1. Introduction

Nichia assembled a white light-emitting diode (w-LED) by means of a blue InGaN LED chip coated with yellow phosphor Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce³⁺) in 1996.¹⁻³ At that time the w-LED was regarded as the next generation light source due to many advantages such as significant power reduction, higher luminous efficacy, longer lifetime and environmental friendliness.⁴ Accordingly, enormous research efforts have been focused on the preparation of high quality w-LEDs.⁵⁻⁶ Compared with Nichia’s assembly method mentioned above, which shows high correlated color temperature (CCT ≈ 7750 K) and a low color rendering index (CRI ≈ 73),⁷ packaging multicolor phosphors on a near-ultraviolet (n-UV) chips can provide relatively high quality white light because the emission spectra can be distributed over the entire visible range (400–800 nm).⁸⁻¹⁰ This means that the study of high-performance single-color phosphor is meaningful.

Researchers have paid great attention to green-emitting phosphors, for instance the cordierite structure phosphor K₀.₅Mg₁.₅Al₄Si₅O₁₃:Eu²⁺,¹¹ the garnet structure phosphors Ca₂La₂Zr₂Ga₃O₁₂:Ce³⁺,¹² Ca₃Y₂ZrAl₂O₁₂:Ce³⁺,¹³ and the commercial green phosphor (Ba,Sr)SiO₄:Eu²⁺. However, there is still room for improvement in some aspects such as wider emission region, better thermal stability and higher quantum efficiency. It is well known that the apatite compound has been utilized as a highly efficient host material for phosphor due to its adjustable crystal structure and its excellent thermal and physicochemical stability.¹⁴⁻¹⁶ Recently, our group has reported a series of apatite solid solution phosphors Ca₁ₓLa₉₋ₓ(SiO₄)₆₋ₓ(PO₄)ₓO₂:Eu²⁺ (x = 0, 2, 4, and 6) whose emitting color can be adjusted from green to blue by changing the ratio of Ca to La. One of these compounds, Ca₆La₄(SiO₄)₂(PO₄)₄O₂:Eu²⁺, show good potential as a commercial green phosphor. Therefore, we consider it worth investigating the crystal structure and luminescence properties of Ca₆La₄(SiO₄)₂(PO₄)₄O₂:Eu²⁺ in more detail.

As discussed above, the novel apatite phosphors Ca₆La₄(SiO₄)₂(PO₄)₄O₂:Eu²⁺ (x = 0.05–0.1) have been synthesized by high-temperature solid state reaction for the first time. The phase purity was examined by XRD and XPS and the crystal structure...
information was analyzed by Rietveld refinement using XRD profiles. In addition, it is the first time that the low-temperature PL and PLE spectra and decay curves were utilized to demonstrate the inclusion of Eu$^{2+}$ in the apatite phosphor. Moreover, the luminescence properties, such as PLE and PL spectra, lifetimes and thermal stability, are discussed in detail. Finally, the novel green phosphor Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ was packaged on a u-UV LED chip (excitation wavelength 385 nm) with commercial red and blue phosphors, demonstrating the potential for it to be utilized in a w-LED.

2. Experiment

2.1 Sample preparation

The apatite phosphors Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:xEu$^{2+}$ ($x = 0.005$, 0.01, 0.02, 0.04, 0.06, 0.08, and 0.1) were synthesized by a conventional high-temperature solid-state method. Based on the stoichiometric amounts of reactants, Ca$_2$CO$_3$ (analytical reagent, AR), La$_2$O$_3$ (AR), SiO$_2$ (AR), NH$_4$H$_2$PO$_4$ (AR) and Eu$_2$O$_3$ (AR) were thoroughly ground in an agate mortar for 15 min. The mixed powders were then preheated for 1 h at 1000 °C in a corundum crucible to eliminate H$_2$O and CO$_2$. Subsequently, the mixtures were sintered at 1500 °C in a reductive atmosphere (H$_2$ 10%, N$_2$ 90%) for 4.5 h. After cooling to room temperature, the sintered samples were ground once again to prepare for further measurements.

