Enhancement of red emission intensity of $Ca_2Al_2SiO_7$:Eu^{3+} phosphor by MoO_3 doping or excess SiO_2 addition for application to white LEDs

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Abstract. $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7$:$0.14Eu^{3+}$ and $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}$:$0.14$ Eu^{3+} were synthesized by solid-state reaction. X-ray powder diffraction, excitation and emission spectra were used to investigate their structures and photoluminescence properties. The results shows that the phosphor $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$ cannot be excited efficiently by light of 393 nm. The introduced Mo ion does not change the position of the excitation peak, but increases both the absorption at 400nm and the emission intensity of Eu^{3+}. The intense red emitting phosphor $Ca_{1.86}Al_2(Si_{0.95}Mo_{0.05})O_7$:$0.14Eu^{3+}$ was obtained, which has 67% enhanced luminous intensity compared to that of the undoped sample $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$. Otherwise, SiO_2 excess of non-stoichiometric phosphors $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}$:$0.14Eu^{3+}$ showed the characteristic pattern of a tetragonal structure with a small SiO_2 concentration. The optimal phosphor of $Ca_{1.86}Al_2Si_{1.1}O_{7.2}$:$0.14Eu^{3+}$ has a luminous intensity about two times higher than that of the original stoichiometric phosphor $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$. We confirmed that the photoluminescence intensity of the obtained phosphors is fairly enhanced by excessive SiO_2. The mechanism of this photoluminescence enhancement is discussed in this paper.

1. Introduction

After a decade of intense research, phosphor-converted light-emitting diodes (pc-LEDs) have attracted worldwide attention owing to their high luminescence efficiency and variety wide range of applications, such as in flashlights, display backlighting, traffic signals, and especially for solid-state lighting. The huge potential market in home lighting encourages the rapid development of pc-LEDs. White-light generation through the diode chips with the help of efficient phosphors has several advantages over the existing incandescent and fluorescent lamps in power efficiency, reliability, long lifetime, low energy consumption, and environmentally friendly characteristics [1-3]. At present, the most common method of preparing a pc-LED is to use the yellow-emitting YAG: Ce^{3+} phosphor with blue InGaN chips to produce the practical white light [4]. However, such white LEDs exhibits a high color temperature and low color-rendering index (Ra<80) because of their weak emission intensity in the red spectral region [5]. This drawback limits white LEDs' applications, such as for indoor illumination and screen display [6]. To warm the white light and improve the color-rendering index and color reproducibility, a promising strategy is to combine a separate red, green, and blue-emitting phosphors with a deep blue/near-UV LED chips. This requires the phosphor materials to have high absorption in the near-UV to blue spectral region. Unfortunately, the red phosphors Y_2O_2S:Eu^{3+} has

poor absorption in the near-UV to blue region and its efficiency is lower than that of the green and blue phosphors [7, 8]. Moreover, the red phosphor is chemically unstable and has a short working lifespan owing to its release of sulfide gas. Therefore, the lack of a proper red phosphor has become a bottleneck in the development of blue or near-UV LED-based white LEDs [9]. Hence, it is very essential to develop a stable and efficient red phosphor with high color purity that can be well coupled with blue and near-UV LEDs. As we know, Eu^{3+} ion is a promising red-emitting rare earth ion, and is a good place to start further discussion [10].

