Single-phased white-light-emitting KCaGd(PO₄)₂:Eu²⁺, Tb³⁺, Mn²⁺ phosphors for LED applications†

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Single-phased white-light-emitting KCaGd(PO₄)₂:Eu²⁺, Tb³⁺, Mn²⁺ phosphors were synthesized by a solid state reaction. By changing the doping contents of Eu²⁺, Tb³⁺ and Mn²⁺, the emission hue could be precisely controlled via the energy transfer mechanism. The structure refinement, luminescence properties as well as their thermal quenching and energy transfer mechanism were firstly investigated. The mechanism of transferring energy between Eu²⁺, Mn²⁺ and Tb³⁺ ions was also discussed in this study. The optimal composition for white-light is KCa(Gd₀.₃Eu₀.₁Mn₀.₁)(Gd₀.₃Tb₀.₁)(PO₄)₂, which gives the CIE coordinates of (0.2984, 0.3171). These results indicate that the KCaGd(PO₄)₂:Eu²⁺, Mn²⁺, Tb³⁺ phosphor could be a promising single-composition phosphor for applications involving white-light NUV LEDs.

Introduction

White light-emitting diodes (WLEDs) by conjunction of the InGaN chip and Y₃Al₅O₁₂:Ce³⁺ phosphor gave another revolution in display and general lighting applications to replace conventional incandescent or fluorescence lamps due to their advantages of being mercury-free, energy saving, high efficiency, and long life.1–3 However, this combination of blue chip and yellow phosphor suffered from the disadvantages of low color-rendering (Ra < 80) due to the scarcity of red emission and different degradation rates of chip and phosphor resulting in chromatic aberration and poor color stability for longer working times. Thus, single-phased white-emitting phosphors for ultraviolet (UV) or near-ultraviolet (NUV) excitations have drawn much attention for solid state lighting due to the merits of excellent Ra and color stability. One of the strategies for generating white light from single-phased phosphors is by doping multi rare-earth ions, as co-doping sensitizers and activators, into the same host. The energy transfer mechanisms of sensitizer/activator pairs, such as Eu²⁺/Mn²⁺, Ce³⁺/Eu²⁺, Ce³⁺/Mn²⁺, Ce³⁺/ Tb³⁺/Mn²⁺ and Eu³⁺/Tb³⁺/Mn²⁺, have been investigated in many hosts, including AₓCa₃SiO₈·Eu²⁺·Mn²⁺ (A = Ca, Sr, Ba),4 Srₓβ₂O₂·Ce³⁺·Eu²⁺,5 Naₓ₀.₄(B₁₂O₄)₃·Ce³⁺·Mn²⁺,6 CaₓGdₓ·(PO₄)₂·SiO₂·Ce³⁺·Tb³⁺·Mn²⁺,7 BaMgxAl₅SiO₄:Eu²⁺·Tb³⁺·Mn²⁺ and so on. Our preliminary research on the energy transfer mechanism between sensitizer and activator includes Ca₅SiO₈·F₂·Eu²⁺·Mn²⁺,9–10 KCa₁₀(PO₄)₂·Eu²⁺·Mn²⁺·Tb³⁺,10 CaₓY(PO₄)₂·Ce³⁺·Eu²⁺,11 CaₓY(PO₄)₂·Ce³⁺·Mn²⁺·Tb³⁺ and CaₓY(GaO)₄·(BO₆)₃·Ce³⁺·Mn²⁺·Tb³⁺ for application in NUV LEDs. Wang et al.14 reported the spectroscopic properties of red-emitting KCa(Y(PO₄)₃):Eu³⁺ phosphors peaking at 616 nm excited in the vacuum ultraviolet (VUV) region. Zhang et al.15 further investigated the VUV-UV spectroscopic properties of a series of RE (RE = Ce³⁺, Eu³⁺ and Tb³⁺)-doped KMLn(PO₄)₂ (M²⁺ = Ca, Sr; Ln³⁺ = Y, La, Lu) phosphors. To the best of our knowledge, the luminescence properties of KCaGd(PO₄)₂:Eu²⁺, Tb³⁺, Mn²⁺ as well as the mechanism of energy transfer have not been reported in the literature.

In our previous work, luminescence properties and the energy transfer mechanism of KCa(Y(PO₄)₃):Eu³⁺, Mn³⁺ phosphors were investigated.16 In this study, we report a novel white-emitting phosphor, KCaGd(PO₄)₂:Eu²⁺, Tb³⁺, Mn²⁺, in which the energy transfer mechanism between blue-emitting Eu³⁺, green-emitting Tb³⁺ and red-emitting Mn²⁺ in the host as well as the Rietveld refinement, thermal quenching and luminescent properties were firstly investigated.

