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Crystal structure and Temperature-Dependent Luminescence Characteristics of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor for White Light-emitting diodes

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The $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor was prepared by the conventional high temperature solid-state reaction. The crystal structure, luminescence and reflectance spectra, thermal stability, quantum efficiency and the application for N-UV LED were studied respectively. The phase formation and crystal structure of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ were confirmed from the powder X-ray diffraction and the Rietveld refinement. The concentration quenching of Eu^{2+} in the $\text{KMg}_4(\text{PO}_4)_3$ host was determined to be 1 mol% and the quenching mechanism was certified to be the dipole-dipole interaction. The energy transfer critical distance of as-prepared phosphor was calculated to be about 35.84 Å. Furthermore, the phosphor exhibited good thermal stability and the corresponding activation energy ΔE was reckoned to be 0.24 eV. Upon excitation at 365 nm, the internal quantum efficiency of the optimized $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ was estimated to be 50.44%. The white N-UV LEDs was fabricated via $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$, green-emitting $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$, and red-emitting $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphors with a near-UV chip. The excellent color rendering index ($R_a = 96$) at a correlated color temperature (5227.08 K) with CIE coordinates of $x = 0.34$, $y = 0.35$ of the WLED device indicates that $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ is a promising blue-emitting phosphor for white N-UV light emitting diodes (LEDs).

Since the first light emitting diode (LED) light source was invented by Nick Holonyak of General Electric, it has drawn more and more attention to apply in solid-state lighting and create an enormous revolution on the lighting industry. Recently, a great attention has been focused on white LEDs as solid-state lighting and as components of display devices because of their low energy consumption, high efficiency, long operational lifetime ($>100\,000$ h), environmental friendliness and high material stability^{1–4}. There are several ways to assemble the white LEDs. The most prevalent strategy is produced by pumping the blue InGaN chip with yellow-emitting $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$ (YAG) phosphor. Nevertheless, high correlated color temperature (CCT) and low color rendering (CRI) index ($R_a < 80$) restrict it to provide sunlight-like illumination due to the deficiency in red emission. In order to generate excellent CRI values and appropriate CCT white light for display or general illumination light sources, the method of pumping blue, green, and red-emitting phosphors with near ultraviolet (N-UV) LEDs has been investigated^{5–7}. Thereinto, the $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ (BAM), which is the most commonly used commercial blue phosphor for N-UV LEDs as high efficiency, suffer from poor thermal stability^{4,8,9}. Accordingly, the development of excellent structure and thermal stability of blue phosphor host for N-UV LEDs is highly desirable.

Eu^{2+} ion is the most frequently used blue-emitting activator in phosphor, which shows broad N-UV excitation and visible emission in a specific host owing to the $4f-5d$ transitions. According to the impact of the strength of the crystal field and covalent, Eu^{2+} can emit light from the ultraviolet to the infrared with broadband emitting fluorescence in different matrixes, and the corresponding fluorescence lifetimes locate commonly in the range of 0.2–2.0 μs ^{10,11}. On basis of these characteristics, multifarious Eu^{2+} -activated phosphors have been widely studied in LED lighting, 3D displays and scintillators in detection devices.

The phosphate $\text{KMg}_4(\text{PO}_4)_3$ compound was first obtained from flux during crystallizing $\text{K}_2\text{MgWO}_2(\text{PO}_4)_2$ by Tomaszewski and co-workers¹². Xiaofeng Lan et al. reported the luminescence properties of Eu^{2+} -activated $\text{KMg}_4(\text{PO}_4)_3$ by combustion-assisted synthesis method in 2012¹³. However, to our best knowledge,

the temperature-dependent luminescence characteristics as well as the application of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ pumped for *n*-UV LEDs have not been investigated. In this paper, the $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor was firstly prepared by the conventional high temperature solid-state reaction method. The crystal structure, reflectance spectra, thermal stability, quantum efficiency and applications in white NUV LED are studied respectively. White LEDs was fabricated by combing an N-UV LED chip ($\lambda_{\text{max}} = 385 \text{ nm}$) with the $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$, along with green and red phosphors, and its optical properties have also been investigated. The results demonstrate that the blue-emitting $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ is a promising blue-emitting phosphor for white N-UV LEDs.

