Synthesis, crystal structure and photoluminescence properties of Eu$^{2+}$-activated RbCaGd(PO$_4$)$_2$ phosphors

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A series of novel double-phosphate compounds RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ were first synthesized by the Pechini-type sol–gel method, and their structure and luminescence properties were characterized in detail. The compound RbCa$_{0.97}$Gd(PO$_4$)$_2$:0.03Eu$^{2+}$ crystallizes in the hexagonal system with space group $P6_222$ and the parameters $a = 7.006(49)$ Å, $c = 6.358(80)$ Å, and $V = 269.969$ Å$^3$, $Z = 1$. Its crystal structure is similar to that of hexagonal LnPO$_4$, where the Rb atom occupies a large tunnel in the lattice and the Ln position is statistically occupied by both Gd and Ca (Eu) atoms. In addition, RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ produces an intense broadband emission from 400 to 600 nm with the CIE coordinates near $(0.2089, 0.2674)$ and assembles a broad excitation spectrum from 250 to 425 nm. The concentration quenching, crystal-field splitting, critical energy transfers distance and thermally stable luminescence properties of RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ phosphors are all discussed, which indicate that this material can be considered as a promising bluish green phosphor for application in white-light UV LEDs.

1. Introduction

Rare-earth doped inorganic phosphors based on their 4f–4f or 5d–4f transitions have attracted much attention in displays, optoelectronic devices and white-light-emitting diodes (w-LEDs).$^{1-4}$ These materials can produce fluorescent radiation efficiently from ultraviolet (UV) to visible light region with good luminescence yield, which makes them a potential application prospect in solid state lighting region, especially the w-LEDs.$^4$ Eu$^{2+}$ is a kind of important activator ions for its broad-band emission in white-light-emitting phosphors originating from the 4f$^6$5d$^1$–4f$^7$ transition, and it can show a wide range of emissions from blue to red color dependent on the structural characteristics of host crystal.$^5-8$ Among the various host crystals, the double-phosphate compounds cause extensive concern in many research groups.

Double phosphates, MNR(PO$_4$)$_2$, where M and N are alkali metal and alkaline earth metal respectively, and R is rare earth element, are isotypic with the corresponding orthophosphates LaPO$_4$ which are well-known to exist in three structures viz., hexagonal, monoclinic and tetragonal phases.$^9$ These phases have several potential applications by doping more different activators for fabrication new compounds because of their environmental friendliness, thermal and chemical stability, and easy synthesis. Hence, lots of studies with double phosphate as host have been performed.$^{10-14}$ For example, Et-Tabirou et al.$^{15}$ reported the structure of ACaLn(PO$_4$)$_2$ ($A = Cs, Rb$ and K) and confirmed that it was hexagonal LaPO$_4$ type in 1980. Vlasse et al.$^{16}$ determined the structure of KCaNd(PO$_4$)$_2$ which was similar to that of hexagonal LnPO$_4$ where the Nd and Ca atoms occupied the Ln position and K atom occupied a large tunnel. Shaolong Tie et al.$^{17}$ first reported the optical properties of Ln$^{3+}$ ions ($Ln = Gd$, Eu and Dy) doped hexagonal KCaR(PO$_4$)$_2$ ($R = Gd$, Y) system with no striking concentration quenching for Eu$^{3+}$ and Gd$^{3+}$ activators. Yen-Chi Chen et al.$^{18}$ reported the KCaGd(PO$_4$)$_2$:Eu$^{3+}$ phosphor as a down-converting phosphor to improve the power conversion efficiency of single crystalline silicon-based photovoltaic cells. Dongling Geng et al.$^{19}$ investigated the optical properties of green-yellow-emitting KSrGd(PO$_4$)$_2$:Ce$^{3+}$, Tb$^{3+}$/Mn$^{2+}$ phosphors with high quantum efficiency. Kang Geng et al.$^{20}$ presented a novel blue-emitting double-phosphate phosphor Cs$_{0.72}$Ca$_{0.72}$Gd$_{1.28}$(PO$_4$)$_2$:Eu$^{2+}$ which could be excited by UV light.

