Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$: a green-emitting oxyfluoride phosphor for white light-emitting diodes

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A novel green-emitting phosphor Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ was synthesized and its photoluminescence (PL) properties were investigated for application in white light-emitting diodes (w-LEDs). This phosphor shows good absorption ranging from the ultraviolet to the blue region and a broad green emission band centered at 502 nm. The concentration quenching mechanism and fluorescence lifetime of Eu$^{2+}$ was centered at 502 nm. The concentration quenching mechanism and fluorescence lifetime of Eu$^{2+}$

1. Introduction

Recently, phosphor conversion white light-emitting diodes (w-LEDs) have been attracted much attention owing to their great advantages over traditional fluorescent lamps and incandescent bulbs, such as long operation time, high energy efficiency, low thermal radiation, and they are mercury free. Most commercial w-LEDs have been based on the combination of a blue LED and yellow phosphor represented by Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce). However, such w-LEDs have low color rendering index (CRI) because they lack a red emitting component. Therefore, w-LEDs fabricated using a near ultraviolet (n-UV) LED (350–420 nm) with three primary color emissions mixed from three individual red, green and blue-emitting phosphors have been investigated to improve the CRI value. Accordingly, the eventual performance of w-LED based devices strongly depends on the luminescence properties of the phosphors used. Therefore the researches on new phosphors excitable by the n-UV light are rapidly increasing and have become one of the hot research topics in the phosphor community. Since the 4f–5d transition of the Eu$^{2+}$ ion is sensitive to the crystal field and covalency, Eu$^{2+}$-doped phosphors generally show superior absorption in the spectral region of 250–400 nm, which is equivalent with the emission of UV and n-UV LED chips, and they also exhibit broad emission bands from blue to red. Many efforts to develop new w-LED phosphors include Eu$^{2+}$-doped silicates, aluminates, nitrides/oxynitrides and some halogen-containing compounds, in order to address issues of higher efficiency, better color rendition and better chemical and thermal stability.

Currently, halogen-containing oxides doped with rare-earth ions have great potential as w-LED phosphors with their adjustable luminescence properties owing to the introduction of halogen ions (F, Cl and Br) in the hosts. Among them, oxy-halides and in particular oxyfluorides, have recently become the renewed focus of exploratory synthesis in the search for new compounds with intriguing luminescence properties after the introduction of rare-earth ions. One recent example for oxyfluoride-based phosphors has been focused on Sr$_3$AlO$_4$F:Ce$^{3+}$, which shows efficient blue-green Ce$^{3+}$ emission under n-UV excitation, and some modified phosphors based on Sr$_3$AlO$_4$F have also been developed. The structural composition for the new Sr$_3$AlO$_4$F host comes from the substitution of F$^-$ for O$^2$-, compensated by Al$^{3+}$ for Si$^{4+}$ substitution in Sr$_3$SiO$_5$. Recent work reported by Im *et al.* shows that solid solution is possible between the nearly isostuctural Sr$_3$AlO$_4$F and Sr$_3$SiO$_5$ compounds, and some excellent luminescence properties have also been reported. Accordingly, we noticed that Ca$_2$Al$_2$SiO$_7$ is a notable phosphor host with tetragonal structure of melilite type. In this structure, if the chemical substitution of F$^-$ for O$^2$-, compensated by Al$^{3+}$ for Si$^{4+}$, is also effective, then a new compound with the chemical composition of Ca$_2$Al$_2$O$_7$F can be obtained. On the basis of the search in the JCPDS database, the preliminary structural data of Ca$_2$Al$_2$O$_7$F can be found, which is completely different from the Ca$_2$Al$_2$SiO$_7$ phase. However, it clearly gives us an effective strategy when screening for new phosphor compositions from well-known phosphor hosts. Herein, we propose that the Ca$_2$Al$_2$O$_7$F phase will be an excellent candidate as a green component for near UV-excited w-LEDs.

