Characterization and luminescence of Eu/Sm-coactivated $CaYAl_3O_7$ phosphor synthesized by using a combustion method*

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A novel red-emitting phosphor, $CaYAl_3O_7$: Eu^{3+}, Sm^{3+}, is synthesized by a combustion method at a low temperature (850 °C), and the single phase of $CaYAl_3O_7$ is confirmed by powder X-ray diffraction measurements. The photoluminescence property results reveal that the red emission intensity of Eu^{3+} is strongly dependent on the Sm^{3+} concentration. Only the Eu^{3+} luminescence is detected in the Eu^{3+}–Sm^{3+} co-doped $CaYAl_3O_7$ phosphor with 393 nm excitation. However, under the characteristic excitation (402 nm) of Sm^{3+}, not only the Sm^{3+} emission but also the Eu^{3+} emission are observed. A possible mechanism of the energy transfer between Sm^{3+} and Eu^{3+} is investigated in detail.

Keywords: $CaYAl_3O_7$, combustion method, photoluminescence, energy transfer

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1. Introduction

Being very energy efficient, compact, easy to install and having a long life span, low maintenance requirements, and vast design capabilities in terms of creating color and atmospheric mood lighting, white light-emitting diodes (WLEDs) are hailed as the next generation of solid state light.[1,2] The WLEDs currently available on the market produce white light by combining the blue light from LED chips with the yellow emission from the most widely applied YAG/Ce phosphor. However, such a combination exhibits a poor color rendering index (< 80) because of the lack of a red light component (above 600 nm). The combination of a near-ultraviolet (UV) InGaN chip (380–410 nm) with blue, green, and red phosphors is another way to generate white light which will yield a high color rendering index and good color reproducibility.[3–5] However, the red light-emitting phosphors for WLEDs are still commercially limited to sulfide-based materials like ZnCdS: Ag, ZnCdS: Ag, Cl, and SrY_2S_4: Eu.[6] Furthermore, those sulfide phosphors are chemically unstable and inefficient. Therefore, a new matrix and system of rare earth (RE) doped WLED phosphor is under study at present.

$CaYAl_3O_7$ has the chemical formula of ABC_3O_7 (A = Ca, Sr, Ba; B = La, Gd, Y; C = Al, Ga) and belongs to the large families that have a melilite structure.[7] Due to their structural features, ABC_3O_7 compounds have been widely investigated as important optical materials. For instance, Singh *et al.*[8] reported the synthesis, characterization, and photoluminescence of Eu^{3+}, Ce^{3+} co-doped $CaLaAl_3O_7$ phosphors. Zhang *et al.*[9] studied the luminescence properties of $SrGdGa_3O_7$: RE^{3+} (RE = Eu, Tb) phosphors and the energy transfer from Gd^{3+} to RE^{3+}. Jiao and Wang[10] discussed a potential red-emitting phosphor $CaSrAl_2SiO_7$: Eu^{3+} for near-ultraviolet light-emitting diodes (n-UV LEDs). In addition, Zhang *et al.*[11] studied the blue light emission from stress-activated $CaYAl_3O_7$: Eu^{2+}, and Zhang *et al.*[12] investigated the electro-mechano-optical luminescence from $CaYAl_3O_7$: Ce^{3+}. Many investigations of rare-earth doped melilite families have also been performed. The studies indicated that the rare-earth doped melilite crystal is an interesting laser host material, having broadened absorption and emission spectra suitable for diode laser pumping and tunable laser generation, respectively.[13] However, as far as we know, Eu^{3+} doped $CaYAl_3O_7$ as a candidate phosphor for UV LEDs has been scarcely investigated.

In general, the synthesis of the $CaYAl_3O_7$ phase requires a high-temperature heat treatment, and it is generally based on the high-temperature sintering method which needs a temperature over 1300 °C.[14,15] In this work, $CaYAl_3O_7$: Eu^{3+} of pure phase is prepared by using a combustion method[16–18] at a low temperature (850 °C). And investigations on further improving the luminescent properties of Eu^{3+} by co-doping with Sm^{3+} are discussed in detail.

2. Experiment

All the raw chemical materials, $Ca(NO_3)_2{\cdot}4H_2O$ (A.R), $Al(NO_3)_3{\cdot}9H_2O$ (A.R), $Y(NO_3)_3{\cdot}6H_2O$ (A.R), Eu_2O_3

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(99.99%), Sm_2O_3 (99.99%), NH_2CH_2COOH (A.R), HNO_3, were used without further purification. $Eu(NO_3)_3$ and $Sm(NO_3)_3$ solutions were first obtained by dissolving Eu_2O_3 and Sm_2O_3 into diluted nitric acid, respectively. NH_2CH_2COOH was added as a fuel. The raw materials were uniformly mixed with aqua distillate in a beaker. Then the solution was poured into an evaporating dish and dried at 95 °C for 8 h. After this, the mixture was rapidly heated to 300 °C and an auto combustion process took place, yielding a yellowish fluffy precursor. The prepared precursor was calcined at temperatures from 500 °C to 850 °C in air.

