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# Research Papers Cr<sup>3+</sup> and Nd<sup>3+</sup> co-activated garnet phosphor for NIR super broadband pc-LED application

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## ABSTRACT

Near-infrared phosphor converted light emitting diodes (NIR pc-LEDs), as a compact light source, play a constructive role in wearable optical biosensing devices. In order to detect the properties of different substances, the NIR emission should be as wide as possible. The typical strategy for broadening the band is the superposition emission of  $Cr^{3+}$  and  $Yb^{3+}$ , the bandwidth of which is 300–320 nm, and it needs to be further broadened. In this paper, NIR Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> garnet phosphor, co-activated by  $Cr^{3+}$  and  $Nd^{3+}$ , is prepared. The emission quantum efficiencies of Nd<sup>3+</sup> at 900 nm and 1060 nm are close to 100%, and the emission band is complementary to that of Yb<sup>3+</sup> at 1030 nm. An efficient super broadband NIR pc-LEDs (47.6 mW@100 mA), with the bandwidth of 350 nm, are achieved. The bandwidth and the efficiency of the pc-LEDs are improved greatly, compared with other reported ones.

## 1. Introduction

Near-infrared (NIR) light source, with continuous emission in 700–1100 nm, is demanded by NIR spectroscopy, which can be applied in food analysis, bio-sensing and medicine [1–8]. Phosphor converted LED (pc-LED) is the most promising one in recent years. The broadband NIR pc-LED is fabricated by integrating the broadband NIR phosphor and blue LED chip. Thus, developing efficient broadband NIR phosphor is particularly important.

Many broadband NIR phosphors have been reported recently [9–31]. They are mainly  $Cr^{3+}$  singly doped materials, such as  $Lu_3Al_5O_{12}$ :  $Ce^{3+}$ ,  $Cr^{3+}$ , [6] ScBO<sub>3</sub>:  $Cr^{3+}$ , [7] Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:  $Cr^{3+}$ , [19] La<sub>2</sub>MgZrO<sub>6</sub>:  $Cr^{3+}$ , [20] Ca<sub>3</sub>Sc<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>:  $Cr^{3+}$ , [21] LiInSi<sub>2</sub>O<sub>6</sub>:  $Cr^{3+}$  [22] and ZnAl<sub>2</sub>O<sub>4</sub>:  $Cr^{3+}$  [23]. In addition, Xia et al. developed Eu<sup>2+</sup> activated K<sub>3</sub>LuSi<sub>2</sub>O<sub>7</sub> phosphor, which showed the emission at 740 nm and a bandwidth of 160 nm [24]. Singly doped phosphors generally showed a bandwidth less than 200 nm, which limited the development of NIR pc-LED applications.

To further broaden the NIR emission band, emitting centers co-doped phosphors were developed. La<sub>3</sub>Ga<sub>5</sub>GeO<sub>14</sub>: Cr<sup>3+</sup>, reported by Liu et al., showed a bandwidth of 330 nm, which was originated from two Cr<sup>3+</sup>

centers. The NIR output power was 18.2 mW at 350 mA drive current [25]. The NIR emission of Ca<sub>3</sub>Sc<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>:  $Cr^{3+}$ ,  $Ln^{3+}$  ( $Ln = Nd^{3+}$ ,  $Yb^{3+}$ ), reported by Yao et al., showed a bandwidth of 330 nm, contributed from the energy transfer from  $Cr^{3+}$  to  $Nd^{3+}$  and  $Cr^{3+}$  to  $Yb^{3+}$ . And the NIR output power was 14.6 mW at 100 mA, corresponding to 4.9% electricity-to-NIR efficiency [26]. Recently, NIR broadband pc-LED with a bandwidth of 210 nm was fabricated by Yao et al., using LiScP<sub>2</sub>O<sub>7</sub>:  $Cr^{3+}$ ,  $Yb^{3+}$  phosphor. And 36 mW NIR output light with 12% electricity-to-NIR efficiency at 100 mA drive current was achieved [27]. Basore et al. fabricated NIR pc-LED using the blend of Gd<sub>3</sub>Sc<sub>1</sub> <sub>5</sub>Al<sub>0.5</sub>.  $Ga_3O_{12}$ :  $Cr^{3+}$ ,  $Yb^{3+}$  and LiInSi<sub>2</sub>O<sub>6</sub>:  $Cr^{3+}$  phosphors. The pc-LED offered a 300 nm NIR bandwidth, and 50 mW NIR output power with 17% electricity-to-NIR efficiency at 100 mA [28]. In our previous work, Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Yb<sup>3+</sup> showed a bandwidth of 320 nm and NIR output light was 41.8 mW at 100 mA drive current, corresponding to 14.3% electricity-to-NIR efficiency [29]. To meet the further demand of applications, the NIR pc-LEDs with broader bandwidth and high electricity-to-NIR efficiency are urgently needed.