To the best of our knowledge, there is no report on the crystal structure and fluorescence properties of the novel double-phosphate compound RbCaGd(PO$_4$)$_2$. RbCaGd(PO$_4$)$_2$ crystallizes in the hexagonal system with space group $P6_222$ under ambient conditions. Therefore, Eu$^{2+}$-doped single-phase RbCaGd(PO$_4$)$_2$ are prepared by the Pechini-type sol–gel technique in this work. Crystal structure, crystallographic occupany of Eu$^{2+}$ in RbCaGd(PO$_4$)$_2$ matrix and their luminescence properties are investigated systematically, which indicates that
the novel RbCaGd(PO₄)₂:Eu²⁺ phosphors can act as potential phosphors for application in w-LEDs.

2. Experimental

2.1 Materials and synthesis

The RbCaGd(PO₄)₂:Eu²⁺ samples were prepared by the Pechini-type sol–gel technique using the following starting materials: Ca(NO₃)₂·4H₂O (A.R.), Rb₂CO₃ (A.R.), Gd₂O₃ (99.99%), Eu₂O₃ (99.99%), (NH₄)₂HPO₄ (A.R.) and C₆H₈O₇ (A.R.) from Beijing Haidian chemical reagent company store. Stoichiometric amounts of Gd₂O₃ and Eu₂O₃ were respectively dissolved in HNO₃ to obtain Gd(NO₃)₃ and Eu(NO₃)₃ solutions. The detailed synthesis process for RbCaₓGd(PO₄)₂:xEu²⁺ where x indicates the content of Eu²⁺ was as follows. Ca(NO₃)₂·4H₂O and Rb₂CO₃ were dissolved in distilled water under stirring and the predetermined amounts of Gd(NO₃)₃, Eu(NO₃)₃, (NH₄)₂HPO₄ and the citric acid (citric acid/metal ion = 2 : 1 in mole) were added successively into the above solution and stirred at 80 °C for 30 min until homogeneous gels formed. After drying at 120 °C for 12 h in an oven, the precursor was ground, heated to 500 °C for 10 h in air, ground again, and calcinated at 1100 °C in air for 5 h in CO reducing atmosphere.

2.2 Measurements and characterization

The phase identification of the as-prepared samples was carried out on the SHIMADZU model XRD-6000 diffractometer at 40 kV and 30 mA and using monochromatic Cu Kα (λ = 0.15406 nm) radiation. The continuous scanning rate (2θ ranging from 10° to 70°) used for phase identification was 4° (2θ) min⁻¹ and the data for the Rietveld analysis were collected in a stepping mode with a step size of 0.02° and 8 s per step over the 2θ range from 10° to 120°. The diffraction patterns were analyzed by the General Structure Analysis System (GSAS). The Fourier transform infrared (FT-IR) measurements were performed on a Spectrum One Paragon 1000 PC spectrometer over the 1500–400 cm⁻¹ region using KBr pellet as background. The room-temperature excitation and emission spectra were recorded on a HITACHI F-4600 fluorescence spectrophotometer with a photomultiplier at 400 V and 150 W Xe lamp as the excitation lamp. And the temperature-dependent luminescence properties were performed by the same spectrophotometer, which was equipped with a self-made heating apparatus and a computer controlled electric furnace. The luminescence decay curve was obtained from a lifetime and steady state spectrophotometer with a self-made heating apparatus and a computer controlled electric furnace. The luminescence decay curve was obtained from a lifetime and steady state spectrophotometer (Edinburgh Instruments Ltd, FL9500) with a 335 nm pulse laser radiation (nano-LED) as the excitation source. The quantum efficiency was measured on an absolute photoluminescence quantum yield measurement system (Nanolog® Fluorolog-3-2-iHR320, Horiba Jobin Yvon) with F-3018 integral sphere.

