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The luminescence properties of novel α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphor prepared in air

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The α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphor was firstly prepared via the conventional high temperature solid-state reaction method and the reduction of Eu^{3+} to Eu^{2+} in air was observed in α-$Mg_2Al_4Si_5O_{18}$: Eu. The phase structure, photoluminescence (PL) properties, the PL thermal stability and the fluorescence decay curves of the samples were investigated, respectively. Emission and excitation spectra were employed to detect the presence of Eu^{2+} ions in the compound. Under the excitation at 365 nm, the phosphor exhibited a broad-band blue emission with peak at 463 nm, which was ascribed to the 4*f*–5*d* transition of Eu^{2+}. It was further proved that the dipole–dipole interactions resulted in the concentration quenching of Eu^{2+} in α-$Mg_2Al_4Si_5O_{18}$: xEu^{2+} phosphors. When the temperature turned up to 150°C, the emission intensity of α-$Mg_2Al_4Si_5O_{18}$: $0.12Eu^{2+}$ phosphor was 59.07% of the initial value at room temperature. The activation energy ΔE was calculated to be 0.21 eV, which proved the good thermal stability of the sample. All the properties indicated that the blue-emitting α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphor has potential application in white LEDs.

1 Introduction

Due to their high luminous efficiency, low power consumption, and environment-friendly characteristics in comparison with traditional incandescent and currently implemented fluorescent lamps, phosphor-converted white light emitting-diodes (pc-*w*LEDs) have received great attention to be a next-generation light source.[1] Currently, commercial *w*-LEDs employ a blue InGaN LED chip with a yellow phosphor of Ce^{3+}-doped yttrium aluminum garnet (YAG: Ce), and are very poor in the color rendering index (CRI) because of the color deficiency in the red region.[2] Consequently, *w*-LEDs fabricated with near ultraviolet (n-UV) LEDs chip and three primary color emissions mixed (red, green and blue) phosphors have been widely investigated.[3]

The luminescent properties of Eu^{2+} ions in various matrix compounds and the reduction processes of Eu^{3+} to Eu^{2+} in phosphor have attracted significant attention in the past decades. [4-9] Normally, the photoluminescence of Eu^{2+} in most silicates host is associated with the $4f \rightarrow 5d$ transitions. Compared with 4*f* orbitals of Eu^{2+}, those of 5*d* orbitals are sensitive to the changes of the crystal field strength due to its existing in the outer shell. The peak positions in the emission spectra depend strongly on the nature of the Eu^{2+} surroundings[9]. Therefore Eu^{2+} can be efficiently excited in a broad spectral range depending on the host lattices in which it is incorporated.

Generally, the reducing atmospheres, such as H_2, H_2/N_2, or CO, is necessary to reduce Eu^{3+} to Eu^{2+} during the annealing process in order to prepare the optical materials activated by Eu^{2+} ions since the raw material of the europium is Eu_2O_3.[6,7] If the reduction of Eu^{3+} to Eu^{2+} can be realized in air condition, it would greatly reduce the cost and increase the safety in preparing of Eu^{2+}-activated phosphor materials. Recently, the reduction of Eu^{3+} to Eu^{2+} in air condition has been reported[8, 10-18]. Since the first reported of an aliovalent substitution method to reduce trivalent rare earth ions Eu^{3+} into divalent ions Eu^{2+} even in air when these ions were doped in alkaline earth borate SrB_4O_7[11] in 1993, there have been significant advances in LEDs. Until now, the phenomena of Eu^{3+} reducing into Eu^{2+} in air have been found in many systems, such as borates (SrB_4O_7: Eu, SrB_6O_{10}: Eu, BaB_8O_{13}: Eu and $CaBPO_5$: Eu)[8,10-13], phosphates ($Ba_3(PO_4)_2$: Eu)[14], sulfates ($BaSO_4$: Eu)[15], aluminates ($Sr_4Al_{14}O_{25}$: Eu)[16] , silicates ($BaMgSiO_4$: Eu)[17] and ZnO-B_2O_3-P_2O_5 glasses[18].

