



The energy transfer from Eu^{2+} to Tb^{3+} in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ and its application in green light emitting diode

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ABSTRACT

A novel green phosphor, $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$, is synthesized by high temperature solid-state reaction. The photoluminescence properties show that there is an efficient energy transfer from Eu^{2+} to Tb^{3+} where Eu^{2+} ions exhibit a strong excitation band between 350 and 420 nm, matching well with the dominant emission band of (n)-UV (390–420 nm) LED, and Tb^{3+} ions give an intense green emitting light. A green LED with CIE chromaticity coordinates ($x=0.283, y=0.383$) were fabricated by coating the $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$ phosphor onto (n)-UV chip emitting at 398 nm. These results demonstrate that Tb^{3+} ion with low 4f–4f absorption efficiency in (n)-UV region can play a role of activator in narrow green emitting phosphor potentially useful in (n)-UV GaN-based LED through efficient energy feeding by allowed 4f–5d absorption of Eu^{2+} with high oscillator strength.

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1. Introduction

It is well known that the invention of white light emitting diodes (LEDs) has brought another revolution to the illumination technology of this century to supersede conventional incandescent or fluorescent lamps because of its excellent properties such as high brightness, reliability, lower power consumption and long life [1,2]. At the present, there are several ways to make the white LEDs [3,4]. One significant scheme is phosphor-converted white LED (pc-wLED) that is further classified into two approaches: blue (440–470 nm) and near (n)-UV (390–410 nm) InGaN chip combined with phosphors. For the blue InGaN chip, the commonly used phosphor is yellow YAG:Ce³⁺. However, such white LEDs encounter low color-rendering index ($R_a < 80$) due to the scarcity of red emission. Besides, the white LED based on blue InGaN chip encounter low color reproducibility on mass manufacturing scale. The n-UV LED is considered more stable and efficient with higher output [5]. It generally emits at wavelength shorter than 400 nm. Therefore the n-UV

LED has little effect on the chromaticity coordinate of pc-wLED, which is generally determined by the visible radiation distribution of phosphor between 380 and 730 nm [6]. In addition, any desirable color LED emitting red, green, blue, etc., can be controlled by choosing different phosphor. The phosphor converted color LED shows some advantages for example, the widely tunable color range from blue to red region, the stable color quality under different operating conditions, especially under different forward-bias currents and during the industrial mass production [7]. Thus, the n-UV pc-LEDs are expected to have great application potential in the field of solid-state lighting.

Nowadays, rare earth ions, especially Ce³⁺ and Eu²⁺ involved with inter-configurational 4f–5d transition, have been widely investigated in many compounds including orthosilicates, akermanites, aluminates, sulfides and oxynitrides/nitrides, etc. [8–12]. However, little is done on trivalent rare earth ions involving with intra-configurational 4f–4f transitions. Recently, Eu³⁺-doped phosphors have been studied for near UV InGaN-based LEDs. For example, oxysulfide ($\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$) [13], molybdates ($\text{Na}_5\text{La}(\text{MoO}_4)_4:\text{Eu}^{3+}$, $\text{Na}_5\text{Eu}(\text{MoO}_4)_4$ and $\text{NaEu}(\text{MoO}_4)_2$) [14] and europium organic complex ($\text{Eu}(\text{TPBDTFA})_2(\text{TPATFA})\text{Phen}$) [15] were developed and the red LEDs were successfully fabricated.

In this paper, our aim is to investigate whether Tb^{3+} ions with low 4f–4f absorption efficiency in (n)-UV region can play a role of activator in a narrow green emitting phosphor potentially useful in (n)-UV GaN-based LEDs. The phenomena of energy transfer