It is noted that the alkaline earth silicate-based inorganic material have been developed to be as the host materials for phosphors because of their various crystal structures, high physical-chemical stability, mild synthesis conditions, and lower production costs than nitrides[11, 12]. In particular, Eu^{3+}-doped $Ca_2Al_2SiO_7$ a compound with a melilite structure, exhibited superior red-emitting properties under near-UV LED excitation [13, 14]. However, in these two papers, two completely different strongest excitation peak positions were reported. One reported the strongest excitation peak for the broad charge transfer transition band (CTB) at around 240–340 nm, and the other reported the strongest excitation peak for the f–f transitions of Eu^{3+} around 394 nm (wavelength of near-UV LED chips), which is considered an important condition in LED. Therefore, a red-emitting phosphor $Ca_2Al_2SiO_7:Eu^{3+}$ was newly synthesized in this work through high-temperature solid-state reaction. The strongest excitation peak was found at the broad CTB around 240–340 nm. In order to strengthen and broaden the absorption to around 350–400 nm to obtain more efficient phosphors for near-UV LED, one approach is doping with heterogeneous metal ions (e.g., W^{6+} or Mo^{6+} ions) for modification of the coordination environment of the Eu^{3+} luminescence center [15, 16]. Thus, we substituted some Si ions with Mo ions in this work. Some reports [17, 18] have focused on molybdate-doped Eu^{3+} because these phosphors have wide and intense charge-transfer absorption bands in the near-UV. Therefore, we synthesized phosphors of $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ type ($0 \leq y \leq 0.3$) with excess SiO_2. We confirmed that the photoluminescence (PL) intensity of the obtained phosphors is fairly enhanced by SiO_2 excess addition. The mechanism of this PL enhancement is discussed in this paper.

2. Experimental

The phosphors $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$, $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ ($0.01 \leq x \leq 0.07$) and $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ ($0 \leq y \leq 0.3$)were prepared by the solid-state reaction technique at high temperature. The starting materials were $CaCO_3$ (A.R.), Al_2O_3 (99%), H_2SiO_3, MoO_3 (99.5%) and Eu_2O_3 (99.99%). A small quantity of H_3BO_3 (about 5 mol%) was added as flux. The samples were prepared sintered at 900°C for 2 h in air. When the material cooled, put them in the tubular furnace and sintered at 1300°C for 8 h in air.

The phase assemblage of the product powders was analyzed using by a Rigaku D/Max-2400 X-ray diffractometer at a scanning rate of 2° min^{-1} and intervals of 0.02° in the 2θ range from 10° to 80° with Nifiltered Cu Ka radiation (λ = 0.15405 nm). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were measured by using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source as the excitation source. All the measurements were performed at room temperature in the air and the spectral bandwidth of both excitation and emission spectrometer was adjusted to 0.50 nm ($\Delta\lambda_{ex} = \Delta\lambda_{em} = 0.50$ nm).

3. Results and discussion

3.1. XRD analysis

A series of XRD patterns of $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ ($0.01 \leq x \leq 0.07$) and JCPDS-35-0755 are shown in figure 1. No impurity phase was detected when Eu^{3+} and Mo^{6+} ions were co-doped into the host lattice, indicating that the obtained samples are all of a single phase of $Ca_2Al_2SiO_7$ with tetragonal structure (space group $p\bar{4}2m$) and are consistent with JCPDS-35-0755 [19]. This indicates that the Ca^{2+} ions can be partly replaced by Eu^{3+} ions and Mo^{6+} can be substituted for Si^{4+} without a change of crystal structure. Based on the effective average ionic radius of the cations (R $_{Eu3+}$ =1.066 Å, R_{Ca2+}

=1.12 Å, CN = 8 and R_{Mo6+} =0.41 Å, R_{Si4+} =0.26 Å, CN = 4) [20]. The results suggested that the samples form solid solutions. We have explained the imbalanced substitution using the Kröger - Vink defect notation [21], which has been reported in $CaSrAl_2SiO_7:Eu^{3+}$ [22] .
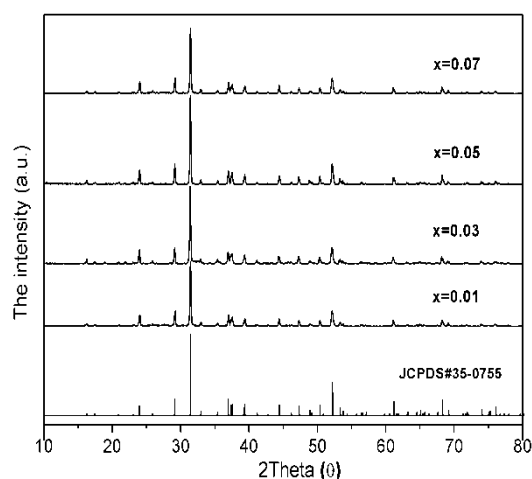

