



Zero-thermal-quenching broadband yellow-emitting Bi³⁺-activated phosphors based on metal to metal charge transfer

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ABSTRACT

Bi³⁺-activated phosphors have been proven to have potential applications foreground in white light-emitting diodes (WLED), plant growth lamps and temperature sensing. Therefore, it is urgent to exploit high-efficiency Bi³⁺-activated phosphors. Herein, a novel broadband yellow-emitting phosphor Ba₂GdGaO₅:Bi³⁺ with high internal quantum efficiency (IQE = 77%) was obtained based on metal to metal charge transfer (MMCT) between Bi³⁺ ground state and Gd³⁺ excited states. The photoluminescence excitation (PLE) spectrum and photoluminescence (PL) spectrum range from 225 nm to 400 nm and 400 nm to 700 nm, respectively, which can avoid the reabsorption phenomenon efficiently. Besides, Ba₂GdGaO₅:Bi³⁺ has superior thermal stability and it shows zero-thermal-quenching at 150 °C. The K⁺ doping hardly changes the thermal stability and can improve the PL intensity to 133.1% when the K⁺ concentration is 2%. Finally, a phosphor-convert WLED (pc-WLED) was simply synthesized by Ba₂GdGaO₅:Bi³⁺ and BaMgAl₁₀O₁₇:Eu²⁺ (BAM:Eu²⁺) phosphors. The doping of Eu³⁺ can significantly enhance the color rendering index (CRI, from 88.1 to 91.5) and reduce the correlated color temperature (CCT, from 4911 K to 4014 K). The above experimental results demonstrated that the phosphor has great application prospect in WLED.

1. Introduction

In recent years, phosphor-converted LED (pc-LED) has developed rapidly and has wide range of applications in various fields [1,2]. The performance of pc-LED depends largely on the optical properties of phosphor, so it is necessary to develop high-performance phosphors [3–5]. At present, the most common phosphor is Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) yellow-emitting phosphor, which can emit white light by combing it with blue LED chip [6–8]. However, this type of WLED has a low CRI (< 75) and high CCT (> 5000 K), and doesn't fulfill the requirements for high-quality white lighting [9,10]. What's more, the strong blue light emitted by blue chip can affect human hormone secretion and harm human eyes [11,12]. A novel strategy using multi-emission phosphors and near-ultraviolet (n-UV) LED chip has been found to be effective in preventing blue light damage [13,14]. The key point of this strategy is to develop efficient n-UV excited phosphors.

Rare earth luminescent materials have been commercialized, such as

Eu²⁺-activated phosphors and Ce³⁺-activated phosphors [15–17]. The PLE spectra of these phosphors usually includes blue and even green regions, and the PLE spectra and PL spectra overlap. These characteristics may lead to reabsorption phenomenon, reduce the luminescence efficiency of pc-LED, resulting in white-light distortion [18,19]. Transition metal Mn⁴⁺-activated fluoride phosphor exhibited bright narrow red emitting, but the excitation spectrum is range from 200 to 600 nm, which also caused reabsorption [20,21]. Furthermore, the preparation process of fluoride phosphor needs to use hydrofluoric acid, which may cause harm to the human body, and lead to environmental pollution [22]. These shortcomings greatly limit the application of this kind of phosphor.

Trivalent bismuth (Bi³⁺), has drawn wide attention owing to the characteristic absorption in the UV region (6s → 6p transition). Bi³⁺ has nearly no absorption in visible region, which can prevent the reabsorption phenomenon [23–25]. Another notable advantage of Bi³⁺ ion is its spectral tunability performance [26–28]. However, this can also lead

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to unpredictable behavior and uncontrollable situations. Both opportunities and challenges exist, and this double-edged sword opens up the possibility of spectrally efficient modulation of Bi^{3+} . The electronic configuration of the element Bi is $[\text{Xe}]4f^{14}5d^{10}6s^26p^3$, in which the 6s orbital loses one electron and the 6p orbital loses two electrons, so the electronic configuration of Bi^{3+} is $[\text{Xe}]4f^{14}5d^{10}6s^06p^0$, and its outermost electron orbital is 6s and 6p. Therefore, because of the naked 6s and 6p outer electrons, Bi^{3+} is sensitive to the surrounding crystal field environment, resulting in multicolor emission [23,29–31]. However, most of Bi^{3+} -activated phosphors represent blue, cyan or green emission, such as $\text{Sc}_2\text{Si}_2\text{O}_7:\text{Bi}^{3+}$ (deep-blue emitting), [32] $\text{CaGdGaO}_6:\text{Bi}^{3+}$ (blue emitting), [33] $\text{Sr}_2\text{GdGaO}_5:\text{Bi}^{3+}$ (cyan emitting), [34] and $\text{Ba}_2\text{LaGaO}_5:\text{Bi}^{3+}$ (green emitting) [35]. Compared with these emission bands, yellow lights have more contribution to improve CRI and reduce CCT of pc-WLED. At present, there is a lack of Bi^{3+} activated phosphors that emit yellow/orange light, and some of the only yellow/orange light still has many drawbacks. Lin reported a series of $\text{ABZn}_2\text{Ga}_2\text{O}_7:\text{Bi}^{3+}$ (A = Ca, Sr; B = Ba, Sr) phosphors with yellow/orange-emitting and achieved excellent CRI of 97.9. Unfortunately, neither IQE (< 25%) nor thermal stability (< 50% at 423 K) is satisfactory, which needs to be further improved [36]. Other yellow/orange phosphors such as $\text{Ba}_2\text{ZnWO}_6:\text{Bi}^{3+}$, $\text{K}_2\text{MgGeO}_4:\text{Bi}^{3+}$ and $\text{SrLaZnO}_{3.5}:\text{Bi}^{3+}$ also have similar defects [37–39]. Consequently, it is of great importance to explore efficient yellow/orange-emitting Bi^{3+} -activated phosphors, not only to fill the gap of Bi^{3+} -activated phosphors, but also to achieve more efficient white light lighting.

Recently, a novel strategy for constructing electron energy levels interact between Bi^{3+} and cations with d^0 or d^{10} configuration was proposed, and the corresponding state is called MMCT state [40]. Bi^{3+} -activated phosphor with the luminescence behavior from MMCT state to Bi^{3+} ground state has large Stokes shift, which can be used to guide the realization of yellow/orange emission. In this work, a broad yellow-emitting $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor was synthesized based on MMCT between Bi^{3+} ground state and Gd^{3+} excited states. This phosphor has excellent comprehensive properties, with IQE up to 77% and zero thermal quenching at 150 °C. In addition, K^+ ions were added as fluxing agent to further improve the emission intensity. When K^+ concentration was 2 mol%, the emission intensity increased to 133% of the original. Finally, a yellow LED was prepared by $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor and 365 nm n-UV chip, which have a high color purity of 82.4%. A pc-WLED with a high CRI of 88.1 and a low CCT of 4911 K was fabricated by $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ and BAM: Eu^{2+} phosphors. Eu^{3+} ion was introduced into the prepared yellow phosphor to further improve the CRI (91.5) and reduce the CCT (4014 K) of the pc-WLED. All the results demonstrated that $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor as a candidate material for achieving high quality WLED.