2.2 Characterization

The X-ray diffraction (XRD) data of the series of phosphors were measured on an X-ray powder diffractometer (D/max-IIIA, Rigaku, Japan) with a stepwise scanning mode over the 2θ range 10°–110° using Cu-K$_\alpha$ radiation (1.5406 Å) with operating voltage 40 kV and current 100 mA. The XRD patterns, used in Rietveld refinement, were acquired with a step size of 0.02° and counting time of 2 s per step. X-ray photoelectron spectroscopy (XPS) measurements were collected with a Kratos Axis Ultra DLD, employing MCP stack & delay-line photoelectron detector with scanned & snapshot spectroscopy modes. The photoluminescence emission (PL) spectrum and the photoluminescence excitation (PLE) spectrum at 298 K and 8 K were measured using a Hitachi F-4600 fluorescence spectrophotometer (Japan) equipped with a 150 W Xe lamp as the excitation source. The temperature-dependent luminescence properties were measured on the same spectrophotometer, which was assembled with a computer-controlled electric furnace and a self-made heating attachment. The room-temperature luminescence decay curves were obtained from a spectrofluorometer (Horiba, Jobin Yvon) using tunable pulsed laser irradiation (nano-LED) as the excitation source. Quantum efficiency was measured by a Fluoromax-4 spectrofluorometer with an integral sphere at room temperature (Horiba, Jobin Yvon).

3. Results and discussion

3.1 Phase formation and structural characteristics

The XRD profiles of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:xEu$^{2+}$ ($x = 0.005–0.1$) phosphors are displayed in Fig. 1. As shown in Fig. 1, all the diffraction spectra do not contain any peaks from impurities or raw materials even at $x = 0.1$, indicating that pure apatite structure phosphors Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:xEu$^{2+}$ ($x = 0.005–0.1$) have been synthesized successfully and that doping of Eu$^{2+}$ does not cause any impurities or phase transitions. Fig. 2 depicts the photoelectron survey spectrum of the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ sample. It contains several photoelectron peaks corresponding to O 2s, Si 2p, P 2p, La 4p 3/2, Ca 2p, Ca 2s, O 1s, La 3d 5/2, La 3d 3/2 and Eu 3d 5/2 emissions. The binding energy was measured to be 1127 eV, which matches well with the signal of Eu$^{2+}$ 3d$_{5/2}$, demonstrating the existence of Eu$^{2+}$.18

Fig. 1 The XRD traces of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:xEu$^{2+}$ ($x = 0.005–0.1$) phosphors.

Fig. 2 Photoelectron survey spectrum of the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ sample. Inset: the high resolution XPS spectrum at Eu 3d$_{5/2}$.
The crystal structure information of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ was determined by the Rietveld refinement method. The observed (x), calculated (red) and difference (gray) XRD profiles for Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ are illustrated in Fig. 3 and the refinement parameters are presented in Table 1. The refinement results further prove that the novel apatite phosphor is a single phase without any impurity or secondary phase and that Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ crystallizes as a hexagonal structure with space group $P6_3/m$. The lattice parameters were determined to be $a = b = 9.536$ Å, $c = 7.026$ Å, $V = 553.35$ Å$^3$ and the refinement $R$ factors finally converged to $R_{wp} = 8.17\%$, $R_{exp} = 1.28\%$, $R_{p} = 6.20\%$, indicating that the refined crystal structure agrees well with the starting model (Ca$_6$La$_4$(SiO$_4$)$_6$). In addition, all atoms positions and occupancy factors for Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ are listed in Table 1.

Fig. 4 illustrates the reflectance spectra of the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$ host and Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ in the range from 200 nm to 800 nm. Obviously, compared with the absorption characteristics of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$ host, which barely absorbs n-UV light, Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ shows a broad absorption band from 200 nm to 450 nm, demonstrating the as-prepared phosphor can efficiently excited by a UV or n-UV LED chip. Furthermore, as shown in the inset of Fig. 4, the band gap of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:0.01Eu$^{2+}$ was estimated to be 3.39 eV.