Figure 1. X-ray diffraction patterns of $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ (0.01≤x≤0.07).
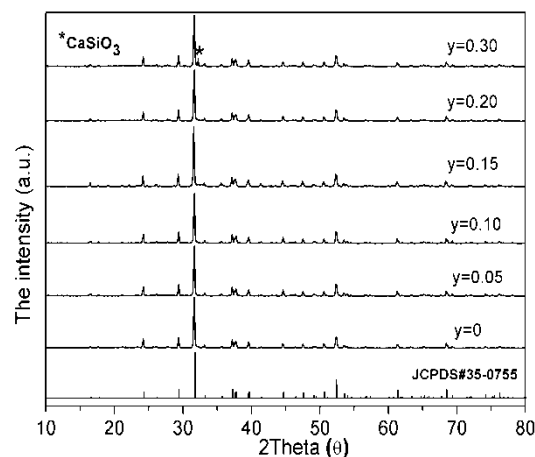
Figure 2. X-ray diffraction patterns of $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ (0≤y≤0.3).

Figure 2 shows the XRD patterns of $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ (0≤y≤0.3). The XRD patterns of the $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ samples the tetragonal structure and are consistent with JCPDS-35-0755. However, with increasing in the SiO_2 content (y≥0.3), a small impurity peak appeared in the region 32-34°, which was assigned to a silicate impurity $CaSiO_3$. The impurity peak observed at larger SiO_2 concentration may be as a result of owing to the SiO_2 in $Ca_{1.86}Al_2SiO_7$ lattice. Therefore, we only investigated the photoluminescence properties of $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ with a small SiO_2 concentration (y<0.3).

3.2. Luminescence properties

We first synthesized $Ca_{2-x}Al_2SiO_7:xEu^{3+}$ phosphors. Owing to the similar photoluminescent character of $Ca_{2-x}Al_2SiO_7:xEu^{3+}$ with different concentrations of Eu^{3+} (x), we only to investigated the luminescent properties of $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$; which the luminescent spectra are shown in figure 3. It can be clearly seen that the excitation spectrum is composed of an intense broad-band centered at about 254 nm and a group of sharp lines in the 300-550 nm longer wavelength rang. The broad-band is ascribed to the charge transfer transition from the 2*p* orbital of the O^{2-} ions to the 4f orbital of the Eu^{3+} ions ($O^{2-}{\rightarrow}Eu^{3+}$), and a group of sharp lines in the 300-550 nm are assigned to the intra-configurational 4*f*–4*f* forbidden transitions of Eu^{3+}: $^7F_0{\rightarrow}^5H_6$ (318 nm), $^7F_0{\rightarrow}^5D_4$ (362 nm), $^5G_4$ (382 nm), $^5L_6$ (393 nm), $^5D_3$(414 nm), $^5D_2$ (464 nm), $^5D_1$ (525 nm) [23]. The emission spectrum of $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$, which was excited by 393 nm, exhibited a well known characteristic Eu^{3+} emission. It consists of several emission lines, among which the main emission line is located at around 614 nm ($^5D_0{\rightarrow}^7F_2$).

In order to strengthen the absorption in ~ 400 nm of the $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$ phosphor, the $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ (0≤x≤0.07) series of samples was investigated. Figure 4 shows the excitation spectra (λ_{em}= 614 nm) of the $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ series of samples. We can see that with increasing Mo^{6+} [24]. Significantly, when the Mo^{6+}-doped concentration is up to 0.05, the sharp peak at 393 nm is about four times higher than that of the original $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$.