Results

XRD Refinement and Crystal Structure. Figure 1 depicts the XRD patterns of the series of as-synthesized $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0, 0.02, 0.06$, and 0.1), and the standard pattern (JCPDS 15-4111) of $\text{KMg}_4(\text{PO}_4)_3$ is shown as a reference. It can be found from the Figure 1 that all XRD patterns agree well with the standard pattern and no other phase is observed, which demonstrates that the single phase of $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ was obtained and the doping of Eu^{2+} ions did not cause any notable impurities or any structural variation. Besides, the main diffraction peaks shift slightly to the higher angle side with increasing Eu^{2+} concentrate, as shown in Figure 1(b). This observation means that the lattice was distorted by substitution the ions which are comparatively big radius in $\text{KMg}_4(\text{PO}_4)_3$ host lattice with Eu^{2+} ions¹⁴. Thus, it is reasonable to assume that Eu^{2+} ($r = 1.25 \text{ \AA}$ for coordinate number (CN) = 8 and $r = 1.17 \text{ \AA}$ for CN = 6) ions substituted the position of K^+ sites ($r = 1.51 \text{ \AA}$ for CN = 8) because both the Mg^{2+} ($r = 0.72 \text{ \AA}$ for CN = 6 and $r = 0.66 \text{ \AA}$ when CN = 5) and P^{5+} ($r = 0.17 \text{ \AA}$ for CN = 4) sites are smaller than the Eu^{2+} ions^{15,16}. For further understanding the phase purity and the occupancy of Eu^{2+} ions on K^+ sites in $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$, the Rietveld refinement of $\text{KMg}_4(\text{PO}_4)_3$ and $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ phosphors were analyzed via the GSAS program as shown in Figure 2. The $\text{KMg}_4(\text{PO}_4)_3$ was served as an initial structural model. The results of Rietveld refinement further demonstrate that neither the host nor the doped 0.06 mol Eu^{2+} ions generated any impurity or secondary phases in $\text{KMg}_4(\text{PO}_4)_3$. The $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ belongs to an orthorhombic structure with the space group $\text{Pnnm}(58)$. For the crystal of $\text{KMg}_4(\text{PO}_4)_3$ host, the lattice parameters were fitted to be $a = 16.3707(7) \text{ \AA}$, $b = 9.5627(4) \text{ \AA}$, $c = 6.1667(5) \text{ \AA}$, cell volume (V) = $965.361(23) \text{ \AA}^3$ and the weighted profile R-factor (R_{wp}), the expected R factor (R_{p}) are 8.86% and 6.86% , respectively. As doped

with Eu^{2+} , the lattice parameters of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ became $a = 16.3563(4) \text{ \AA}$, $b = 9.5570(2) \text{ \AA}$, $c = 6.1663(1) \text{ \AA}$ and $V = 963.904(67) \text{ \AA}^3$. The refinement data converged to $R_{\text{wp}} = 10.54\%$ and $R_{\text{p}} = 7.97\%$, as summarized in Table 1. The volumetric constriction with increasing Eu^{2+} doping concentration also indicates that the Eu^{2+} occupied the K^+ ions sites.

Figure 3 illustrates the crystal structure of $\text{KMg}_4(\text{PO}_4)_3$ and the coordination environment of the K^+ ions. The compound of $\text{KMg}_4(\text{PO}_4)_3$ is consist of PO_4 tetrahedra, MgO_6 octahedra and MgO_5 polyhedra which are linked by P–O–Mg bridges. The K^+ ions are located in the tunnels along *b*-axis and surrounded by the three-dimensional framework forming via interconnected polyhedra. As presented in Figure 3c, the K^+ ions in $\text{KMg}_4(\text{PO}_4)_3$ are eight-fold coordinated by oxygen ions with $4g$ position and *m* site symmetry.

Reflectance and Photoluminescence properties of the $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ phosphor at RT. The reflectance spectra of $\text{KMg}_4(\text{PO}_4)_3$ host and $\text{KMg}_4(\text{PO}_4)_3:0.05\text{Eu}^{2+}$ are presented in Figure 4a. The $\text{KMg}_4(\text{PO}_4)_3$ host shows an energy absorption band ranging from 200 to 300 nm, and a high reflection ranging from 300 to 700 nm. The band gap of the virgin $\text{KMg}_4(\text{PO}_4)_3$ is calculated by using the following formula:¹⁷

$$[F(R_{\infty})h\nu]^n = C(h\nu - E_g) \quad (1)$$

in which $h\nu$ means the energy per photon, C is a proportional constant and E_g represents the value of the band gap, $n = 1/2$ stands for an indirect allowed transition, 2 means a direct allowed transition, $3/2$ represents a direct forbidden transition, or 3 indicates an indirect forbidden transition, $R_{\infty} = R_{\text{sample}}/R_{\text{standard}}$. The $F(R_{\infty})$ means the Kubelka–Munk function which can be formulated to the following equation:

$$F(R_{\infty}) = \frac{K}{S} = \frac{(1-R)^2}{R} \quad (2)$$

where K , S , and R represent the absorption, scattering, and reflectance parameter, respectively. As illustrated in Figure 4b, the band gap energy of $\text{KMg}_4(\text{PO}_4)_3$ host is estimated to be about 5.74 eV from the extrapolation of the line for $[F(R_{\infty})h\nu]^2 = 0$. As Eu^{2+} ions were introduced into the host, strong broad absorption appeared in the $250\text{--}400 \text{ nm}$ N-UV range, which is matched well with the excitation spectrum.

The photoluminescence emission (PL, $\lambda_{\text{ex}} = 300$ and 365 nm) and excitation (PLE, $\lambda_{\text{em}} = 450 \text{ nm}$) spectra of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ are also depicted in Figure 4a. The PLE spectrum of $\text{KMg}_4(\text{PO}_4)_3$:

Figure 1 | (a) XRD patterns of the as-prepared samples $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0, 0.02, 0.06$, and 0.1) and the standard pattern (JCPDS 15-4111). (b) The detailed XRD patterns ranging from 10° to 12° for the same samples.

Figure 2 | Powder XRD pattern (×) of (a) $\text{KMg}_4(\text{PO}_4)_3$ host and (b) $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ samples with their corresponding Rietveld refinement (solid line) and residuals (bottom).

0.06Eu^{2+} presents a broad hump ranging at 250–400 nm, which originates from the $4f^7-4f^65d$ transition of Eu^{2+} ions. It indicates that the broad excitation spectrum of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ matches well with the emission of the commercial N-UV chip (365–420 nm). The PL spectra of the $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ phosphor present a 52.2 nm full width at half-maximum (FWHM) broad blue emission band extending from 400 to 525 nm peaking at 450 nm, which is assigned to the $4f^65d-4f^7$ transition of the Eu^{2+} ions. Moreover, The PL of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ detected under 365 nm is similar to that under 300 nm in addition to the difference of the relative intensity, which verifies that the Eu^{2+} ions occupy the same lattice site (K^+ sites) in $\text{KMg}_4(\text{PO}_4)_3$ host¹⁸. Above result is in accord with the conclusion from Rietveld refinement. The CIE chromaticity coordinates of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ and commercial BAM phosphors under 365 nm UV excitation are illustrated in Figure 5. The color coordinates of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ and BAM are calculated to be ($x = 0.1507$, $y = 0.0645$) and ($x = 0.1471$, $y = 0.0628$), respectively. The inset shows the digital photograph of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphor under a 365 nm UV lamp, which indicates $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor can be used as a blue-emitting phosphor for w -LEDs application.

As Figure 4a shows, the PL and PLE spectra of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ overlap partially, which demonstrates the existence of energy transfer between $\text{Eu}^{2+}-\text{Eu}^{2+}$ ¹⁹. As we know, two main mechanisms can be explanatory for the resonant energy-transfer:

exchange interaction or electric multipolar interaction²⁰. In order to further investigate the process of energy transfer between activators or between sensitizer and activator, the Eu^{2+} concentration-dependent PL spectra of $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$) phosphors under 365 nm light excitation are shown in Figure 6. The optimal doping concentration of Eu^{2+} for the PL intensity in $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ is 1% mol. When the doping content of Eu^{2+} exceeded 0.01 mol%, the PL intensity began to decrease because of the concentration quenching effect which is due to the energy consumed via energy transfer from one activator to another²¹. Thus, the critical distance (R_c) for energy transfer among Eu^{2+} is necessary to obtain for further understanding the concentration quenching interaction mechanism. The value of the critical distance (R_c) can be reckoned via the following equation:²²

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

where V means the unit cell volume, x_c represents the concentration of activator ion where the quenching occurs and N is the number of the K^+ ion in per unit cell. For the $\text{KMg}_4(\text{PO}_4)_3$ host, $x_c = 0.01$, $N = 4$, and $V = 965.361 \text{ \AA}^3$, hence, the value of R_c is calculated to about 35.84 Å. Owing to the typical critical distance of the exchange interaction is about 5 Å and the exchange interaction only fits the energy transfer of forbidden transitions^{5,23}. Therefore, the electric multipolar