2. Experiment section

2.1. Materials and synthesis

The raw materials of these phosphor are BaCO_3 (99.99%, Aladdin), Gd_2O_3 (99.99%, Aladdin), Ga_2O_3 (99.99%, Aladdin), Bi_2O_3 (99.99%, Aladdin), K_2CO_3 (99.99%, Aladdin), and Eu_2O_3 (99.99%, Aladdin). All of these phosphors $\text{Ba}_2\text{GdGaO}_5:x \text{ mol}\% \text{Bi}^{3+}$ ($x = 0, 0.5, 1, 2, 3, 4, 5$), $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, y \text{ mol}\% \text{K}^+$ ($y = 0, 0.5, 1, 1.5, 2$), $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, n \text{ mol}\% \text{Eu}^{3+}$ ($n = 0, 0.5, 1, 2, 3, 4, 5$) were prepared by high-temperature solid-state method. The experiment steps are as follows: i) An analytical balance was used to weigh these ingredients by stoichiometric ratio, and then placed them in an agate mortar. ii) 2–3 mL anhydrous ethanol was added in agate mortar and ground them adequately for 40 minutes. iii) The mixture was poured into a corundum crucible and placed in the muffle furnace, the sintering condition was 1300 °C/6 h. iv) After the furnace cooled to its natural temperature, the specimens were taken and ground to a fine powder for subsequent testing. The pc-LEDs were fabricated by $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$,

BAM: Eu^{2+} phosphors and 365 nm n-UV chips. The steps are as follows: i) The epoxy resin A and B were combined in a ratio of 1:2. ii) The phosphors and epoxy resin are thoroughly mixed until thick. iii) The mixture was coated on LED chips and placed in an oven at 90 °C for 18 hours. After drying, pc-LEDs were obtained.

2.2. Characterization

X-ray diffraction (XRD) data were recorded using an Aries X-ray diffractometer (PANalytical, Netherlands) fitted with monochromatic $\text{Cu K}\alpha$ radiation (40 kV, 15 mA). The increment between steps of 2θ was 0.022° , and the duration of each counting period was 18.87 s. Rietveld refinement was accomplished by using TOPAS 4.2. PL and PLE spectra were measured on an F-4700 fluorescence spectrometer (Hitachi, Japan). Temperature-dependent PL spectra were recorded by an F-4700 fluorescence spectrometer with a heat controller (Orient KOJI, China). X-ray photoelectron spectroscopy (XPS) spectrum was measured on an X-ray photoelectron spectrometer (Thermo escalab 250Xi, U.S.). IQE and decay time were collected using a FLS-1000 fluorescence spectrometer (Edinburgh, U.K.). Diffuse reflection (DR) and electroluminescence (EL) spectra were obtained by ultraviolet and visible spectrophotometer (Shimadzu, Japan) and photoelectric test system (Everfine, China), respectively.

3. Results and discussion

3.1. Crystal structure and phase purity

Fig. 1 is the crystal structure diagram and Rietveld refinement pattern of $\text{Ba}_2\text{GdGaO}_5$ host material. The refinement results (Table 1 and Table 2) indicate that all diffraction peaks can be indexed by monoclinic cell ($P2_1$) with parameters close to $\text{Ba}_2\text{NdAlO}_5$. Therefore, this structure was used as the starting model for the Rietveld. The refinement was performed using TOPAS 4.2. When the sites of Nd^{3+} and Al^{3+} ions were occupied by Gd^{3+} and Ga^{3+} ions, respectively, the target material $\text{Ba}_2\text{GdGaO}_5$ was obtained. Refinements remained stable and gave low R-factors ($R_{wp} = 6.13$, $R_p = 4.66$, $R_B = 0.9$ and $\chi^2 = 1.36$). Crystal structure $\text{Ba}_2\text{GdGaO}_5$ consists of GdO_6 distorted octahedra which joints with GaO_4 tetrahedra forming 3D net, and Ba^{2+} ion locates in holes of this 3D net. Bi^{3+} tends to substitute six-coordination sites instead of four-coordination sites. Additionally, the ionic radius of Bi^{3+} (CN = 6, $r =$

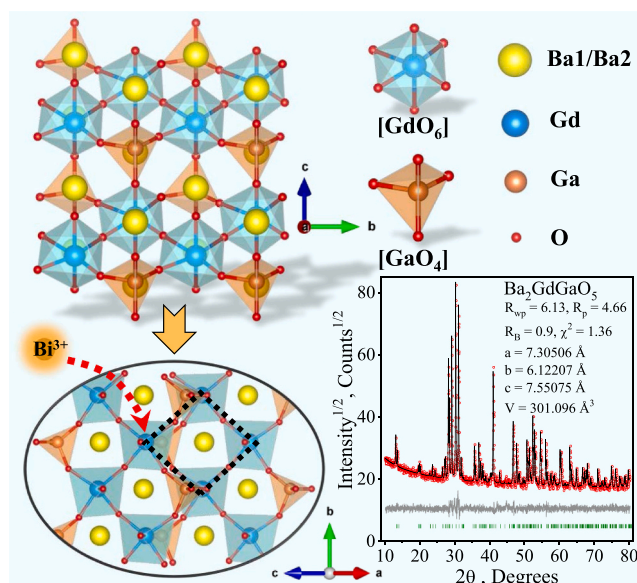


Fig. 1. Crystal structure in different crystal axis directions and XRD Rietveld refinements of $\text{Ba}_2\text{GdGaO}_5$ host material.

Table 1
Main parameters of processing and refinement of the Ba₂GdGaO₅.

sample	Space Group	Cell parameters (Å), Cell Volume (Å ³)	R _{wp} , R _p , R _B , χ ²
Ba ₂ GdGaO ₅	P2 ₁	a = 7.30506(15), b = 6.12207(12), c = 7.55075(15), V = 301.096(11)	6.13, 4.66, 0.9, 1.36

Table 2
Main bond lengths (Å) of Ba₂GdGaO₅.