The crystal structure of 2 × 2 × 2 unit cells, the coordination environments of a single unit cell and the coordination environments of cation sites in Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ are displayed in Fig. 5a–d. As observed from Fig. 5a, Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$ has a layered structure and two types of cation sites included in it, the inner-laminar site labeled M(I) with the local symmetry $C_3$ and the inter-laminar site labeled M(II) with the local symmetry $C_6$. Furthermore, Fig. 5b–d depicts the coordination environments of these cation sites. The M(I) site (located at position 4f), surrounded by 9 oxygen atoms, forms a mono-capped square antiprism and connects with the tetrahedral PO$_4$/SiO$_4$ groups. On the other hand, the M(II) site (located at position 6h) surrounded by 7 oxygen atoms forms a pentagonal bipyramid and connects with each other through vertices. Furthermore, considering the effective ionic radii (Å) of Ca$^{2+}$ ($R_{\text{CN}=9} = 1.38$, $R_{\text{CN}=7} = 1.06$), La$^{3+}$ ($R_{\text{CN}=9} = 1.21$, $R_{\text{CN}=7} = 1.10$) and Eu$^{2+}$ ions ($R_{\text{CN}=9} = 1.3$, $R_{\text{CN}=7} = 1.2$), Eu$^{2+}$ is expected to substitute the Ca$^{2+}$ site in the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ crystal structure based on its similar ion radius and valence.

### Table 1 Results of structure refinement of CLSPO:0.01Eu$^{2+}$

| Atom | Site | $x$  | $y$  | $z$  | Occupancy |
|------|------|-----|-----|-----|-----------|
| La1  | 6h   | 0.227(2) | 0.983(3) | 0.25 | 0.617 |
| Ca1  | 6h   | 0.227(2) | 0.983(3) | 0.25 | 0.368 |
| Eu1  | 6h   | 0.227(2) | 0.983(3) | 0.25 | 0.005 |
| La2  | 4f   | 2/3 | 1/3 | 0.0024(1) | 0.060 |
| Ca2  | 4f   | 2/3 | 1/3 | 0.0024(1) | 0.935 |
| Eu2  | 4f   | 2/3 | 1/3 | 0.0024(1) | 0.005 |
| Si   | 6h   | 0.406(8) | 0.375(1) | 1/4 | 1/3 |
| P    | 6h   | 0.406(8) | 0.375(1) | 1/4 | 2/3 |
| O1   | 6h   | 0.591(2) | 0.464(2) | 1/4 | — |
| O2   | 6h   | 0.339(2) | 0.493(2) | 1/4 | — |
| O3   | 12i  | 0.344(1) | 0.261(1) | 0.072(1) | — |
| O4   | 2a   | 0   | 0   | 1/4 | — |

3.2 Photoluminescence characteristics

The PLE spectrum of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ (monitored at 500 nm) and the PL spectra of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:2Eu$^{2+}$ (x = 0.005–0.1) (under 365 nm excitation) are displayed in Fig. 6a and b, respectively. Due to the 4f$^7$ → 4f$^6$5d$^1$ transition of Eu$^{2+}$, the PLE spectrum depicts a broad excitation band ranging from 280 nm to 400 nm with a maximum value at 330 nm, indicating that the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ phosphor can be suitably excited by a n-UV LED chip. The PL spectrum consists of an asymmetric broad emission band peaking at 500 nm, which is ascribed to the electric dipole-allowed transition of Eu$^{2+}$ from the lowest level of the 5d excited state to the 4f ground state. In general, the asymmetric emission band is due to the different coordination environments of Eu$^{2+}$. As shown in Fig. 6c, the asymmetric emission band of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:0.01Eu$^{2+}$ has been resolved...
Fig. 5 (a) The crystal structure of $2 \times 2 \times 2$ unit cells of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:Eu$^{2+}$, (b) the coordination environments in a single unit cell, (c) the coordination environment of the M(I) site with the local symmetry $C_3$ and (d) the M(III) site with the local symmetry $C_5$.

Fig. 6 (a) The PLE spectrum of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:0.01Eu$^{2+}$, (b) the PL spectra of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:xEu$^{2+}$ ($x = 0.005$–$0.1$) and (c) two Gaussian components of the peak of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$:0.01Eu$^{2+}$. 
into two Gaussian components peaking at 492 nm (I1) and 593 nm (I2). Thus, the low-temperature (8 K) PLE and PL spectra of Ca₆La₄(SiO₄)₂(PO₄)₄O₂:0.01Eu²⁺ are displayed in Fig. 7a and b to demonstrate the existence of the different Eu²⁺ sites. Consequently, the PL spectrum at low temperature contains two component peaks located at 529 nm and 584 nm and the shape of PLE spectrum was found to be identical to that of measured at room temperature. These features further prove that Eu²⁺ occupies two types of Ca²⁺ sites to form different emitting centers. Moreover, due to the existence of multi-emitting centers, the Ca₆La₄(SiO₄)₂(PO₄)₄O₂:Eu²⁺ phosphor shows a wider emission band compared with the BaMgSiO₄:Eu²⁺ and Ca₅Y₂Zr₂Al₃O₁₂:Ce³⁺ green phosphors and it reaches a similar level as the commercial green phosphor (Ba,Sr)SiO₄:Eu²⁺.