Table 1 | Main parameters of processing and refinement of $\text{KMg}_4(\text{PO}_4)_3$ host and $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ samples

Compound	$\text{KMg}_4(\text{PO}_4)_3$	$\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}$
Sp.Gr.	<i>Pnmm</i>	<i>Pnmm</i>
a , Å	16.3707(7)	16.3563(4)
b , Å	9.5627(4)	9.5570(2)
c , Å	6.1667(5)	6.1663(1)
α , °	90	90
β , °	90	90
γ , °	90	90
V , Å ³	965.361(23)	963.904(67)
2θ -interval, °	5–90°	5–90°
R_{wp} , %	8.86	10.54
R_p , %	6.86	7.97
χ^2	2.511	2.844

Figure 3 | Crystal structures of $\text{KMg}_4(\text{PO}_4)_3$. The view of the $\text{KMg}_4(\text{PO}_4)_3$ (a) along the [001] Direction, (b) perpendicular to the [010] direction, and the (c) coordination geometry of anions around the K^+ ions.

interactions are dominant in the energy transfer process. The interaction type can be estimated via the following equation:²⁴

$$\frac{1}{x} = K \left[1 + \beta(x)^{\frac{\theta}{3}} \right]^{-1} \quad (4)$$

in which x is the concentration of activation, which is not less than the critical concentration, I/x is the emission intensity (I) per

activator concentration (x); K and β are constants under the same excitation condition of host lattice; and θ is a function of electric multipolar character. $\theta = 6, 8, 10$ for dipole–dipole ($d-d$), dipole–quadrupole ($d-q$), quadrupole–quadrupole ($q-q$) interactions, respectively. In order to estimate the θ value, the dependence of $\lg(I/x)$ on $\lg(x)$ is illustrated in the inset of Figure 6. A relatively linear relation can be observed and the slope of the straight line is fitting to

Figure 4 | (a) Excitation and emission spectra of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ ($\lambda_{\text{em}} = 450$ nm for excitation and $\lambda_{\text{ex}} = 300$ and 365 nm for emission); Diffuse reflection spectra of $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0$ and 0.06); (b) Absorption spectra of $\text{KMg}_4(\text{PO}_4)_3:0.06\text{Eu}^{2+}$ matrix calculated by the Kubelka–Munk equation. All spectra were taken at RT.

Figure 5 | CIE coordinates of the $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphor and the commercial BAM:Eu^{2+} . The inset shows a digital photograph of the blue-emitting $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ sample.

-1.4911 which equals to $-\theta/3$. Hence, the value of θ is 4.4733 , which is close to 6 , demonstrating that the interaction type in $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ is dipole-dipole interactions.

To further explore the energy transfer process, the room temperature luminescence decay curves of Eu^{2+} ions in $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$

($x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$; $\lambda_{\text{ex}} = 365 \text{ nm}$, $\lambda_{\text{em}} = 450 \text{ nm}$) were measured, as shown in Figure 7. The decay curves can be fitted with an approximate single-exponential decay model as:

$$I = I_0 + A \exp(-t/\tau) \quad (5)$$

where I_0 represents the initial emission intensity when t is 0 and τ means the lifetime. The average lifetimes of Eu^{2+} ions of $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0.005, 0.01, 0.02, 0.04, 0.06, 0.08$) were estimated to be $1.246, 1.262, 1.245, 1.176, 1.163$ and $1.161 \mu\text{s}$, respectively. All measured decay times are reasonable for the $5d-4f$ allowed transition of Eu^{2+} in solids ($\sim 1 \mu\text{s}$). Besides, the decay time increases to maximum, when the concentration of Eu^{2+} increases to 0.01 , and then the decay time reduces acutely, indicating an efficient energy transfer between Eu^{2+} ions and causing concentration quenching^{25,26}.

Influence of Temperature on emission intensity and FWHM. The thermal quenching of luminescence is one of important technological parameters to be considered for phosphor materials applied in high power LEDs, because it significantly affects the light output and service life. The temperature-dependent PL spectra of the $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ excited by 365 nm N-UV light is depicted in Figure 8. With increasing temperature (30°C – 300°C), the emission intensity decreases from 100% to 74.26% of that at 30°C , and the FWHM of the emission band increases from 50.34 to 60.42 nm . The inset of Figure 8 illustrates the comparison of the thermal luminescence quenching of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ with that of commercial BAM:Eu^{2+} and the FWHM of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ emission as a function of the temperature. As shown in Figure 8, it can be found only 9% decay at 150°C for $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$, which indicates that the thermal stability of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ is superior to that of commercial BAM:Eu^{2+} below 200°C and this phosphor could be used as a promising phosphor for high-power LED application. To better understand the thermal quenching process, the configurational coordinate diagram can be used to

Figure 6 | PL spectra for $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0.005$ – 0.08) phosphors. The inset shows the fitting line of $\lg(I/x)$ versus $\lg(x)$ in $\text{KMg}_4(\text{PO}_4)_3:x\text{Eu}^{2+}$ ($x = 0.005$ – 0.08) phosphors beyond the quenching concentration.