Ba ₂ GdGaO ₅			
Ba1—O1	2.679(36)	Ba1—O2 ⁱ	3.0746(44)
Ba1—O2 ⁱⁱ	3.133(39)	Ba1—O3 ^f	3.202(65)
Ba1—O3 ⁱⁱⁱ	2.625(68)	Ba1—O4 ^{iv}	3.430(46)
Ba1—O4 ⁱⁱⁱ	2.706(60)	Ba1—O5 ^v	2.758(48)
Ba1—O5 ⁱⁱⁱ	3.284(60)	Ba2—O1	3.0977(42)
Ba2—O2	2.689(38)	Ba2—O3	2.89(10)
Ba2—O3 ⁱⁱⁱ	2.92(10)	Ba2—O4	2.700(43)
Ba2—O4 ^{vi}	3.439(58)	Ba2—O5	3.449(43)
Ba2—O5 ^{vii}	2.707(59)	Gd—O1	2.416(36)
Gd—O2 ⁱⁱⁱ	2.301(44)	Gd—O3 ^j	2.151(93)
Gd—O3 ⁱⁱⁱ	2.264(81)	Gd—O4 ⁱ	2.231(56)
Gd—O5	2.329(49)	Ga—O1 ^{vii}	1.827(47)
Ga—O2 ^{viii}	1.891(41)	Ga—O4	1.871(50)
Ga—O5	1.897(58)		

1.03 Å) is similar to that of Gd³⁺ (CN = 6, r = 0.938 Å). Therefore, Bi³⁺ is supposed to occupy GdO₆ site to form a luminescent center, resulting in a yellow phosphor Ba₂GdGaO₅:Bi³⁺.

Fig. 2a shows XRD patterns of phosphors doped with different concentrations of Bi³⁺. All diffraction peaks match well with the calculated result, demonstrating that doping the material with Bi³⁺ from 0 mol% to 5 mol% doesn't affect its structure. Fig. 2b is the XRD patterns of Ba₂GdGaO₅:3 mol%Bi³⁺, y mol%K⁺ (y = 0, 0.5, 1, 1.5, 2) phosphors and all these samples are pure phase. Fig. 2c is the XRD patterns of Eu³⁺ ions co-doped with different concentrations. The Bi³⁺ ion concentration stays at 3 mol%, and the Eu³⁺ ion concentration ranges from 0 mol% to 5 mol%. A series of Ba₂GdGaO₅:3 mol%Bi³⁺, n mol%Eu³⁺ (n = 0–5) phosphors are obtained. Their XRD has basically no change, proving that all the samples are well synthesized.

3.2. Luminescence performance

Fig. 3a illustrates the PLE spectra of Ba₂GdGaO₅:x mol%Bi³⁺ phosphors. The excitation band is predominantly located in the near

ultraviolet range between 300 and 400 nm. The excitation peak is 342 nm and is attributed to the ¹S₀→³P₁ transition of Bi³⁺. The excitation is in good agreement with the emission band of commercial n-UV chip. In addition, there is a weak excitation band range from 225 nm to 275 nm, which ascribe to ¹S₀→¹P₁ transition. As shown in Fig. 3b, the emission spectra of Ba₂GdGaO₅:x mol%Bi³⁺ phosphors show broadband emission from 380 nm to 700 nm with peak at 547 nm. As the concentration of Bi³⁺ increases, the PL intensity of the phosphor initially increased, but subsequently decreased. The maximum intensity was achieved at x = 3 mol%. The reduction of PL intensity is caused by the concentration quenching produced by the high concentration of Bi³⁺ ion. To enhance comprehension of concentration quenching's mechanism, we calculated the critical distance via the subsequent equation: [41,42]

$$R_c \approx 2 \times \left(\frac{3V}{4\pi x_c n} \right)^{\frac{1}{3}} \quad (1)$$

where the V is cell volume, x_c is critical doping concentration, n represent the available site occupied by the activator ion. In this material, V, x_c and n are 301.096 Å³, 0.03 and 2, respectively. The critical distance was calculated to be 21.241 Å, which beyond the exchange interaction distance (5 Å). Hence, multiple interaction is considered to have a significant impact on concentration quenching between Bi³⁺ ions. According to Dexter's theory, when the concentration burst is a multiple interaction, the strength of this interaction can be determined by the intensity of its luminescence spectrum. To obtain Fig. 6(a), we fit lg(I/x) and lg(x) using the following equation: [5,43]

$$\frac{I}{x} = k[1 + \beta(x)^{\theta}]^{-1} \quad (2)$$

where k and β represent certain excitation conditions and specific matrix crystals, x represents the doping concentration of Bi³⁺, and I represents the luminescence intensity of the phosphor of the corresponding concentration of x. The slope of the fitted line in Fig. 3c was obtained by calculation to be -1.1765, and so the value of θ was calculated to be 3.5295, which is closer to 6. Therefore, it can be proved that the concentration burst mechanism in Ba₂GdGaO₅:Bi³⁺ phosphor is caused by dipole-dipole interactions. [44] Fig. 3d is the relationship between emission intensity and Bi³⁺ doping concentration. Moreover, the peak value of the PL spectra is slightly shifted when the concentration of Bi³⁺ increases. As mentioned above, the luminescence behavior of Bi³⁺ ion is closely related to the change of crystal field environment. Different concentrations of Bi³⁺ ions doped will affect the crystal field environment around the luminescence center, leading to slight changes in the