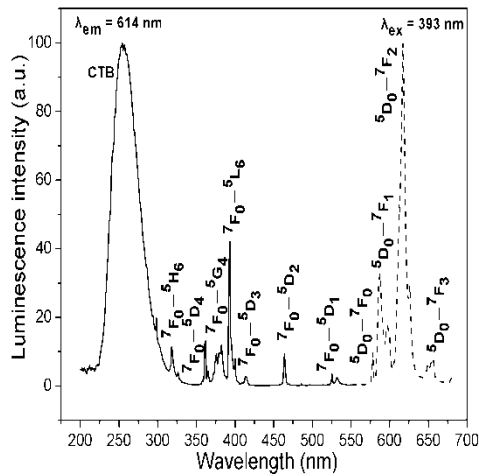**Figure 3.** Excitation and emission spectra of $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$.
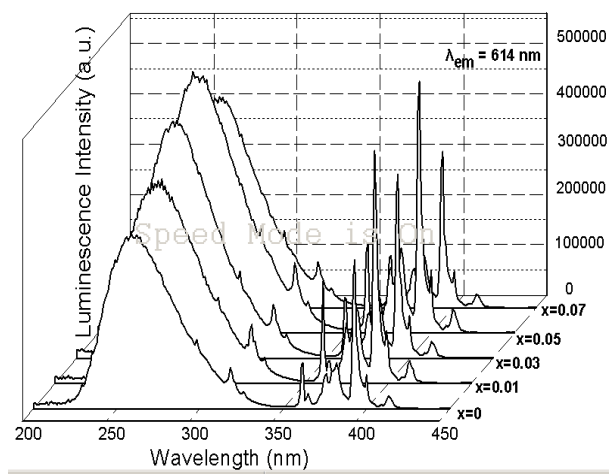
Figure 4. Excitation spectra of $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7$:$0.14Eu^{3+}$ ($0 \leq x \leq 0.07$) with different doping concentration x of Mo^{6+}.

The comparison of emission intensity ($^5D_0 \rightarrow {}^7F_2$ transition) under 393 nm excitation for $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7$: $0.14Eu^{3+}$ ($0 \leq x \leq 0.07$) is shown in Table1. With the increase of the component of Mo^{6+}, the maximum emission intensity appears at x = 0.05. This can be primarily estimated that the presence of Mo, whose ionic radii is different from Si, results in somewhat diverse about the sub-lattice structure around the luminescent center ions, which may realize the optimum lattice environment for the energy transfer and luminescence of Eu^{3+} to some certain degree. The intensity for $Ca_{1.86}Al_2(Si_{0.95}Mo_{0.05})O_7$:$0.14Eu^{3+}$ was enhanced by 67% compared to that of the undoped sample $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$. However, an increase in the concentration of Mo^{6+} ions lowers the crystallinity of the phosphors and results in the formation of more defects, which would increase the probability of nonradiative transitions.

Table 1. Comparison of emission intensity ($^5D_0 \rightarrow {}^7F_2$) of $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7$: $0.14 Eu^{3+}$ ($0 \leq x \leq 0.07$) (λ_{ex} = 393 nm).

Composition	Relative Intensity (100%)
$Ca_{1.86}Al_2SiO_7$: $0.14 Eu^{3+}$	100
$Ca_{1.86}Al_2(Si_{0.99}Mo_{0.01})O_7$: $0.14 Eu^{3+}$	121
$Ca_{1.86}Al_2(Si_{0.97}Mo_{0.03})O_7$: $0.14 Eu^3$	142
$Ca_{1.86}Al_2(Si_{0.95}Mo_{0.05})O_7$: $0.14 Eu^{3+}$	167
$Ca_{1.86}Al_2(Si_{0.93}Mo_{0.07})O_7$: $0.14 Eu^{3+}$	138

The luminescent properties of excess SiO_2 in the $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}$:$0.14Eu^{3+}$ were researched by the luminescent spectra at room temperature. Owing of $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}$:$0.14Eu^{3+}$ with different values of y, we just use the spectra of $Ca_{1.86}Al_2Si_{1.1}O_{7.2}$:$0.14Eu^{3+}$ for example. Figure 5 shows the excitation and emission spectra of $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$. The strongest excitation peak is located at 393 nm, which is attributed to the characteristics of the transition absorption peak ($^7F_0$-$^5L_6$) of Eu^{3+}. The relationship of the relative intensity of 393 nm and the change in SiO_2 excess (y) is illustrated in the inset of figure 5. The relative intensities were increased with increasing excessive SiO_2 concentration (from y = 0.05 to 0.1) and also the non-stoichiometric phosphor $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}$: $0.14Eu^{3+}$ with y = 0.1 mol exhibited the strongest luminous intensity, which is about twice as high as that of the original stoichiometric phosphor $Ca_{1.86}Al_2SiO_7$:$0.14Eu^{3+}$. However, as y continues to increase, the luminous intensity gradually declines. As a result, we can consider that an appropriate