Experimental

Materials and synthesis

The KCaGd(PO₄)₂ host and a series of rare-earth doped KCaGd(PO₄)₂ phosphors were synthesized by solid state reactions. These phosphors were prepared from a mixture of K₂CO₃ (A. R.), CaCO₃ (A. R.), Gd₂O₃ (A. R.), (NH₄)₂HPO₄ (A. R.),
Eu₂O₃ (A. R.), Tb₄O₇ (A. R.) and MnO (A. R.) in the stoichiometric composition. The weighed powder was mixed in an agate mortar and placed in an alumina crucible. This crucible was heated at 1250 °C for 8 h under a reducing atmosphere of 15% H₂/85% N₂, and cooled slowly to room temperature.

Materials characterization

The crystal structure and phase purity of KCaGd(PO₄)₂ were characterized by using powder synchrotron radiation in the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The structure refinement of the KCaGd(PO₄)₂ sample was further investigated by the GSAS program. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured using a Spex Fluorolog-3 Spectrofluorometer (Instruments S.A., N.J., U.S.A) equipped with a 450 W Xe light source and double excitation monochromators. The samples were excited under 45° incidence, and the emitted fluorescence was detected with a Hamamatsu Photonics R928 type photomultiplier perpendicular to the excitation beam. The CIE chromaticity coordinates for all samples were measured with a Laiko DT-101 color analyzer equipped with a CCD detector (Laiko Co., Tokyo, Japan). Thermal quenching measurements were investigated using a heating apparatus (THMS-600) in combination with the PL equipment.

Results and discussion

Crystal structure

Vlasse et al. reported the X-ray single crystal structure data of KCaNd(PO₄)₂.¹⁷ To consider the similar ionic radii and stronger luminescence, Nd atoms were replaced by Gd atoms in this study. Fig. 1 shows experimental, calculated, and difference results in Rietveld refinement XRD patterns of the KCaGd(PO₄)₂ host lattice at room temperature by the GSAS program. The initial parameters of refinement for the KCaGd(PO₄)₂ sample were referred from the single crystal data of KCaNd(PO₄)₂ (ICSD-35098). The single-phase of KCaGd(PO₄)₂ was successfully synthesized in this study, crystalized as an hexagonal structure with space group of P6₃22 (Table 1). For KCaGd(PO₄)₂, the lattice constants were determined to be a = 6.94273(5) Å, b = 6.94273(3) Å, c = 6.34659(1) Å, and cell volume was obtained to be 264.931(7) Å³. All atom positions, fraction factors and thermal vibration parameters were refined with convergence and well satisfied the reflection condition, \( \chi^2 = 3.249 \), \( R_p = 4.21\% \), \( R_{wp} = 7.08\% \). The results show the effect of atomic replacement on the lattice constants and cell volume. Through Gd replacement, the lattice constants and cell volume are smaller than KCaNd(PO₄)₂.

Changes of cation in the host lattice might be the reason for changes in emission wavelength. The smaller cation leads to the possibility that the radius of RE-O changes, which then makes the emission wavelength shift. The inset in Fig. 1 shows the crystal structure of KCaGd(PO₄)₂. The di-valance ions occupied the large empty tunnels of the lattice and the trivalence position was statistically occupied by both Gd³⁺ and Ca²⁺ ions, which results in chains of edge sharing [Ca,Gd]O₈ polyhedra interconnected by corner sharing.

Photoluminescence properties

Fig. 2a shows the PL and PLE spectra of the as-synthesized KCaGd(PO₄)₂:1%Eu²⁺ phosphor. The inset in Fig. 2a shows the phosphor photo excited at 365 nm in the UV box. First of all, the PL spectrum of KCaGd(PO₄)₂:1%Eu²⁺ exhibited a single and intense blue emission peak at 463 nm due to the 4f–5d transition of Eu²⁺ ions occupied 8-coordinated Ca²⁺ sites in the lattice. The phosphor image shown in the inset of Fig. 2a exhibited an intense blue color under excitation of 365 nm in the UV box. The PLE spectrum of KCaGd(PO₄)₂:1%Eu²⁺ shown in Fig. 2a gives a broad hump between 268 and 420 nm, which is typically attributed to the 4f–5d electronic dipole allowed transitions of Eu²⁺ with the electronic configuration of 4f⁷–5d¹. The broad excitation spectrum indicates that KCaGd(PO₄)₂:Eu²⁺ phosphors could be excitable by both UV

| Table 1 Refinement structure parameters of KCaGd(PO₄)₂ at room temperature |
|-----------------------------|-------------------------------|-------------------------------|------------------------------|
| KCaGd(PO₄)₂                |                               |                               |
| Crystal system:             | hexagonal                     |                               |
| Space group:                | P6₃22                         |                               |
| Cell parameters:            | a = 6.94273(5) Å              | b = 6.94273(3) Å              |
|                            | c = 6.34659(1) Å              | \( \gamma = 120^\circ \)     |
|                            | \( x = 90^\circ \)             | \( \beta = 90^\circ \)        |
| Cell volume:                | 264.931(7) Å                 |                               |
| \( \chi^2 = 3.249 \)       |                               |                               |
| \( R_p = 4.21\% \)         |                               |                               |
| \( R_{wp} = 7.08\% \)      |                               |                               |