In theory, the width of the crystal-field splitting of the Eu²⁺ 5d level is the main influence on the position of the Eu²⁺ emitting energy level, i.e., the lower the lowest crystal-field position, the lower the emission energy. The major difference between the 4f and 6h site is that the 6h site has a free oxygen ion, which does not belong to any silicate group. Therefore, the binding strength is not saturated compared with the 4f site resulting in the average covalency of the 6h site being higher than that of the 4f site. Consequently, Eu²⁺ will have lower emission bands when located at the 6h site than when at the 4f site and the higher energy emission band (492 nm) can be assigned to Eu²⁺ (4f) while the lower energy emission band (539 nm) is derived from Eu²⁺ (6h). This inferred conclusion can be further demonstrated by an empirical relationship proposed by Van Uitert: 

$$ E (\text{cm}^{-1}) = Q^* \left[ 1 - \left( \frac{V}{4} \right)^{1/3} \times 10^{-((nE_{Eu})/80)} \right] $$  

where $E$ represents the position of the d-band edge energy for rare-earth ions (cm⁻¹), $Q$ is the position energy for the lower d-band edge for the free ion (34,000 cm⁻¹ for Eu²⁺); $V$ is the activator ion valence (for Eu²⁺ $V = 2$), $n$ represents the number of anions in the immediate shell about the Eu²⁺ ion, $r$ is the host cation radius that is replaced by the Eu²⁺ ion (in Å), and $E_0$ is the electron affinity of the atoms that form anions (in eV). In general, due to the complexity of the local crystal structure, the exact energy levels of Eu²⁺ at a specific site are hard to calculate precisely. However, it can be deduced approximately that the value of $E$ is proportional to the quantity of $n$ and $r$. For the as-prepared phosphors, $r$ is equal because both of the substitutions occurring at cation sites are that Ca²⁺ is replaced by Eu²⁺. Therefore, the band peak at 492 nm is ascribed to the 4f⁵5d¹ → 4f⁶ transition of Eu²⁺ occupying the M(I) site with nine-coordination, whereas the longer wavelength band can be attributed to Eu²⁺ occupying the M(II) site with nine-coordination.

In addition, as shown in Fig. 6b, with the increase of doping concentration of Eu²⁺, the peak emission wavelength shows an obvious red-shift from 498 to 510 nm. The red-shift phenomenon is mainly due to the variation in the crystal-field splitting of Eu²⁺. In this regard, the crystal-field splitting of Eu²⁺ can be determined as obeying:

$$ D_q = \frac{z^2r^4}{6R^6} $$

where $D_q$ is a measure of the energy level separation, $z$ represents the charge or valence of the anion, $R$ is the distance from the central ion to its ligands, $e$ is the charge of an electron, and $r$ is the radius of the d wave function. For the d₅(O₡⁻)⁰ orbital, while $z$, $e$ and $r$ are equal, then $D_q$ is merely a function of $1/R^6$. Along with the small Ca²⁺ substituted by the larger Eu²⁺, the distance between Eu²⁺ and O²⁻ becomes shorter and the magnitude of the crystal-field strength increases. The concentration dependence of the PL intensity of the as-prepared samples Ca₆La₄(SiO₄)₂(PO₄)₄O₂:xEu²⁺ ($x = 0.005–0.1$) are depicted in Fig. 8. With the increase of Eu²⁺ content, the PL intensity shows an increase at first and it reaches the maximum value at $x = 0.01$. Subsequently, the intensity tends to decrease gradually due to the concentration quenching effect. Thus, the optimized concentration of Eu²⁺ was confirmed to be 0.01.

