



Photoluminescence properties and the self-reduction process of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ phosphor

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ABSTRACT

$\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ anorthite phosphor was synthesized by the traditional solid state reaction. In the air-sintered phosphor, the Eu ions were partial self-reduced to Eu^{2+} , which contributed to the observation of the blue (Eu^{2+}) and the red (Eu^{3+}) emission in $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ phosphor. To further investigate the photoluminescence properties and the self-reduction mechanism of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ phosphor, the adjustment of the valence state of Eu ions by controllable approaches was studied. In addition, $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ phosphor shows a tunable emission from reddish to bluish region under ultraviolet excitation, which implies that it could be applied as potential phosphor for near ultraviolet light emitting diode.

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1. Instruction

The ever-increasing energy-saving demands drive the advance of lighting technology, especially for the solid state lighting such as light emitting diode (LED) [1]. It is well known that the invention of LED has brought another significant revolution to the illumination of this century to supersede conventional incandescent or fluorescent lamps because of its excellent properties such as high brightness, reliability, lower power consumption, and long life. At present, one significant scheme is phosphor-converted LED (pc-LED) by combing blue (440–470 nm) or near ultraviolet NUV (390–410 nm) chips with the down-converting phosphors [2]. Recent efforts to develop new LED phosphors include oxide [3–5], oxyfluoride [6–8], nitride [9–12], and oxynitride [13–15], hosts. Despite many successes, continued efforts are still required to address issues of higher efficiencies, better color rendition, and adjustment of optical properties.

Silicates are suitable hosts of phosphors because of their high physical and chemical stability, especially their excellent water-resistant property. The luminescence of rare earth ions in the silicate host has been studied for a long time, such as rare earth ions doped M_2SiO_4 [16–19], $\text{M}_2(\text{Mg}, \text{Zn}, \text{Zr})\text{Si}_2\text{O}_7$ [20–22], $\text{M}_3\text{MgSi}_2\text{O}_8$ [23–25] ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$). Wu et al. prepared $\text{Sr}_{1.97-x}\text{Ca}_x\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}, \text{Dy}^{3+}$ phosphors and concluded that both the wavelength of the emission

and the afterglow time are controllable [26]. Ma et al. proposed a functional solid-state lighting lamp utilizing a NUV LED chip and $\text{A}_3\text{MgSi}_2\text{O}_8:\text{Eu}^{2+}, \text{Mn}^{2+}$ ($\text{A} = \text{Ca}, \text{Sr}, \text{Ba}$) phosphors which emit blue and red lights to meet the basic irradiation needs to plants [27]. Recently, the alkaline-earth feldspars of $\text{MAl}_2\text{Si}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) aluminosilicate have drawn much attention for their excellent luminescence properties [28–31]. Wang et al. reported Eu^{2+} and Dy^{3+} co-activated $\text{CaAl}_2\text{Si}_2\text{O}_8$ as a long afterglow phosphor [32]. Furthermore, the $\text{Eu}^{2+} \rightarrow \text{Mn}^{2+}$ energy transfer mechanism in $\text{CaAl}_2\text{Si}_2\text{O}_8$ was described by Yang et al. who demonstrated $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}, \text{Mn}^{2+}$ can be systematically tuned to generate white light under ultraviolet radiation [33]. In our study, it is interesting to find that the Eu^{3+} and Eu^{2+} coexist in the air-synthesized $\text{CaAl}_2\text{Si}_2\text{O}_8$. Despite Zhang et al. reported the realization of the reduction of Eu^{3+} to Eu^{2+} in the alkaline-earth metal aluminum silicates $\text{MAl}_2\text{Si}_2\text{O}_8$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$), however, the luminescence properties of the coexisted $\text{Eu}^{3+}/\text{Eu}^{2+}$ and the self-reduction process of Eu ions doped $\text{CaAl}_2\text{Si}_2\text{O}_8$ were not yet well understood. More importantly, if light qualities, including peak positions and intensity ratio of blue to red light, are able to be adjusted in controllable approaches, which enable us to tailor the optimal spectrum requirements for different species of solid state lighting. Therefore, we investigated the photoluminescence properties, valence state controlling and color chromaticity properties of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ phosphor in the present work. Our results give some further evidence for the self reduction mechanism and demonstrated that $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ can emit tunable light under UV excitation, which could provide potential application in NUV LED.