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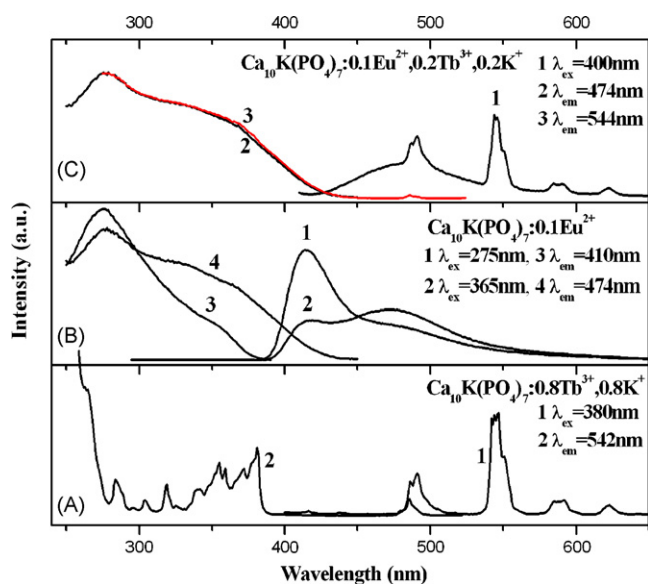


Fig. 1. PL and PLE spectra of $\text{Ca}_{8.4}\text{K}(\text{PO}_4)_7:0.8\text{Tb}^{3+},0.8\text{K}^+$ (A), $\text{Ca}_{9.9}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+}$ (B) and $\text{Ca}_{8.3}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+},0.2\text{Tb}^{3+},0.2\text{K}^+$ (C).

in phosphors were extensively observed [16–18], especially, those from Ce^{3+} to Tb^{3+} . However, energy transfer from Eu^{2+} to Tb^{3+} is rarely seen except in $\text{KLn}_3\text{F}_{10}$ ($\text{Ln} = \text{Y}, \text{Lu}$) [19]. In this paper, the energy transfer from Eu^{2+} to Tb^{3+} in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ was systematically investigated and a green emitting $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$ phosphor was developed for the first time. The phosphor-converted green LED was also successfully fabricated by combining ultraviolet GaInN chip and $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$.

2. Experimental

2.1. Syntheses

Eu^{2+} or Tb^{3+} singly doped and $\text{Eu}^{2+}-\text{Tb}^{3+}$ co-activated $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ phosphors were prepared by conventional solid-state reaction technique. The starting materials were CaCO_3 (A.R.), CaHPO_4 (A.R.), anhydrous CaCl_2 (A.R.), Eu_2O_3 (99.99%), Tb_4O_7 (99.99%) and K_2CO_3 (A.R.). When the trivalent Tb^{3+} ions are doped in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, additional K_2CO_3 serves as a charge compensation reagent. Stoichiometric amounts of the raw materials were thoroughly mixed in an agate mortar by grinding and then sintered at 873 K for 3 h, followed by regrinding. Finally, they were fired at 1573 K in a reducing atmosphere (10% $\text{H}_2/90\%$ N_2) for 4 h.

2.2. Characterizations

The phase purity of the as-prepared phosphors was investigated by X-ray powder diffraction spectroscopy (XRD) with a Rigaku D/max 2200 vpc X-ray diffractometer with $\text{Cu K}\alpha$ radiation at 40 kV and 30 mA. The XRD patterns were collected in the range $10^\circ \leq 2\theta \leq 80^\circ$. The XRD patterns of Eu^{2+} or Tb^{3+} singly doped and $\text{Eu}^{2+}-\text{Tb}^{3+}$ co-activated $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ phosphors confirm of a single phase of $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ (JCPDS 45-0138).

The decay curves were recorded by a FLS920-Combined Fluorescence Lifetime and Steady State Spectrometer (Edinburgh Instruments). The room temperature photoluminescence (PL), photoluminescence excitation (PLE) spectra were measured by a Fluorolog-3 spectrofluorometer (Jobin Yvon Inc/specx) equipped with a 450 W Xe lamp and double excitation monochromators.

2.3. Characterization of green LED

The green LEDs were fabricated by combining InGaN-based ultraviolet LEDs (Cree Inc., C395-MB290, 12 mW, $\lambda_{\text{em}} = 395$ nm) and as-synthesized phosphors. Their optical properties were evaluated by a LED-1100 Spectral/Goniometric Analyzer (Labsphere Inc.) under a direct current of 20 mA at room temperature.