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and NUV chips for LED applications. Fig. 2b displays the PL spectra of KCaGd(PO₄)₂:Eu²⁺ phosphors with different doping concentrations of Eu²⁺. The inset of Fig. 2b demonstrates the PL intensity of KCaGd(PO₄)₂:Eu²⁺ phosphors as a function of Eu content. The results indicate that the optimal doping concentration of Eu²⁺ in the KCaGd(PO₄)₂ host was 1 mol%. The PL intensity decreased as long as the concentration exceeded the critical concentration due to the phenomena of concentration quenching. As a result, the critical energy transfer distances between Eu²⁺ ions in the phosphor can be calculated by the following equation:

$$R_c = 2\left(\frac{3V}{4\pi x_c Z}\right)^{1/3}$$  (1)

where $x_c$ is the critical concentration, $Z$ is the number of cation sites in the unit cell, and $V$ is the volume of the unit cell. In this case, $V = 264.93$ Å³, $Z = 1$ and the critical doping concentration of Eu²⁺ in the KCaGd(PO₄)₂ host was found to be 0.01. Thus, $R_c$ of Eu³⁺ was then determined to be 36.98 Å.

The quantum efficiencies of composition-optimized phosphors-KCaGd(PO₄)₂:1%Eu²⁺ and the blue-emitting commodity of the BaMgAlO₁₇:Eu²⁺ phosphor are measured by integrating spheres under the excitation wavelength of 365 nm. The quantum efficiencies of KCaGd(PO₄)₂:1%Eu²⁺ and BaMgAlO₁₇:Eu²⁺ were determined to be 13.2% and 94.5%, respectively. The luminescence intensity and quantum efficiency of the as-synthesized phosphor could be further improved by using synthetic process optimization and choices of fluxes.

The temperature dependence of luminescence for the KCaGd(PO₄)₂:1%Eu²⁺ under 365 nm excitation is shown in Fig. 3a. The activation energy ($E_a$) can be expressed by:

$$\ln\left(\frac{I_o}{I}\right) = \ln A - \frac{E_a}{kT}$$  (2)

where $I_o$ and $I$ are the luminescence intensities of the KCaGd(PO₄)₂:1%Eu²⁺ phosphor (by integrating the area of each spectrum) at room temperature and testing temperature, respectively; $A$ is constant; $k$ is the Boltzmann constant (8.617...
The inset displays the relation between $\ln(I_0/I)$ and $1/T$. From the slope value, the $E_a$ was obtained to be 0.038 eV. Fig. 3b further shows the thermal quenching of Eu$^{2+}$ emission intensity in $\text{KCaGd(PO}_4\text{)}_2$ and Eu$^{2+}$ emission in commercial BaMgAl$_{10}$O$_{17}$ phosphor (BAM). At 100 °C, the luminescent intensity of K$\text{CaGd(PO}_4\text{)}_2$:Eu$^{2+}$ is about 84.2% of that of the BAM phosphor. The fair thermal stability compared with the BAM phosphor demonstrated that the K$\text{CaGd(PO}_4\text{)}_2$:Eu$^{2+}$ blue-emitting phosphor could be applied for high power LED applications.

Energy transfer mechanism

Fig. 4 shows the emission mechanism of $\text{KCaGd(PO}_4\text{)}_2$:1%Eu$^{2+}$, $x$%Mn$^{2+}$ phosphors ($x = 0, 1, 3, 5, 7$ and $10$) under 365 nm excitation. The inset in Fig. 4 displays the energy transfer efficiency with different Eu$^{2+}$/Mn$^{2+}$ ratios in the K$\text{CaGd(PO}_4\text{)}_2$ host. By co-doping Eu$^{2+}$ and Mn$^{2+}$ in the host, the phosphors generated blue and red emission bands centered at 462 nm ($4f^{5}5d^{1} \rightarrow 4f^{7}$ transition of Eu$^{2+}$) and 650 nm ($^{4}T_{1}(^{4}G) \rightarrow ^{6}A_{1}(^{6}S)$ transition of Mn$^{2+}$). The intensity of the Eu$^{2+}$ blue emission at 462 nm decreased as the Mn$^{2+}$ content increased to $x$. The intensity of the red emission at 650 nm increased as the Mn$^{2+}$ content increased, reached a maximum at $x = 3$ mol%, and then decreased when $x$ exceeded 3 mol%. The apparent decrease in the PL intensity for Mn$^{2+}$ with $x > 3$ mol% is primarily due to the concentration quenching effect. The energy transfer efficiency of Eu$^{2+}$ and Mn$^{2+}$ as a function of Mn$^{2+}$ concentration showed that the energy transfer efficiency increased with the increase of Mn$^{2+}$ concentration.