In this study,  $Cr^{3+}$  and  $Nd^{3+}$  co-activated  $Ca_2LuZr_2Al_3O_{12}$  (CLZA) is fabricated via high temperature solid state reaction. Its emission

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Received 1 November 2021; Received in revised form 19 January 2022; Accepted 18 February 2022 Available online 19 February 2022 0025-5408/© 2022 Elsevier Ltd. All rights reserved. spectrum including a  $Cr^{3+}$  emission band, at 800 nm, and a group of Nd<sup>3+</sup> emission lines, distributed in range of 870–1100 nm and excited by energy transfer (ET) from  $Cr^{3+}$  to Nd<sup>3+</sup>. Optical properties and thermal stabilities of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:  $Cr^{3+}$ , Nd<sup>3+</sup> are analyzed. A widely distributed NIR emission with a bandwidth of 350 nm is achieved. The as fabricated pc-LED offers 22.3% electricity-to-NIR efficiency at 10 mA, and the efficiency decreases to 16.2% at 100 mA with 47.6 mW NIR output power. The research data indicates that optical performance has greatly improved, compared with ever reported ones.

## 2. Experiment

# 2.1. Materials and synthesis

 $\rm Nd^{3+}$  and  $\rm Cr^{3+}$  co-activated  $\rm Ca_2LuZr_2Al_3O_{12}$  phosphors are synthesized via the high-temperature solid state reaction.  $\rm CaCO_3$  (99.99%),  $\rm Lu_2O_3$  (99.9%),  $\rm ZrO_2$  (99.99%),  $\rm Al_2O_3$  (99.9%),  $\rm Cr_2O_3$  (99.99%), and  $\rm Nd_2O_3$  (99.9%) are used as raw materials. The accurately weighed mixtures are grinded and put into the tube furnace heating by 3 °C/min, and protected by 10%H<sub>2</sub>/N<sub>2</sub> gas flow. At first, the temperature raised to 900 °C, maintaining 1 h, and then raised to 1600 °C, maintaining 4 h. The final products, some green powders, are acquired after cooling down to room temperature. The PC-LED is fabricated by 460 nm chip and the blend of two NIR phosphor. The Ca\_2LuZr\_2Al\_3O\_{12}:8%Cr^{3+}, 2%Nd<sup>3+</sup> phosphors, Ca\_2LuZr\_2Al\_3O\_{12}:8%Cr^{3+}, 2%Yb^{3+} phosphors and epoxide resin were fully mixed with 1:1:2 weigh ratio, then put it on the 460 nm chip, and then solidified at 200 °C for 20 min.

## 2.2. Characterization

The crystal pattern of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> is detected by X-ray diffraction (XRD) (Bruker D8 Focus diffract meter, in the 20 range from 15° to 75° with Cu Kα radiation ( $\lambda$ =1.54056 Å) operating at 40 kV, 30 mA); Photoluminescence excitation spectra are measured by FLS900 spectrometer (Edinburgh Instruments, U.K.); Photoluminescence spectra and the temperature-dependent properties are measured by HAAS2000 photoelectric spectrometer (350–1100 nm, EVERFINE, China), equipped with an excitation source (a 455 nm laser diode (LD)) and a THMS600E cooling-heating platform (77–873 K, Linkam Scientific Instruments, UK); The emission lifetime of Cr<sup>3+</sup> and Nd<sup>3+</sup> are measured by TRIAX 550 spectrometer, a pulsed laser as an excitation source; The photoelectric properties of the pc-LEDs are measured by HAAS2000 photoelectric measuring system (350–1100 nm, EVERFINE, China); The

internal quantum efficiency (IQE) is measured using an absolute photoluminescence quantum yield measurement system (Quantaurus-QY Plus C13534–12, Hamamatsu Photonics).