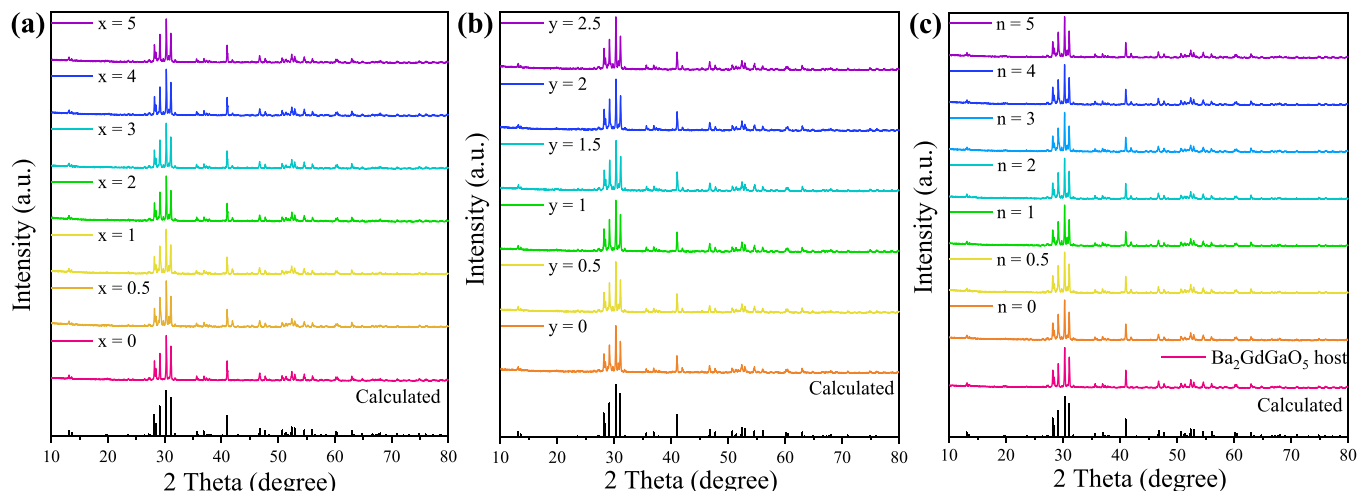


Fig. 2. XRD patterns of (a) the Ba₂GdGaO₅:x mol%Bi³⁺, (b) the Ba₂GdGaO₅:3 mol%Bi³⁺, y mol%K⁺ and (c) the Ba₂GdGaO₅:3 mol%Bi³⁺, n mol%Eu³⁺ phosphors.

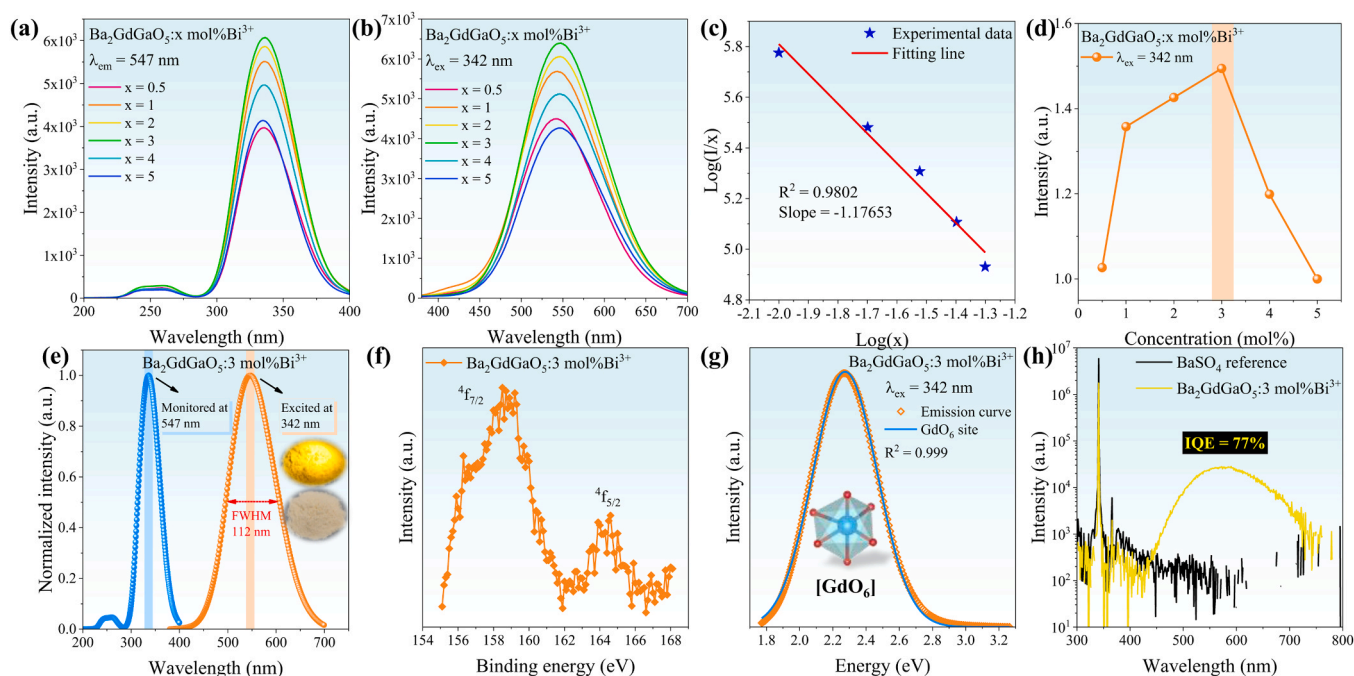


Fig. 3. (a) PLE and (b) PL spectra of $\text{Ba}_2\text{GdGaO}_5:x \text{ mol}\% \text{Bi}^{3+}$ phosphors. (c) The relationship between $\text{Log}(I/x)$ and $\text{Log}(x)$. (d) The relationship between emission intensity and Bi^{3+} doping concentration. (e) PLE and PL spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and its photographs. (f) The XPS spectrum. (g) Gaussian fitting of the PL spectrum of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ under excitation of 342 nm. (h) The IQE of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$.

crystal field splitting strength, resulting in peak displacement phenomenon. Fig. 3e illustrates the optimal PL and PLE spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor. The full width at half-maximum (FWHM) of PLE spectrum reaches 112 nm and has a large Stokes shift. Hence, the PLE spectrum and PL spectrum hardly overlap, which can effectively avoid reabsorption. The illustrations are pictures of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor under natural light and 365 nm n-UV light. It can be seen that the phosphor is milky white under natural light, while it shows strong yellow light emission under n-UV light.

The XPS spectrum (Fig. 3f) shows that the $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor has a characteristic peak near 159 eV and 164 eV, which is attributed to $\text{Bi}^{3+} 4f_{7/2}$ and $\text{Bi}^{3+} 4f_{5/2}$. This result proves that the valence state of bismuth element is trivalent. To further confirm the occupation of Bi^{3+} and the number of luminescent centers, a Gaussian fitting is carried out for the PL spectrum of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor. As shown in Fig. 3g, the spectral curve can be well fitted by a single peak and the value of R^2 is as high as 0.999, which indicates that the fitting result is reliable. Therefore, it can be confirmed that Bi^{3+} ion will only replace GdO_6 site to form one luminescent center. The quantum efficiency is a key index to evaluate the luminescence performance of phosphor. In Fig. 3h, in contrast to the white board coated with BaSO_4 , the IQE of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor reaches 77% under the excitation of 342 nm n-UV light. This test results show that it has excellent luminescent properties. Relevant equation as follows:[45]

$$\eta_{\text{IQE}} = \frac{\int L_s}{\int E_R - \int E_s} \quad (3)$$

where η_{IQE} and L_s are the value of IQE and PL spectrum, respectively. E_R and E_s represent the spectrum of the excitation light with and without sample in integrating sphere.