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2. Experimental

High purity of CaCO_3 (A.R), Al_2O_3 (A.R), SiO_2 (A.R), Eu_2O_3 (99.99%) were employed as the raw materials. Small quantities of H_3BO_3 (A.R/5%) were added as a flux. The raw materials were intimately mixed in the requisite proportions. The mixtures were first calcined at 900°C and then sintered at 1420 , 1450 and 1480°C for 4 h in ambient atmosphere, respectively.

The phases of samples were identified by X-ray powder diffraction (XRD) with Ni-filtered $\text{CuK}\alpha$ radiation at a scanning step of 0.02 in the 2θ range from 10° to 80° . A Hitachi F-7000 fluorescence spectrophotometer was used to record excitation and emission spectra. All powder samples weight was kept constant (0.5 g). The powder samples were compacted and excited under 45° incidence and emitted fluorescence was detected perpendicular to the excitation beam. All the measurements were carried out at room temperature.

3. Results and discussion

All the samples are characterized to be single phase by XRD. Fig. 1a shows the XRD patterns of selected samples. All the diffraction peaks can be indexed to the phase of $\text{CaAl}_2\text{Si}_2\text{O}_8$ (JCPDS 41-1486). No impurity phase is observed, implying that the small

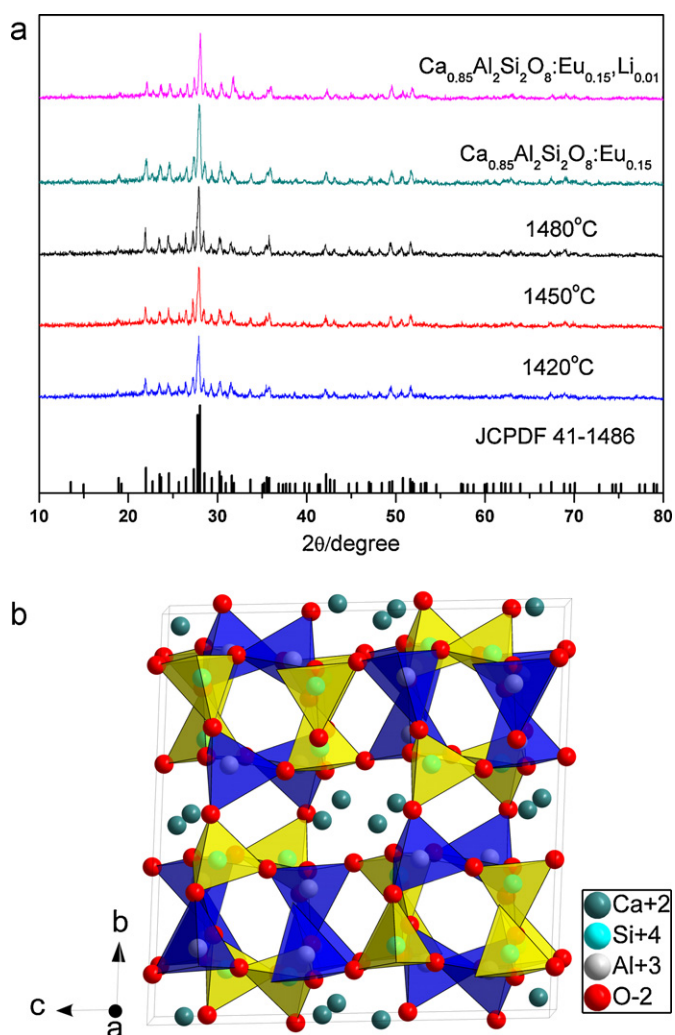


Fig. 1. (a) XRD spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ obtained at different temperature in air (sample a–c) and with and without Li^+ when the Eu ions concentration equal to 1.5 mol% (sample d and e). (b) The crystal structure of $\text{CaAl}_2\text{Si}_2\text{O}_8$ phosphor.