3. Results and discussion

Fig. 1 shows PL and PLE spectra of singly doped Eu^{2+} or Tb^{3+} and $\text{Eu}^{2+}-\text{Tb}^{3+}$ co-activated $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ phosphors. For

$\text{Ca}_{8.4}\text{K}(\text{PO}_4)_7:0.8\text{Tb}^{3+},0.8\text{K}^+$, the emission spectrum monitoring at 379 nm shows a characteristic optical transitions of Tb^{3+} ion, which are situated at about 486, 542, 587, 619 nm, due to $\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 6, 5, 4, 3$). The weak emissions ${}^5\text{D}_3 \rightarrow {}^7\text{F}_J$ ($J = 5, 6$) of Tb^{3+} at 416 and 432 nm, respectively, are also observed in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ with 8 mol% of Tb^{3+} ions, which may be due to the lower ν_{max} of phonon in this host. Monitoring at 542 nm, The PLE spectrum consists of many sharp peaks in the wavelength range from 280 to 380 nm, due to the forbidden 4f–4f transitions of Tb^{3+} ions. For $\text{Ca}_{9.9}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+}$, the PL spectra consist of two emission bands at 410 and 470 nm, both attributed to 5d \rightarrow 4f transitions of Eu^{2+} . The emission spectra of Eu^{2+} shows the distinct features when monitored at different excitation wavelength: the dominating emission is at about 410 nm when monitored at 275 nm while that at around 474 nm when monitored at 365 nm. The PLE spectra of Eu^{2+} , monitored at different emission at 410 and 474 nm, also present the distinguishable behavior. Therefore, it can be concluded Eu^{2+} ions occupy at least two different cation sites in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$, denoted as Eu_1 (410 nm) and Eu_2 (474 nm). It is reasonable because there are four different crystallographically independent Ca^{2+} sites with different coordination numbers (CN = 6, 8 and 9) [20].

Nowadays, the commercial n-UV LEDs show a ultraviolet light at around 390–410 nm. As shown in Fig. 1A, it can be seen that Tb^{3+} shows no absorption beyond 380 nm, meaning that Tb^{3+} singly doped phosphate is not suitable for the application of n-UV LED. Contrarily, the PLE spectra of Eu^{2+} ion (Fig. 1B) matches well with the emission of n-UV LEDs, suggesting that Eu^{2+} singly doped phosphate has potential application in the field of n-UV LEDs. However, the comparison of the PL spectrum of $\text{Ca}_{9.9}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+}$ and PLE spectrum of $\text{Ca}_{8.4}\text{K}(\text{PO}_4)_7:0.8\text{Tb}^{3+},0.8\text{K}^+$ reveals spectral overlap between the emission band of Eu^{2+} at longer wavelength (at about 474 nm) and the absorption transition of Tb^{3+} (${}^7\text{F}_6 \rightarrow {}^5\text{D}_4$ located at 486 nm). Therefore, the effective resonance energy transfer from Eu^{2+} to Tb^{3+} in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ is expected. Fig. 1C shows the PL and PLE spectra of $\text{Eu}^{2+}-\text{Tb}^{3+}$ co-activated $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$ phosphors. Monitoring at 400 nm excitation, both the broad emission band of Eu^{2+} and the sharp emission peaks of Tb^{3+} (${}^5\text{D}_4 \rightarrow {}^7\text{F}_J$ ($J = 6, 5, 4, 3$)) are observed. The shapes of PLE spectra of $\text{Ca}_{8.3}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+},0.2\text{Tb}^{3+},0.2\text{K}^+$, monitored at 474 and