3. Results and discussion

3.1 Phase analysis

The XRD patterns of the synthesized RbCaGd(PO₄)₂:Eu²⁺ phosphors and the Joint Committee on Powder Diffraction Standards (JCPDS) reference card of RbCaGd(PO₄)₂ are depicted in Fig. 1(a). The diffraction patterns of the synthesized samples can be indexed to the standard card of RbCaGd(PO₄)₂ (JCPDS, Fig. 1 XRD patterns of the as-prepared RbCaGd(PO₄)₂:Eu²⁺ phosphors (a), Rietveld structure analysis (b) of the selected RbCaGd(PO₄)₂:0.03Eu²⁺ phosphor and crystal structure (c) of RbCaGd(PO₄)₂.
For the first time, the crystal structure of RbCaGd(PO₄)₂ was determined. The crystal structure of double phosphate of RbCa₀.₉₇Gd(PO₄)₂:0.03Eu²⁺ host lattice is refined using the computer software GSAS. The Rietveld structure of the RbCa₀.₉₇Gd(PO₄)₂:0.03Eu²⁺ and the single crystal data of the ICSD-35098-KCaNd(PO₄)₂ phase model are shown in Fig. 1(b). No impurity phase is detected and the fractional atomic coordinates, occupancy, and isotropic thermal parameters of RbCa₀.₉₇Gd(PO₄)₂:0.03Eu²⁺ are presented in Table 1. Rb⁺ and Gd³⁺ are designed to occupy the sites of K⁺ and Nd³⁺, respectively, due to the similar ion radius and equal valence. Table 1 also lists the fractional atomic coordinates, occupancy, and isotropic thermal parameters of RbCa₀.₉₇Gd(PO₄)₂ viewed from the c axis and the coordination environment around Rb⁺ and Ca²+/Gd³⁺ are shown in Fig. 1(c). Rb⁺ is coordinated by 8O located along the c axis whereas Ca²+/Gd³⁺ is coordinated to 8O with the distorted D₂ point symmetry forming the chains of -(Ca²+/Gd³⁺)-(PO₄)&&(Ca²+/Gd³⁺)– running along the c-axis which forms the edge sharing [Ca₂GdO₄] polyhedral chains interconnected by corner sharing. These interconnected chains leave large open channels, which is occupied by Rb atom with oxygen lined tunnels parallel to the c axis.

The FT-IR spectra of the double phosphates are shown in Fig. 2(a). Due to small amounts of the dopant ions, the spectra of the doped and undoped samples are similar, therefore only one representative spectrum for RbCaGd(PO₄)₂:Eu²⁺ is shown in this figure. The singlet strong absorption band centered at 1074 cm⁻¹ attributes to the asymmetric stretching of PO₄ groups, while the symmetric stretching of the same groups manifests at the 1001 cm⁻¹. Two bands centered at 609 and 503 cm⁻¹ are due to the asymmetric deformation modes of PO₄ groups, and a single band centered at 414 cm⁻¹ is due to symmetric deformation modes of PO₄ groups. The FT-IR results show that all vibrations originate from the anion groups of PO₄ units, and one of the characteristic feature of the phosphates is the low number of absorption bands. Some similar results have been observed in the other types of hexagonal phosphates.⁴¹,⁴²

### 3.2 Photoluminescence properties of the RbCaGd(PO₄)₂:Eu²⁺ phosphors

The PLE and PL spectra of the RbCaGd(PO₄)₂:0.03Eu²⁺ are displayed in Fig. 2(b). The PLE spectrum monitored at 476 nm exhibits two obvious bands from 250 to 425 nm, which originate from the electron transition from the ground state 4f⁰ to the crystal-field split 4f⁵d levels of Eu²⁺ in the host lattice. Upon excitation at 334 nm, all of the emission spectra of RbCaGd(PO₄)₂:xEu²⁺ show a similar band board from 435 to 600 nm peaking at 476 nm attributable to the transitions between the 5d excited state and 4f ground state. In order to further understand the origin of the emission centered at 476 nm, the experiential equation of Van Uitert is adopted to fit the emission peak and excitation edge data²³ and the crystallographic site substituted by Eu²⁺ in RbCaGd(PO₄)₂ is investigated theoretically:

