

## RESEARCH ARTICLE

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

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Cr<sup>3+</sup>-activated broadband near-infrared (NIR) phosphors usually show controllable and excellent photoluminescence (PL) properties, but their poor thermal stability remains a big challenge. Herein, a series of Lu<sub>3-x</sub>Ca<sub>x</sub>Ga<sub>5-x</sub>Si<sub>x</sub>O<sub>12</sub>:Cr<sup>3+</sup> garnet phosphors with tunable and abnormal thermal quenching performance have been successfully proposed. It is found that both the crystal field strength and calculated energetic difference between <sup>4</sup>T<sub>2</sub> and <sup>2</sup>E states decrease obviously with increasing [Ca<sup>2+</sup>-Si<sup>4+</sup>] co-substitution, resulting in the thermal occupation of the <sup>4</sup>T<sub>2</sub> state and broadened PL spectra. More importantly, the Lu<sub>3-x</sub>Ca<sub>x</sub>Ga<sub>5-x</sub>Si<sub>x</sub>O<sub>12</sub>:Cr<sup>3+</sup> phosphors show improved PL thermal stability depending on the different thermal population between <sup>4</sup>T<sub>2</sub> and <sup>2</sup>E states, and the mechanism is investigated in detail. The PL intensity of the optimal sample reaches up to 125% and 121% at 425 K and 475 K compared with that at 300 K, respectively, which is much better than those of most Cr<sup>3+</sup>-activated broadband NIR phosphors. A NIR phosphor-converted light-emitting diode (NIR pc-LED) has been fabricated using the as-prepared thermally stable phosphor and its application in bio-imaging and night vision is demonstrated.

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## 1. Introduction

Nowadays, NIR spectroscopy is widely used in many fields of our daily life, such as food quality analysis, night vision, medical imaging, plant growth, and so on.<sup>1</sup> Among the various NIR sources, NIR pc-LEDs have received much attention due to the merits of high efficiency, small size, energy saving, environmentally friendly nature and tunable PL properties over the traditional ones (NIR LEDs, tungsten and halogen lamps).<sup>2,3</sup> As a key component of NIR pc-LEDs, the PL properties of phosphors have a great influence on the performance of LED devices.<sup>4</sup> It is known that the working temperature of the LED device can reach up to above 100 °C (even 150 °C) because of accumulated heat from the chip.<sup>5</sup> The PL intensity of NIR phosphors usually decreases obviously due

to enhanced non-radiative transition with increasing temperature,<sup>6</sup> leading to a decreased device performance. Therefore, the development of NIR phosphors with improved thermal stability is quite important for further applications.<sup>7</sup>

Cr<sup>3+</sup>-activated NIR phosphors usually show strong absorption (<sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>) in the blue light region, which can match well with that of the commercial blue LED chip.<sup>8</sup> In addition, the broadband NIR emission (peak position and bandwidth) of Cr<sup>3+</sup> can be easily tuned depending on the crystal field strength, due to its unique 3d<sup>3</sup> electron configuration.<sup>4,9</sup> Thanks to the above characteristics, Cr<sup>3+</sup> is considered to be an ideal NIR emitter and has been extensively explored in recent years. For example, Na<sub>3</sub>ScF<sub>6</sub>:Cr<sup>3+</sup> (λ<sub>em</sub> = 774 nm, FWHM ≈ 108 nm, and I<sub>425K</sub> ≈ 27%) shows a high Cr<sup>3+</sup> doping concentration (35.96%) and the internal quantum efficiency (IQE) and external quantum efficiency (EQE) are as high as 91.5% and 40.82%, respectively.<sup>10</sup> Through lithium ion compensation, Mg<sub>4</sub>Ta<sub>2</sub>O<sub>9</sub>:Cr<sup>3+</sup> (λ<sub>em</sub> = 842 nm, FWHM ≈ 167 nm, and I<sub>425K</sub> ≈ 25%) reaches a record EQE of 61.25%.<sup>11</sup> Compounds with a garnet structure are popular hosts for Cr<sup>3+</sup> ions due to the wide bandgap, high structural rigidity and adjustable composition, such as Gd<sub>2.4</sub>Lu<sub>0.6</sub>Ga<sub>4</sub>AlO<sub>12</sub>:Cr<sup>3+</sup> (λ<sub>em</sub> = 728 nm, FWHM ≈ 107 nm, and I<sub>425K</sub> ≈ 75%),<sup>12</sup> CaLu<sub>2</sub>Mg<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup> (λ<sub>em</sub> = 765 nm, FWHM ≈ 120 nm, and I<sub>425K</sub> ≈ 82%),<sup>13</sup> and Gd<sub>3</sub>Sc<sub>2</sub>Ga<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup> (λ<sub>em</sub> = 760 nm, FWHM ≈ 120 nm, and I<sub>425K</sub> ≈ 86%).<sup>14</sup> Although the above-mentioned Cr<sup>3+</sup>-activated broadband NIR phosphors show

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† Electronic supplementary information (ESI) available: The excitation spectra, FWHM, decay curves and temperature-dependent spectra of Lu<sub>3-x</sub>Ca<sub>x</sub>Ga<sub>5-x</sub>Si<sub>x</sub>O<sub>12</sub>:Cr<sup>3+</sup>; XRD patterns, PL intensity, PLE and temperature-dependent 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); electroluminescence spectrum of the LED device. See DOI: <https://doi.org/10.1039/d4qm00395k>

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excellent PL properties and high luminous efficiency, the poor thermal stability still remains a big challenge before practical application, especially for high-power devices.