Figure 7 | Decay lifetime tests of $\text{KMg}_4(\text{PO}_4)_3:\text{xEu}^{2+}$ ($x = 0.05\text{--}0.08$) detected at 450 nm for Eu^{2+} emission.

respond to this phenomenon. As the temperature increases, the interaction of electron-phonon is intensive. Along with the enhancing of phonon interaction, more electrons can be thermally activated to the crossover between the $4f^65d$ excited state and $4f^7$ ground state, whereupon release the energy by generating lattice vibration²². The excellent thermal stability of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ may relate to the indurative structure which is combined with PO_4 tetrahedra, MgO_6 octahedra and MgO_5 polyhedra via P-O-Mg bridges to form the three-dimensional framework. In this indurative structure, the energy of the electrons in the excited state is difficult to release via lattice vibration, which means smaller Stokes shift in a configurational coordinate diagram model and higher activation energy (ΔE)²⁷. The activation energy can be estimated

by using the Arrhenius equation:²⁸

$$\ln\left(\frac{I_0}{I}\right) = \ln A - \frac{\Delta E}{kT} \quad (6)$$

in which I_0 and I are the luminescence intensity of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ at room temperature and a given temperature, respectively; A is a constant; k is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV K}^{-1}$). From above equation, the ΔE is calculated to be about 0.24 eV (Figure 9).

The temperature-dependent of emission FWHM is related to the configuration coordinate model and the Boltzmann distribution, and can be expressed by:^{18,29}

$$\text{FWHM}(T) = W_0 \times \sqrt{\coth \frac{hv}{2kT}} \quad (7)$$

$$W_0 = \sqrt{8\ln 2} \times hv \times \sqrt{S} \quad (8)$$

where W_0 is the FWHM at 0°C , hv represents the vibrational phonon energy, S means the Huang–Rhys parameter, and k is the Boltzmann constant. With the temperature increase, the excited electrons spread to higher vibration levels and the radiative transitions from these different levels cause the emission band broadening.

Quantum efficiency and Electroluminescence properties of White-Light LED Lamp. Quantum efficiency of phosphors is another important technological parameter for practical application. The internal quantum efficiency (QE) of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ were measured and calculated by the following equations:³⁰

$$\eta_{\text{QE}} = \frac{\int L_s}{\int E_R + \int E_s} \quad (9)$$

in which L_s represents the luminescence emission spectrum of the sample; E_R is the spectrum of the excitation light from the empty integrated sphere (without the sample); E_s means the excitation

Figure 8 | Temperature-dependent PL spectra of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$. The inset shows a comparison of thermal quenching of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ with that of $\text{BAM}:\text{Eu}^{2+}$ and dependence of the FWHM of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ emission on temperature.

Figure 9 | The plot of $\ln(I_0/I)$ vs. $1/T$ of the $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphors.

spectrum for exciting the sample. As given in Figure 10, the internal QE of the $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphor is estimated to be about 50.44% under 365 nm excitation. As a comparison, the internal QE of commercial $\text{BaM}:\text{Eu}^{2+}$ phosphor is detected at the same condition and calculated to about 88.99%. The QE of $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ can be further improved by optimization of the preparation conditions, because the QE depends closely on the prepared conditions, crystalline defects, particle size and morphology of the phosphor^{31,32}.

