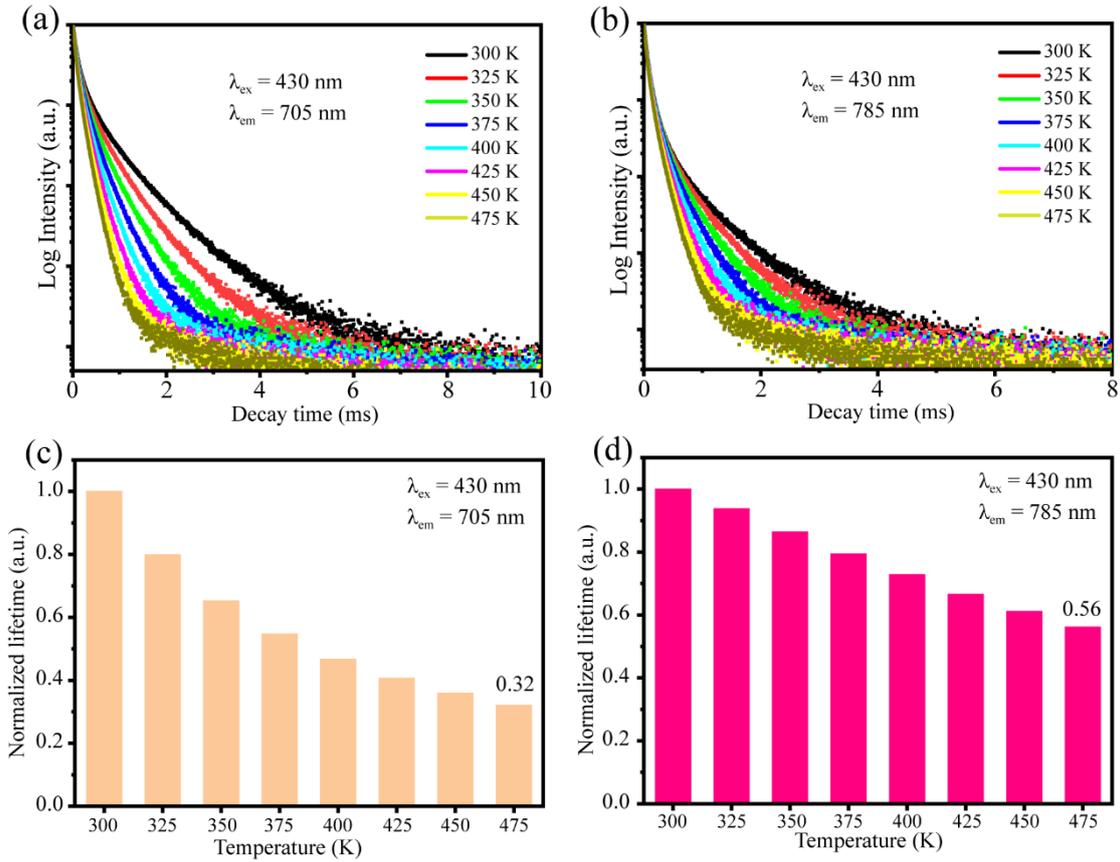
**Fig. S3.** PLE spectra of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.5$ ).