The energy transfer mechanism between Eu$^{2+}$ and Mn$^{2+}$ can be investigated via Dexter’s energy transfer formula of multipolar interaction and the following relation can be obtained:20

$$\frac{I_{S_0}}{I_S} \propto C^{3/3}$$

where $I_{S_0}$ and $I_S$ are the luminescence intensities of the sensitizer Eu$^{2+}$ with and without activator Mn$^{2+}$ present, and $C$ is then Mn$^{2+}$ ion concentration. The plots of $(I_{S_0}/I_S)$ versus $C^{3/3}$ with $x = 6, 8, 10$ correspond to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively. Fig. 5a and 5b illustrate the relationships between $(I_{S_0}/I_S)$ versus $C^{3/3}$, revealing linear relationships for both $x = 6$ and 8. These fitting results indicate that the energy transfer from sensitizer Eu$^{2+}$ to activator Mn$^{2+}$ accompanies both electric dipole–dipole and electric dipole–quadrupole interactions, which is similar to that observed in some references.21,22

Owing to the gap between blue-emission of Eu$^{2+}$ at 462 nm and red-emission of Mn$^{2+}$ at 650 nm in the K$\text{CaGd(PO}_4\text{)}_2$ host, the CRI value is very poor. Thus, we introduce green-emitting Tb$^{3+}$ ions into the K$\text{CaGd(PO}_4\text{)}_2$:Eu$^{2+}$,Mn$^{2+}$ phosphor to generate a high quality white color. Fig. 6 shows the PL spectra of K$\text{CaGd(PO}_4\text{)}_2$:1%Eu$^{2+}$,10%Mn$^{2+}$,y%Tb$^{3+}$ phosphors ($y = 1, 5, 10, 20$) excited at 365 nm.
(y = 1, 5, 10, 20) excited at 365 nm. As shown in Fig. 6, the typical Tb3+ emission is due to the $^5D_4 \rightarrow 7F_J$ ($J = 6, 5, 4, 3$), which are $^5D_4 \rightarrow 7F_6 (483, 490, 493 nm)$, $^5D_4 \rightarrow 7F_5 (543, 555 nm)$, $^5D_4 \rightarrow 7F_4 (585, 590 nm)$, $^5D_4 \rightarrow 7F_3 (621, 627 nm)$, respectively. Fig. 7 and Table 2 summarize the CIE chromaticity diagram of the single-phased emission-tunable phosphor KCaGd(PO4)2:1%Eu2+,x%Mn2+,y%Tb3+ under 380 nm excitation. The corresponding CIE coordinates are shown in Fig. 7. The CIE coordinates of point 9 in Fig. 7 with the composition of K(Ca0.89Eu0.01Mn0.1)(Gd0.9Tb0.1)(PO4)2 are (0.2984, 0.3171), which are very close to the CIE coordinates of white light.

Fig. 8 shows the decay life time of KCaGd(PO4)2:x%Eu2+ phosphors ($x = 1, 3, 5, 7$ and 10) under excitation of 380 nm. The time decay was fitted well by the first-order exponential decay mode. The time constants of $t$ of Eu2+ were determined to be 817 ns, 758 ns, 678 ns, 631 ns and 571 ns for 1, 3, 5, 7 and 10% Eu, respectively. The result indicate that Eu2+ was substituted into one coordinated site, which is consistent with our inference that Eu2+ should occupy Ca2+ ions due to the consideration of ionic radii matching.

**Conclusions**

This study reports the synthesis of a novel single-phase white light-emitting NUV LED KCaGd(PO4)2:Eu2+,Tb3+,Mn2+ phosphor using a solid state reaction. The energy transfer from Eu2+ to Mn2+ in the KCaGd(PO4)2 host was resonant type via a non-radiative dipole–quadrupole mechanism. A white light could be generated by co-doping Eu2+, Mn2+ and Tb3+ ions. The optimal-composition for white light is K(Ca0.89Eu0.01Mn0.1)(Gd0.9Tb0.1)(PO4)2, which gives the CIE coordinates of (0.2984, 0.3171). These results indicate that the KCaGd(PO4)2:Eu2+,Mn2+,Tb3+ phosphor could be a promising single-composition phosphor for applications involving white-light NUV LEDs.

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**Notes and references**