amount of doped rare earth ions have almost no effect on the $\text{CaAl}_2\text{Si}_2\text{O}_8$ phase. Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ was reported to be crystallized in a triclinic crystal system with space group $I\bar{1}$ [34]. In the crystal lattice, there are six crystallographically independent cation sites, namely, four Ca^{2+} sites, one Al^{3+} site, and one Si^{4+} site. Al and Si atoms both occupy tetrahedral sites with four coordinated oxygen atoms, while one type of Ca^{2+} ion occupies an octahedral site with six oxygen atoms and other Ca^{2+} ions occupy three kinds of polyhedral sites with seven coordinated oxygen atoms with different Ca–O bond distance. The crystal structure of $\text{CaAl}_2\text{Si}_2\text{O}_8$ was shown in the inset of Fig. 1b. Based on the effective ionic radii (r) of cations with different coordination number (CN) reported by Shannon [35], Eu ions are expected to occupy the Ca^{2+} sites preferably, because the ionic radii of Eu^{2+} ($r = 1.17\text{ \AA}$ when $\text{CN} = 6$ and $r = 1.20\text{ \AA}$ when $\text{CN} = 7$) and Eu^{3+} ($r = 0.947\text{ \AA}$ when $\text{CN} = 6$ and $r = 1.01\text{ \AA}$ when $\text{CN} = 7$) are close to that of Ca^{2+} ($r = 1.00\text{ \AA}$ when $\text{CN} = 6$, $r = 1.06\text{ \AA}$ when $\text{CN} = 7$). Since both four-coordinated Al^{3+} ($r = 0.39\text{ \AA}$) and Si^{4+} ($r = 0.26\text{ \AA}$) sites are too small for Eu ions to occupy, therefore we conclude that the Eu ions tends to prefer the Ca^{2+} sites due to size consideration.

The photoluminescence (PL) and the photoluminescence excitation (PLE) spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ prepared in air atmosphere is depicted in Fig. 2. The PL spectrum of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ behaves in a mixed emissions consisting of both a band emission around 423 nm and line-emissions at 592 , 613 and 654 nm . Due to the limitation of the instrument of our spectra, when the emission spectra were recorded under 393 nm , the emission at 423 nm could not be recorded complete. The peaked line-emissions at 592 , 613 and 654 nm could be ascribed to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_J$ ($J = 1, 2, 3$) transitions of Eu^{3+} , respectively. However, the origin of the blue emission from either the $\text{CaAl}_2\text{Si}_2\text{O}_8$ host or Eu ions needs to be clarified. To illustrate the blue emission, the PL spectra for the pure host were exhibited in Fig. 2, it was found that the emission intensity of the host around 423 nm was somehow low, which could be neglected compare with the Eu doped $\text{CaAl}_2\text{Si}_2\text{O}_8$. Therefore, it is reasonable to ascribe the 423 nm peaked band emission to $4f^65d^1(t_{2g})-4f^7({}^8\text{S}_{7/2})$ transition of Eu^{2+} , while the shoulder peaks located at 468 and 511 nm could be originated from Eu ions which substituted Ca^{2+} at different polyhedral sites as discussed above. To further illustrate the self-reduction process, PLE monitored at different emission peaks of 423 nm and 613 nm of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ were recorded as shown in Fig. 2 as well, the distinct excitation peaks of the broad and line absorption peaks mean that the peaks derived from different luminescent centers of the characteristic excitation of Eu^{2+} ($4f \rightarrow 5d$ transitions [36]) and

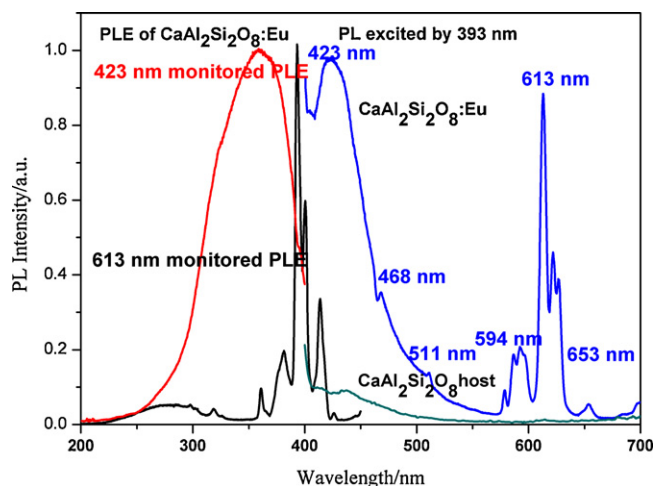


Fig. 2. PL spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ and $\text{CaAl}_2\text{Si}_2\text{O}_8$ host and PLE spectra of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}$ monitored at different emission peaks.

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