In general, concentration quenching can occur in a compound by obeying two mechanisms: exchange interaction and multipolar interaction. In consequence, as shown in Fig. 9, the concentration quenching originates from energy loss at a ‘killer’ center owing to the transfer of excitation energy among activators at a

![Fig. 7](image-url)

Fig. 7 (a) Low-temperature (8 K) PLE and (b) PL spectra of Ca₆La₄(SiO₄)₂(PO₄)₄O₂:0.01Eu²⁺.
where $V$ is the volume of the unit cell, $x_c$ is the critical concentration of Eu$^{2+}$ ions and $N$ is the number of total Eu$^{2+}$ sites in the unit cell. For Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_2$:Eu$^{2+}$, $V = 552.5$ Å$^3$ and $N = 13$. Thus, the $R_{Eu-Eu}$ distance was determined to be 25.32, 20.09, 15.95, 12.66, 11.06, 10.05, 9.33 and 8.78 Å when $x = 0.005$, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1, respectively. Accordingly, this indicates that with the increase in doping concentration of Eu$^{2+}$, $R_{Eu-Eu}$ decreases and the crystal-field splitting of the Eu$^{2+}$ 5d bands increased, leading to a continuous increase in the red-shift with the Eu$^{2+}$ dopant concentration. The critical concentration ($x_c$) of Eu$^{2+}$ was determined to be 0.01 mol, therefore, the $R_c$ value for energy transfer was calculated to be 20.09 Å.

Room temperature decay curves of the as-prepared phosphors, under excitation at 365 nm, were measured and are plotted in Fig. 10. Each decay curve can be well fitted with a second-order exponential function by the following equation:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$$  (5)

where $I$ presents the luminescence intensity; $A_1$ and $A_2$ are constants; $t$ is time and $\tau_1$ and $\tau_2$ are the lifetimes for the exponential components. Furthermore, the average lifetime constant ($\tau^*$) can be calculated as follows:

$$\tau^* = (A_1 \tau_1^2 + A_2 \tau_2^2)/(A_1 \tau_1 + A_2 \tau_2)$$  (6)

The measured lifetimes monitored at 500 nm were calculated to be 412.9, 429.1, 383.4, 336.5, 257.5, 125.3 and 54.1 ns with Eu$^{2+}$ contents = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08 and 0.1, respectively. One can observe that with the increase of Eu$^{2+}$ concentration, the measured lifetimes of Eu$^{2+}$ increase to a maximum when $x = 0.01$ and then decrease rapidly. This phenomenon is a typical sign of energy transfer and concentration quenching.

The measured lifetime is also related to the total relaxation rate by:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + A_{nr} + P_t$$  (7)

where $\tau_0$ is the radiative lifetime; $A_{nr}$ presents the non-radiative rate ascribed to multi-phonon relaxation and $P_t$ is the energy transfer rate between Eu$^{2+}$ ions. The distance between Eu$^{2+}$ ions decreases with the increase of Eu$^{2+}$ concentration, resulting in the increases of energy transfer rate between Eu$^{2+}$ and the probability of energy transfer to luminescent ‘killer’ sites. Consequently, the lifetimes show a gradually decreasing trend with the increase of Eu$^{2+}$ concentration. Moreover, the two decay components ($\tau_1$ and $\tau_2$) were detected in both the room-temperature and low-temperature decay curves, further demonstrating that Eu$^{2+}$ occupies two different Ca$^{2+}$ sites in Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_2$:O$_2$ host.

In general, temperature is the factor that has a great influence on the emitting intensity of a phosphor. Therefore, thermal stability is one of the important characteristics that needs to be taken into consideration before recommending the phosphor for potential applications. The PL spectra of the temperature dependence experiment are shown in Fig. 11. As we can observe from Fig. 11, the luminescence intensity shows a gradual decrease when the sample was heated and the phosphor still maintains 55% of the emitting intensity at 150 °C compared with the initial intensity.
at room temperature (25 °C). Therefore, it shows better thermal stability than the garnet phosphor Ca$_2$LaZr$_2$Ga$_3$O$_{12}$:Ce$^{3+}$ and the commercial green phosphor Ba$_2$SiO$_4$:Eu$^{2+}$. On the other hand, the full width at half maximum (FWHM) of the PL spectra increases from 56 nm up to 75 nm during this temperature increase. The increase of FWHM can be explained by a configuration coordinate diagram, a physical model, that electron–phonon interaction will enhanced and the population of higher vibration levels will increase when the temperature rises,\textsuperscript{18} and then, the excited luminescent center is thermally activated and release non-radiative through the crossover between the excited states and the ground states with the help of phonons. In consequence, the luminescence is quenched due to the enhanced population density of phonons, which also causes the broadening of the PL spectra.\textsuperscript{4,17}