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2. Experimental

2.1. Materials and synthesis

The Ca$_2$Al$_3$O$_6$F host compound and Ca$_{2-x}$Al$_3$O$_6$F:xEu$^{2+}$ phosphors were synthesized by a high-temperature solid-state reaction method. The starting materials were CaCO$_3$ (Aldrich, 99.9%), Al$_2$O$_3$ (Aldrich, 99.9%), CaF$_2$ (Aldrich, 99.9%) and Eu$_2$O$_3$ (Aldrich, 99.995%). In a typical procedure, all the starting materials were mixed and ground according to the given stoichiometric ratio. A slight excess of CaF$_2$ (5 wt% beyond stoichiometry) is necessary to compensate for loss of F source at high temperature. After the mixtures were ground thoroughly in an agate mortar, they were placed into an alumina crucible and then were fired at 1250 °C in a reducing atmosphere (N$_2$–H$_2$ 95:5) for 4 h. After this, the samples were furnace-cooled to room temperature, and ground again into powder for subsequent use.

2.2. Characterization methods

The crystal structure determination of the as-prepared Ca$_2$Al$_3$O$_6$F compound was performed by X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer with Cu-K$_\alpha$ radiation ($\lambda = 1.5418$ Å). The data were collected over a 2θ range from 5 to 100° at intervals of 0.02° with a scanning time of 5 s per step. The structural parameters of Ca$_2$Al$_3$O$_6$F were refined by the Le Bail method using the General Structure Analysis System (GSAS) software. The solid-state $^{27}$Al MAS nuclear magnetic resonance (NMR) spectrum was collected on a 500 MHz Varian Unity Inova wide bore NMR spectrometer equipped with a 4 mm rotors. The Larmor frequency for $^{27}$Al was 104.3 MHz using a Bruker D2 PHASER diffractometer with Cu-K$_\alpha$ radiation. After this, the samples were furnace-cooled to room temperature. The samples were ground thoroughly in an agate mortar, and then they were fired at 1250 °C in a reducing atmosphere (N$_2$–H$_2$ 95:5) for 4 h. After this, the samples were furnace-cooled to room temperature, and ground again into powder for subsequent use.

3. Results and discussion

3.1. Crystal structure and band-structure characterizations of the Ca$_2$Al$_3$O$_6$F phase

The Ca$_2$Al$_3$O$_6$F compound was reported for the first time by Leary in 1962, which has hexagonal structure with $a = b = 17.29$ Å, $c = 7.01$ Å, and the cell volume $V = 1814.84$ Å$^3$. Leary found that this new compound can be crystallized from the CaO–Al$_2$O$_3$–CaF$_2$ melt. However, very little research has been done on the Ca$_2$Al$_3$O$_6$F compound after that, especially, there is no work in relation with the crystal structure analysis. Very recently, Sahoo et. al. found that the Ca$_2$Al$_3$O$_6$F phase possibly grew under the epitaxial effect of hexagonal calcium fluorapatite (Ca$_6$(PO$_4$_3)F) when aluminum was previously added to the reaction mixture for the preparation of Ca$_6$(PO$_4$_3)F. Even so, we also knew little about the structural information and luminescence properties of the rare-earth doped Ca$_2$Al$_3$O$_6$F host.

In this work, we have carefully prepared Ca$_2$Al$_3$O$_6$F by a solid-state method. The crystallographic data cannot be found in existing databases, and we therefore performed an XRD refinement by Le Bail fitting for the as-prepared Ca$_2$Al$_3$O$_6$F phase with the initial unit cell parameters. Fig. 1 shows the experimental, calculated and difference plots of Le Bail refinement of powder XRD patterns of Ca$_2$Al$_3$O$_6$F. Based on this, the structure of Ca$_2$Al$_3$O$_6$F was assigned to the crystalline hexagonal system with space group $P6_3/mmc$. The lattice constants are $a = b = 17.3255(2)$ Å, $c = 7.0006(1)$ Å, and $V = 1819.26(2)$ Å$^3$, $Z = 12$. The reliability parameters of refinement are $R_{wp} = 10.6\%$, $R_p = 5.77\%$, $\chi^2 = 3.64$, which can verify the phase purity of the as-prepared sample. Solid-state NMR is sensitive to the local order of nuclei, and it can be performed to study their connection environment. We therefore measured the $^{27}$Al MAS NMR spectrum to study the local structure of Al atoms in the Ca$_2$Al$_3$O$_6$F phase. The isotopic chemical shift in the NMR spectrum is known to be mainly sensitive to the coordination number of the cation: Al$^{VI}$ gives $\delta_{iso} \approx 0$–20 ppm and Al$^{IV}$ gives $\delta_{iso} \approx 70$–80 ppm. As found from Fig. 2, one peak at 77.6 ppm is observed, matching well with the value in the literature for 4-fold coordinated Al atoms. The presence of the [AlO$_4$] tetrahedra can be confirmed, as also demonstrated in the inset of Fig. 2. Although the phase purity and the local environment of aluminum atoms in Ca$_2$Al$_3$O$_6$F have been characterized and proved, the detailed crystal structure should be further investigated in future work.