In this work, a series of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  phosphors with tunable and abnormal thermal quenching performance are designed and presented. It is found that the temperature-dependent luminescence properties of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  can be controlled by the thermal population of the  $^4\text{T}_2$  energy level, which is highly related to the energetic difference between  $^4\text{T}_2$  and  $^2\text{E}$  states.

## 2. Experimental section

### 2.1 Synthesis

A series of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.010\text{Cr}^{3+}$  ( $x = 0-0.5$ ) phosphors were synthesized by a traditional high-temperature solid-state reaction method.  $\text{Lu}_2\text{O}_3$  (99.995%),  $\text{CaCO}_3$  (A.R.),  $\text{SiO}_2$  (99.95%),  $\text{Cr}_2\text{O}_3$  (A.R.),  $\text{Ga}_2\text{O}_3$  (99.99%) and  $\text{NH}_4\text{Cl}$  (A. R.) were used as raw materials without further purification. The raw materials were weighed stoichiometrically (0.3 wt% of  $\text{NH}_4\text{Cl}$  as flux) and finely ground in an agate mortar for 20 min. The mixture was transferred to a corundum crucible and sintered at 1300 °C for 5 h. After cooling to room temperature, the samples were reground for further characterization.  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:x\text{Cr}^{3+}$  ( $x = 0.005-0.040$ ) phosphors were synthesized similarly according to the above procedures.

### 2.2 Characterization

The phase purity and crystal structure of the samples were confirmed using a Bruker D8 Advance X-ray diffractometer

(XRD) operating with a Cu K $\alpha$  radiation source ( $\lambda = 1.5405 \text{ \AA}$ ) under 40 kV and 40 mA. Measurements were carried out at room temperature over  $5-90^\circ 2\theta$  range. Rietveld refinement was performed using TOPAS-Academic V5 software. The PL excitation (PLE) spectra, PL spectra, and PL decay curves were measured on a FLS1000 spectrometer (Edinburgh Instruments, a 450 W Xe900 continuous xenon lamp as the excitation source) equipped with a thermo-electronic cooled ( $-22 \text{ }^\circ\text{C}$ ) R928P photomultiplier (PMT) from Hamamatsu and a MercuryITC temperature controller (Oxford).

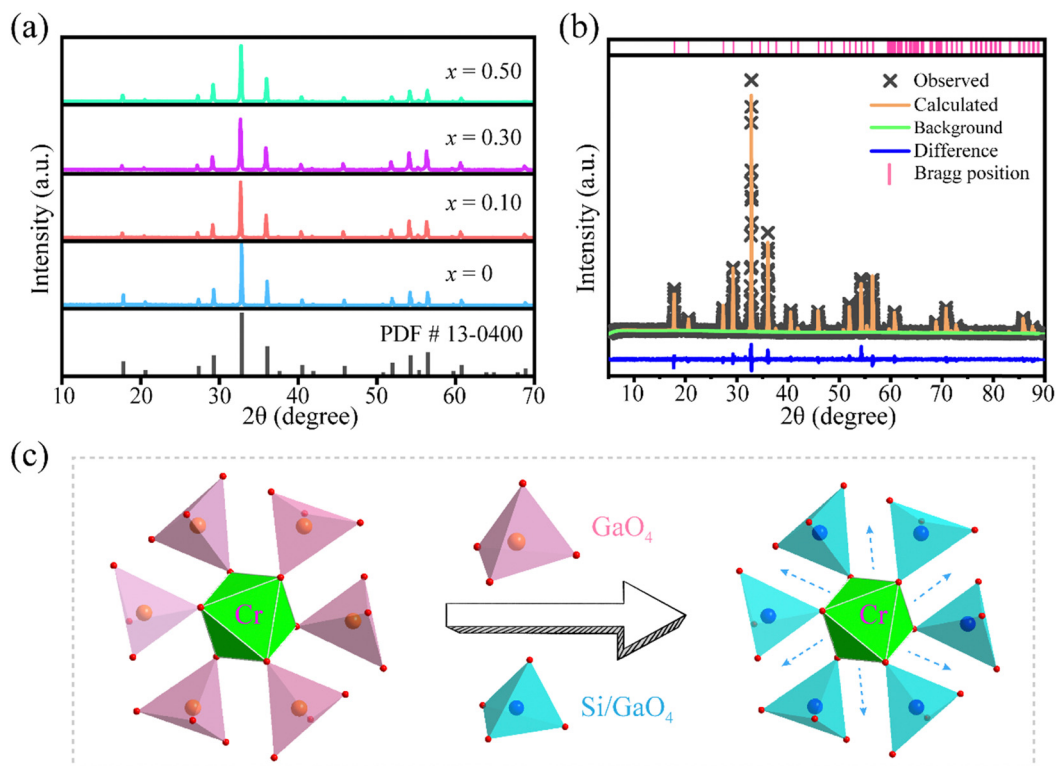
### 2.3 LED fabrication

The NIR pc-LED device was fabricated by coating the prepared NIR phosphor on an InGaN blue chip (450 nm, 1 W) with a mass ratio of the phosphor to epoxy resin of 1:1. The current-dependent electroluminescence and output power were collected using an ATA-1000 photoelectric measuring system (EVERFINE, China).