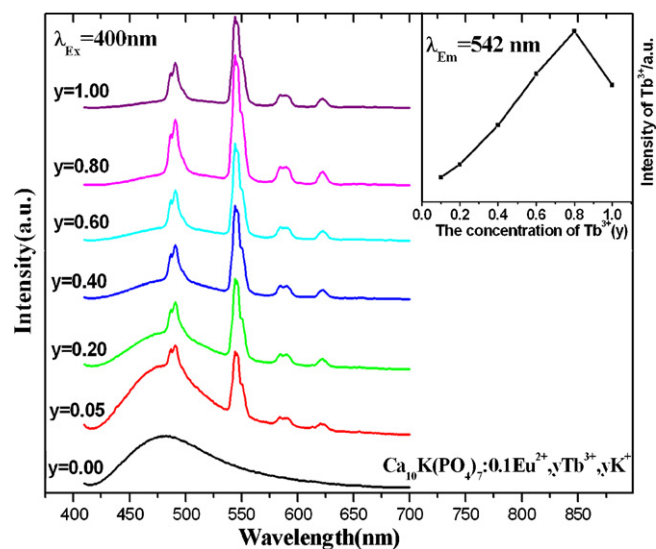


Fig. 2. The emission spectra ($\lambda_{\text{ex}} = 400$ nm) of $\text{Ca}_{9.9-2y}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+},y\text{Tb}^{3+},y\text{K}^+$ ($y = 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0$); inset is the dependence of the peak intensity of Tb^{3+} (${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ located at 544 nm) and the maximum intensity of the emission band of Eu^{2+} (located 474 nm) on Tb^{3+} concentration (y) in $\text{Ca}_{9.9-2y}\text{K}(\text{PO}_4)_7:0.1\text{Eu}^{2+},y\text{Tb}^{3+},y\text{K}^+$.

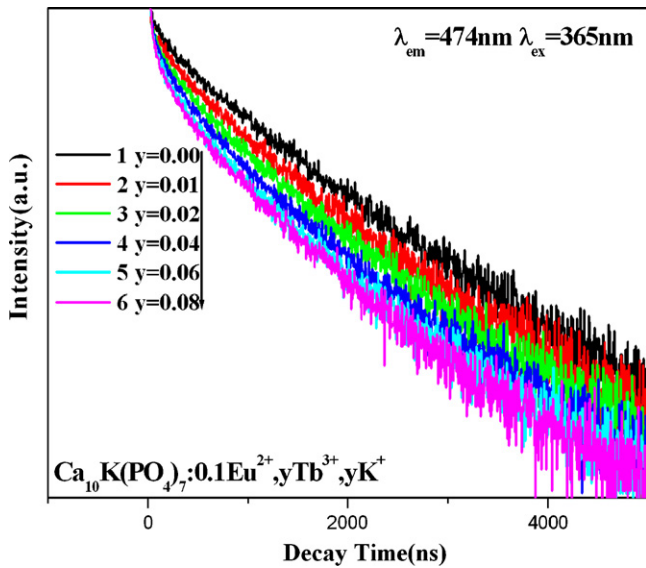


Fig. 3. The concentration effects of Tb^{3+} ions on the lifetime of Eu^{2+} ion in $Ca_{9.9-2y}K(PO_4)_7:0.1Eu^{2+},yTb^{3+},yK^+$ ($y=0, 0.1, 0.2, 0.4, 0.6, 0.8$) ($\lambda_{ex}=365$ nm, $\lambda_{em}=474$ nm).

544 nm (curve 2 and curve 3 in Fig. 1C), are almost the same as that of $Ca_{9.9}K(PO_4)_7:0.1Eu^{2+}$ (curve 4 in Fig. 1B), indicating that the energy transfer from Eu^{2+} at Eu_2 site to Tb^{3+} appears. It is therefore expected that Tb^{3+} ions can serve as activator of green-emitting phosphor by energy feeding of Eu^{2+} ions that can be directly excited by 400 nm emission of UV LED.

In order to optimize the green-emitting performance of the as-synthesized phosphors so that they can be potentially applied in n-UV LED with dominating emission at around 400 nm, a series of $Ca_{9.9-2y}K(PO_4)_7:0.1Eu^{2+},yTb^{3+},yK^+$ ($0 \leq y \leq 1.0$) phosphors were prepared and their luminescent properties were systematically investigated. The emission spectra ($\lambda_{ex}=400$ nm) of $Ca_{9.9-2y}K(PO_4)_7:0.1Eu^{2+},yTb^{3+},yK^+$ are shown in Fig. 2. It can be seen that the characteristic sharp emission of Tb^{3+} ($^5D_4 \rightarrow ^7F_J$ ($J=6,$