The diffuse reflection spectrum of the Ca$_2$Al$_3$O$_6$F host compound was measured and is shown in Fig. 3. The absorption spectra $F(R)$ were obtained from the reflection spectra by using the Kubelka–Munk function: $F(R) = (1 - R)^2/2R = K/S$, where R, K and S are the reflectivity, the absorption coefficient and the scattering coefficient, respectively. It is found that the diffuse reflection spectra show a plateau of high reflection in the wavelength range of 250–800 nm and then starts to decrease dramatically from 250 to 200 nm, that can be attributed to the host absorption band. The host absorption of Ca$_2$Al$_3$O$_6$F derived from Fig. 3 is evaluated to be around 6.2 eV (200 nm). Furthermore, the vacuum ultraviolet (VUV) excitation ($\lambda_{em} = 315$ nm) and emission ($\lambda_{ex} = 192$ nm) spectra of the Ca$_2$Al$_3$O$_6$F host are also given in Fig. 3. The excitation peak at 192 nm should correspond to the band gap energy in Ca$_2$Al$_3$O$_6$F host, and the estimated host
The absorption (band gap) energy is determined as 6.46 eV by using the relation
\[ E = \frac{hc}{\lambda} \]
where \( h = 6.63 \times 10^{-34} \text{ J s} \) and \( c = 3 \times 10^8 \text{ m s}^{-1} \). By comparing the band gap energy of \( \text{Ca}_2\text{Al}_3\text{O}_6\text{SiO}_4 \) (5.74 eV), the band gap of \( \text{Ca}_2\text{Al}_3\text{O}_6\text{F} \) host is larger than that of \( \text{Ca}_2\text{Al}_2\text{SiO}_7 \) owing to the introduction of \( \text{F}^- \) with lower charge and higher electronegativity compared to \( \text{O}^2- \), as well as because of the smaller size of [AlO4] tetrahedra compared to that of [SiO4] tetrahedra.

### Table 1

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### 3.2. Refection and photoluminescence spectra of Eu\(^{2+}\) doped \( \text{Ca}_2\text{Al}_3\text{O}_6\text{F} \) phosphor

Fig. 4 shows the diffuse reflection spectra of \( \text{Ca}_{2-x}\text{Al}_3\text{O}_6\text{F}:x\text{Eu}^{2+} \) with different Eu\(^{2+}\) concentrations.
there are obvious differences in the spectral profiles of Eu-doped samples compared to that of the Ca$_2$Al$_3$O$_6$F host. For the samples doped with Eu$^{2+}$, there are two obvious absorption bands in the wavelength range of 220–320 and 320–500 nm, due to the 4f–5d transition of Eu$^{2+}$ ions. With the increase of Eu$^{2+}$ concentration, the absorption intensities in this series of samples increase, which provides further confirmation of the absorption originating from Eu$^{2+}$ ions.