## 3. Results and discussion

### 3.1. Crystal structure of $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}$

The phase purity of as-prepared  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  ( $x = 0-0.5$ ) phosphors was examined by X-ray diffraction (XRD). All the diffraction peaks are in good agreement with the standard data of  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  (PDF no. 13-0400) and no impurity peaks are observed (Fig. 1a), indicating that the co-substitution of  $[\text{Lu}^{3+}-\text{Ga}^{3+}]$  by  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  has almost no influence on the crystal structure.



**Fig. 1** (a) XRD patterns of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  ( $x = 0-0.5$ ). (b) The Rietveld refinement of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  ( $R_p = 6.00\%$ ,  $R_{wp} = 10.23\%$ ). (c) The crystal structure.

The Rietveld refinement (Fig. 1b) is performed using  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  as the starting model, and the small residual factors ( $R_p = 6.00\%$ ,  $R_{wp} = 10.23\%$ , Table S1, ESI†) further confirm the good phase purity.  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}$  crystallize in the same space group  $Ia\bar{3}d$  (no. 230) as the  $\text{Lu}_3\text{Ga}_5\text{O}_{12}$  garnet and there are three kinds of polyhedra in the garnet structure:  $(\text{Lu}/\text{Ca})\text{O}_8$  dodecahedra,  $\text{GaO}_6$  octahedra and  $(\text{Ga}/\text{Si})\text{O}_4$  tetrahedra (Fig. 1c).  $\text{Cr}^{3+}$  ions ( $r = 0.615 \text{ \AA}$ , CN = 6) prefer to replace the octahedral  $\text{Ga}^{3+}$  site ( $r = 0.62 \text{ \AA}$ , CN = 6) due to the similar radius. The  $(\text{Ga}/\text{Cr})\text{O}_6$  octahedra might be enlarged and distorted (Fig. 1c) due to the much smaller ionic radius of  $\text{Si}^{4+}$  ( $r = 0.26 \text{ \AA}$  and CN = 4) than  $\text{Ga}^{3+}$  ( $r = 0.47 \text{ \AA}$  and CN = 4), indicating a weakening crystal field strength,<sup>15</sup> and then a broadened emission can be anticipated with increasing  $x$  values in  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  phosphors.

Fig. S1 (ESI†) presents the SEM and elemental mapping images of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  phosphors, which show an irregular shape with several hundred nanometers in size. All the elements such as Lu, Ga, Ca, Si, O and Cr are found to be distributed uniformly in the matrix.

### 3.2. PL properties of $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$

To investigate the influence of  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  co-substitution on the PL properties, the emission spectra of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  are studied in detail. It can be seen that the room-temperature PL spectrum of  $\text{Lu}_3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$  is dominated by a sharp emission peaked at 705 ( $R_1$  line) and 691 nm ( $R_2$  line) corresponding to

${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition of  $\text{Cr}^{3+}$  (Fig. 2a). Meanwhile, the broadband emission from 620 to 830 nm comes from  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition.<sup>16</sup> With increasing  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  co-substitution, the PL intensity of the broadband  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  emission increases significantly (Fig. 2b), leading to an increased value (from 43 to 150 nm, Fig. S2, ESI†) of full width at half maximum (FWHM).

The spectral broadening of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  is probably related to the decrease of crystal field strength with  $x$  value. As is well known, the energy of the  ${}^4\text{T}_2$  level of  $\text{Cr}^{3+}$  is lower than that of the  ${}^2\text{E}$  level when exposed to a weak crystal field, according to the Tanabe–Sugano diagram for the  $3d^3$  electron configuration (Fig. 2c), and the PL spectra consist of an intense broadband emission band. The energy of the  ${}^2\text{E}$  level is lower as a result of a strong crystal field, and the PL spectra consist of a sharp emission line. When  $\text{Cr}^{3+}$  ions are exposed to intermediate crystal fields, both emission bands are visible in the PL spectra. Therefore, to further explore the influence of  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  co-substitution on the PL properties, the crystal field splitting parameters ( $Dq$  and  $B$ ) of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  ( $x = 0-0.5$ ) are calculated from the PL excitation spectra (PLE, Fig. S3, ESI†) with the following equations:<sup>17,18</sup>

$$10Dq = E({}^4\text{T}_2) = E({}^4\text{A}_2 \rightarrow {}^4\text{T}_2) \quad (1)$$