\[
E = Q \left[ 1 - \left( \frac{V}{4} \right)^{\frac{3}{10}} \right]^{10} \text{eV}
\]

where E is the energy of the d-band edge for rare earth ions (cm⁻¹) equivalent to the wavelength of 470 nm, V is the valence of the activator (Eu²⁺) with V = 2, Q represents the energy of the lower d-band edge of the free ions (34 000 cm⁻¹ for Eu²⁺), n is the coordination number of the “active” ion (Eu²⁺), r is the effective radius of the host replaced by the “active” ion, Eₐ is the constant electron affinity of the atoms that form anions in the same host. Here, Eₐ is 2.5 eV as reported from other phosphate systems and as discussed above, Eu²⁺ occupies the Ca²⁺ site in the RbCaGd(PO₄)₂ host and the effective ionic radii of Ca²⁺ is 1.12 Å. The calculated n is 7.9 which means that Eu²⁺ has eight coordination elements.

The PL spectra of the RbCaGd(PO₄)₂:xEu²⁺ are displayed in Fig. 3(b). Excited by 334 nm irradiation, all of the emission spectra of RbCaGd(PO₄)₂:xEu²⁺ show a similar spectral profiles due to the 4f–5d transition of Eu²⁺. But the peak red-shifts as the concentration of Eu²⁺ increases gradually. It originates from the change in the crystal field strength as shown in the following:²⁴

\[
Dq = \frac{z^2r^4}{6R^6}
\]

### Table 1 Fractional atomic coordinates, occupancy, and isotropic thermal parameters of RbCaGd(PO₄)₂ obtained by GSAS Rietveld refinement using powder X-ray diffraction data at room temperature

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>U₁₁₁/Å²</th>
<th>Multiplicity</th>
</tr>
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<tr>
<td>Rb</td>
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<td>1/2</td>
<td>0.5</td>
<td>0.071(91)</td>
<td>3c</td>
</tr>
<tr>
<td>Ca</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.483(12)</td>
<td>0.007(97)</td>
<td>3c</td>
</tr>
<tr>
<td>Eu</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.016(63)</td>
<td>0.007(97)</td>
<td>3b</td>
</tr>
<tr>
<td>Gd</td>
<td>1/2</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.007(97)</td>
<td>3c</td>
</tr>
<tr>
<td>P</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>1.0</td>
<td>0.011(79)</td>
<td>3d</td>
</tr>
<tr>
<td>O</td>
<td>0.4348(45)</td>
<td>0.1356(84)</td>
<td>0.3529(56)</td>
<td>1.0</td>
<td>0.028(01)</td>
<td>12k</td>
</tr>
</tbody>
</table>

* Space group: P6₃22 – hexagonal; a = 7.006(49) Å, c = 6.358(80) Å, V = 269.969 Å³; α = 90°, γ = 120°; 2θ-interval = 10–120°; Rwp (%) = 8.62, Rp (%) = 6.34, x² = 2.01.
where $D_q$ is the crystal field strength, $e$ is the charge of an electron, $r$ is the radius of the central ions, $d$ is the wave function, $z$ is the charge or valence of the anion, and $R$ is the bond distance between the central ion and ligands. Based on this equation, a shorter bond length increases the crystal field strength when the crystal environment is homologous. When Ca$^{2+}$ is substituted by the larger Eu$^{2+}$, the distance between Eu$^{2+}$ and O$^{2-}$/C$^{2-}$ becomes shorter and the crystal field strength increases. As a result, the emission wavelength red-shifts with increasing Eu$^{2+}$ concentrations.

The concentration dependence of the emission intensity of the phosphors on Eu$^{2+}$ is demonstrated in the inset of Fig. 3(a). The PL emission intensity increases, reaches a maximum at the Eu$^{2+}$ concentration of 0.03, and decreases afterwards due to concentration quenching. Concentration quenching is due to the energy transfer from one activator to another. So it is necessary to calculate the critical transfer distance ($R_c$) of the activator and quenching site. The optimum Eu$^{2+}$ concentration can be used to determine concentration quenching caused by energy transfer mechanisms such as exchange interaction.