The cordierite is a magnesium/aluminium aluminosilicate with the crystallo-chemical formula $Mg_2^{[6]}Al_3^{[4]}(Si_5Al^{[4]}O_{18})$[19], which have a complex structure with six tetrahedral units [Si/AlO_4]. Binding of the tetrahedral units is ensured by the [MgO_6] octahedral and [AlO_4] tetrahedral. The cordierite has several polymorphic modifications. A low temperature modification (β-$Mg_2Al_4Si_5O_{18}$) crystallizes in the orthorhombic

system, a metastable modification (μ-$Mg_2Al_4Si_5O_{18}$, crystallizes from glass below 925°C)[20] crystallizes in the hexagonal and a high temperature modification (α-$Mg_2Al_4Si_5O_{18}$) crystallizes in the hexagonal system. [21]

Magnesium cordierite, $Mg_2Al_4Si_5O_{18}$, have been used more frequently as promising ceramic material over the past several years attribute to easy preparation, chemical and thermal durability and mechanical properties resistant to corrosion at higher temperature.[22-24] Piriou et al.[25] and Thim et al.[26] have studied luminescent properties of magnesium cordierite ($Mg_2Al_4Si_5O_{18}$) doped with Eu^{3+} ion prepared by sol–gel without any flux at 1300°C and 1200°C, respectively, and they all found the weak broad peak in the range of 420–570 nm. However, they have not further investigated about the broad peak in the range of 420–570 nm. Additionally, no further researches on the luminescence properties of $Mg_2Al_4Si_5O_{18}$ have been reported so far. In this study, the $Mg_2Al_4Si_5O_{18}$: Eu^{2+} was prepared in air via using the conventional high temperature solid-state reaction method. The phase structure and luminescence properties of the blue-emitting (peak at 463nm) α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphors and the mechanism of the Eu^{3+} to Eu^{2+} reduction in α-$Mg_2Al_4Si_5O_{18}$ were studied in detail. These results indicate that the sample has good performance for *w*-LEDs application and it is of great significance for energy conservation.

2 Experimental

The $Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphors were prepared by conventional solid-state method with a stoichiometric quantities of MgO (A. R.), Al_2O_3 (A. R.), H_2SiO_3 (A. R.), Eu_2O_3 (A. R.), La_2O_3 (A. R.) (An excess of 8 *wt*% of La_2O_3 was added as flux). The selected starting materials were mixed and ground homogeneously according to the given stoichiometric ratio in the agate mortar, and then some mixtures were fired at 1300 °C in an alumina crucible for 6 hours in air. Other mixtures were sintered at the same temperature and time in the thermal carbon-reducing atmosphere (TCRA). The crystalline phases of synthesized products were examined by X-ray diffraction (XRD; D8 Advance diffractometer, Germany), using Cu-Kα1 radiation (λ = 1.5406 Å) with a step of 0.02° (2θ) and a scanning rate of 2 °·min^{-1}. The emission and the excitation spectra were recorded on a Hitachi F-4600 fluorescence spectrofluorimeter.