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

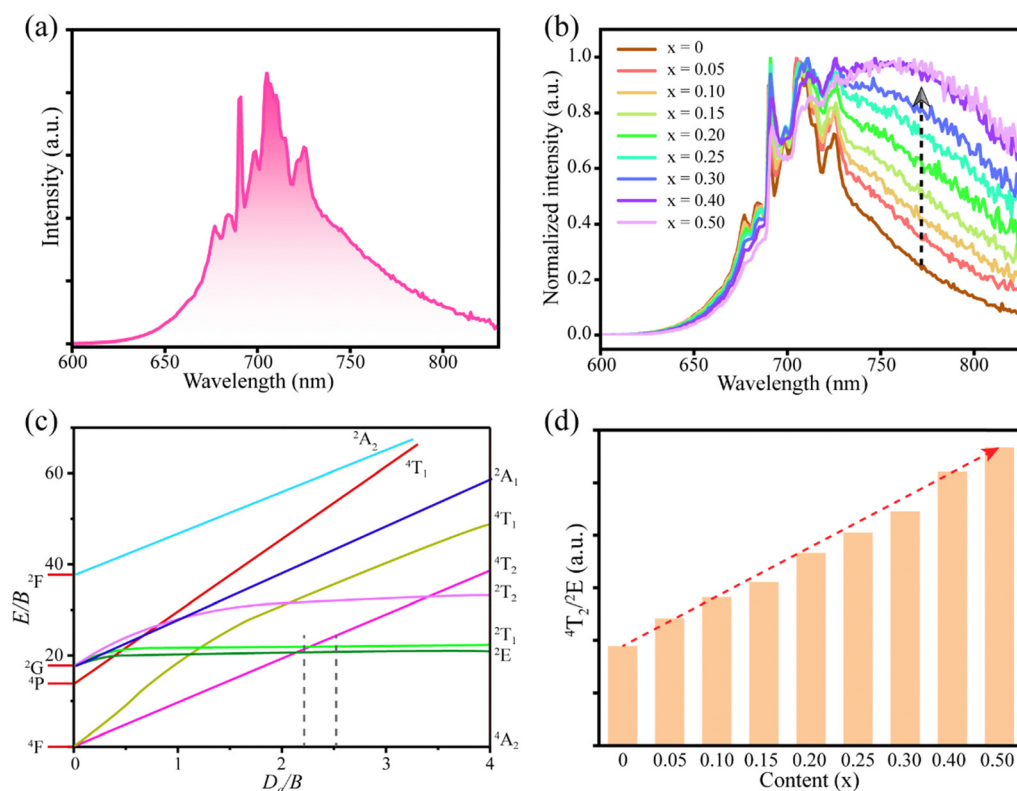


Fig. 2 (a) Emission spectrum of  $\text{Lu}_3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$  ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ). (b) Emission spectra ( $\lambda_{\text{ex}} = 430 \text{ nm}$ ) of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  ( $x = 0-0.5$ ). (c) Tanabe–Sugano diagram of  $\text{Cr}^{3+}$  ions in an octahedral coordination. (d) Fluorescence intensity ratio (FIR) of  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  to  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  [ $I({}^4\text{T}_2)/I({}^2\text{E})$ ] transitions of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  ( $x = 0-0.5$ ).

**Table 1** Crystal field splitting parameter  $Dq$ , Racah parameter  $B$  and values of energy levels of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.5$ )

| $x$  | $Dq$ ( $\text{cm}^{-1}$ ) | $B$ ( $\text{cm}^{-1}$ ) | $Dq/B$ | $\Delta_1$ ( $\text{cm}^{-1}$ ) | $S\hbar\omega$ ( $\text{cm}^{-1}$ ) | $\Delta_2$ ( $\text{cm}^{-1}$ ) |
|------|---------------------------|--------------------------|--------|---------------------------------|-------------------------------------|---------------------------------|
| 0    | 1652.89                   | 655.07                   | 2.52   | 2344.53                         | 1551.25                             | 793.28                          |
| 0.05 | 1639.34                   | 667.91                   | 2.45   | 2209.05                         | 1592.36                             | 616.69                          |
| 0.1  | 1631.32                   | 680.03                   | 2.40   | 2148.91                         | 1648.02                             | 500.89                          |
| 0.15 | 1626.02                   | 680.84                   | 2.39   | 2115.89                         | 1674.10                             | 441.79                          |
| 0.2  | 1623.38                   | 684.91                   | 2.37   | 2109.47                         | 1709.93                             | 399.54                          |
| 0.25 | 1618.12                   | 685.71                   | 2.36   | 2116.53                         | 1742.04                             | 374.49                          |
| 0.3  | 1612.90                   | 693.89                   | 2.32   | 2064.33                         | 1749.85                             | 314.48                          |
| 0.4  | 1602.56                   | 702.92                   | 2.28   | 1960.94                         | 1733.48                             | 227.46                          |
| 0.5  | 1594.90                   | 715.45                   | 2.23   | 1923.72                         | 1706.64                             | 217.08                          |

$$\Delta E = E(^4T_1) - E(^4T_2) = E(^4A_2 \rightarrow ^4T_1) - E(^4A_2 \rightarrow ^4T_2) \quad (3)$$

Here,  $Dq$  and  $B$  represent the crystal field strength and repulsive force between 3d electrons, respectively.<sup>16</sup> The calculated results are shown in Table 1. It can be seen that the  $Dq/B$  values of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$  decrease from 2.52 to 2.23 with increasing  $x$ , indicating that a decreased crystal field strength is obtained with increasing  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  co-substitution. The weakened crystal field strength downshifts the  $^4T_2$  energy level (Fig. 2c), due to which the possibility of thermal population at the  $^4T_2$  state will increase compared with that at the  $^2E$  state,<sup>15</sup> leading to an increased fluorescence intensity ratio (FIR) of  $^4T_2 \rightarrow ^4A_2$  to  $^2E \rightarrow ^4A_2$  [ $I(^4T_2)/I(^2E)$ ] transitions (Fig. 2d). The decreased lifetime of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  (Fig. S4, ESI<sup>†</sup>) is another evidence for the thermally populated  $^4T_2$  energy level.<sup>19</sup>

To further analyze the PL properties of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  in detail, a configurational coordinate diagram