#### 3. Results and discussion

## 3.1. XRD patterns and crystal structure

The XRD patterns of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup>, xNd<sup>3+</sup> (x = 0-8%) are shown in Fig. 1a. The XRD peaks shift to the left as the increase of x. This is because Nd<sup>3+</sup> has replaced Lu<sup>3+</sup> in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup>, Nd<sup>3+</sup>, and the radius of Nd<sup>3+</sup> (1.109 Å) is larger than that of Lu<sup>3+</sup>(0.977 Å) [32]. A weak XRD peak (asterisk) of ZrO<sub>2</sub> is also detected at around 30°. Previous studies show that Cr<sup>3+</sup> does not emit in ZrO<sub>2</sub> [19, 29]. Thus, the influence of ZrO<sub>2</sub> on luminescent properties of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:Cr<sup>3+</sup>, Nd<sup>3+</sup> can be ignored. The crystal structure diagram of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> and coordinate environments of Ca<sup>2</sup>+/Lu<sup>3+</sup>, Zr<sup>4+</sup> and Al<sup>3+</sup> are shown in Fig. 1b. The crystal structure of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> is a garnet, as shown. The Ca<sup>2+</sup>/Lu<sup>3+</sup> connects with 8 oxygen atoms to form a [CaO<sub>8</sub>] polyhedron. Zr<sup>4+</sup> forms a [ZrO<sub>6</sub>] octahedron. Al<sup>3+</sup> forms a [AlO<sub>4</sub>] tetrahedron.

## 3.2. Luminescence properties and energy transfer

The excitation and emission spectra of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8% Cr<sup>3+</sup>, monitored at 800 nm, are showed in Fig. 2a. From the picture, three excitation bands, at 300 nm, 460 nm and 640 nm, can be observed, which are assigned to  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  (from  ${}^{4}P$  orbit),  ${}^{4}A_{2g} \rightarrow {}^{4}T_{1g}$  (from  ${}^{4}F$ ) and  ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}$  (from  ${}^{4}F$ ) transitions of  $Cr^{3+}$ , respectively [29]. The weak excitation peak at 698 nm is originated from  ${}^{4}A_{2g} \rightarrow {}^{2}E_{g}$  transition. The emission spectrum of Ca2LuZr2Al3O12: 8%Cr3+ shows a broadband at 800 nm, originated from  ${}^{4}T_{2g}({}^{4}F) \rightarrow {}^{4}A_{2g}$  transition of  $Cr^{3+}$ . The excitation and emission spectra of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 4%Nd<sup>3+</sup> can be found in Fig. 2b, in which a group of emission lines are observed. The line of 850–950 nm is originated from  ${}^{4}F_{3/2} \rightarrow {}^{4}I_{9/2}$  transition of Nd<sup>3+</sup>, 1050–1150 nm is  ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$  and 1300–1450 nm is  ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ [33–35]. The excitation spectrum of Nd<sup>3+</sup> shows series lines, which are originated from transitions of  $Nd^{3+}$ , from  ${}^{4}I_{9/2}$  to the  ${}^{4}F_{3/2}$  or upper energy levels. The overlap of  $Nd^{3+}$  excitation peaks and the  $Cr^{3+}$  emission band indicates the possibility of energy transfer from  $Cr^{3+}$  to  $Nd^{3+}$ . The excitation spectrum of  $Cr^{3+}$  and  $Nd^{3+}$  co-doped  $Ca_2LuZr_2Al_3O_{12}$  are shown in Fig. 2c and the energy transfer process is more evident, as shown. Moreover, the diffuse reflection spectra of the Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:



Fig. 1. XRD patterns of  $Ca_2LuZr_2Al_3O_{12}$ :8% $Cr^{3+}$ , xNd<sup>3+</sup> (x = 0-8%) (a) and structure diagram of  $Ca_2LuZr_2Al_3O_{12}$  and coordinate environments of  $Ca^{2+}/Lu^{3+}$ ,  $Zr^{4+}$  and  $Al^{3+}$  (b). The symbol \* represents the peak due to  $ZrO_2$ .



Fig. 2. Excitation and emission spectra of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:8%Cr<sup>3+</sup> (a), Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 4%Nd<sup>3+</sup> (b) and Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 4%Nd<sup>3+</sup> (c).