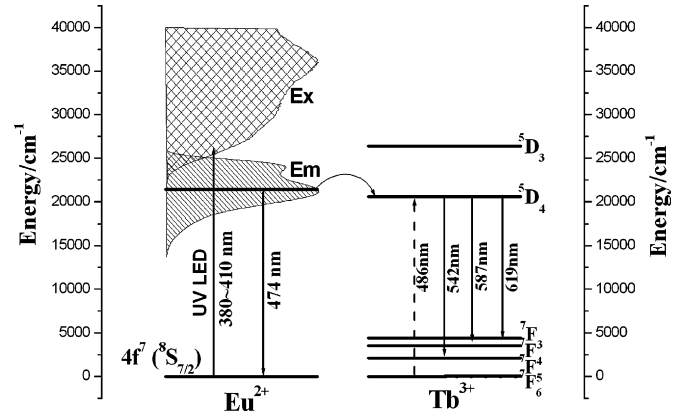


Fig. 4. The schematic diagram of energy transfer in $Ca_{10}K(PO_4)_7:Eu^{2+},Tb^{3+}$.

5, 4, 3)) becomes stronger and stronger when the concentration of Tb^{3+} ions increases and the broad emission band of Eu^{2+} ions located around 474 nm decreases gradually. As shown in the inset of Fig. 2, the optimal concentration of Tb^{3+} ions is about 8 mol%, and excess Tb^{3+} ions will lead to its concentration quenching.

Fig. 3 shows the concentration effects of Tb^{3+} ions on the lifetime of Eu^{2+} in $Ca_{9.9-2y}K(PO_4)_7:0.1Eu^{2+},yTb^{3+},yK^+$ ($y=0, 0.1, 0.2, 0.4, 0.6$). It can be seen that the decay curves of Eu^{2+} ion are well fitted with a second order exponential equation: $I(t) = I_0 + A \exp(-t/\tau_1) + B \exp(-t/\tau_2)$ where I and I_0 are the luminescence intensity initially and at t , A and B are constants, and τ_1 and τ_2 are lifetimes). It is obvious that with the increasing amount of Tb^{3+} ions, the lifetime of Eu^{2+} ions gradually decreases. In the absence of Tb^{3+} , the lifetimes of Eu^{2+} ion are 0.16 and 1.12 μs . When the amount of codopant Tb^{3+} is up to 0.8 mol%, the lifetimes of Eu^{2+} ion are 0.06 and 0.76 μs . Such behavior indicates that the excitation energy of these Eu^{2+} ions is transferred to Tb^{3+} ions.

Fig. 4 shows schematic diagram of energy transfer in $Ca_{10}K(PO_4)_7:Eu^{2+},Tb^{3+}$. As shown in Fig. 1, the broad-band emission of Eu^{2+} at 474 nm (Eu_2 site) covers with the excitation peak of Tb^{3+} at 486 nm. The overlap indicates that there is likely to be