The phases of the obtained samples were identified by X-ray powder diffraction (XRD) with Cu $K\alpha$ (λ = 1.54060078 Å) radiation in scanning steps of 0.02° in the 2θ range from 10° to 90° (Bruker D8-Advance, operated at 40 kV and 40 mA). The photoluminescence (PL) spectra were measured by using a HITACHI F-7000 fluorescence spectrophotometer using a static 150 W Xe lamp as the excitation source. All measurements were carried out at room temperature.

3. Results and discussion

3.1. Crystal structure

Figure 1 shows the XRD patterns of $CaYAl_3O_7$ (CYA) synthesized at different temperatures ranging from 500 °C to 850 °C, Eu^{3+} doped and Eu^{3+}/Sm^{3+} co-doped $CaYAl_3O_7$ are also exhibited. At a synthesizing temperature of 500 °C, no $CaYAl_3O_7$ phase is detected as shown in Fig. 1, indicating that the $CaYAl_3O_7$ phase cannot be obtained at this temperature. With synthesizing temperature increasing, the $CaYAl_3O_7$ phase is gradually formed. All the diffraction peaks can be indexed to be of the $CaYAl_3O_7$ phase at 850 °C, which exhibits a tetragonal structure (space group $P\bar{4}21m$, $a = 7.684$ Å, $c = 5.037$ Å, and $V = 297.45$ Å^3).[19] Moreover, for the diffraction patterns of $CaYAl_3O_7$: Eu^{3+} and $CaYAl_3O_7$: Eu^{3+}, Sm^{3+}, all of the diffraction peaks are found to be in good agreement with those reported in JCPDS file 49-0605 regardless of the introduction of Eu^{3+} and Sm^{3+}, indicating that no impurity phase is present. Based on the effective ionic radii (r) of cations with different coordination numbers (CN) reported by Shannon,[20] the radii of Eu^{3+} (0.947 Å) and Sm^{3+} (0.958 Å) are more similar to those of Ca^{2+} (1.00 Å) and Y^{3+} (0.900 Å) than that of Al^{3+} (0.535 Å) which is too small for Eu^{3+} and Sm^{3+} ions to occupy. And with regard to the charge balance, we propose that Eu^{3+} and Sm^{3+} ions are expected to and, in fact, occupy the Y^{3+} sites preferably.

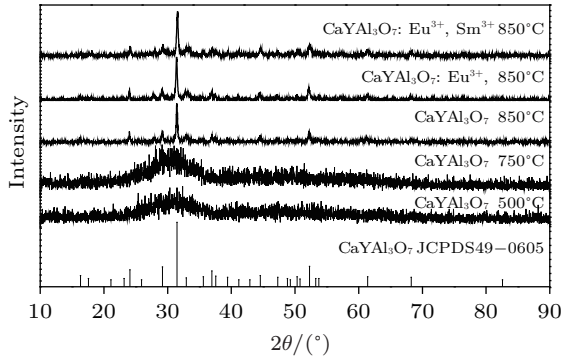


Fig. 1. Powder XRD patterns of CYA (JCPDS 49-0605), CYA, CYA: Eu^{3+}, and CYA: Eu^{3+}, Sm^{3+}.

3.2. Photoluminescence properties of $CaYAl_3O_7$: Eu^{3+}

The excitation and emission spectra of $CaY_{0.96}Al_3O_7$: 0.04Eu are shown in Fig. 2. Figure 2 shows the excitation spectrum ($\lambda_{em} = 617$ nm) of $CaY_{0.96}Al_3O_7$: 0.04Eu, which exhibits a broad charge-transfer (CT) band extending from 210 nm to 310 nm. The CT band corresponds to an electron transfer from an oxygen 2p orbital of O^{2-} to an empty 4f orbital of Eu^{3+}. The sharp lines of several groups of absorptions peaked at about 318 nm, 361 nm, 381 nm, 393 nm, 414 nm, and 464 nm are assigned to the $^7F_0$–$^5H_6$, $^7F_0$–$^5D_4$, $^7F_0$–$^7L_5$, $^7F_0$–$^5L_6$, $^7F_0$–$^5D_3$, and $^7F_0$–$^5D_2$ transitions of Eu^{3+}, respectively. As shown in Fig. 2(b), under 393 nm excitation, there are five main sharp emission peaks around 590 nm, 598 nm, 617 nm, 656 nm, and 703 nm in the emission spectrum, which correspond to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$, 1, 2, 3, 4) transitions of Eu^{3+} $4f^6$ electron configuration, respectively.[21–25]