8%Cr, Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr, 4%Nd, Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 1%Nd phosphors were shown in the Fig. S1. The excitation spectrum of Nd<sup>3+</sup> emission at 1061 nm in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup> is identical to that of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, indicating that Nd<sup>3+</sup> is excited mainly by energy transfer from Cr<sup>3+</sup> in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup>. The energy level diagram of

 $Cr^{3+}$  and  $Nd^{3+}$  with the energy transfer process is illustrated in Fig. S2. The emission spectra of  $Ca_2LuZr_2Al_3O_{12}$ : 8% $Cr^{3+}$ ,  $xNd^{3+}$  (x= 0–10%), under 455 nm excitation, are shown in Fig. 3a. From the figure, the  $Nd^{3+}$  emission lines are rising and the  $Cr^{3+}$  emission bands are falling as the increasing of x. The IQEs of the total NIR emissions are



**Fig. 3.** Luminescent properties of  $Ca_2LuZr_2Al_3O_{12}$ :8%Cr<sup>3+</sup>, xNd<sup>3+</sup> (x = 0-10%): (a) Emission spectra under 455 nm excitation, (b) IQEs for different x, (c) Decay curves of Nd<sup>3+</sup> emission and (d) Decay curves of Cr<sup>3+</sup> emission after pulse excitation at 460 nm.

measured for different x, as shown in Fig. 3b, it can be found that there is an IQE enhancement from 69.1% to 74.6%, as the increasing of x from 0 to 1%. The result is the consequence of energy transfer from  $Cr^{3+}$  to the more efficient Nd<sup>3+</sup> emitting center. The emission efficiency of Nd<sup>3+</sup> can be calculated using the fluorescence lifetime and radiative lifetime of Nd<sup>3+</sup>. The fluorescence lifetime of Nd<sup>3+</sup> in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, xNd<sup>3+</sup> is 260 µs for x = 1%, as shown in Fig. 3c. The radiative lifetime and the emission spectra of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 1%Nd<sup>3+</sup> at 77 K were shown in Fig. S3 and Fig. S4. It can be seen that the radiative lifetime is close to the lifetime of  $Ca_2LuZr_2Al_3O_{12}\!\!:\,1\%\text{Nd}^{3+}$  at 77 K, which is measured to be 263  $\mu$ s. Then, the quantum emission efficiency of Nd<sup>3+</sup> in Ca\_2LuZr\_2Al\_3O\_{12}: 8%Cr<sup>3+</sup>, 1%Nd<sup>3+</sup> is calculated to be 98.9%, close to 1, which is indeed much higher than that (69.1%) of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%  $Cr^{3+}$ . Hence, the emission of  $Nd^{3+}$ , instead of  $Cr^{3+}$ , through energy transfer from Cr<sup>3+</sup> will lead to the enhancement of overall IQE, which is attributed to the restriction of the non-radiation transition. In addition, the efficiency of energy transfer ( $\eta_{ET}$ ), radiation ( $\eta_{R}$ ) and non-radiation  $(\eta_{NR})$  of  $Cr^{3+}$  at various Nd<sup>3+</sup> concentrations are shown in Fig. S5. However, as doped concentration of  $Nd^{3+}$  is higher than 1%, the IQE is decreased, which is attributed to the waste of some excitation energies induced by increase of  $Nd^{3+}$ .

The efficiency of energy transfer can be calculated by the following equation, [36–39] which is based on the intensity decrease of  $Cr^{3+}$  emission (Fig. 3a) or lifetime shortening (Fig. 3d) of it, with the increase of x in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, xNd<sup>3+</sup>.

$$\eta_{ET} = 1 - I_{Cr} / I_{Cr_0} \tag{1}$$

$$\eta'_{ET} = 1 - \tau_{Cr} / \tau_{Cr_0}$$
 (2)

Where  $I_{Cr}$  and  $I_{Cr_0}$  is  $Cr^{3+}$  emission intensity,  $\tau_{Cr}$  and  $\tau_{Cr_0}$  is  $Cr^{3+}$  emission lifetime in the presence of and in the absence of Nd<sup>3+</sup>, respectively. The calculated values of energy transfer efficiency are very close, as shown in Fig. 4a. The average of the two efficiencies,  $\overline{\eta}_{ET}$ , is adopted in this paper. Based on the kinetic analysis of energy transfer,  $I_{Nd}/I_{Cr}$  can be expressed by

$$\frac{I_{Nd}}{I_{Cr}} = \frac{\overline{\eta}_{ET} \cdot \eta_{Nd}}{(1 - \overline{\eta}_{ET}) \cdot \eta_{Cr_o}}$$
(3)

Where  $I_{Nd}$  and  $I_{Cr}$  are emission intensity of Nd<sup>3+</sup> and Cr<sup>3+</sup>,  $\eta_{Nd}$  and