(Fig. 3a) is constructed based on the obtained spectral characteristics.  $\Delta_1$  is the energetic difference between the  $R_1$  line and the maximum of the  $^4A_2 \rightarrow ^4T_2$  PLE band.<sup>20</sup> The energetic difference  $\Delta_2$  between  $^4T_2$  and  $^2E$  electronic manifolds, which determines the thermal occupation of the  $^4T_2$  energy level, can be obtained from the following relationship:<sup>21,22</sup>

$$\Delta_2 = \Delta_1 - S\hbar\omega \quad (4)$$

where  $S$  and  $\hbar\omega$  are the Huang-Rhys factor and effective phonon energy, respectively. The values of  $S$  and  $\hbar\omega$  can be calculated using the following equations:<sup>23</sup>

$$\Delta E = (2S - 1)\hbar\omega \quad (5)$$

$$\Gamma(T) = 2.35\hbar\omega \sqrt{S \coth\left(\frac{\hbar\omega}{2kT}\right)} \quad (6)$$

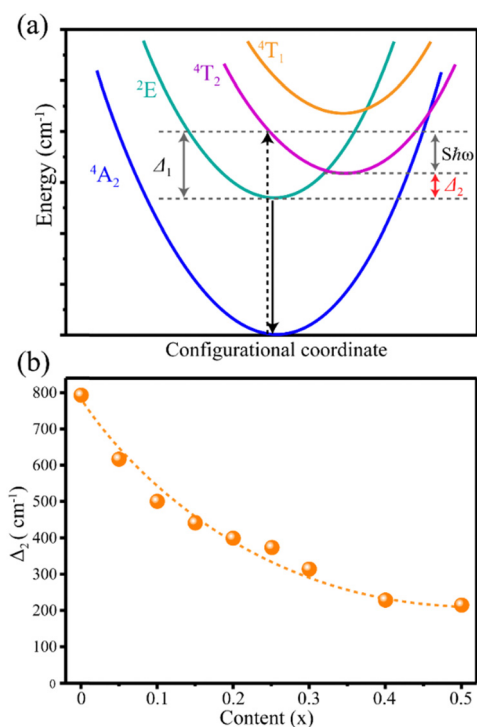
where  $\Delta E$  is the Stokes shift (energy difference between the first absorption and corresponding emission bands) and  $\Gamma(T)$  is the FWHM of the emission band at temperature  $T$ . The  $\Delta_2$  values of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  are calculated according to the above equations and the results are shown in Fig. 3b. It can be seen that the values of  $\Delta_2$  decrease with increasing  $x$ , indicating a higher probability of  $^2E \rightarrow ^4T_2$  transition (*i.e.* thermally populated  $^4T_2$  state) which is consistent with the enhanced  $^4T_2 \rightarrow ^4A_2$  broadband emission and increased FIR of  $I(^4T_2)/I(^2E)$  of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  (as shown in Fig. 2b and d).

### 3.3. Thermal stability of $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:\text{Cr}^{3+}$

The PL intensity of phosphors usually shows a decreasing trend due to enhanced non-radiative transition with increasing temperature, which is a major obstacle for their application. Therefore, it is of great importance to develop NIR phosphors with improved thermal stability. In previous work,<sup>24</sup> it is verified that the PL thermal stability of  $\text{Cr}^{3+}$  can be optimized by the electron occupation between  $^4T_2$  and  $^2E$  states. As discussed above, the energetic difference  $\Delta_2$  and crystal field strength (Table 1) between  $^4T_2$  and  $^2E$  states (thermal population of the  $^4T_2$  state) of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  can be easily tuned by co-substitution of  $[\text{Lu}^{3+}-\text{Ga}^{3+}]$  by  $[\text{Ca}^{2+}-\text{Si}^{4+}]$ , which may provide an alternative way for improving the thermal stability.

In order to evaluate the influence of  $[\text{Ca}^{2+}-\text{Si}^{4+}]$  co-substitution on thermal stability, the temperature-dependent PL spectra of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0, 0.15$  and  $0.30$ ) are studied in detail (Fig. 4 and Fig. S5, ESI<sup>†</sup>). On the one hand, it is noted that the integrated PL intensity of all  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0, 0.15$  and  $0.30$ ) samples increases first and then decreases with increasing temperature (Fig. 4a-c). On the other hand, the thermal stability of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  becomes better and better with increasing  $x$  and the PL intensity at  $x = 0.30$  reaches up to 125% and 121% at 425 K and 475 K compared with that at 300 K (Fig. 4c), respectively, which is much better than those of most  $\text{Cr}^{3+}$ -activated broadband NIR phosphors (Table 2).

To understand the mechanism behind the abnormal thermal stability, the PL spectra are deconvoluted into separate  $^4T_2 \rightarrow ^4A_2$  broadband and  $^2E \rightarrow ^4A_2$  sharp-line emissions for all



**Fig. 3** (a) Schematic configurational coordinate diagram and (b) energy difference between  $^4T_2$  and  $^2E$  states of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{4.99-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0-0.5$ ).