**Fig. S4.** PL decay curves of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.4$ ).

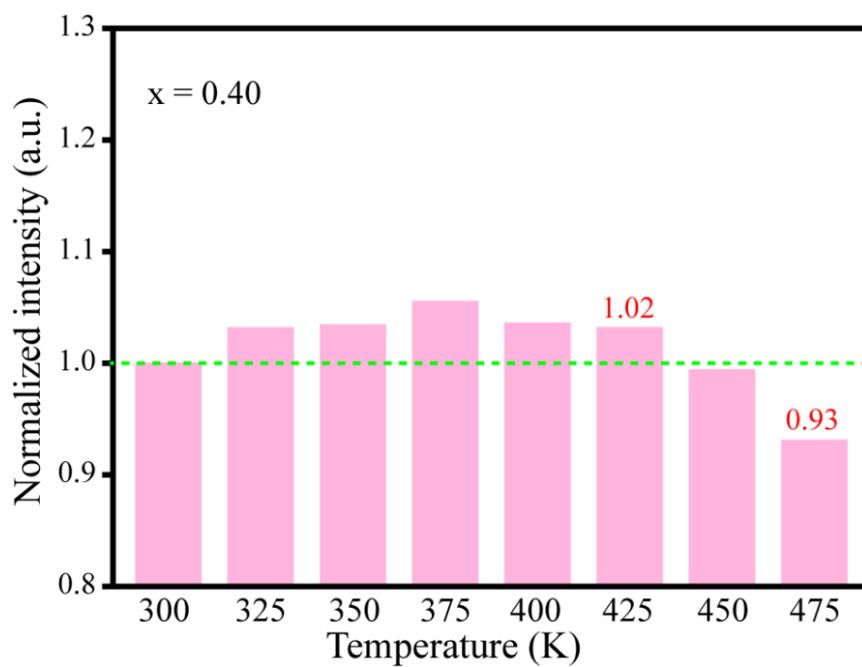


**Fig. S5.** PL spectra of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_3\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.3$ ) as a function of temperature (300-475 K).

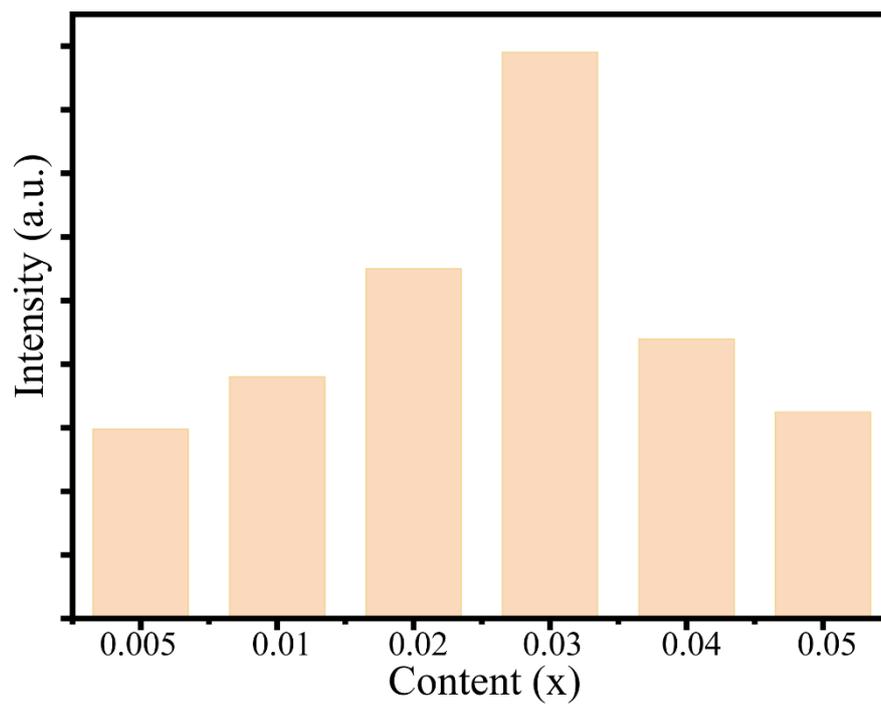


**Fig. S6.** Decay curves of (a)  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  ( $\lambda_{\text{em}} = 705$  nm) and (b)  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  ( $\lambda_{\text{em}} = 785$  nm) transitions of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  as a function of temperature. Normalized lifetime (the lifetime at 300 K is set as 1) of (c)  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  ( $\lambda_{\text{em}} = 705$  nm) and (d)  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  ( $\lambda_{\text{em}} = 785$  nm) transitions of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  as a function of temperature.