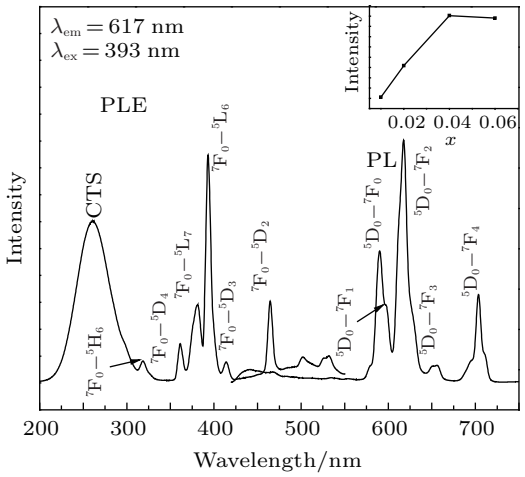


Fig. 2. Excitation and emission spectra for $CaY_{0.96}Al_3O_7$: 0.04Eu^{3+} phosphors, the inset shows the intensity at 617 nm of $CaY_{1-x}Al_3O_7$: xEu^{3+} ($x = 0.01$, 0.02, 0.04, 0.06) versus the concentration of Eu^{3+} ions.

In many cases, concentration quenching is due to the energy transfer from one activator to another until energy sinking in the lattice is reached. As the concentration of the Eu^{3+} ions increases, the distance between Eu^{3+} ions becomes smaller, which favors the nonradiative pathway by energy transfer among Eu^{3+} ions.[26–28] Hence we calculate the critical distance (R_c) between Eu^{3+} ions for energy transfer by using the relation given by Blasse *et al.*[29]

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

where V is the volume of the unit cell, x_c is the critical concentration of activator ions, and N is the number of formula units per unit cell. For the $CaYAl_3O_7$ host, the critical distance for energy transfer, R_c, is estimated to be about 19 Å, which corresponds to the Y^{3+}–Y^{3+} distance (16 Å) calculated from the $CaYAl_3O_7$ host matrix crystal structure, which further demonstrates that Eu^{3+} occupies the Y^{3+} crystal site and the best doping concentration of Eu^{3+} is 0.04.

3.3. Energy transfer of Eu/Sm-coactivated $CaYAl_3O_7$ phosphor

Figure 3 shows the excitation spectra of $CaYAl_3O_7$: Eu^{3+} and $CaYAl_3O_7$: Eu^{3+}, Sm^{3+} phosphors. As shown in Fig. 3, the introduction of Sm^{3+} into the red-emitting phosphors can generate a strong excitation line at 402 nm (monitored at 617 nm of Eu^{3+}) due to the $^6H_{5/2} \rightarrow {}^4F_{7/2}$ transition of Sm^{3+}, thereby extending the excitation region.[30,31] It is indicated that the absorption energy of Sm^{3+} at 402 nm may be transferred to Eu^{3+}. With the aim of further confirming the influence of co-doping with Sm^{3+}, the emission spectra of $CaYAl_3O_7$: Eu^{3+}, Sm^{3+} are shown in Fig. 4. In Fig. 4, the emission peaks at 617 nm grow with the increase of the Sm^{3+} concentration up to 0.01 and then decrease when the Sm^{3+} concentration is beyond 0.01. As a result, it is speculated that there exists an energy transfer from Sm^{3+} to Eu^{3+} and we confirm that the best concentration of Sm^{3+} in $CaYAl_3O_7$: Eu^{3+} is 0.01.

Figure 5 shows the normalized emission spectra of $CaY_{0.95}Al_3O_7$: $0.04Eu^{3+}$, $0.01Sm^{3+}$, $CaY_{0.96}Al_3O_7$: $0.04Eu^{3+}$, and $CaY_{0.99}Al_3O_7$: $0.01Sm^{3+}$ phosphors excited at different wavelengths. Figures 5(a) and 5(b) display the emission spectra of Eu^{3+} and Sm^{3+}, respectively. Figure 5(c) exhibits the emission spectrum of the phosphor co-doped with Eu^{3+} and Sm^{3+} excited at 393 nm of Eu^{3+}, whereas the main emission peaks of Sm^{3+} are not observed in Fig. 5(c). It implies that Sm^{3+} cannot be effectively excited by 393 nm, and the efficient energy transfer from Eu^{3+} ions to Sm^{3+} ions does not occur. While the characteristic emission peaks of Eu^{3+} are observed in the emission spectrum excited at 402 nm of Sm^{3+} (Fig. 5(d)). Meanwhile, the emission of Sm^{3+} ions is also excited at 402 nm. It means the occurrence of efficient energy transfer from Sm^{3+} ions to Eu^{3+} ions. The emissions of the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions of Eu^{3+} ions have been observed.[30,32,33] Comparing Fig. 5(c) with Fig. 5(d), we propose that the energy transfer between Sm^{3+} and Eu^{3+} is unidirectional and irreversible. It implies that the energy transfer wastage between Sm^{3+} and Eu^{3+} is very low.