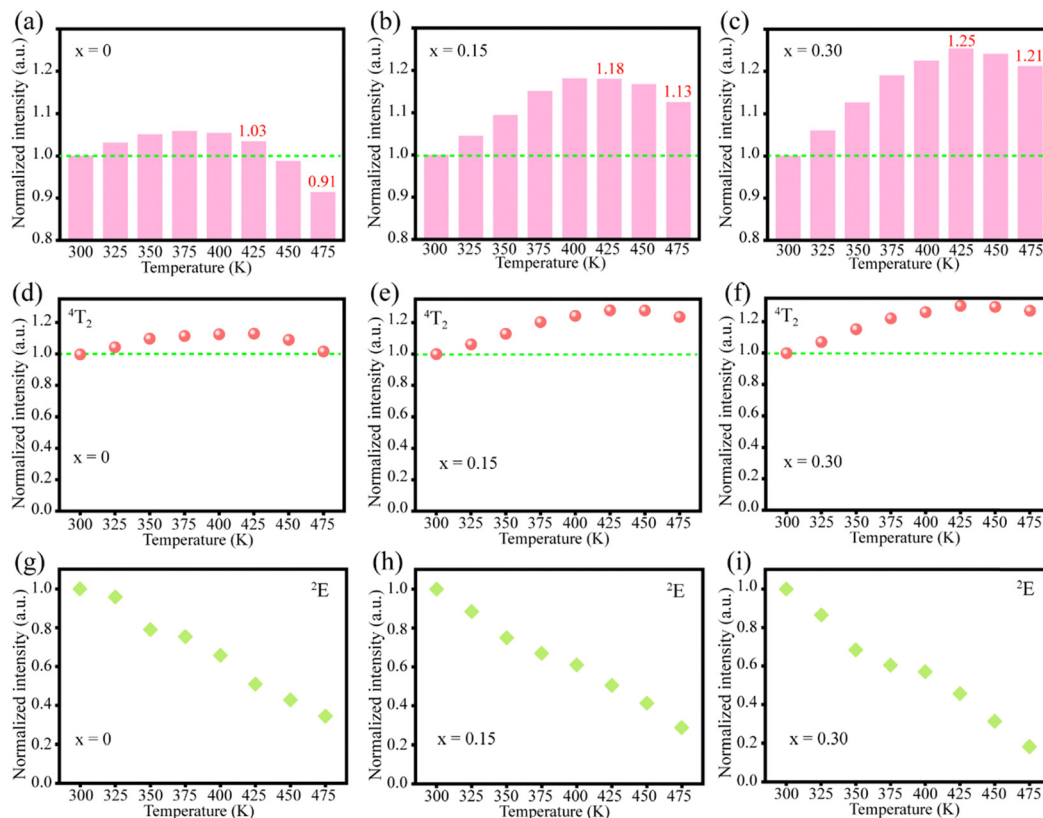


Fig. 4 Normalized PL intensity of (a)–(c)  ${}^4T_2 + {}^2E \rightarrow {}^4A_2$ , (d)–(f)  ${}^4T_2 \rightarrow {}^4A_2$  and (g)–(i)  ${}^2E \rightarrow {}^4A_2$  transitions of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  as a function of temperature (300–475 K) with  $x = 0, 0.15$  and  $0.30$ , respectively.

temperatures.<sup>22</sup> The PL intensity of the  ${}^4T_2 \rightarrow {}^4A_2$  broadband emission (Fig. 4d–f) exhibits a similar trend to the corresponding total PL intensity (Fig. 4a–c), while the  ${}^2E \rightarrow {}^4A_2$  sharp-line emission (Fig. 4g–i) decreases monotonically with  $x$ . In the  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}$  system, the  ${}^2E$  state can serve as a reservoir for the higher lying  ${}^4T_2$  state.<sup>19</sup> The electrons will migrate from the  ${}^2E$  to  ${}^4T_2$  energy level with increasing temperature and reach a new thermal equilibrium, leading to a thermally populated  ${}^4T_2$  state (which can be further verified by the decay curves in Fig. S6, ESI†). This explains why  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  phosphors exhibit an abnormal thermal stability before 425 K. At higher temperatures, the  ${}^4T_2 \rightarrow {}^4A_2$  broadband emission dominates the PL spectra and then a

traditional thermal quenching phenomenon is observed due to the increased non-radiative rate of the  ${}^4T_2$  level.

The improved thermal stability of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  ( $x = 0, 0.15$  and  $0.30$ ) with increasing  $x$  is due to the different energetic difference  $\Delta_2$  between  ${}^4T_2$  and  ${}^2E$  states which has a great influence on the initial thermal equilibrium between  ${}^4T_2$  and  ${}^2E$  energy levels (*i.e.* FIR of  $I({}^4T_2)/I({}^2E)$ ) and determines the thermal quenching performance at elevated temperatures. The PL intensity of  ${}^2E \rightarrow {}^4A_2$  sharp-line emission is strong at large  $\Delta_2$  values (small  $x$ ), whose decrease has a great influence on the whole PL intensity with increasing temperature. Then the  ${}^2E \rightarrow {}^4T_2$  transition strengthens with decreasing  $\Delta_2$  (increasing  $x$ ). Finally, the  ${}^2E \rightarrow {}^4T_2$  transition has little influence on the thermal quenching performance due to the insufficient  ${}^2E$  electrons for smaller  $\Delta_2$  values. That is why the thermal stability of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  decreases when  $x > 0.30$  (Fig. S7, ESI†). In this work, it is obvious that  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  phosphors have optimal  $\Delta_2$  values and the best thermal stability when  $x = 0.30$ .