excess of SiO_2 can effectively enhance the luminous intensity of phosphors. This is because while the high-temperature solid-phase synthesis silicates phosphors, the SiO_2 is very easy to volatilization. According to the stoichiometric ratio of component preparation phosphors will because low SiO_2 is easy to form some defects [25, 26]. Even at low doping concentrations, the presence of these defects can also cause luminescent quenching [27]. Therefore, an appropriate excess of SiO_2 can make up for defects to some extent [25], reducing the probability of the nonradiative transition so as to improve the luminous intensity of phosphors.
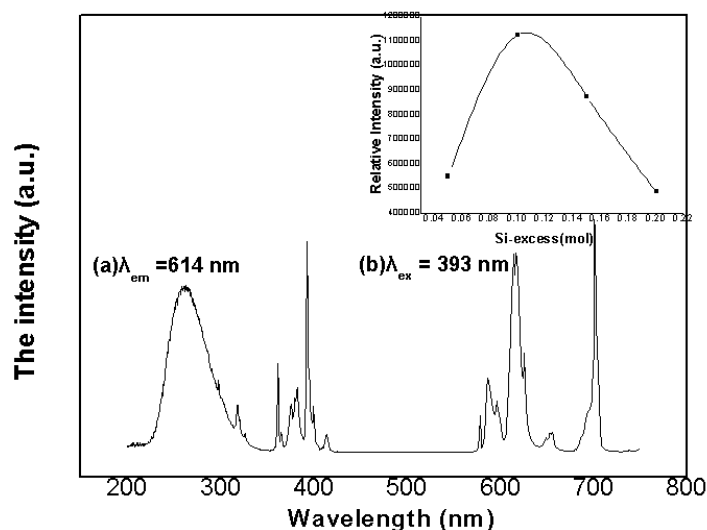

Figure 5. Excitation and Emission spectra of $Ca_{1.86}Al_2Si_{1.1}O_{7.2}:0.14Eu^{3+}$ (the inserted figure shows the relationship between relative intensity of 393 nm and the change of SiO_2 excess in $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ ($0.05 \leq y \leq 0.2$)).

4. Conclusions

A new red-emitting phosphors $Ca_{1.86}Al_2(Si_{1-x}Mo_x)O_7:0.14Eu^{3+}$ ($0.01 \leq x \leq 0.07$) and $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ ($0 \leq y \leq 0.3$), was successfully synthesized. Our experimental data indicated that the phosphor $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$ cannot be excited 393 nm light. In order to strengthen the absorption of the phosphors at around 400 nm, Mo ion was introduced. The obtained phosphor $Ca_{1.86}Al_2(Si_{0.95}Mo_{0.05})O_7:0.14Eu^{3+}$ shows good absorption at 393 nm and enhanced emissions, which the luminous intensity was enhanced by 67% compared to that of the undoped sample $Ca_{1.86}Al_2SiO_7:0.14Eu^{3+}$. Moreover, non-stoichiometric phosphors $Ca_{1.86}Al_2Si_{1+y}O_{7+2y}:0.14Eu^{3+}$ ($0 \leq y \leq 0.3$) show the tetragonal structure (space group $p\overline{4}2m$) with a small SiO_2 concentration ($y < 0.3$). An appropriate excess of SiO_2 can make up for the defects to a certain extent, reducing the probability of the nonradiative transition so as to improve the luminous intensity of phosphors. Therefore, these red phosphors $Ca_{1.86}Al_2(Si_{0.95}Mo_{0.05})O_7:0.14Eu^{3+}$ and $Ca_{1.86}Al_2Si_{1.1}O_{7.2}:0.14$ Eu^{3+} are considered as an prominent red-emitting phosphor for LEDs.

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