Fig. 5 presents the excitation [photoluminescence excitation (PLE); $\lambda_{\text{ex}} = 312, 350$ and $400$ nm] spectra of the Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor. The PLE
spectra have a broad band between 260 and 440 nm, and there are three excitation peaks around 312, 350 and 400 nm, which correspond to 4f–5d transitions of Eu$^{2+}$ ions, making target samples interesting for application in n-UV w-LEDs. The observed excitation band is also consistent with the diffuse reflection spectrum of Ca$\text{_{2−x}}$Al$_x$O$_6$F:$x$Eu$^{2+}$ phosphors, as shown in Fig. 4. The emission spectra are broad with a maximum at about 502 nm (green emission) under different excitation wavelengths of 312, 350 and 400 nm, showing the green emission in which the emission band corresponds to the transition from the 4f$^n$5d excited state to the 4f$^n$ ground state of a Eu$^{2+}$ ion. The full-width at half-maximum (FWHM) of the PL spectrum of Ca$\text{_{2−x}}$Al$_x$O$_6$F:$x$Eu$^{2+}$ is around 70 nm, and the calculated Stokes shift is about 8650 cm$^{-1}$. As is also shown in Fig. 5, all the emission spectra have no significant variation in the spectra configuration except for the emission intensity, which means there is only the one type of emission centre in this phosphor. In order to further understand the origin of the emission centre at 502 nm, the well-known experiential equation given by Van Uitert has been used to qualitatively analyze the present experimental result. According to the report of Van Uitert, for Eu$^{2+}$ in suitable matrices, eqn (1), provides a good fit to the emission peak and excitation edge data. Based on this equation, the possible crystallographic site substituted by Eu$^{2+}$ in Ca$\text{_{2−x}}$Al$_x$O$_6$F can be investigated theoretically.

$$E = Q \left[ 1 - \left( \frac{V}{4} \right)^{\frac{1}{2}} \cdot 10^{\frac{Q x}{80}} \right]$$

(1)

In the above eqn (1), $E$ represents the position of the d-band edge in energy for the rare-earth ion (cm$^{-1}$), $Q$ is the position in energy for the lower d-band edge for the free ion (34 000 cm$^{-1}$ for Eu$^{2+}$), $V$ is the valence of the “active” cation, here $V = 2$ for Eu$^{2+}$. $E_0$ is the electron affinity of the atoms that form anions, which is different when Eu$^{2+}$ is introduced into different anion complexes with various coordination numbers. Here, $E_0$ is approximately determined as 2.5, as reported in other melilite structures,$^{11}$ $n$ is the number of anions in the immediate shell around the “active” cation, and $r$ is the radius of the host cation (Ca$^{2+}$) replaced by the “active” cation (Eu$^{2+}$). Therefore, we used eqn (1) and calculated emission wavelengths of Eu$^{2+}$ in different Ca$^{2+}$ sites, as given in Table 1. As can be seen from Table 1, when Ca$^{2+}$ is situated in different environments, the calculated values are different. When these Ca$^{2+}$ sites are replaced by Eu$^{2+}$, the positions of the emission peaks are different. By comparing the measured emission wavelengths of Eu$^{2+}$ in Ca$\text{_{2−x}}$Al$_x$O$_6$F host, we can infer that the green emission at 502 nm is due to a seven-coordinated Eu$^{2+}$ luminescence center.

3.3. Eu$^{2+}$ concentration dependent PL emissions and lifetimes of Ca$\text{_{2−x}}$Al$_x$O$_6$F:Eu$^{2+}$ phosphors

Fig. 6a shows the PL spectra of Ca$\text{_{2−x}}$Al$_x$O$_6$F:$x$Eu$^{2+}$ (0.005 ≤ $x$ ≤ 0.2) phosphors. The experimental optimal Eu$^{2+}$ concentration ($x$) in Ca$\text{_{2−x}}$Al$_x$O$_6$F:$x$Eu$^{2+}$ was found to be 0.05, from which the PL intensity begins to decrease with increasing Eu$^{2+}$ concentration due to the concentration quenching effect as indicated in the inset of Fig. 6a which plots the emission intensity of Ca$\text{_{2−x}}$Al$_x$O$_6$F:$x$Eu$^{2+}$ phosphors as a function of the Eu$^{2+}$ content. The emission intensity increases with Eu$^{2+}$ content and reaches a maximum critical value at $x = 0.05$. However, the intensity decreased gradually as the Eu$^{2+}$ content increased beyond the critical concentration. It is accepted that concentration quenching is mainly caused by energy transfer among Eu$^{2+}$ ions, the probability of which increases as the concentration of Eu$^{2+}$ increases. If we consider energy transfer between two identical centers, the critical distance ($R_c$) is defined as the distance for which the probability of energy transfer equals the probability of radiative emission of Eu$^{2+}$, as pointed out by Blasse.$^{32}$ Eqn (2) can be used to calculate the $R_c$ value,