Considering the higher thermal stability (Fig. 3c) and PL intensity (Fig. S8, ESI†) of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  at  $x = 0.30$ , a series of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  with various  $\text{Cr}^{3+}$  concentrations were prepared (Fig. S9, ESI†) to further optimize the PL properties (Fig. 5a). The PL intensity of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$  reaches its maximum value at  $x = 0.02$  (Fig. S10, ESI†) and then decreases owing to the concentration

Table 2 Thermal stability of  $\text{Cr}^{3+}$ -activated broadband NIR phosphors

| Phosphors  | $\lambda_{\text{em}}$ (nm) | $I_{423\text{K}}$ (%) | Ref.      |
|--|----------------------------|-----------------------|-----------|
| $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7}\text{Si}_{0.3}\text{O}_{12}:\text{Cr}^{3+}$ | 748                        | 125                   | This work |
| $\text{Y}_3\text{In}_2\text{Ga}_3\text{O}_{12}:\text{Cr}^{3+}$                             | 760                        | 100                   | 25        |
| $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}:\text{Cr}^{3+}$                            | 770                        | 97.4                  | 26        |
| $\text{GaTaO}_4:\text{Cr}^{3+}$  | 840                        | 60                    | 27        |
| $\text{ScBO}_3:\text{Cr}^{3+}$   | 800                        | 51                    | 28        |
| $\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12}:\text{Cr}^{3+}$                            | 750                        | 99                    | 29        |
| $\text{K}_2\text{NaInF}_6:\text{Cr}^{3+}$  | 774                        | 78.3                  | 30        |
| $\text{K}_2\text{NaIScF}_6:\text{Cr}^{3+}$   | 765                        | 89.6                  | 31        |
| $\text{ScF}_3:\text{Cr}^{3+}$  | 853                        | 85.5                  | 32        |

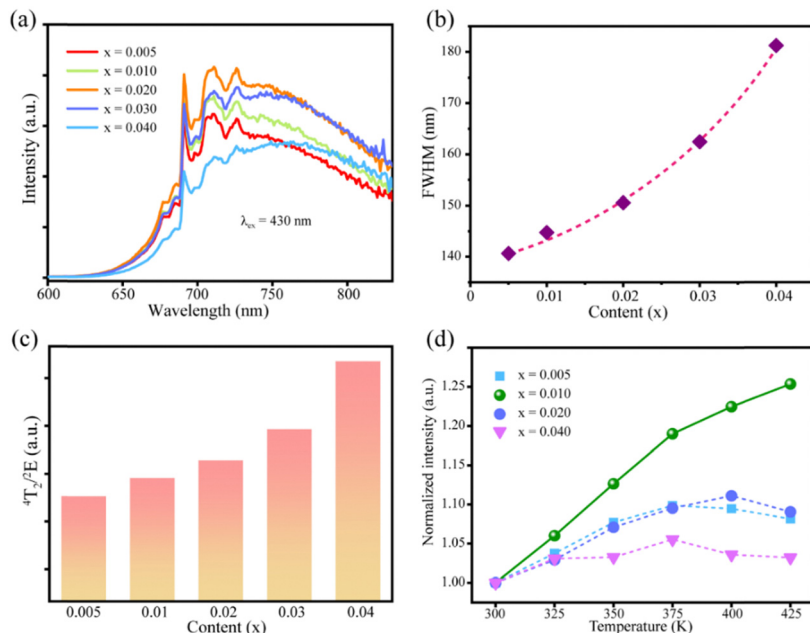


Fig. 5 (a) Emission spectra, (b) FWHM and (c) FIR of  ${}^4T_2$   ${}^4A_2$  to  ${}^2E \rightarrow {}^4A_2$  transitions of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{xCr}^{3+}$  ( $x = 0.005$ – $0.040$ ). (d) Normalized PL intensity of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{xCr}^{3+}$  as a function of temperature (300–425 K).

quenching effect. Moreover, it is found that both the FWHM (from 140 to 182 nm, Fig. 5b) and FIR (Fig. 5c) of  $I({}^4T_2)/I({}^2E)$  show an increasing trend as the  $\text{Cr}^{3+}$  concentration increases, just like that of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$  (Fig. 2b, d). But the reason for the increased  ${}^4T_2 \rightarrow {}^4A_2$  broadband emission with increasing  $\text{Cr}^{3+}$  content is different from that of  $\text{Lu}_{3-x}\text{Ca}_x\text{Ga}_{5-x}\text{Si}_x\text{O}_{12}:0.01\text{Cr}^{3+}$

(which is due to a decreased crystal field strength). In this case, the normalized PLE spectra of  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{xCr}^{3+}$  almost overlap with each other (Fig. S11 (ESI<sup>+</sup>), implying an unchanged crystal field strength). It is considered that the distance between  $\text{Cr}^{3+}$  and  $\text{Cr}^{3+}$  ions in  $\text{Lu}_{2.7}\text{Ca}_{0.3}\text{Ga}_{4.7-x}\text{Si}_{0.3}\text{O}_{12}:\text{xCr}^{3+}$  decreases with increasing  $\text{Cr}^{3+}$  concentration, which is conducive