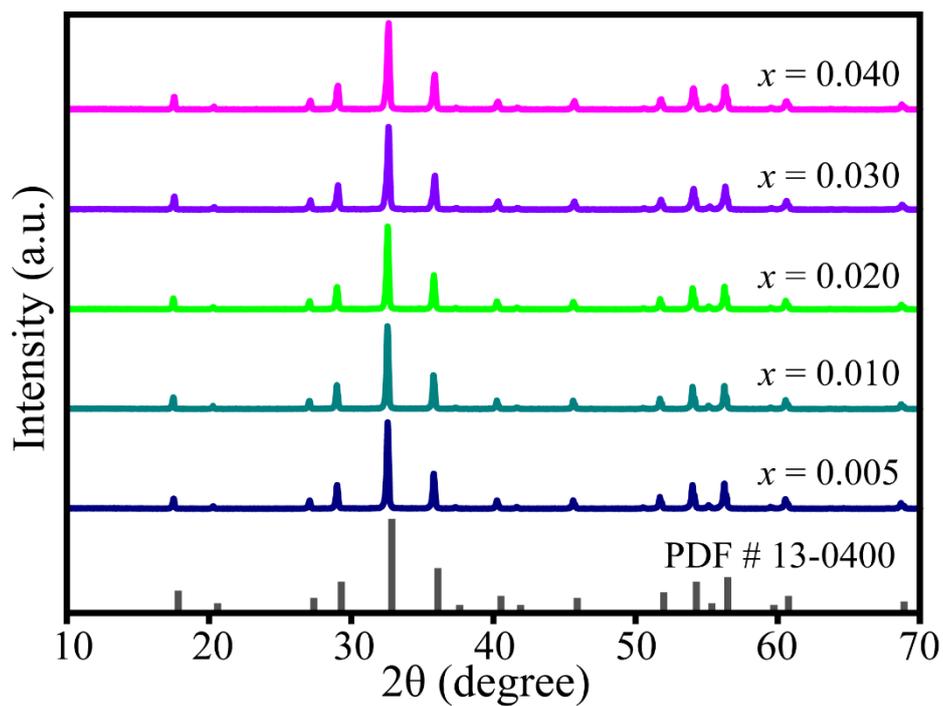
It can be seen from **Fig. S6** that the lifetime of both  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  and  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transitions decreases with temperature from 300 to 475 K due to enhanced nonradiative transitions. Furthermore, it should be noted that the decrease rate of the lifetime of  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition is much higher than that of  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ , which means that the efficiency of electron migration from  ${}^2\text{E}$  to  ${}^4\text{T}_2$  states is much higher than the nonradiative  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition, indicating that the radiative  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  broadband emission can be possibly strengthened at high temperatures.



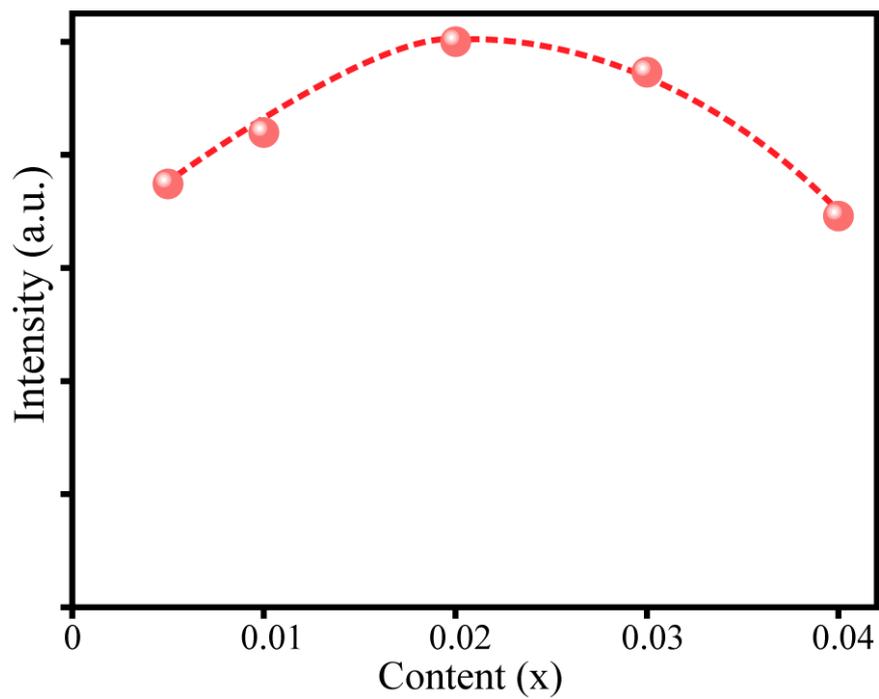
**Fig. S7.** PL intensity of  $\text{Lu}_{2.6}\text{Ca}_{0.4}\text{Ga}_{4.6}\text{Si}_{0.4}\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0.40$ ) as a function of temperature (300-475 K).