3 Results and Discussion

3.1 Phase Structure of the Samples

Figure 1 shows the XRD patterns of $Mg_2Al_4Si_5O_{18}$ [Fig. 1(a)], $Mg_2Al_4Si_5O_{18}$: 0.16Eu [Fig. 1(b)], the standard pattern (JCPDS 84-1222) of α-$Mg_2Al_4Si_5O_{18}$ and the standard pattern (JCPDS 13-0294) of β-$Mg_2Al_4Si_5O_{18}$. As the Fig. 1 shows, the characteristic peak between the JCPDS card No. 13-0294 (β-phase) and No. 84-1222 (α-phase) look like similar, while there are some difference to distinguish that the phosphor is either β-$Mg_2Al_4Si_5O_{18}$ or α-$Mg_2Al_4Si_5O_{18}$. It is obviously shows that the amount of characteristic peaks of β-phase is more than α-phase (Such as: 23.14° and 37.88°) and XRD patterns of $Mg_2Al_4Si_5O_{18}$ don't have any peaks on 23.14° and 37.88°. In addition, some peaks of No. 13-0294 would form the double peak phenomenon due to the distance of characteristic peaks are close [Such as: (26.34°, 26.43°), (28.32°, 28.48°) and (29.37°, 29.41°, 29.64°)], while the formation of peaks of $Mg_2Al_4Si_5O_{18}$ on 26.19°, 28.28° and 29.36° are symmetrical single peaks. It indicates that the phosphors we prepared are α-$Mg_2Al_4Si_5O_{18}$ (hexagonal) which crystallize in a hexagonal cell, with the space group P6/mcc, and has a hexagonal structure with the cell parameters of a = 9.794 Å, b = 9.794 Å, c = 9.339 Å, V = 775.70 $Å^3$ and Z = 2.[27] The miller indices for each XRD pattern are demonstrated in Fig. 1(a). It also can be seen that all the diffraction peaks of compounds are all well indexed to the standard pattern of α-$Mg_2Al_4Si_5O_{18}$, indicating that the obtained sample is single phase and the doping caused by a small amount of Eu ions did not cause the structural variation. In the α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphor system, Piriou et al[25] had demonstrated that the Eu ion cannot inside the structure channels at room temperature and it is assumed that Eu^{2+} (r = 0.117 nm when coordinate number (CN) = 6) ions occupied the Mg (r = 0.072 when CN = 6) sites because both the Al^{3+} (r = 0.039 nm) and the Si^{4+} (r = 0.026 nm) sites are too small to take the Eu^{2+} ions.[28]

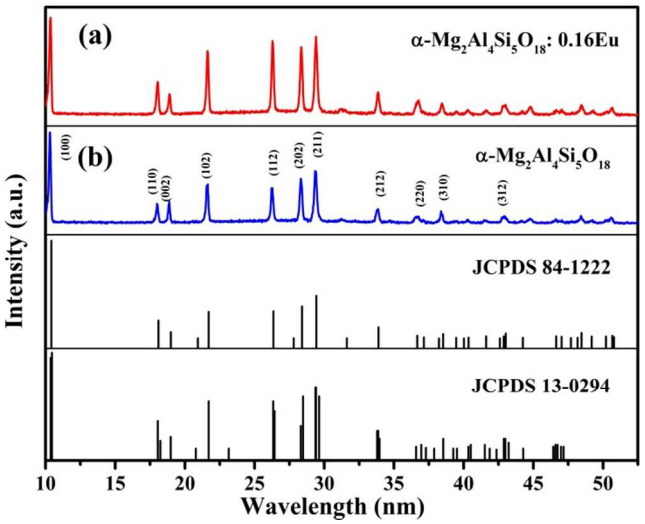

Fig. 1 XRD patterns of α-$Mg_2Al_4Si_5O_{18}$: 0.16Eu (a), α-$Mg_2Al_4Si_5O_{18}$ (b), the standard pattern (JCPDF84-1222) of α-$Mg_2Al_4Si_5O_{18}$, and the standard pattern (JCPDF13-0294) of β-$Mg_2Al_4Si_5O_{18}$.

3.2 Luminescence properties

It is well known that the emission of Eu^{2+} ion in a solid state compound generally originated from the transition of $4f^65d \rightarrow 4f^7$ with a broad band character. However, the emission of Eu^{3+} ion shows a narrow band character in the spectral region of 570–750 nm corresponding to $^5D_0$–^7F_J (J = 0–4) transitions. [17] In consequence, the existence of Eu^{2+} ions in phosphor compounds can be detected by luminescent measurements.