In the preparation of phosphors, adding a small amount of flux materials is beneficial to reduce the sintering temperature. In addition, the flux materials can also cause the carbonate or nitrate in the raw material to decompose more thoroughly and improve the crystallinity of the resulting phosphor particles. Thus, it is beneficial to enhance the luminescent performance of phosphor. Alkali metal ions are common flux

materials and have been successfully utilised in various phosphor systems to enhance their luminescence performance, such as $\text{CaYGaO}_4:\text{Bi}^{3+}$ and $\text{BaScO}_2\text{F}:\text{Bi}^{3+}$ phosphors. As shown in Fig. 4a-d, we co-doped K^+ ion as flux materials to improve the PL intensity of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor. Fig. 4b-c display the PL spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$, y mol% K^+ phosphors excited at 342 nm and 365 nm, respectively. The PL intensity all increase with K^+ concentration doping. We plotted the relationship between emission intensity and K^+ ion concentration in Fig. 4d. When the concentration of K^+ reaches 1.5 mol%, the intensity increases to 121.1% of the initial intensity excited at 342 nm. Moreover, under the excitation of 365 nm, the PL intensity can enhance to 133.1% when y = 2 mol%. As mentioned above, the K^+ doping has no effect on the phase (in Fig. 2b). Therefore, the function of K^+ ions is to act as a flux to improve the crystallinity of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor and thus improve the luminescent intensity. Fig. 4e presents the decay lifetime curves of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$, 2 mol% K^+ phosphors monitored at 547 nm at room temperature. Both of these phosphors possess only one luminescent center, hence their decay curves fit perfectly with a single exponential function, as shown below:[46–48]

$$I(t) = I_0 \times A \exp\left(-\frac{t}{\tau}\right) \quad (4)$$

where $I(t)$ and I_0 are the PL intensity at time t and time 0, respectively. A and τ are constant and decay time of fluorescence lifetime, respectively. The lifetime values of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$, 2 mol% K^+ phosphors are calculated to be 351.21 ns and 347.48 ns. It can be seen from Fig. 4e that the lifetime value of doped K^+ hardly changes. Fig. 4f gives the DR spectra of $\text{Ba}_2\text{GdGaO}_5$, $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$, 2 mol% K^+ phosphors. The obvious absorption band around 250 nm in the host material is attributed to the electron transition between the valence and conduction bands. After doping Bi^{3+} ion, the absorption of these phosphors in the n-UV region (250–400 nm) is significantly stronger, and the absorption wavelength matches well with the excitation spectrum. The optical bandgap of $\text{Ba}_2\text{GdGaO}_5$ can be calculated through:[49–51]

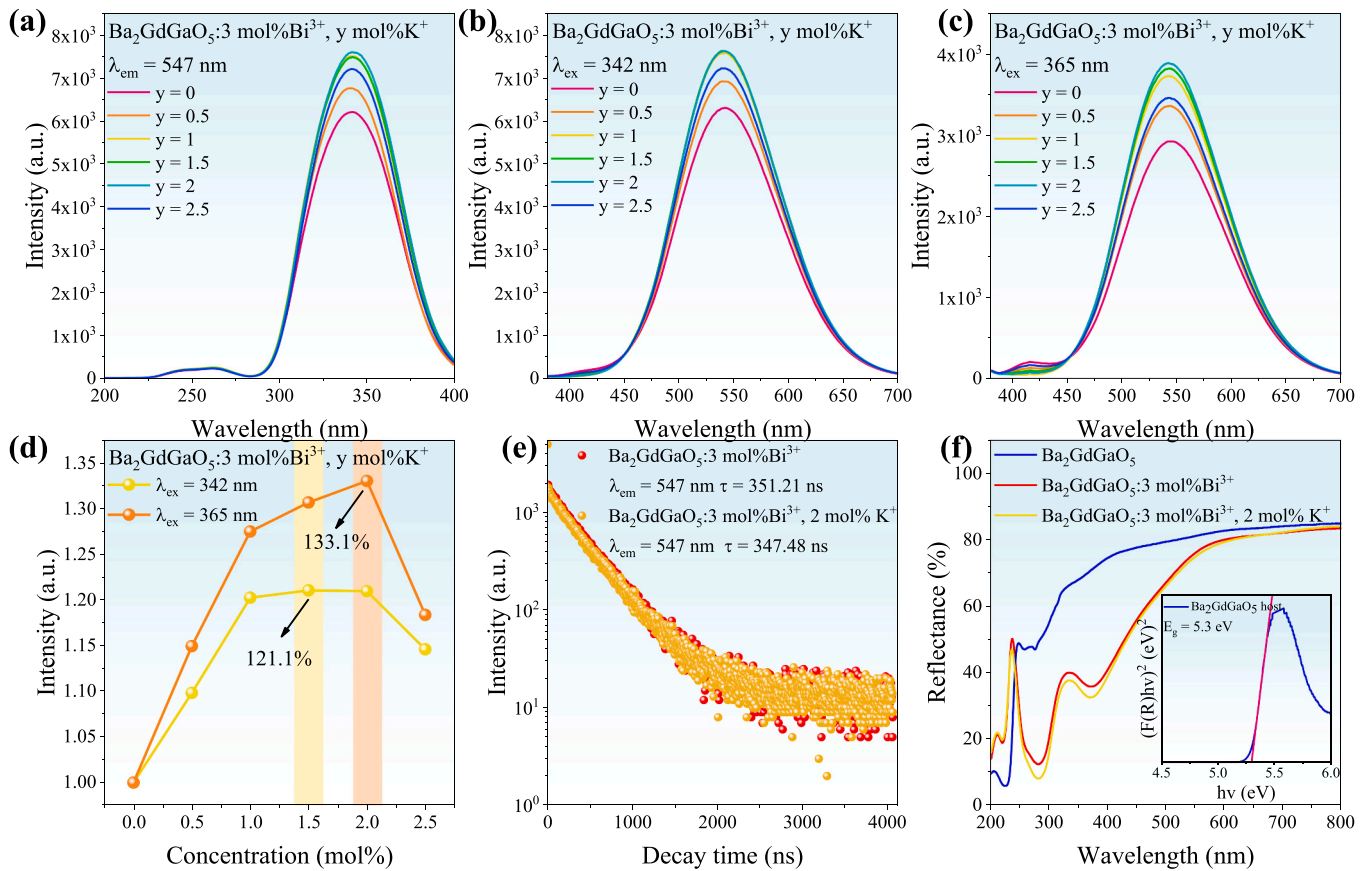


Fig. 4. (a) PLE and (b-c) PL spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, y \text{ mol}\% \text{K}^+$ phosphors. (d) The relationship between emission intensity and K^+ doping concentration. (e) The decay curves of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$ phosphors. (f) DR spectra of $\text{Ba}_2\text{GdGaO}_5$, $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$, insert figure is the calculation of optical band gap.

$$F(R) = (1 - R)^2 / 2R \quad (5)$$

$$(F(R)hv)^{\frac{1}{n}} = A(hv - E_g) \quad (6)$$

where $F(R)$, R , hv and E_g represent absorption, reflection (%), photon energy and optical band gap, respectively. It is known that similar Ba_2YGaO_5 material is a direct bandgap,[52] so the n value is 1/2, and the band gap value is calculated to be 5.3 eV (illustration in Fig. 4f).