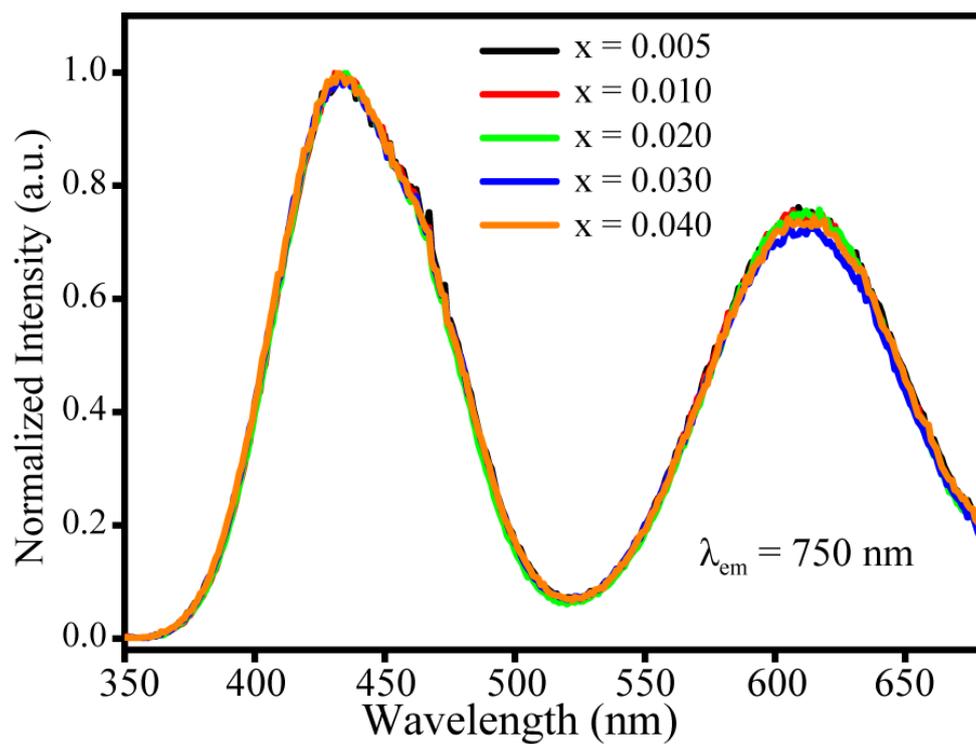
**Fig. S8.** PL intensity of Lu<sub>3-x</sub>Ca<sub>x</sub>Ga<sub>5-x</sub>Si<sub>x</sub>O<sub>12</sub>:0.01Cr<sup>3+</sup> (x = 0-0.5).