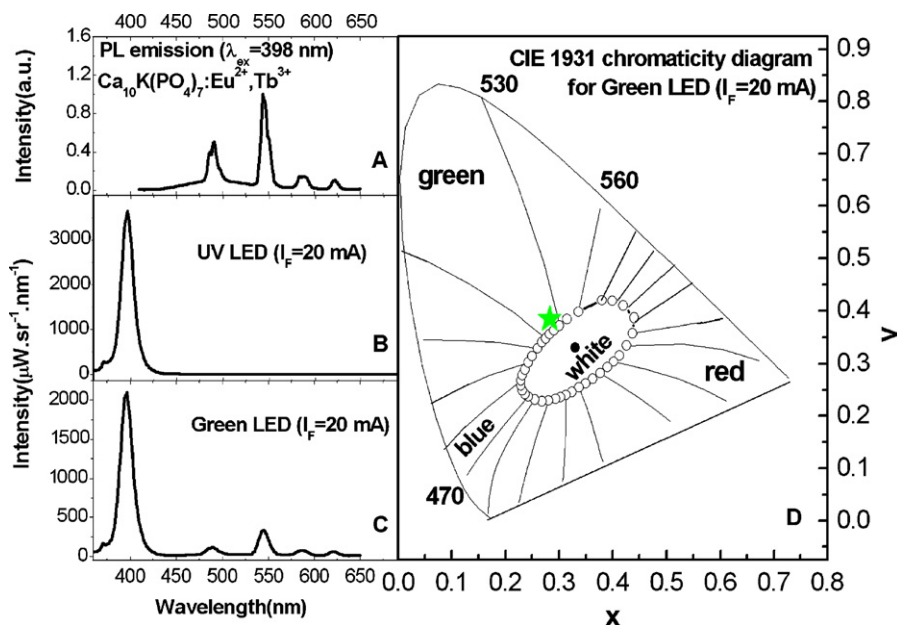


Fig. 5. The PL spectra of $Ca_{10}K(PO_4)_7:Eu^{2+},Tb^{3+}$ phosphor (A), the electroluminescence spectra of naked UV LED (B) and the fabricated green pc-LED (C) by combining with $Ca_{10}K(PO_4)_7:Eu^{2+},Tb^{3+}$ phosphor and UV LED under 20 mA forward-bias current, and the 1931 CIE chromaticity diagram (D) of the as-fabricated green pc-LED under $I_F = 20$ mA.

the radiative or non-radiative resonant energy transfer. However, it seems impossible for the resonant radiative transfer because the absorption transition of ${}^7F_6 \rightarrow {}^5D_4$ located at 486 nm has very weak oscillator strength. In addition, it is reasonable that the lifetime of the donor will remain constant in the presence of the acceptor if the resonant radiative transfer is involved [21]. In present case, the lifetime of Eu^{2+} ion as donor decreases with the increasing amount of Tb^{3+} ion as acceptor. It is therefore concluded that the energy transfer mechanism is likely to be ascribed to resonant non-radiative transfer from the lowest excited level of Eu^{2+} to the excited 5D_4 level of Tb^{3+} as shown in Fig. 4.

The emission spectrum of green emitting LED that was fabricated by combining $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+}$ phosphor with the 398-nm InGaN chip under 20 mA forward-bias current (I_F), is shown in Fig. 5. The characteristic emission peaks of Tb^{3+} (486, 542, 587, 619 nm) can be clearly observed in the emission spectrum of the green pc-LED, which is consistent with the PL spectra of $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+}$ phosphor. From the comparison of the emission intensity of near-UV-LED chip at 395 nm as shown in Fig. 5B and C, it is seen that its intensity decreases from 3700 (Fig. 5B) to 2300 mW/sr/nm (Fig. 5C), indicating that $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+}$ phosphor has efficient absorption to the 395-nm InGaN chip. The remaining UV light can be used to excited blue and red phosphor for the white LEDs that combine with n-UV chip and RGB phosphors. As illustrated in Fig. 5D, the color coordinate of as-fabricated pc-LED is ($x=0.283, y=0.383$) under $I_F=20$ mA, which is located in green area and very close to the white light ellipse. The properties of the as-fabricated green LED also demonstrate that the pc-LEDs are alternatives to the semiconductor green LEDs for applications in lighting, signal and indicator, etc.

4. Conclusions

A novel green-emitting phosphate $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$ was reported for the first time. There are at least two luminescent centers, Eu_1 at 410 nm and Eu_2 at 474 nm and the efficient energy transfer from Eu^{2+} (Eu_2 site) to Tb^{3+} exists in $\text{Ca}_{10}\text{K}(\text{PO}_4)_7$. The $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+},\text{K}^+$ phosphor exhibit the efficient broad absorption band of Eu^{2+} and an intense green emission of Tb^{3+} . The green LED with the color coordinate of ($x=0.2835, y=0.3855$) was successfully fabricated based on $\text{Ca}_{10}\text{K}(\text{PO}_4)_7:\text{Eu}^{2+},\text{Tb}^{3+}$ and n-UV

chip. It demonstrates that Tb^{3+} ion with low 4f–4f absorption efficiency in (n)-UV region can play the role of activator in narrow green emitting phosphor potentially useful in (n)-UV GaN-based LED through efficient energy feeding by allowed 4f–5d absorption of Eu^{2+} with high oscillator strength.

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