$$R_c \approx 2 \left( \frac{3V}{4\pi x N} \right)^{\frac{1}{3}}$$

(2)

where $R_c$ corresponds to the mean separation between the nearest Eu$^{2+}$ ions at $x_c$. Using $V = 1819.26$ Å$^3$, $N = 12$, and $x_c = 0.05$, the critical transfer distance of Eu$^{2+}$ in Ca$\text{_{2−x}}$Al$_x$O$_6$F is calculated to be 17.96 Å. Based on this result, it can be inferred that the mechanism of exchange interaction plays no role in
energy transfer between Eu$^{2+}$ ions in the Ca$_2$Al$_3$O$_6$F phosphor since the exchange critical interaction is dominant only for short distances (typical critical distances of 5 Å). Therefore, as a consequence, the energy transfer in the present case will occur only by electric multipolar interaction. According to Dexter’s theory, there are three multipole–multipole interactions: dipole–
dipole, dipole–quadrupole and quadrupole–quadrupole, respectively. The emission intensity ($I$) of multipolar interaction can be determined from the change of the emission intensity from the emitting level with multipolar interaction, which follows eqn (3):\(^{33,34}\)

$$I/x = K[1 + \beta(x)^{4/3}]^{-1} \quad (3)$$

where $I$ is the emission intensity, $x$ is the concentration of the activator ions, $K$ and $\beta$ are constants for the same excitation conditions, and $\theta$ is a function of multipole–multipole interaction, taking values of 0 (dipole–dipole), 8 (dipole–quadrupole) or 10 (quadrupole–quadrupole). To get a correct $\theta$ value for the two emission centers, the dependence of log($I/x$) on log($x$) is plotted, which yields a straight line with a slope equal to $-\theta/3$. Because the critical quenching concentration of Eu$^{2+}$ ($x$) has been determined as about 0.05 in Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphor, $I/x$ is plotted as a function of $x$ for $x > 0.05$. The dependence of log($I/x$) on log($x$) is linear in Fig. 6b with a slope of $-2.18$. Therefore, the value of $\theta$ is calculated as approximately 6, which indicates that the dipole–
dipole interaction is the dominant concentration quenching mechanism of Eu$^{2+}$ emission in the Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphor.

Fluorescence decay curves of Ca$_{2-x}$Al$_x$O$_6$F:xEu$^{2+}$ phosphors ($x = 0.005, 0.01, 0.03, 0.05, 0.06, 0.10$ and 0.20) excited at 370 nm are also measured and depicted in Fig. 7. The decay curve can be well fitted with a first-order exponential decay mode by use of eqn (4):\(^{35}\)

$$I(t) = I_0 + A \exp(-t/\tau) \quad (4)$$

where $I$ and $I_0$ are the luminescence intensity at time $t$ and 0, $A$ is a constant, $\tau$ is the time, and $\tau$ is the decay time for an exponential component. On the basis of eqn (4) and decay curves, the decay times were determined to be 0.68, 0.56, 0.51, 0.47, 0.43, 0.37 and 0.25 μs for Ca$_{2-x}$Al$_x$O$_6$F:xEu$^{2+}$ phosphors with different Eu$^{2+}$ doped concentrations, respectively, as is also shown in Fig. 7. Considering that Eu$^{2+}$ in this series of Ca$_2$Al$_3$O$_6$F compounds should have similar chemical environment, as expected the measured decay time is nearly the same. However, the decay time begins to decrease gradually with further increasing Eu$^{2+}$ concentration. Therefore, the nonradiative and self-absorption rate of the internal doped ions evidently increase when activators cross the critical separation between donor (activator ion) and acceptor (quenching site).\(^{36}\)

3.4. Temperature-dependent photoluminescence, SEM, CIE and quantum efficiency of Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphors

In order to further investigate the possible practical application of the Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphor, some key parameters, such as the temperature-dependent photoluminescence, microstructure and morphology, CIE value and quantum efficiency of Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphors have also been studied and measured.

