

A strong green-emitting phosphor: $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ for UV-excited white light-emitting-diodes

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$\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors are synthesized by the solid reaction method, and the phases and luminescence properties of the obtained phosphors are well characterized. The emission spectra of $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ exhibit the typical emissions of Tb^{3+} . Concentration quenching of Tb^{3+} is not observed in $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$, likely because the shortest average distance of $\text{Tb}^{3+}-\text{Tb}^{3+}$ in $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ is adequately long such that energy transfer between $\text{Tb}^{3+}-\text{Tb}^{3+}$ ions cannot take place effectively. This result indicates that $\text{K}_3\text{Tb}(\text{PO}_4)_2$ phosphors have potential application in near ultraviolet (n-UV)-convertible phosphors for white light-emitting diodes.

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Light-emitting diodes (LEDs) were first reported in 1960s and have since then drawn significant attention from the research community. White light LEDs (w-LEDs) are considered next-generation illumination resources because of their high efficiency, compactness, long operational lifetime, and environment-friendliness^[1]. Currently, the commercial method of generating white light involves combination of a blue InGaN LED chip and a yellow-emitting phosphor (YAG:Ce³⁺)^[2]. However, low color-rendering indices and high correlated color temperatures attributed to the lack of red light seriously affect the quality of white light obtained from LEDs^[3]. To address these issues, a near-ultraviolet (n-UV) LED (350-420 nm) coated with tricolor phosphors that can provide superior color uniformity with a high color-rendering index and excellent light quality was recently developed^[4]. Thus, exploration of novel tricolor phosphors for n-UV applications is an important part of the development of w-LEDs.

Tb^{3+} ions are frequently applied as activators of green emission because of their predominant $^5\text{D}_4-^7\text{F}_5$ transition peak at around 542 nm. However, the intensities of Tb^{3+} emissions are restricted by concentration quenching in most host materials. An inorganic phosphate with the general formula $\text{K}_3\text{R}(\text{PO}_4)_2$ ($\text{R}=\text{Nd}$, Eu , and Tb) and showing no concentration quenching of luminescence even under large amounts of doped activators has been proposed^[5]. This structure belongs to the general formula $M_3\text{R}(\text{PO}_4)_2$, where M is an alkali metal cation and R is a trivalent rare-earth cation. Zhao *et al.*^[6] reported the crystal structure of $\text{K}_3\text{Gd}(\text{PO}_4)_2$ in detail. Ju *et al.*^[5] studied a reddish orange-emitting phosphor $\text{K}_3\text{Eu}(\text{PO}_4)_2$ and indicated that concentration quenching does not take place in this system even when the doping concentration of Eu^{3+} reaches 100%. Similar phenomena were observed by Mikhailik *et al.*^[7], who studied the luminescence properties of $\text{K}_3\text{Tb}(\text{PO}_4)_2:\text{Eu}$ excited under Vacuum ultraviolet (VUV). However, while the

absence of concentration quenching in $M_3\text{R}(\text{PO}_4)_2$ phosphor has been reported, little information is available to explain the mechanism of non-concentration quenching. In this letter, we investigate the photoluminescence (PL) properties of $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors and attempt to describe the mechanism of non-concentration quenching. $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors may serve as green-emitting phosphors for future n-UV w-LEDs because of their high luminance emission.

$\text{K}_3\text{Gd}_{1-x}(\text{PO}_4)_2:x\text{Tb}^{3+}$ ($x=0, 0.25, 0.4, 0.5, 0.6, 0.7, 0.8, 1$) phosphors were synthesized by the conventional solid-state method. Analytical reagent-grade K_2CO_3 , Gd_2O_3 , TbF_3 , and $\text{NH}_4\text{H}_2\text{PO}_4$ were employed as raw materials. The chemicals were weighed out, mixed homogeneously using an agate mortar for 30 min, and then placed in an alumina crucible. This crucible was heated at 950 °C for 6 h under an air atmosphere and slowly cooled to room temperature.