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![Image](image_url)

**Fig. 2** The FT-IR spectrum (a), PL and PLE spectra (b) of the RbCaGd(PO$_4$)$_2$:0.03Eu$^{2+}$ phosphor.

**Fig. 3** PL spectra (a) and relationship (b) of log($I_v$) vs. log($I_0$/$I_v$) for the RbCaGd(PO$_4$)$_2$:xEu$^{2+}$ (x = 0.01, 0.03, 0.05, 0.08 and 0.10) phosphors, emission spectra (c) of RbCaGd(PO$_4$)$_2$:0.03Eu$^{2+}$ excitation under 334 nm at different temperature and (d) activation energy of thermal quenching.

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radiation reabsorption, or multipole–multipole interaction and $R_e$ can be estimated with geometrical consideration according to the following formula:\textsuperscript{25}

$$R_e \approx 2 \left[ \frac{3V}{4\pi x_c N} \right]^{1/3}$$

(3)

where $N$ is the number of host ions in the unit cell, $V$ is the unit cell volume of the unit cell, and $x_c$ is the atom fraction of the activator at which quenching occurs. In the RbCaGd(PO$_4$)$_2$ host, the crystallographic parameters are $V = 269.980$ Å$^3$, $N = 1$, and $x_c = 0.03$. According to eqn (3), the critical distance $R_e$ is determined to be 28.81 Å indicating that the nonradiative concentration quenching takes place among two nearest Eu$^{2+}$ via electric multipolar interactions based on the Dexter theory. In order to further investigate the energy transfer mechanism, the interaction type between the sensitzers or between the sensitizer and activator is confirmed by eqn (4):\textsuperscript{26}

$$I/I_0 = k[1 + \beta(x)^{\theta_3}]^{-1}$$

(4)

In this equation, $I$ is the emission intensity, $x$ is the activator concentration which is not less than the critical concentration, $k$ and $\beta$ are constants under the same excitation conditions for a given host crystal, and $\theta = 6, 8, 10$ for the dipole–dipole (d–d), dipole–quadrupole (d–q), or quadrupole–quadrupole (q–q) interactions, respectively. To obtain the correct $\theta$, the dependency between $\log(I/I_0)$ and $\log(x)$ based on eqn (4) is plotted in Fig. 3(b). The slope of the straight line is determined to be $-1.78$ and $\theta$ is calculated to be 5.34 that is close to 6, indicating that the dipole–dipole interaction is the major concentration quenching mechanism in RbCaGd(PO$_4$)$_2$:Eu$^{2+}$. The temperature dependence of luminescence from the RbCaGd(PO$_4$)$_2$:0.03Eu$^{2+}$ phosphor under 334 nm excitation is presented in Fig. 3(c). As the temperature goes from 30 °C up to 150 °C, the PL intensity diminishes to 37% of the initial value. In general, the configurational coordinate diagram is used to explain thermal luminescence quenching as the excited luminescence center is thermally activated through the crossing point between the ground state and the excited state. This nonradiative transition depends strongly on the temperature resulting in reduction in the emission intensity. When the temperature is increased, the intensity decreases and the full-width at half-maximum (FWHM) increases as described by the Boltzmann distribution function as follows:\textsuperscript{27}

$$FWHM(T) = W_0 \sqrt{\text{coth} \left( \frac{hw}{2kT} \right)}$$

$$W_0 = \sqrt{8 \ln 2(hw)\sqrt{S}}$$

(5)

(6)