First, for application in high power LEDs, the thermal quenching property of a phosphor is an important parameter to be considered. Fig. 8 shows the emission spectra of the Ca$_{1.95}$Al$_x$O$_6$F:0.05Eu$^{2+}$ phosphor at various temperatures. It can be seen that the Ca$_{1.95}$Al$_x$O$_6$F:0.05Eu$^{2+}$ phosphor shows a relatively poor thermal stability upon heating. The PL intensity of Ca$_{1.95}$Al$_x$O$_6$F:0.05Eu$^{2+}$ phosphor at 150 °C is only about 39% of its initial value, as given in the inset of Fig. 8. The thermal quenching is caused by thermally activated cross-over from the 4$^5$Sd-excited state to the 4$^5$G ground state and can be explained by the thermal quenching mechanism using a configurational coordinate diagram.\(^{37}\) Additionally, the emission wavelength shows slight blue shifting with increasing temperature (Fig. 8). This can be explained by thermally active phonon-assisted excitation from lower energy sublevels to higher-energy sublevels in the excited states of Eu$^{2+}$.

In order to understand the temperature dependence of emission intensity and to determine the activation energy for thermal quenching, the Arrhenius equation (eqn (5)) was fitted to the thermal quenching data of the Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor.\(^{38}\)

$$I_T = \frac{I_0}{1 + c \exp(-\Delta E/kT)} \quad (5)$$

In eqn (5), $I_0$ is the initial emission intensity, $I_T$ is the intensity at different temperatures, $\Delta E$ is activation energy of thermal quenching, $c$ is a constant for a certain host, and $k$ is the Boltzmann constant ($8.629 \times 10^{-5} \text{eV}$). Fig. 9 plots the relationship of log($I_0/I_T - 1$) vs. 1000/$T$ for the present Ca$_{2-x}$Al$_x$O$_6$F:0.05Eu$^{2+}$ phosphor, which is linear with a slope of $-4.256$. According to eqn (5), the activation energy $\Delta E$ of Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor was calculated to be 0.37 eV.

The morphologies of the selected crystalline Ca$_{1.95}$Al$_3$O$_6$F:
F:0.05Eu$^{2+}$ phosphors were determined using SEM (Fig. 10). It is found that the particles have uniform smooth morphology and narrow size distribution with diameters of the particles between 3 and 8 μm. It is believed that such morphology will be very helpful in practical terms in the fabrication of white LEDs devices. The CIE chromaticity coordinates for Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphors excited at 365 nm were determined in our work. The CIE coordinates are calculated to be (0.171, 0.470), and the results obtained are shown in the CIE diagram of Fig. 11. A digital photo of the Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor under 365 nm UV lamp is shown in the inset of Fig. 11 revealing an intense green light. Additionally, we have also measured the internal quantum efficiency (QE) of Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor according to the reported method.\(^{39,40}\) From the results of Fig. 12 the internal QE value can be calculated by eqn (6):

$$\eta_{\text{QE}} = \frac{\int L_S}{\int E_R - \int E_S} \quad (6)$$

where $L_S$ is the luminescence emission spectrum of the sample; $E_S$ is the spectrum of the light used for exciting the sample; $E_R$ is the spectrum of the excitation light without the sample in the sphere; and all the spectra were collected using the sphere on the FLS920 fluorescence spectrophotometer. The measured internal QE of Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor is determined as 34% under 400 nm excitation. Moreover, the QE can be improved by
controlling the particle size, size distribution, morphology and crystalline defects through optimization of the processing conditions and chemical composition.

4. Conclusions

In conclusion, we have synthesized and studied a new green-emitting phosphor Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$. The phase purity and local structure behaviors have been characterized by XRD and $^{27}$Al MAS NMR spectroscopy. The overall luminescence performance of Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ has been evaluated. Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ shows strong and broad absorption in the near UV regions and the optimum excitation band is located in the 260–420 nm region. Under excitation at 400 nm, the phosphor gives bright green emission peaking at around 502 nm. The dipole–dipole interaction is the concentration quenching mechanism of Eu$^{2+}$ emission in the Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphor. The temperature-dependent luminescence properties, CIE values and the typical morphology of the selected Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ phosphors have been investigated in detail. The measured internal QE of Ca$_{1.95}$Al$_3$O$_6$F:0.05Eu$^{2+}$ phosphor is determined to be 34% under 400 nm excitation. The above results indicate that Ca$_2$Al$_3$O$_6$F:Eu$^{2+}$ is a good candidate for the green component in n-UV-excited w-LEDs.

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