The phases of the obtained samples were identified by X-ray powder diffraction (XRD) with $\text{Cu K}\alpha$ ($\lambda=0.15418$ nm) radiation at a scanning step of 0.02° in the 2θ range from 10° to 60°; the instrument was operated at 36 kV and 30 mA (Rigaku Model D/max-2200). The PL and PL excitation spectra of the phosphors were measured with a HITACHI F-7000 fluorescence spectrophotometer using a static 150-W Xe lamp as the excitation source. All of the measurements were carried out at room temperature.

Figure 1 shows the XRD patterns of the $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors. Analysis of the XRD patterns obtained confirms that the compounds are of a single phase. The $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ orthophosphates recovered are isotopic to monoclinic $\text{K}_3\text{Gd}(\text{PO}_4)_2$ (PDF#49-1085) or $\text{K}_3\text{Tb}(\text{PO}_4)_2$ (PDF#50-1769) with a space group of $\text{P}2_1/\text{m}$ (11). No detectable impurity peaks within the whole range of Tb^{3+} concentrations studied are observed. The crystal structure of $\text{K}_3\text{Gd}(\text{PO}_4)_2$ belongs to a monoclinic crystal system with a space group of $\text{P}2_1/\text{m}$

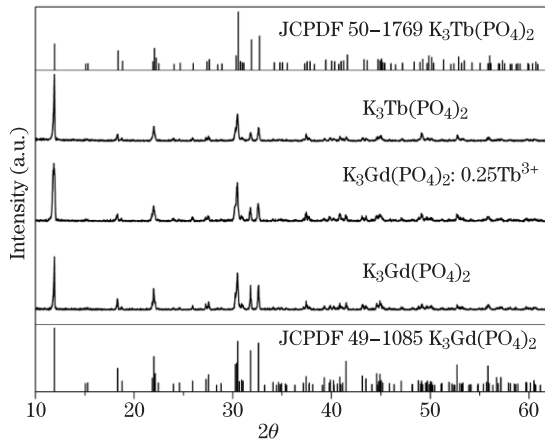


Fig. 1. XRD patterns of some phosphor samples.

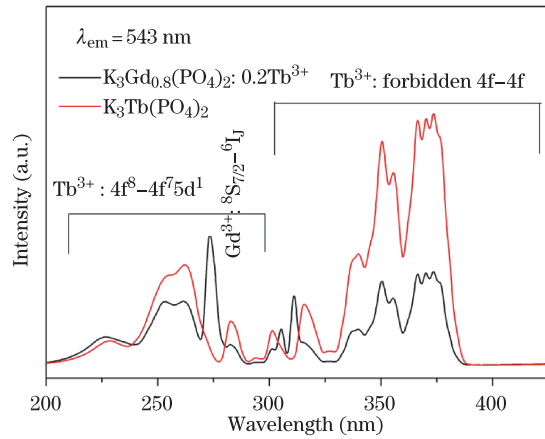


Fig. 2. (Color online) Excitation spectra of $\text{K}_3\text{Gd}_{0.8}(\text{PO}_4)_2:0.2\text{Tb}^{3+}$ and $\text{K}_3\text{Tb}(\text{PO}_4)_2$.

($Z=2$). According to the effective ionic radii of cations with different coordination numbers reported by Shannon^[8], the ionic radius of seven-coordinated Gd^{3+} is 0.100 nm, and the ionic radius of seven-coordinated Tb^{3+} is 0.098 nm. Three different K^+ sites with coordination numbers of 9, 10, 11 and radii of 0.155, 0.159, and 0.164 nm, respectively, are observed. These sites are too large for Tb^{3+} ions to occupy. Considering the principles of ionic radii matching, Tb^{3+} ions must substitute Gd^{3+} sites in the $\text{K}_3\text{Gd}(\text{PO}_4)_2$ host.