Figure 2 depicts the photoluminescence (PL), photoluminescence excitation (PLE) and reflectance spectra of α-$Mg_2Al_4Si_5O_{18}$: *x*Eu prepared in air. Although the precursor for europium was trivalent from Eu_2O_3 and the samples were prepared by annealing at 1300 °C in air condition, it seems that the europium exists in divalent state in the compound. The PLE monitoring by 463 nm is composed of one strong absorption peak at 275 nm in the spectral range from 200 to 450 nm, which is attributed to $4f^7(^8S_{7/2})$–$4f^65d$ transitions of the doped Eu^{2+} ions. PL spectrum shows that α-$Mg_2Al_4Si_5O_{18}$: *x*Eu phosphor exhibits similar blue emission band peaked at 463 nm under the excitation at 365 nm, which belongs to the typical emission of Eu^{2+} ions ascribed to $4f^65d$-$4f^7$ transitions.[10] As shown in Fig. 2, there are a part of overlap between the PL and PLE spectra of α-$Mg_2Al_4Si_5O_{18}$: *x*Eu, indicates the existence of energy transfer between Eu^{2+}–Eu^{2+}.[29] In the reflection spectra, the α-$Mg_2Al_4Si_5O_{18}$ host material shows a high reflection in the visible range. As Eu^{2+} ions were doped into the host, a strong broad absorption appeared in the range of 200–400 nm near-UV, which assigned to the $4f^7$-$4f^65d^1$ absorption of Eu^{2+} ions. The results confirm that the phosphor can match well with the emission of diffuse reflection spectrum. Additionally, we synthesized the α-$Mg_2Al_4Si_5O_{18}$: Eu^{2+} phosphor in TCRA, and detected its PL and PLE spectra (Fig. 2) for further verification of the existence of Eu^{2+} ions in α-$Mg_2Al_4Si_5O_{18}$: Eu prepared in air. By comparing the spectral characteristics of the PL and PLE between the air and TCRA, the shapes and positions of the PL and PLE are almost the same. However, as the inset of Fig. 2 shows, a very weak emission, which peaked at 740 nm and originated from the transition of $^5D_0$-$^7F_3$ from Eu^{3+}, could be observed from the enlarged emission spectra. It can be seen clearly that most of the Eu^{3+} have been reduced to Eu^{2+} during the annealing process, while a very small amount of Eu^{3+} also exist. Hence, it indicated that the incomplete reduction of Eu^{3+} which prepared in air might be the main reason of decrement of intensity of PL from air to TCRA and it confirmed by Peng et al.[16] and Liu et al.[30]. Consequently, we can conclude that the reduction of Eu^{3+} to Eu^{2+} in air took place in α-$Mg_2Al_4Si_5O_{18}$: Eu during the preparation at high temperature.

As we can also find from the excitation spectrum, the broad-band excitation character from 200-450 nm verified that the phosphor can match well with the emission of n-UV chip. The CIE color coordinate for the α-$Mg_2Al_4Si_5O_{18}$ phosphor under 365 nm UV excitation is calculated to be (0.1674, 0.1700). These results mean that the phosphor can be used as a blue-emitting phosphor for *w*-LEDs application.

The emission (λ_{ex} = 365 nm) spectra of α-$Mg_2Al_4Si_5O_{18}$: *x*Eu (*x* = 0.02, 0.04, 0.08, 0.12, 0.16) phosphors at room temperature were presented in Fig. 3. As found in Fig. 3, with an increase of Eu concentration up to 4 mol%, the intensities increase to maximum and then the emission intensity decreased with further increasing concentration, which is caused by the concentration quenching effect. From the emission spectra, the dependence of the emission intensity on the concentration of