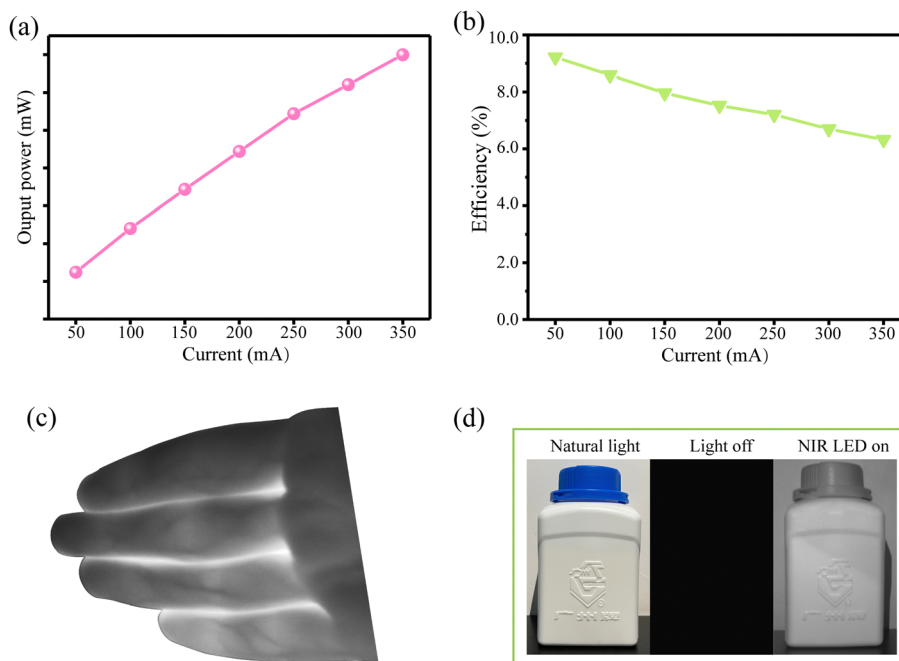


Fig. 6 (a) Output power and (b) photoelectric conversion efficiency of the fabricated NIR-LED device as a function of driven current. (c) Photograph of fingers taken with the NIR camera under irradiation of the LED device. (d) Photographs of a bottle under natural light and NIR LED light captured with a visible camera (left and middle) and the NIR camera (right).

to the electron migration from the  ${}^2E$  to  ${}^4T_2$  state, thus resulting in a thermally populated  ${}^4T_2$  state (*i.e.* enhanced  ${}^4T_2 \rightarrow {}^4A_2$  broadband emission) at higher  $Cr^{3+}$  content.<sup>24</sup>

Due to the varying FIR values of  $I({}^4T_2)/I({}^2E)$  of  $Lu_{2.7}Ca_{0.3}Ga_{4.7-x}Si_{0.3}O_{12}:xCr^{3+}$ , it is necessary to investigate the thermal stability. The temperature-dependent PL spectra of  $Lu_{2.7}Ca_{0.3}Ga_{4.7-x}Si_{0.3}O_{12}:xCr^{3+}$  are measured and shown in Fig. 5d and Fig. S12 (ESI<sup>†</sup>). As expected, the thermal stability of  $Lu_{2.7}Ca_{0.3}Ga_{4.7-x}Si_{0.3}O_{12}:xCr^{3+}$  becomes better before  $x = 0.010$  and then decreases due to the gradually exhausting  ${}^2E$  electrons at higher  $Cr^{3+}$  concentration. From the obtained results, it can be inferred that both the  $\Delta_2$  value and  $Cr^{3+}$  concentration have a significant influence on the thermal stability of  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:Cr^{3+}$ .

### 3.4. NIR pc-LED applications

Considering the excellent thermal quenching behavior of the as-prepared samples, a NIR pc-LED was fabricated by combining a  $Lu_{2.7}Ca_{0.3}Ga_{4.7}Si_{0.3}O_{12}:Cr^{3+}$  phosphor with a commercial blue InGaN chip and the electroluminescence spectrum is shown in Fig. S13 (ESI<sup>†</sup>). The NIR output power (Fig. 6a) increases monotonously from 50 to 350 mA, while the photoelectric conversion efficiency decreases slightly (Fig. 6b). The NIR light from the LED device can penetrate human fingers easily and the blood vessels can be observed clearly (Fig. 6c). In addition, with the aid of a NIR camera, the words on the bottle surface are clearly distinguished by using the packaged NIR pc-LED as the light source (Fig. 6d). The above results indicate that the as-prepared sample can be potentially used in the fields of bio-imaging and night vision.

## 4. Conclusions

In summary,  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:Cr^{3+}$  phosphors with tunable PL properties and abnormal thermal stability were synthesized by a high-temperature solid-state method. The FWHM of the PL spectra of  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:Cr^{3+}$  broadens from 43 to 150 nm due to the enhanced  ${}^4T_2 \rightarrow {}^4A_2$  emission, resulting from a decreased crystal field strength. The calculated energetic difference ( $\Delta_2$ ) between  ${}^4T_2$  and  ${}^2E$  states also shows a decreasing trend with increasing  $[Ca^{2+}-Si^{4+}]$  co-substitution, leading to a thermally populated  ${}^4T_2$  state. Based on the different thermal population of the  ${}^4T_2$  state, the thermal stability of  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:Cr^{3+}$  can be easily tuned. With the optimal  $[Ca^{2+}-Si^{4+}]$  co-substitution,  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:0.01Cr^{3+}$  ( $x = 0.30$ ) shows an abnormal thermal quenching performance and the PL intensity can reach up to 125% and 121% at 425 K and 475 K compared with that at 300 K, respectively. In addition, it is found that the  ${}^4T_2/{}^2E$  thermal population and PL thermal stability of  $Cr^{3+}$  can be further optimized by the  $Cr^{3+}$  concentration. Finally, a NIR pc-LED based on the  $Lu_{3-x}Ca_xGa_{5-x}Si_xO_{12}:Cr^{3+}$  phosphor shows excellent performance in bio-imaging and night vision.

## Data availability

The data supporting this article have been included as part of the ESI.<sup>†</sup>

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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