In main lattice $\text{Ba}_2\text{GdGaO}_5$, the interaction of Bi^{3+} dopants with the nearest neighbouring Ga^{3+} and Gd^{3+} ions results in the appearance of two d-energy level states in the bandgap corresponding to $\text{Bi}^{3+}-\text{Ga}^{3+}$ MMCT and $\text{Bi}^{3+}-\text{Gd}^{3+}$ MMCT, respectively. These abundant electron leaps result in significant photoluminescent properties of Bi^{3+} -activated $\text{Ba}_2\text{GdGaO}_5$. At the same time, we calculated the values of the d-energy states ($\text{Bi}^{3+}-\text{Ga}^{3+}$ MMCT and $\text{Bi}^{3+}-\text{Gd}^{3+}$ MMCT) using the empirical equations proposed by Philippe Boutinaud:[23,40]

$$\text{MMCT}(\text{Bi}^{3+}, \text{cm}^{-1}) = \frac{\chi_{\text{CN}=4}(\text{Ga}^{3+})}{d_{\text{corr}}} \quad (7)$$

which is valid for 4-coordinated Ga^{3+} metals, and

$$\text{MMCT}(\text{Bi}^{3+}, \text{cm}^{-1}) = \frac{\chi_{\text{CN}>4}(\text{Gd}^{3+})}{d_{\text{corr}}} \quad (8)$$

which is valid for 6-coordinated Gd^{3+} metals, and

$$d_{\text{corr}} = d_{\text{host}} + \frac{1}{2}[r(\text{Bi}^{3+}) - r(\text{host})] \quad (9)$$

In these equations, $\chi_{\text{CN}=4}(\text{Ga}^{3+})$ and $\chi_{\text{CN}=6}(\text{Gd}^{3+})$ represent the optical electronegativity of Ga^{3+} and Gd^{3+} , respectively. The variable

d_{host} represents the shortest key length of $\text{Bi}^{3+}-\text{Gd}^{3+}$. The variables r (Bi^{3+}) and $r(\text{host})$ represent the ionic radius of Bi^{3+} and the ionic radius of Bi^{3+} occupying the matrix cation Gd^{3+} , respectively.[40] Based on the above equations and data in Table 3, the $\text{Bi}^{3+}-\text{Ga}^{3+}$ MMCT value is approximately 47714 cm^{-1} (210 nm) in the ultraviolet. This value should be disregarded. The $\text{Bi}^{3+}-\text{Gd}^{3+}$ MMCT value is approximately 40748 cm^{-1} (245 nm), which corresponds to the weak peak in the excitation spectrum (250 nm). Hence, it can be concluded that $\text{Bi}^{3+}-\text{Gd}^{3+}$ MMCT contributes to luminescence. Luminescence mechanism diagram of $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor is shown in Fig. 5. Under the excitation of n-UV light, the electrons transition from the ground state of $^1\text{S}_0$ to the excited state of $^3\text{P}_1$. After which the nonradiative relaxation occurs to the lowest position of the MMCT state and a large Stokes shift creates. Finally, the electrons return to their ground state by a radiative transition, accompanied by intense yellow light emission. The MMCT state comes from the interaction between Bi^{3+} levels and the Gd^{3+} (d^0 configuration) excited states.

3.3. Spectral tunability and zero-thermal-quenching performance

To achieve the spectral tunability performance, we continue to doping another activator Eu^{3+} to get $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, n \text{ mol}\%$

Table 3

Theoretical energy values of the MMCT states of $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ from the semi-empirical model.

sample	$\chi_{\text{CN}} (\text{M}^{n+})$	$d_{\text{corr}} (\text{\AA})$	MMCT (cm^{-1})
$\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$	1.386(Gd^{3+})	4.425($\text{Bi}^{3+}-\text{Gd}^{3+}$)	40748
	1.755(Ga^{3+})	4.095($\text{Bi}^{3+}-\text{Ga}^{3+}$)	47714

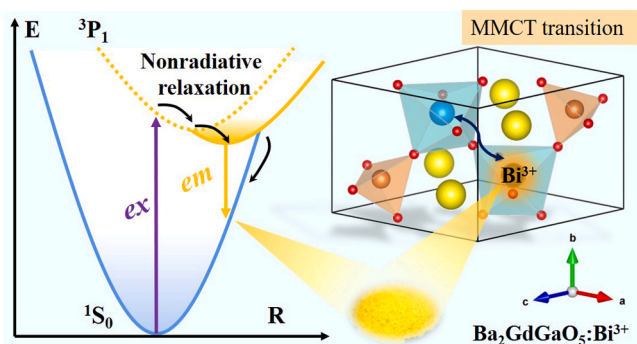


Fig. 5. Luminescence mechanism diagram of $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor.

Eu^{3+} ($n = 0-5$) phosphors. It has been previously analyzed that doping of Eu^{3+} will not affect their phase (in Fig. 2c). The PL spectra are exhibited in Fig. 6a, as the concentration of Eu^{3+} increases, the emission of several typical Eu^{3+} ions at 600 nm narrow band red light gradually enhanced. When $n = 4$ mol%, the red light reaches maximum. However, when the concentration increased further, the red light began to weaken, which may be due to the competition between Bi^{3+} and Eu^{3+} ions. According to CIE chromaticity coordinates (Fig. 6b), with increasing Eu^{3+} ion concentration, the chrominance coordinates are gradually moving towards the red zone. The corresponding phosphor photographs are shown in Fig. 6c. Under 365 nm n-UV light, the color of these phosphors gradually changes from yellow light to orange red light. These phosphors still appear milky white under natural light, and no significant changes have occurred.