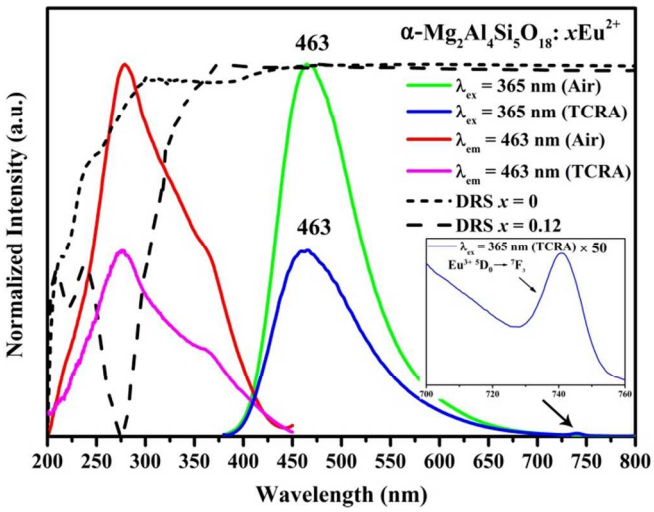

Fig. 2 The excitation and emission spectra of α-$Mg_2Al_4Si_5O_{18}$: $0.12Eu^{2+}$ (λ_{em} = 454 nm for excitation and λ_{ex} = 365 nm for emission) prepared in air and in TCRA; the diffuse reflection spectrum of α-$Mg_2Al_4Si_5O_{18}$: xEu^{2+}(*x* = 0 and 0.12). The range of 700-760 nm of emission spectra prepared in TCRA was amplified by factor of 50. All spectra were taken at RT.

Eu^{2+} is shown in the inset of Fig. 3. Thus, the optimum Eu-doping concentration is about 4 mol% for obtaining the strongest PL emission intensity. In addition, a red-shift of the peak wavelength is observed as the concentration of Eu^{2+} increases gradually, which could originate from the variations of the crystal field strength surrounding the activators.[31,32] When the doping concentration of Eu^{2+} increases, the inter-atomic distance between the two activators become shorter and the interaction is enhanced; as a result, the 5*d* band of Eu^{2+} is decreased, and finally the emission wavelength is red-shifted with increasing Eu^{2+} concentration. [33] The mechanism of the interaction between sensitizers or between sensitizer and activator can be expressed by the following equation[34,35]:

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

where *x* is the activator concentration, which is not less than the critical concentration; *I*/*x* is the emission intensity (*I*) per activator concentration (*x*); *K* an α are constants for the same excitation condition of host crystal; and θ is a function of multipole-multipole interaction. According to the previous reports, θ = 3 means the energy transfer among the nearest-neighbor ions and θ = 6, 8 and 10 corresponds to dipole–dipole (d–d), dipole–quadrupole (d–q), and quadrupole –quadrupole (q–q) interactions, respectively.[36] As the Fig. 4 shows, the relationship between the lg(I/x) and lg(x) shows a relatively linear and the slope of straight line is measured to be -1.8446 which equals -θ/3. Thus the value of θ can be calculated to be 5.5337, which is close to 6 that means the quenching results from dipole–dipole interactions in α-$Mg_2Al_4Si_5O_{18}$: *x*Eu.

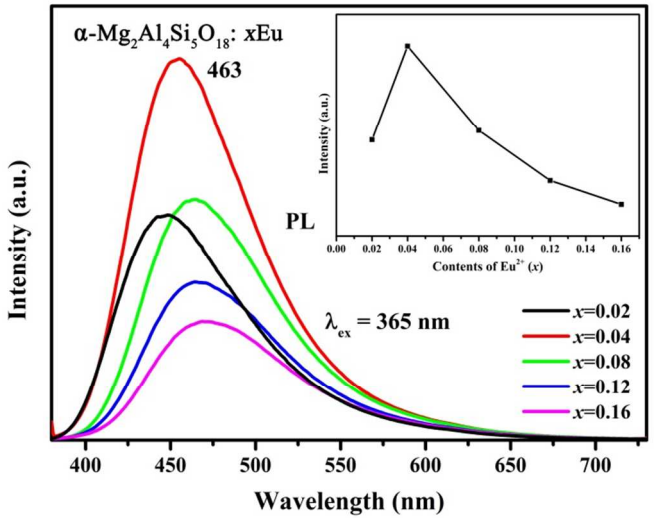

Fig. 3 The emission spectra of α-$Mg_2Al_4Si_5O_{18}$: *x*Eu (*x* = 0.02, 0.04, 0.08, 0.12 and 0.16). The inset shows the dependence of the emission intensity on the concentration of Eu^{2+}.