To demonstrate the potential application of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor, the electroluminescent spectrum of white LED lamp which was fabricated via using N-UV LED chips ($\lambda_{\text{max}} = 385 \text{ nm}$) combining

Figure 11 | EL spectrum of a white-emitting N-UV-LED chip (385 nm) comprising of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ (blue), $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ (green) and $\text{CaAlSiN}_3:\text{Eu}^{2+}$ (red) phosphors driven by a 2 mA current.

with blue-emitting $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphor, green-emitting $(\text{Ba,Sr})_2\text{SiO}_4:\text{Eu}^{2+}$ phosphor, and red-emitting $\text{CaAlSiN}_3:\text{Eu}^{2+}$ phosphor was measured as given in Figure 11 with forward bias current of 2 mA. The CIE color coordinates, correlated color temperature (CCT) and color rendering index (R_a) of this fabricated WLED lamp are determined to be (0.34, 0.35), 5227.08 and 96, respectively. The R_a was decided from the full set of the first eight CRIs shown in Table 2. The appropriate CCT value (5227.08) and high R_a value (96) demonstrate that the $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ can be a promising candidate for a blue-emitting phosphor for application of WLEDs.

Figure 10 | Excitation line of BaSO_4 and emission spectrum of the $\text{KMg}_4(\text{PO}_4)_3:0.01\text{Eu}^{2+}$ phosphor collected by an integrating sphere. The inset shows the magnification of the emission spectrum.

Table 2 | Full Set of 14 CRIs and the Ra of the Fabricated WLED

R _o	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10	R11	R12	R13	R14
96	96	98	98	94	96	94	96	92	77	95	89	96	96	99

Discussion

In conclusion, we report a systematic study on the preparation and crystal structure analysis of blue-emitting $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ phosphor and investigate their reflectance spectra, thermal stability, quantum efficiency and applications in N-UV LED. The phase composition and crystal structure of $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ were determined via the powder X-ray diffraction patterns and Rietveld refinement analysis. The optimal Eu^{2+} doping concentration in the $\text{KMg}_4(\text{PO}_4)_3$ host is 1 mol%. The critical energy transfer distance of this phosphor was calculated to be about 35.84 Å and the concentration quenching mechanism is proved to be the dipole-dipole interaction. The investigation results also reveal that the as-prepared phosphor shows good thermal stability, and the internal quantum efficiency is 50.44%. The white N-UV LEDs packaged by an N-UV chip with blue-emitting $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$, green and red-emitting phosphors generate white light with high color rendering index ($R_a = 96$) and an appropriate correlated color temperature (5227.08 K). These results demonstrate that $\text{KMg}_4(\text{PO}_4)_3:\text{Eu}^{2+}$ is a promising blue-emitting phosphor for N-UV LEDs.

Methods

Materials and Synthesis. A variety of blue-emitting $\text{KMg}_4(\text{PO}_4)_3:\text{xEu}^{2+}$ phosphors were prepared via a traditional high-temperature solid-state reaction. The constituent raw materials KH_2PO_4 (A. R.), MgO (A. R.), $\text{NH}_4\text{H}_2\text{PO}_4$ (A. R.) and Eu_2O_3 (A. R.) were weighed in stoichiometric proportions and ground homogeneously in agate mortar. Firstly, the mixtures were preheated at 600°C for 2 h in a muffle furnace in air to release NH_3 , CO_2 , and H_2O . Then, the precursor was reground and heated at 1000°C for 6 h in the thermal carbon reducing atmosphere (TCRA). Finally the furnace cooled to room temperature and the mixtures were ground in an agate mortar.

Materials Characterization. X-ray powder diffraction (XRD) patterns of the final products were identified on a D8 Advance diffractometer (Bruker Corporation, Germany) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm) radiation. High quality XRD data for Rietveld refinement were collected by step scanning rate (8 s per step with a step size of 0.02°) over a 2θ range from 5° to 100° . The photoluminescent excitation/emission (PLE/PL) spectra were detected by a Hitachi F-4600 fluorescence spectrophotometer (Japan) equipped using 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 diffuse reflectance spectra were obtained by a Varian Cary-5000 UV-vis-NIR spectrophotometer attached with an integral sphere. The room-temperature luminescence decay curves were obtained from a spectrofluorometer (Horiba, Jobin Yvon TBXPS) using a tunable pulse laser radiation (nano-LED) as the excitation. Quantum efficiency was measured by a fluoromax-4 spectrofluorometer (Horiba, Jobin Yvon) with an integral sphere at room temperature.