The thermal quenching resistance of phosphors is also an important index to evaluate their luminescent properties. The temperature-dependent emission spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$ phosphors are presented in Fig. 7. The PL spectra in the range of 25 °C to 300 °C at 342 nm excitation were measured. With the increase of temperature, the PL intensity of these two phosphors both initially increase and then decrease. The normalized temperature-dependent PL spectra (Fig. 7b, e) show a blue shift in the peak wavelength of both phosphors from 547 nm blue to 527 nm and from 551 nm blue to 531 nm, respectively. The reason for this phenomenon may be the increase in population of higher vibrational levels of the local Bi^{3+} radiation center with increasing temperature. Moreover, as the temperature increases, the lattice will expand and the crystal field will weaken, resulting in blue shift of spectra. In the next stage, we calculated the integral area of the emission spectra and expressed it as

the Integrated PL intensity, as shown in Fig. 7 f. When the temperature reaches 150 °C, the Integrated PL intensity of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$ maintained 101% and 98.2% of the initial intensity respectively, achieving zero thermal quenching. When the temperature reaches 250 °C, the luminescent thermal quenching can still be about 20%. In the actual production application, the luminous intensity of phosphor at 85 °C and 105 °C is an important index to evaluate the lamp bead. We conducted relevant tests, as shown in Fig. 7 f. It can be found that the luminescent intensity of the phosphor $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ at 85 °C and 105 °C is 107% and 108% of that at room temperature (25 °C), respectively. Meanwhile, the luminescent intensity of phosphor $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$ at both 85 °C and 105 °C were 100% of that at room temperature. The slight change of thermal stability is related to the modification of grain after adding the flux. Therefore, these phosphors have strong thermal quenching resistance. This abnormal heat quenching may be attributed to the defects of the host material, which can capture photons and generate thermal stimulation radiation benefits. The defect energy level dominates when the temperature is high and it can compensate the light loss caused by thermal quenching. Therefore, the luminescent intensity will increase first. When the temperature is too high, thermal quenching is dominant, so the luminescence intensity decreases.

3.4. WLED application

To verify the application possibility of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor, a series of pc-LED were prepared with 365 nm n-UV chips. In Fig. 8a, the first is the EL spectrum of pc-LED prepared with $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ phosphor. It exhibits a broadband yellow light emitting with a color purity of 82.4% and corresponding CIE coordinates of (0.4527, 0.4877). A pc-WLED (LED2) was obtained by combining this phosphor with commercial BAM: Eu^{2+} . The CIE coordinate was (0.3472, 0.3490), CCT was 4911 K, and CRI reached 88.1. By introducing Eu^{3+} ions and increasing the red part of the spectrum, a LED3 with higher CIR of 91.5 was obtained. The CIE coordinate of the LED3 was shifted to the red light region (0.3737, 0.3530), and the CCT further decreased to 4014 K, which was typical warm white light emitting.

4. Conclusion

In conclusion, a novel zero-thermal-quenching broadband yellow-emitting Bi^{3+} -activated $\text{Ba}_2\text{GdGaO}_5:\text{Bi}^{3+}$ phosphor was synthesized based on MMCT transition. The FWHM is 112 nm and the IQE reaches 77%. When the temperature is heated up to 150 °C, the PL intensity can be maintained at 101% of normal temperature. The corresponding

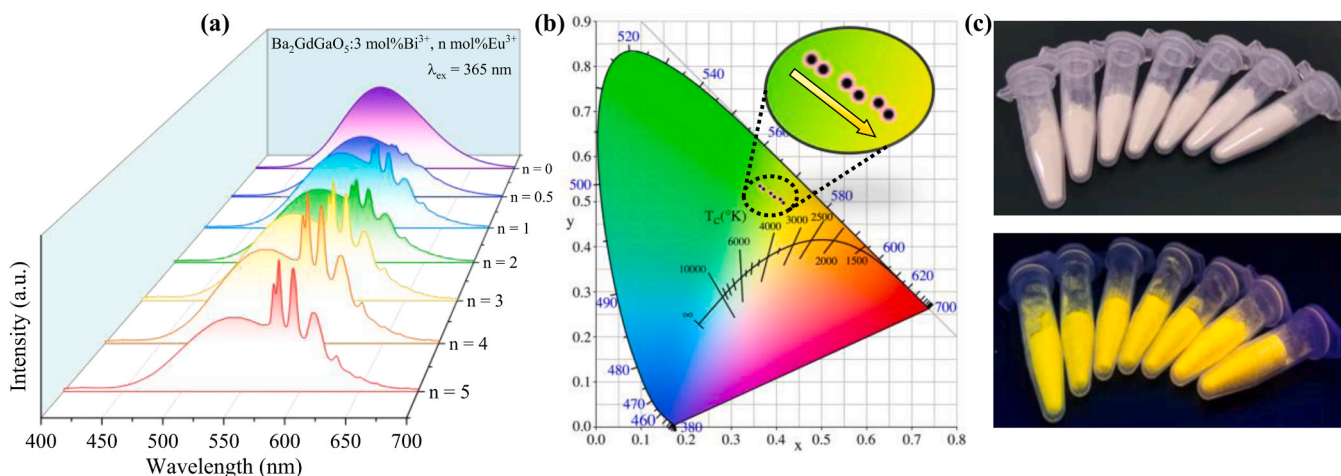


Fig. 6. (a) The PL spectra and (b) CIE chromaticity of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, n \text{ mol}\% \text{Eu}^{3+}$ ($n = 0-5$) phosphors. (c) The photographs under natural light and 365 nm n-UV light.