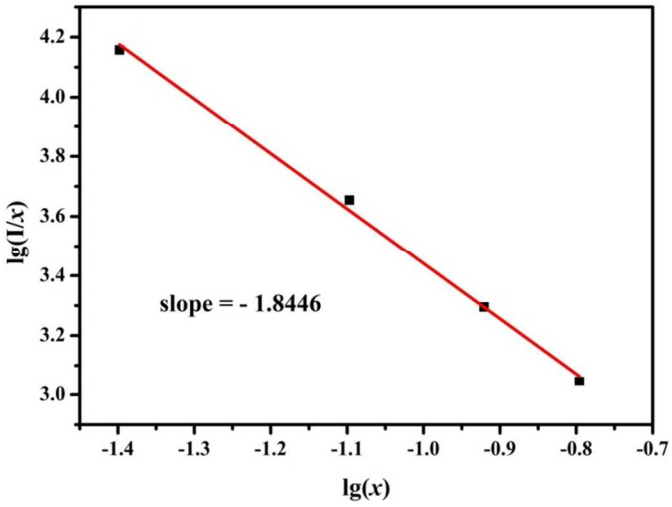

Fig. 4 The relationship between the lg (I/x) and lg (x) of α-$Mg_2Al_4Si_5O_{18}$: *x*Eu^{2+}

In general, the thermal stability of the phosphor plays an important role in solid-state lighting and has a significant influence on the light output and CRI. The temperature-dependent emission spectra under 365 nm excitation of α-$Mg_2Al_4Si_5O_{18}$: 0.12Eu^{2+} prepared in air are shown in Fig. 5. The intensity of the emission spectrum decreases with temperature increment. The emission intensities of α-$Mg_2Al_4Si_5O_{18}$: 0.12Eu^{2+} decrease to 56.95% of the initial emission intensity, which is regarded as 100%, with the increasing temperature up to 150°C. To further investigate the relationship between the photoluminescence and the temperature and to calculate the activation energy from the thermal quenching, the activation energy was calculated using the Arrhenius equation[37,38]:

$$I_T = \frac{I_0}{1+c\exp\left(-\frac{\Delta E}{kT}\right)} \quad (2)$$

where I_0 is the initial emission intensity of the phosphor at room temperature, I_T is the emission intensity at different temperatures, c is a constant, ΔE is the activation energy for the thermal quenching, and k is the Boltzman's constant (8.62×10^{-5} eV). As shown in Fig. 6, the activation energy ΔE of the thermal quenching of α-$Mg_2Al_4Si_5O_{18}$: 0.12Eu^{2+} was calculated as 0.21 eV via plotting $\ln[(I_0/I) - 1]$ against 1/kT, where a straight slope equals -ΔE.

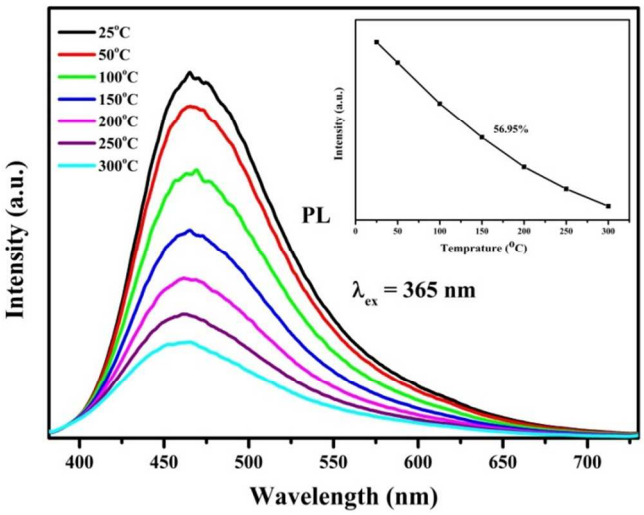

Fig. 5 The emission spectra of α-$Mg_2Al_4Si_5O_{18}$: 0.12Eu^{2+} prepared in air at different temperatures. The inset shows the emission intensities as a function of the temperature.