- Bergh, A., Craford, G., Duggal, A. & Haitz, R. The Promise and Challenge of Solid-State Lighting. *Phys. Today*. **54**, 42–47 (2001).
- Brinkley, S. E. *et al.* Robust Thermal Performance of $\text{Sr}_2\text{Si}_5\text{N}_8:\text{Eu}^{2+}$: an Efficient Red Emitting Phosphor for Light Emitting Diode Based White Lighting. *Appl. Phys. Lett.* **99**, 241106 (2011).
- Krings, M., Montana, G., Dronskowski, R. & Wickleder, C. $\alpha\text{-SrNCN}:\text{Eu}^{2+}$ - A Novel Efficient Orange-Emitting Phosphor. *Chem. Mater.* **23**, 1694–1699 (2011).
- Gwak, S. J., Arunkumar, P. & Im, W. B. A New Blue-Emitting Oxohalide Phosphor $\text{Sr}_4\text{OCl}_6:\text{Eu}^{2+}$ for Thermally Stable, Efficient White-Light-Emitting Devices under Near-UV. *J. Phys. Chem. C*. **118**, 2686–2692 (2014).
- Chiu, Y. C. *et al.* $\text{Ca}_2\text{PO}_4\text{Cl}:\text{Eu}^{2+}$: an Intense Near-Ultraviolet Converting Blue Phosphor For White Light-Emitting Diodes. *J. Mater. Chem.* **20**, 1755–1758 (2010).
- Li, H. F. *et al.* $\text{Sr}_{1.7}\text{Zn}_{0.3}\text{CeO}_4:\text{Eu}^{3+}$ Novel Red-Emitting Phosphors: Synthesis and Photoluminescence Properties. *ACS Appl. Mater. Interfaces*. **6**, 3163–3169 (2014).
- Xia, Z. G. & Liu, R. S. Tunable Blue-Green Color Emission and Energy Transfer of $\text{Ca}_2\text{Al}_2\text{O}_6\text{F}:\text{Ce}^{3+}$, Tb^{3+} Phosphors for Near-UV White LEDs. *J. Phys. Chem. C*. **116**, 15604–15609 (2012).