Figure 2 shows the excitation spectra of $\text{K}_3\text{Gd}_{0.8}(\text{PO}_4)_2:0.2\text{Tb}^{3+}$ and $\text{K}_3\text{Tb}(\text{PO}_4)_2$ phosphors obtained by monitoring 543-nm emissions. The broad band at 210–275-nm corresponds to the spin-allowed transition from the 4f state to the 5d state of Tb^{3+} ions, while sharp lines in the range of 300–400 nm are ascribed to excitation due to forbidden f-f transitions of the Tb^{3+} ion^[9]. The sharp line located at about 273 nm in the spectrum of $\text{K}_3\text{Gd}_{0.8}(\text{PO}_4)_2:0.2\text{Tb}^{3+}$ is attributed to the $8^8\text{S}_{7/2}-6^6\text{I}_J$ transition of Gd^{3+} and dominates the spectrum^[10]. However, when Gd^{3+} ion sites are occupied entirely by Tb^{3+} ions, as in the excitation spectrum of $\text{K}_3\text{Tb}(\text{PO}_4)_2$, the Gd^{3+} excitation peak disappears and the 4f–4f transitions of Tb^{3+} increase tremendously. The maximum excitation intensity is located at about 373 nm, which matches with n-UV chip.

Figure 3 shows the emission spectra of $\text{K}_3\text{Gd}_{1-x}(\text{PO}_4)_2:x\text{Tb}^{3+}$ excited at 373 nm. Emission peaks located at 485, 543, 586, and 623 nm correspond to the typical emissions of Tb^{3+} ions, which are associated with $5^5\text{D}_4-7^7\text{F}_J$ ($J=6, 5, 4$, and 3) characteristic transitions^[11]. In the inset in Fig. 3, the Tb^{3+} emission intensity observed at 543 nm increases gradually with increasing Tb^{3+} content and achieves a maximum value even when Tb^{3+} ions entirely occupy the Gd^{3+} sites. This result indicates that concentration quenching does not take place in the host. To the best of our knowledge, concentration quenching is caused by energy transfer among activators, that is, energy transfer occurs from one activator to another until an energy sink in the lattice is reached^[12]. Therefore, a possible reason for the absence of concentration quenching is that energy transfers between $\text{Tb}^{3+}-\text{Tb}^{3+}$ in $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ do not occur effectively. According to Blasse, to achieve the critical concentration, the shortest average distance between activator ions must be equal to the critical distance R_0 ^[13]. When the activator concentration exceeds the critical concentration, the shortest average distance between activator ions is less than the critical distance and energy transfer takes place, resulting in concentration quenching. The critical distance of $\text{Tb}-\text{Tb}$ can be calculated using the concentration equation:

$$R_0 = 2 \left[\frac{3V}{4\pi X_c N} \right]^{1/3},$$

where X_c is the critical concentration, N is the number of cations in the unit cell, and V is the volume of the unit cell. Because of the absence of concentration quenching in $\text{K}_3\text{Tb}(\text{PO}_4)_2$, X_c was taken as 100%. Substituting the experimental and analytical values of V , N , and X_c (0.3936 nm³, 2, and 100%, respectively) into the equation, the critical distance is determined to be about 0.722 nm.

The absence of concentration quenching under UV excitation is usually related to the structure of the host. Thus, the crystal structure of $\text{K}_3\text{Gd}(\text{PO}_4)_3$ was constructed by utilizing its fractional atomic coordinates. Gd ions in $\text{K}_3\text{Gd}(\text{PO}_4)_3$ form a two-dimensional (2D) layer structure. In one layer, one Gd ion is surrounded by ten neighboring Gd ions, and the distances between ions are $d_1=d_2=1.37031$ nm, $d_3=d_4=0.48620$ nm, $d_5=d_6=0.56206$ nm, $d_7=d_8=0.63586$ nm, and $d_9=d_{10}=0.94452$ nm. The shortest average distance