Figure 7 presents the room temperature decay curves of the Eu^{2+} luminescence in α-$Mg_2Al_4Si_5O_{18}$: *x*Eu with different Eu contents (*x* = 0.02–0.16) upon excitation at 365 nm. The entire decay curve can be well fitted to a second-order exponential decay model by the following equation[39]:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 (-t/\tau_2) \quad (3)$$

where I is the luminescence intensity; A_1 and A_2 are constants; t is time; and τ_1 and τ_2 are the lifetimes for the exponential components. Further, the average lifetime constant (τ*) can be calculated as

$$\tau^* = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2) \quad (4)$$

The obtained lifetimes monitored at 365 nm were calculated to be 613.02, 775.23, 610.01, 433.00 and 320.70 ns with Eu content = 2, 4, 8, 1.2 and 1.6 mol%, respectively. With an increase of Eu concentration up to 4 mol%, the measured lifetime τ of Eu^{2+} 5*d*–4*f* emission increase to maximums, and then decline sharply, which is a typical sign of energy transfer, and causes concentration quenching.[37] The measured lifetime is also related to the total relaxation rate by: [40,41]

$$\frac{1}{\tau} = \frac{1}{\tau_0} + A_{nr} + P_t \quad (5)$$

where τ_0 is the radiative lifetime; A_{nr} is the nonradiative rate due to multiphonon relaxation; P_t is the energy transfer rate between Eu^{3+} ions. The distance between Eu^{2+} ions decreases with the increasing Eu^{2+} concentration. Thus, the energy transfer rate between Eu^{2+}-Eu^{2+} and the probability of energy transfer to luminescent killer sites increases.[42] In consequence the lifetimes are shortened with increasing Eu^{2+} concentration.

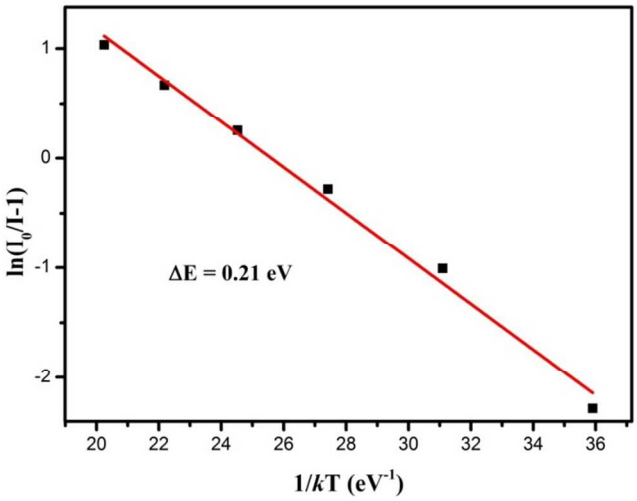

Fig. 6 The Arrhenius fitting of the emission intensity of α-$Mg_2Al_4Si_5O_{18}$: $0.12Eu^{2+}$ phosphor and the calculated activation energy (ΔE) for thermal quenching.

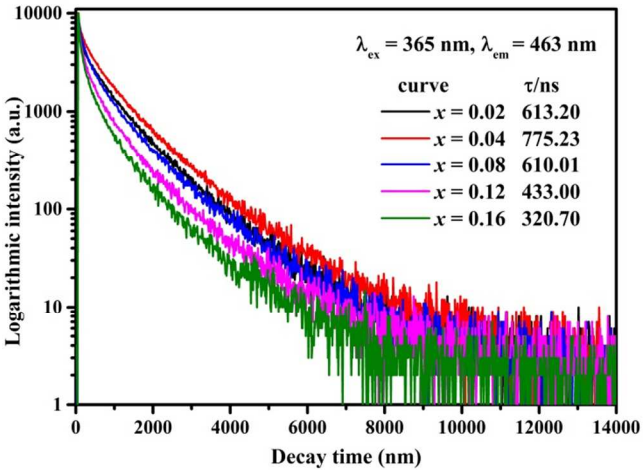

Fig. 7 The decay curves of α-$Mg_2Al_4Si_5O_{18}$: xEu (x = 0.02 – 0.16) monitored at 463 nm.