Luminescence efficiency is an important technological parameter for the application of a phosphor. The internal quantum efficiency (QE) of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$ was measured and calculated to be 57.73%. It is higher than that of K$_{0.5}$Mg$_{1.5}$Al$_4$Si$_5$O$_{13}$:Eu$^{2+}$ (48.3%)\textsuperscript{11} and Ca$_2$LaZr$_2$Ga$_3$O$_{12}$:Ce$^{3+}$ (35.2%), but lower than the commercial green phosphor (Ba,Sr)SiO$_4$ (79%).\textsuperscript{12} In general, the QE can be further optimized by improving the preparation conditions because the QE depends closely on crystalline defects, particle sizes and the morphology of the phosphor.\textsuperscript{8,37} To demonstrate the potential application, the electroluminescent spectrum of w-LED lamp is displayed in Fig. 12. The self-made lamp was fabricated by coating Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$, BAM:Eu$^{2+}$ and CaAlSiN$_3$:Eu$^{2+}$ phosphors on a n-UV chip ($\lambda_{ex} = 385$ nm). The CIE color coordinates, CCT and Ra of the self-fabricated w-LED lamp were calculated to be (0.37, 0.37), 4253 K and 86, respectively. The relatively high Ra value (86) and appropriate CCT value (4253 K) demonstrate that the Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ can be a promising candidate for a green-emitting phosphor for the application of w-LEDs.

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Fig. 10  (a) Room-temperature and (b) low-temperature decay curves of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:0.01Eu$^{2+}$.

Fig. 11  Temperature-dependent spectra of Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$ ranging from 25 °C to 175 °C.

Fig. 12  EL spectrum of a white-emitting n-UV chip (385 nm) comprising Ca$_6$La$_4$(SiO$_4$)$_2$(PO$_4$)$_4$O$_2$:Eu$^{2+}$, BAM:Eu$^{2+}$ and CaAlSiN$_3$:Eu$^{2+}$ phosphors driven by 30 mA current. Inset: digital images of the LED package with and without powder input.
4. Conclusion

A novel apatite structure green phosphor Ca₆La₄(SiO₄)₂(PO₄)₂Eu²⁺ has been synthesized by a high-temperature solid-state reaction method. The phase purity and elemental valency were examined according XRD and XPS. The crystal structure information was refined by Rietveld refinement using the high quality XRD traces. The refinement parameters, all atom positions and occupancy factors for Ca₆La₄(SiO₄)₂(PO₄)₂:0.01Eu²⁺ were presented and the coordination environments of the two types of cation sites were discussed in detail. In the section on luminescence properties analysis, the asymmetric emission spectrum, which is attributed to the electric dipole-allowed transition of the Eu²⁺ ions from excited 5d state to the 4f ground state, was resolved into two Gaussian components peaking at 492 nm and 593 nm, demonstrating the existence of two emitting centers. Moreover, this result was further proved by low-temperature luminescence experiments. Based on the coordination environments analysis and an empirical relation proposed by Van Uitert, we propose that the higher energy emission band (492 nm) will be detected when Eu²⁺ is located at the 4h site and the lower energy emission band (593 nm) is derived from the Eu²⁺ ion occupying the 6h site. The optimized Eu²⁺ concentration was confirmed to be x = 0.01, the R₂ is calculated to be 20.09 Å and the energy transfer between Eu²⁺ is of the exchange interaction type. The phosphor shows good thermal stability, it maintain 55% of its emitting intensity at 150 °C compared with room temperature. Finally, the Ca₆La₄(SiO₄)₂(PO₄)₂Eu²⁺ phosphor was fabricated with commercial red (CaAlSiN₃:Eu²⁺) and blue (BAM:Eu²⁺) phosphors on a n-UV chip excited at 385 nm; the CIE color coordinates, CCT and Ra of the self-fabricated w-LED lamp were calculated to be (0.37, 0.37), 4253 K and 86, respectively. This proves that this green phosphor has the potential to be used in a w-LED lamp.

Acknowledgements

This study was sponsored by the National Natural Science Foundation of China (Grant No. 51472223), the Program for New Century Excellent Talents in University of Ministry of Education of China (Grant No. NCET-12-0951) and the Fundamental Research Funds for the Central Universities (Grant No. 2652015020 and Grant No. 2652015008).

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