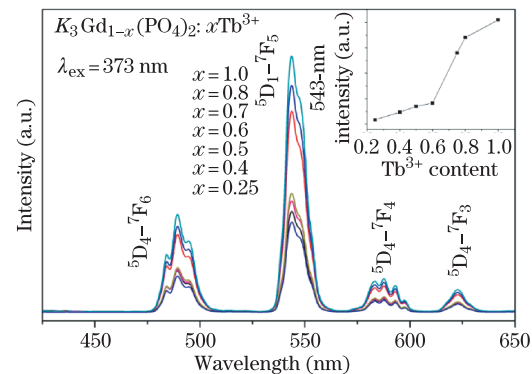


Fig. 3. (Color online) Emission spectra of $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ with different Tb^{3+} doping contents. Inset: Relationship between Tb^{3+} emission at 543 nm and Tb^{3+} content.

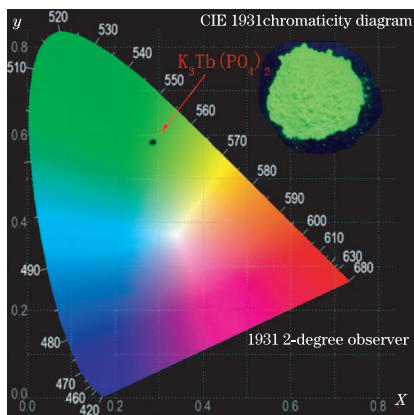


Fig. 4. (Color online) Representation of the CIE chromaticity coordinates of $\text{K}_3\text{Tb}(\text{PO}_4)_2$ phosphors under 373 nm excitation and a digital photo of $\text{K}_3\text{Tb}(\text{PO}_4)_2$ under 365 nm UV lamp excitation.

between Gd ions is then calculated as 0.800 nm by taking the average of these distances. When Tb ions occupy all of the lattice sites of Gd ions, the average distance of Tb–Tb is similar to that of Gd–Gd. Apparently, it is longer than critical distance of Tb^{3+} – Tb^{3+} calculated through concentration equation, which demonstrates energy transfer cannot happen between Tb ions. As such, concentration quenching cannot take place in the $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphor. The quantum efficiency of $\text{K}_3\text{Tb}(\text{PO}_4)_2$ is about 69.4%, which is a relatively high value, because of the absence of concentration quenching in the phosphor. These results indicate that $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors may be used as green LED phosphors.

Figure 4 shows the CIE chromaticity coordinates of $\text{K}_3\text{Tb}(\text{PO}_4)_2$ under 312-nm excitation as calculated using Zolix Color Convert software; a digital photograph of the same phosphor under 365-nm UV lamp excitation is also provided. The CIE coordinates of $\text{K}_3\text{Gd}(\text{PO}_4)_2:x\text{Tb}^{3+}$ ($x=0.25, 0.4, 0.6, 0.8, 1$) are calculated as follows: (0.296, 0.574), (0.300, 0.589), (0.301, 0.590), (0.299, 0.579), (0.297, 0.585). These CIE coordinates are nearly identical and may be found in the yellowish-green region. The photo obtained shows intense green light, which indicates that $\text{K}_3\text{Tb}(\text{PO}_4)_2$ phosphors have potential application as UV-convertible green phosphors in w-LEDs.

In summary, $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors are prepared by the solid reaction method, and the luminescence properties and CIE coordinates of the resultant products are investigated. Phase analysis of the phosphors is also performed. Concentration quenching is not observed in the $\text{K}_3\text{Gd}(\text{PO}_4)_2:\text{Tb}^{3+}$ phosphors because the shortest average distance of Tb^{3+} – Tb^{3+} in $\text{K}_3\text{Tb}(\text{PO}_4)_2$ is adequately long such that energy transfer between Tb^{3+} – Tb^{3+} ions cannot take place effectively. This result indicates that $\text{K}_3\text{Tb}(\text{PO}_4)_2$ phosphors have potential application as n-UV-convertible phosphors for white LEDs.

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