3.3 The mechanism of reduction Eu^{3+}→Eu^{2+} in α-$Mg_2Al_4Si_5O_{18}$: Eu prepared in air

The reduction of Eu^{3+} to Eu^{2+} in α-$Mg_2Al_4Si_5O_{18}$: Eu in air can be explained with the charge compensation mechanism.[8,16] When Eu^{3+} ions were doped into α-$Mg_2Al_4Si_5O_{18}$, the Mg^{2+} ions would be substituted non-equivalently. For the purpose of maintaining charge balance, three Mg^{2+} ions must be replaced by two Eu^{3+} ions. Thus, each substitution of every two Eu^{3+} ion would create one vacancy defect V_{Mg}'' with two negative charges, and two positive defects of $Eu_{Mg}^{\cdot}$ in the structure. Then the vacancy of V_{Mg}'' and the two $Eu_{Mg}^{\cdot}$ defects would act as the donor of electrons and the acceptor of electrons, respectively. Consequently, under the thermal stimulation, the negative charges in vacancy defects of V_{Mg}'' would be transferred into Eu^{3+} sites and reduce Eu^{3+} to Eu^{2+}. The whole process of the charge compensation mechanism could be expressed as follows:

$$3Mg^{2+} + 2Eu^{3+} \rightarrow V_{Mg}'' + 2Eu_{Mg}^{\cdot} \quad (6)$$

$$V_{Mg}'' \rightarrow V_{Mg}^{x} + 2e \quad (7)$$

$$2Eu_{Mg}^{\cdot} + 2e \rightarrow 2Eu_{Mg}^{x} \quad (8)$$

Moreover, tetrahedral anion group composed by [Si/AlO_4] and [AlO_4] also played a role of shield for Eu^{2+} against the oxidation under the annealing process. Fig. 8 exhibits the crystal structures of hexagonal α-$Mg_2Al_4Si_5O_{18}$.[43] The reduced Eu^{2+} ions substituted the Mg^{2+} ions in [MgO_6] octahedral. The [MgO_6] octahedral was surrounded by the tetrahedral framework structure which consists of corner-shared tetrahedral of [Si/AlO_4] and [AlO_4].[44] For these reduced Eu^{2+} ions are located in the octahedral of 3-D network, it could effectively resist the attack of oxygen to Eu^{2+} ions and can stabilize Eu^{2+} ions.

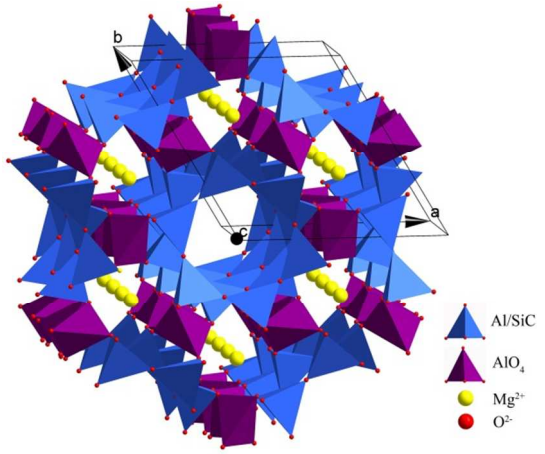

Fig. 8 The crystal structures of α-$Mg_2Al_4Si_5O_{18}$.

4 Conclusions

As a summarization, the blue-emitting α-$Mg_2Al_4Si_5O_{18}$: xEu phosphors were prepared in air via a high temperature solid-state reaction method. The phosphor exhibited a blue emission band peaked at 463 nm ascribed to the 4*f*–5*d* transition of Eu^{2+}. As for α-$Mg_2Al_4Si_5O_{18}$: $x$$Eu^{2+}$, the critical quenching concentration of Eu^{2+} was about 4 mol%, and the corresponding concentration quenching mechanism was verified to be the dipole–dipole interaction. The activation energy ΔE was

calculated to be 0.21 eV, which proved the good thermal stability of the sample. The color coordinate was (0.1674, 0.1700), indicating that the α-$Mg_2Al_4Si_5O_{18}$: Eu phosphor can be regarded as a blue-emitting phosphor for WL-LEDs application. The reduction of Eu^{3+} to Eu^{2+} in α-$Mg_2Al_4Si_5O_{18}$: Eu prepared in air was explained with the charge compensation model and the structures of 3-D networks composed by [Si/AlO_4] and [AlO_4] tetrahedra are possible for maintaining of the reduction (Eu^{3+}-Eu^{2+}) when samples were prepared in air at high temperature.

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