- Zhu, P. *et al.* Effect of SiO_2 Coating on Photoluminescence and Thermal Stability $\text{BaMgAl}_{10}\text{O}_{17}:\text{Eu}^{2+}$ under VUV and UV Excitation. *Opt. Mater.* **30**, 930–934 (2008).
- Im, W. B., Kim, Y.-I., Yoo, H. S. & Jeon, D. Y. Luminescent and Structural Properties of $(\text{Sr}_{1-x}\text{Ba}_x)_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}$: Effects of Ba Content on the Eu^{2+} Site Preference for Thermal Stability. *Inorg. Chem.* **48**, 557–564 (2008).
- Dorenbo, P. Energy of the First $4f^7-4f^55d$ Transition of Eu^{2+} in Inorganic Compounds. *J. Lumin.* **104**, 239–260 (2003).
- Chen, J. *et al.* The Luminescence Properties of Novel $\alpha\text{-Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{2+}$ Phosphor Prepared in Air. *Rsc Adv.* **4**, 18234–18239 (2014).
- Tomaszewski, P. E., Maczka, M., Majchrowski, A., Waskowska, A. & Hanuza, J. Crystal Structure and Vibrational Properties of $\text{KMg}_4(\text{PO}_4)_3$. *Solid State Sci.* **7**, 1201–1208 (2005).
- Lan, X. F., Wu, Q. Q., Chen, Y. Y. & Tang, W. J. Luminescence Properties of Eu^{2+} -Activated $\text{KMg}_4(\text{PO}_4)_3$ for Blue-Emitting Phosphor. *Opt. Mater.* **34**, 1330–1332 (2012).
- Chen, J., Liu, Y. G., Fang, M. H. & Huang, Z. H. Luminescence Properties and Energy Transfer of Eu/Mn -Coactivated $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ as a Potential Phosphor for White-Light LEDs. *Inorg. Chem.* **53**, 11396–11403 (2014).
- Piriou, B., Chen, Y. F. & Vilminot, S. Site-Selective Spectroscopy in Eu^{3+} Doped α -cordierite. *Eur. J. Solid State Inorg. Chem.* **35**, 341–355 (1998).
- Thim, G. P., Brito, H. F., Silva, S. A., Oliveira, M. A. & Felinto, M. C. Preparation and Optical Properties of Trivalent Europium Doped into Cordierite using The Sol-Gel Process. *J. Solid State Chem.* **171**, 375–381 (2003).
- Jiang, Z. Q., Wang, Y. H. & Wang, L. S. Enhanced Yellow-to-Orange Emission of Si-Doped $\text{Mg}_3\text{Y}_2\text{Ge}_3\text{O}_{12}:\text{Ce}^{3+}$ Garnet Phosphors for Warm White Light-Emitting Diodes Sensors and Displays: Principles, Materials, and Processing. *J. Electrochem. Soc.* **157**, J155 (2010).
- Liu, C. M. *et al.* High Light Yield of $\text{Sr}_6(\text{Si}_3\text{O}_{12})\text{Cl}_2:\text{Eu}^{2+}$ under X-ray Excitation and Its Temperature-Dependent Luminescence Characteristics. *Chem. Mater.* **26**, 3709–3715 (2014).
- Wang, D. Y., Huang, C. H., Wu, Y. C. & Chen, T. M. $\text{BaZrSi}_3\text{O}_9:\text{Eu}^{2+}$: A Cyan-Emitting Phosphor with High Quantum Efficiency for White Light-Emitting Diodes. *J. Mater. Chem.* **21**, 10818–10822 (2011).
- Huang, C. H. & Chen, T. M. A Novel Single-Composition Trichromatic White-Light $\text{Ca}_3\text{Y}(\text{GaO})_3(\text{BO}_3)_4:\text{Ce}^{3+}$, Mn^{2+} , Tb^{3+} Phosphor for UV-Light Emitting Diodes. *J. Phys. Chem. C*. **115**, 2349–2355 (2011).
- Im, W. B. *et al.* $\text{Sr}_{2.975-x}\text{Ba}_x\text{Ce}_{0.025}\text{AlO}_6\text{F}$: A Highly Efficient Green-Emitting Oxyfluoride Phosphor for Solid State White Lighting. *Chem. Mater.* **22**, 2842–2849 (2010).
- Blasse, G. Energy Transfer in Oxidic Phosphors. *Philips Res. Rep.* **24**, 131 (1969).
- Dexter, D. L. A Theory of Sensitized Luminescence in Solids. *J. Chem. Phys.* **21**, 836–850 (1953).
- Blasse, G. Energy Transfer in Oxidic Phosphors. *Phys. Lett.* **28**, 444–445 (1968).
- Xie, R. J., Hirosaki, N., Kimura, N., Sakuma, K. & Mitomo, M. 2-Phosphor-Converted White Light-Emitting Diodes using Oxynitride/Nitride Phosphors. *Appl. Phys. Lett.* **90**, 191101–191101-3 (2007).
- Geng, D. L. *et al.* Color Tuning via Energy Transfer in $\text{Sr}_3\text{In}(\text{PO}_4)_3:\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Mn}^{2+}$ Phosphors. *J. Mater. Chem.* **22**, 14262–14271 (2012).
- Lv, W. Z. *et al.* Synthesis, Structure, and Luminescence Properties of $\text{K}_2\text{Ba}_7\text{Si}_{16}\text{O}_{40}:\text{Eu}^{2+}$ for White Light Emitting Diodes. *J. Phys. Chem. C*. **118**, 4649–4655 (2014).
- Huang, C. H., Liu, W. R. & Chen, T. M. Single-Phased White-Light Phosphors $\text{Ca}_9\text{Gd}(\text{PO}_4)_7:\text{Eu}^{2+}$, Mn^{2+} under Near-Ultraviolet Excitation. *J. Phys. Chem. C*. **114**, 18698–18701 (2010).
- Henderson, B. & Imbusch, G. F. Optical Spectroscopy of Inorganic Solids. *Optical Spectroscopy of Inorganic Solids* Clarendon Press, Oxford, U.K., 1989.
- Xu, Y. S. *et al.* Efficient Near-Infrared Down-Conversion in $\text{Pr}^{3+}-\text{Yb}^{3+}$ Codoped Glasses and Glass Ceramics Containing LaF_3 Nanocrystals. *J. Phys. Chem. C*. **115**, 13056–13062 (2011).
- Dexter, D. X. & Schulman, J. H. Theory of Concentration Quenching in Inorganic Phosphors. *J. Chem. Phys.* **22**, 1063–1070 (1954).
- Bachmann, V., Ronda, C., Oeckler, O., Schnick, W. & Meijerink, A. Color Point Tuning for (Sr, Ca, Ba) $\text{Si}_2\text{O}_7\text{N}_2:\text{Eu}^{2+}$ for White Light LEDs. *Chem. Mater.* **21**, 316–325 (2009).

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Author contributions

Y.G.L. and J.C. conceived the project. J.C. and H.K.L. designed and performed the experiments. J.C., L.F.M. and M.H.F. analyzed the data. J.C. and Z.H.H. wrote the manuscript. All the authors discussed the results and commented on the manuscript at all stages.

Additional information

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