In the above equations, $hw$ is the energy of the lattice vibration that interacts with the electronic transition, $W_0$ is the FWHM at 0 K, $k$ is Boltzmann's constant, and $S$ is the Huang–Rhys–Pekar parameter showing the strength of the electron–lattice coupling. It is postulated that $hw$ is the energy of the vibrational levels of the 4f$^7$ ground state or 4f$^6$5d excited state of Eu$^{2+}$. As the temperature is increased, the electron–phonon interaction becomes dominant and a higher temperature increases the FWHM of the emission line. The activation energy ($E$) of thermal quenching can be estimated by the Arrhenius equation:\textsuperscript{28}

$$I(T) \approx \frac{I_0}{1 + c \exp \left( \frac{-E}{kT} \right)}$$

(7)

where $I_0$ is the initial PL intensity of the phosphor, $I(T)$ is the intensity at the given temperature, $c$ is a constant for a certain host, $k$ is Boltzmann's constant ($8.62 \times 10^{-5}$ eV), and $E$ is the activation energy of thermal quenching. Fig. 3(d) plots the relationship of $\ln(I_0/I_0) - 1$ vs. $1/kT$, where the straight slope is equal to $-E$ and the activation energy $E$ of RbCaGd(PO$_4$)$_2$:0.03Eu$^{2+}$ is 0.3117 eV. A red shift behavior is observed as the temperature goes up and it can be explained by the semi-empirical Varshni equation:\textsuperscript{29}

$$E(T) = E_0 - \frac{aT^2}{T + b}$$

(8)

where $E_0$ is the energy difference between the excited and ground states at 0 K, $E(T)$ is the energy difference at temperature $T$, and $a$ and $b$ are fitting parameters. The covalent bond between the luminescent center and ligand ions becomes stronger and the interaction between electrons is reduced due to the expansion of the electron clouds, resulting in the decreased crystal field as the temperature is increased. Moreover, the symmetry of the luminescent center is distorted so that the Jahn–Teller effect is dominant. Splitting of the degenerate excited state or ground state causes these two effects which drive the emission peak shift to lower energies.

Fig. 4 presents the decay curves of the Eu$^{2+}$ luminescence in RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ with different Eu contents (0.1–0.10 mol%) upon excitation at 335 nm. In this work, the decay time of all the samples are characterized by average lifetime ($\tau^*$), which can be calculated based on the following expression:\textsuperscript{30}

![Fig. 4 Decay curves of Eu$^{2+}$ in RbCaGd(PO$_4$)$_2$:xEu$^{2+}$ phosphors (excited at 335 nm, monitored at 467 nm).](image-url)
where $I(t)$ is the luminescence intensity at a time $t$. According to the equation, the effective lifetime $\tau^*$ is determined to be 0.978, 0.927, 0.884, 0.845 and 0.767 s for RbCaGd(PO$_4$)$_2$:xEu$^{2+}$ with $x = 0.01, 0.03, 0.05, 0.08$ and $0.10$, respectively. Those results are reasonable for the allowed 5d–4f transition of Eu$^{2+}$ ions, which is known occurring in less than a microsecond. The lifetime for the Eu$^{2+}$ ions decrease monotonically with increasing Eu$^{2+}$ concentration due to the increase of the nonradiative and self-absorption rate of the internal doped ions when activators cross the critical separation between activator ion and quenching site.

The $x$ and $y$ values of CIE chromaticity coordinates for RbCaGd(PO$_4$)$_2$:xEu$^{2+}$ ($x = 0.01, 0.03, 0.05, 0.08$ and $0.10$) were calculated and presented in Table 2. The results obtained is shown in CIE chromaticity diagram of Fig. 5. Besides, the images of phosphors excited by 365 nm are also given in the inset of Fig. 5. The emission light can be clearly observed by the naked eye. The chromaticity coordinates for naked eye. The chromaticity coordinates for RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ are $(0.2169, 0.2543)$. The series of phosphors show a board band at 476 nm due to the 4f–5d transition. The calculated $R_c$ for the energy transfer from one Eu$^{2+}$ to another Eu$^{2+}$ in the phosphor, which is electrostatic multipolar interaction, is 28.81 Å. Concentration quenching resulting from the dipole–dipole interaction is observed. With increasing of the Eu$^{2+}$ concentration, the CIE coordinates slightly shift from greenish blue $(0.2169, 0.2543)$ to bluish green $(0.2639, 0.3097)$ position. These results suggest that the RbCaGd(PO$_4$)$_2$:Eu$^{2+}$ exhibits a potential application in the solid-state lighting field.

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### References