 $\eta_{Cr_0}$  are the quantum efficiency of Nd<sup>3+</sup> and Cr<sup>3+</sup> at the absence of Nd<sup>3+</sup>, respectively. Hence, a proportional relationship between  $\eta_{Nd}\cdot\bar{\eta}_{ET}/(1-\bar{\eta}_{ET})$  and  $I_{Nd}/I_{Cr}$  can be observed, as shown in Fig. 4b. Meanwhile, Fig. 4c shows the dependence between  $\bar{\eta}_{ET}/(1-\bar{\eta}_{ET})$  and x, and the slope is 1 for small x and 2 for higher x. This result is in good consistent with the Dexter's expression of energy transfer[40].

The mechanism of energy transfer is analysed based on the decay curve of  $Cr^{3+}$  emission using Inokuti-Hirayama formula: [37, 41]

$$I = I_0 \exp\left[-\frac{4}{3}\pi\Gamma\left(1-\frac{3}{s}\right)N_a\alpha^{\frac{3}{2}I^{\frac{3}{2}}}\right]$$
(4)

Where *I* and *I*<sub>0</sub> are the decay curve of  $Cr^{3+}$  in the presence of and in the absence of Nd<sup>3+</sup>, respectively. *s* is a coefficient with values of 6 (for dipole–dipole interactions), 8 (dipole–quadrupole interactions) and 10 (quadrupole-quadrupole interactions), respectively. *N*<sub>a</sub> is the number of acceptor ions (Nd<sup>3+</sup>) per unit volume Fig. 4.d-4i show a linear dependence between log{-*ln*[*I*/*I*<sub>0</sub>]} and log(*t*), with the slop of 3/*s*. Thus, *s* is close to 6, indicating the dipole–dipole interaction between Cr<sup>3+</sup> and Nd<sup>3+</sup> in energy transfer process.

## 3.3. Thermal stability

The emission spectra, at different temperatures, of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, *x*Nd<sup>3+</sup> (x = 0, 1% and 8%) are depicted in Fig. S6 and Fig. 5. As shown, the quenching temperature increases from 450 K up to 550 K as the increasing of x, from 0 to 10%. On one hand, the quenching temperature increasing indicates that Nd<sup>3+</sup> emission has a high thermal stability, compared with Cr<sup>3+</sup>, which is in accordance with high IQE of Nd<sup>3+</sup>. On the other hand, the thermal de-excitation of Cr<sup>3+</sup> can be suppressed by energy transfer, as our previous study has shown. [29, 42-44]

## 3.4. Super-broadband NIR pc-LED

The Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup> converted NIR pc-LED is fabricated and its emission spectra, NIR output powers and power conversion efficiencies are measured at different drive currents, as shown in Fig. S7. The emission spectrum of the Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup> pc-LED appears a deep cavity around 1000 nm, which is not a good broadband NIR



**Fig. 4.** (a) The *x* dependence of  $Cr^{3+}$ ,  $Nd^{3+}$  emission intensity, energy transfer efficiencies calculated based on  $Cr^{3+}$  emission intensity, lifetimes, and the average of it. (b) The dependence of  $\eta_{Nd}\overline{\eta}_{ET}/(1-\overline{\eta}_{ET})$  on luminescence intensity ratio  $I_{Nd}/I_{Cr}$ . (c)  $\log(x)$  dependence on  $\log(\overline{\eta}_{ET}/(1-\overline{\eta}_{ET}))$ . And (d-i) the relationship between  $Log[-Ln(I(t)/I_0(t))]$  and Log(t) of  $Ca_2LuZr_2Al_3O_{12}$ : 8% $Cr^{3+}$ , xNd<sup>3+</sup> (x = 0.01-0.10).