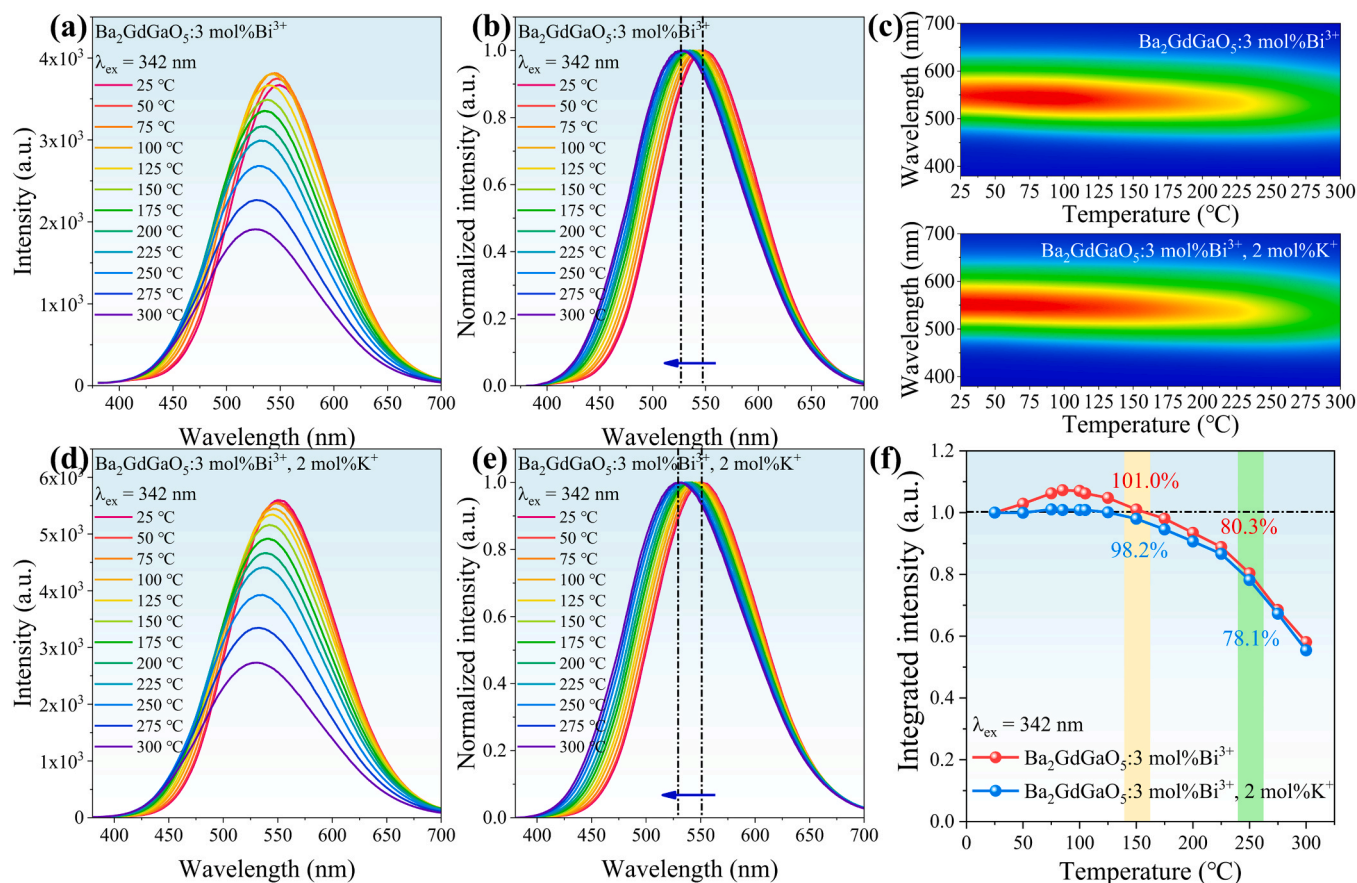


Fig. 7. (a-b) Temperature-dependent and normalized temperature-dependent PL spectra from 25 °C to 300 °C of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$. (c) Temperature-dependent PL spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$. (d-e) Temperature-dependent and normalized temperature-dependent PL spectra of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$. (f) Integrated emission intensity as a function of temperature of $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}$ and $\text{Ba}_2\text{GdGaO}_5:3 \text{ mol}\% \text{Bi}^{3+}, 2 \text{ mol}\% \text{K}^+$.

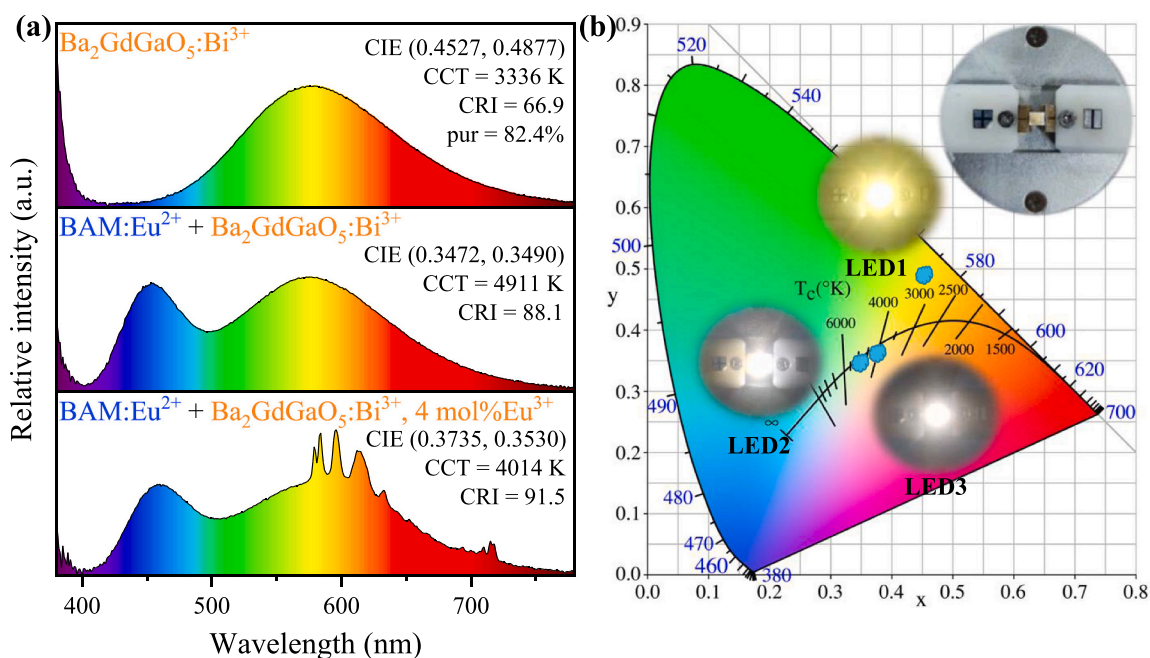


Fig. 8. (a) EL spectra of as-fabricated pc-LED. (b) CIE chromaticity coordinates and pc-LED photographs.

relationship between crystal structure and luminescent mechanism is studied in detail. K^+ doping as flux can improve the crystallinity of the material, and thus enhance the PL intensity of $Ba_2GdGaO_5:3 \text{ mol\%Bi}^{3+}$ phosphor to 133.1% excited at 365 nm. Finally, through the preparation of pc-WLED, the application potential in the field of warm white light is demonstrated. A pc-WLED is prepared by combining $Ba_2GdGaO_5:3 \text{ mol\%Bi}^{3+}$ with $BAM:Eu^{2+}$ phosphor, which shows a CRI of 88.1 and a CCT of 4911 K. The CRI is increased to 91.5 and the CCT is lowered to 4014 K by doping with Eu^{3+} , and the warm white light emission is obtained.

Author contributions

Ke Chen and Peixin Gao contributed equally to this work. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

CRediT authorship contribution statement

Peixin Gao: Writing – review & editing, Writing – original draft. **Zengtao Zhang:** Writing – review & editing. **Yibiao Ma:** Writing – review & editing. **Zan Luo:** Writing – review & editing. **Ke Chen:** Writing – review & editing, Writing – original draft. **Zhi Zhou:** Supervision, Resources. **Maxim S Molokeev:** Methodology, Data curation. **Mao Xia:** Supervision, Resources.

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.

Data Availability

Data will be made available on request.

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