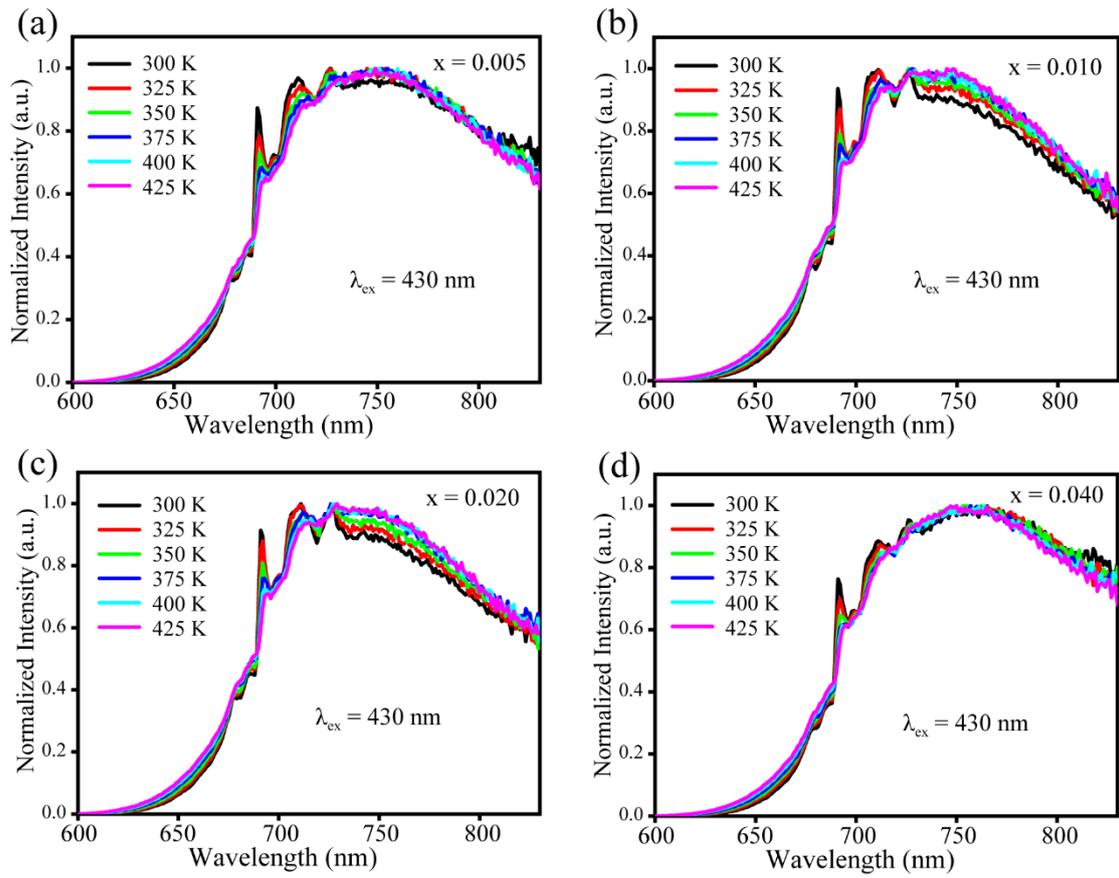
**Fig. S9.** XRD patterns of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:x\text{Cr}^{3+}$  ( $x = 0.005$ - $0.040$ ).



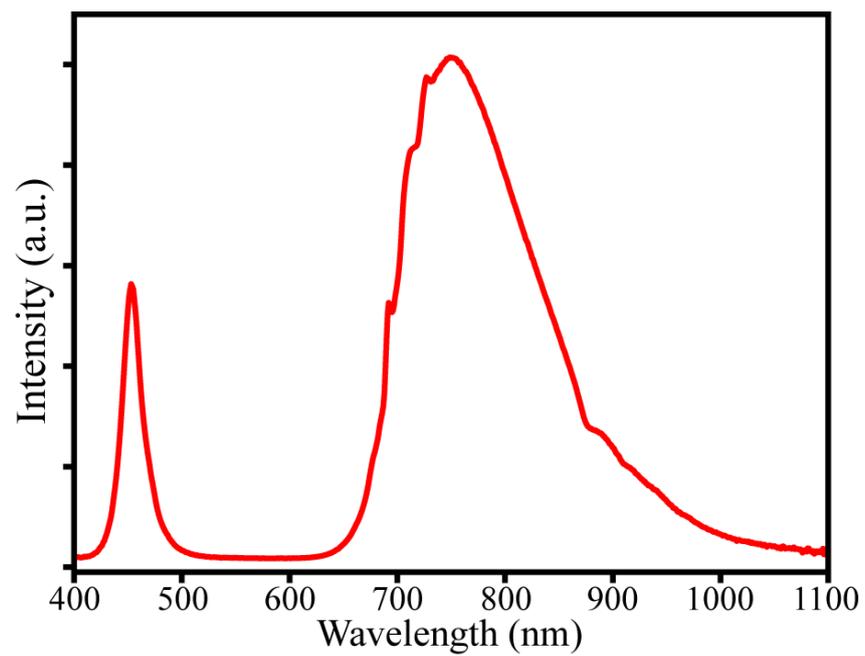
**Fig. S10.** PL intensity of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:x\text{Cr}^{3+}$  ( $x = 0.005\text{-}0.040$ ).



**Fig. S11.** PLE spectra of Lu<sub>2.7</sub>Ca<sub>0.3</sub>Ga<sub>4.7-x</sub>Si<sub>0.3</sub>O<sub>12</sub>:xCr<sup>3+</sup> (x = 0.005-0.040).



**Fig. S12.** PL spectra of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{xCr}^{3+}$  ( $x = 0.005\text{-}0.040$ ) as a function of temperature (300-425 K).



**Fig. S13.** Electroluminescence spectrum of the fabricated NIR-LED device (300 mA).