Fig. 5. Emission spectra at different temperatures for x = 0 (a), 1% (b) and 8% (c), and temperature dependence of the total emission intensity (d).

light source. To broaden the band with no obvious deficiency of spectral component within it, a NIR super-broadband pc-LED is fabricated, using the blend of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 2%Nd<sup>3+</sup> and Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 2%Yb<sup>3+</sup> phosphors as fluorescence converter. The NIR emission spectra of the blend phosphor pc-LED (Fig. 6a) is just the superposition of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 2%Nd<sup>3+</sup> emission (Fig. 6b) and Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 2%Nd<sup>3+</sup> emission (Fig. 6b) and Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: 8%Cr<sup>3+</sup>, 2%Nd<sup>3+</sup> emission (Fig. 6c), exhibiting improved spectral distribution compared to both of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup> pc-LED (Fig. S7) and Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Yb<sup>3+</sup> pc-LED [29]. The bandwidth is 350 nm, broader than that (320 nm) of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Yb<sup>3+</sup> pc-LED, [29] due to the appearance of the strong Nd<sup>3+</sup> emission band at 1060 nm, and it is longer than the wavelength (1030 nm) of Yb<sup>3+</sup> emission. The emission spectra of the pc-LED including a blue band, from LED chip, and a NIR emission band from the phosphor blend. The emission systams table, as shown in Fig. 6a.

Fig. 6d manifests the dependence of electricity-to-NIR light conversion efficiency and the NIR light output power on drive current for the pc-LED. The conversion efficiency reaches 22.3% at 20 mA, with the NIR output power of 11.8 mW, 16.2% at 100 mA and the NIR light output power is 47.6 mW. The bandwidth and power conversion efficiency of the present pc-LED are improved, compared to the NIR pc-LEDs [29–31] ever reported at the same drive current. The decrease of electricity-to-NIR light conversion efficiency is caused by the well-known efficiency droop of blue LED chip rather than phosphor degradation.

## 4. Conclusion

Blue light excitable NIR Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>: Cr<sup>3+</sup>, Nd<sup>3+</sup> phosphors are prepared by solid state reaction. From the emission spectra of the phosphors, we can see a band at 800 nm of Cr<sup>3+</sup> emission and a group of Nd<sup>3+</sup> emission bands, with quantum emission close to 100%, distributed in range of 850–1100 nm, excited by energy transfer from Cr<sup>3+</sup> to Nd<sup>3+</sup>. The IQE and thermal stability are both improved by adding Nd<sup>3+</sup> in Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub> Cr<sup>3+</sup>, due to the energy transfer from Cr<sup>3+</sup> to the more efficient Nd<sup>3+</sup>. The IQE is promoted from 69.1% to 74.6% and the quenching temperature is increased from 450 K to 550 K. Energy transfer is governed by dipole–dipole interaction.

NIR super-broadband pc-LED is fabricated, and the blend of  $Ca_2LuZr_2Al_3O_{12}$ : 8%Cr<sup>3+</sup>, 2%Nd<sup>3+</sup> and  $Ca_2LuZr_2Al_3O_{12}$ : 8%Cr<sup>3+</sup>, 2% Yb<sup>3+</sup> phosphors are fluorescence converter. The NIR emission spectrum of the blend phosphor pc-LED exhibits improved spectral distribution, compared to both of Ca\_2LuZr\_2Al\_3O\_{12}: Cr<sup>3+</sup>, Nd<sup>3+</sup> pc-LED and Ca\_2LuZr\_2Al\_3O\_{12}: Cr<sup>3+</sup>, Yb<sup>3+</sup> pc-LED. The bandwidth reaches 350 nm, broader than that (320 nm) of Ca\_2LuZr\_2Al\_3O\_{12}: Cr<sup>3+</sup>, Yb<sup>3+</sup> pc-LED. The electricity-to-NIR light conversion efficiency of the blend phosphor pc-LED reaches 22.3%, at 20 mA drive current, with a NIR output power



**Fig. 6.** Emission spectra of pc-LED under different drive currents (a),  $Ca_2LuZr_2Al_3O_{12}$ :  $8\%Cr^{3+}$ ,  $2\%Nd^{3+}$  (b),  $Ca_2LuZr_2Al_3O_{12}$ :  $8\%Cr^{3+}$ ,  $2\%Yb^{3+}$  (c). The light-red region represents the spectral extension to the longer wavelength due to appearance of Nd<sup>3+</sup> emission band at 1060 nm. (d) Dependence of NIR output power and electricity-to-NIR light conversion efficiency on drive current for the pc-LED.

of 11.8 mW, 16.2% at 100 mA with the NIR light output power of 47.6 mW. The bandwidth and power conversion efficiency of the present pc-LED are improved, compared to the NIR pc-LEDs ever reported. Our researches suggest the great potential of Ca<sub>2</sub>LuZr<sub>2</sub>Al<sub>3</sub>O<sub>12</sub>:  $Cr^{3+}$ , Nd<sup>3+</sup> phosphors for super broadband NIR pc-LEDs.

#### **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Supplementary materials

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