We also study the energy transfer mechanism between Sm^{3+} and Eu^{3+}. The diagram in Fig. 6 shows how the rare-earth ions in the $CaY_{0.95}Al_3O_7$: $0.04Eu^{3+}$, $0.01Sm^{3+}$ phosphor absorb energy (n-UV light) and emit red light. If the $CaY_{0.95}Al_3O_7$: $0.04Eu^{3+}$, $0.01Sm^{3+}$ phosphor is excited by 393 nm, corresponding to the $^7F_0 \rightarrow {}^5L_6$ of Eu^{3+}, the Eu^{3+} ion absorbs energy by itself and the energy state moves to the lowest excited energy level ($^5D_0$) through relaxation. Finally, a red emission occurs through the $^5D_0 \rightarrow {}^7F_J$ transition. On the other hand, when an electron in the $^4F_{7/2}$ level of Sm^{3+} is excited by 402 nm light, the excited one is relaxed to the $^4G_{5/2}$ level, which is the lowest excited level of Sm^{3+}. Then the energy in the $^4G_{5/2}$ level of Sm^{3+} is transferred to the $^5D_0$ level

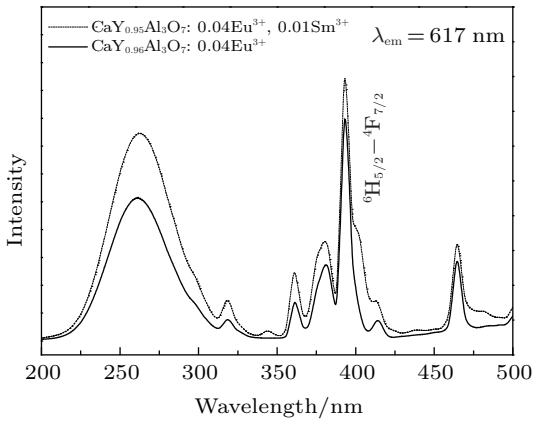


Fig. 3. Excitation spectra of $CaY_{0.96}Al_3O_7$: $0.04Eu^{3+}$ and $CaY_{0.95}Al_3O_7$: $0.04Eu^{3+}$, $0.01Sm^{3+}$ phosphors (monitored at 617 nm).

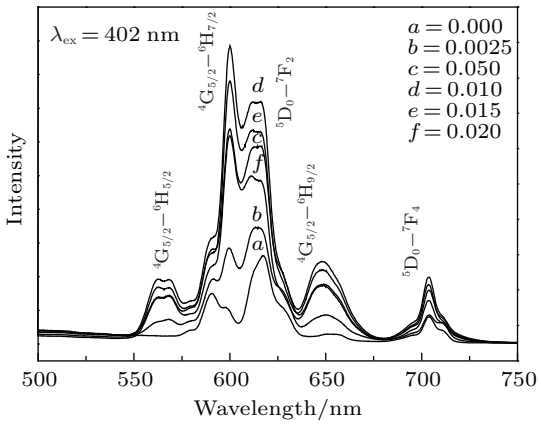


Fig. 4. Emission spectra of $CaY_{1-0.04-x}Al_3O_7$: $0.04Eu^{3+}$, xSm^{3+} ($x =$ 0.000–0.020) phosphors (excited at 402 nm).

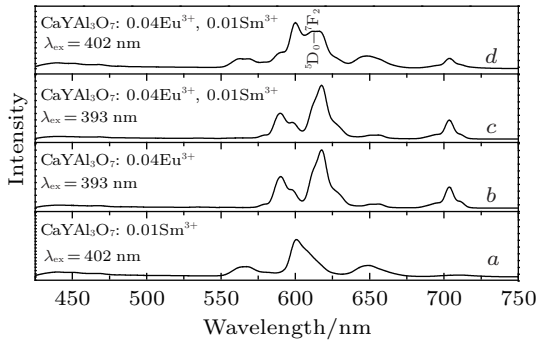


Fig. 5. Emission spectra of $CaY_{0.95}Al_3O_7$: $0.04Eu^{3+}$, $0.01Sm^{3+}$, $CaY_{0.96}Al_3O_7$: $0.04Eu^{3+}$, and $CaY_{0.99}Al_3O_7$: $0.01Sm^{3+}$ phosphors excited at different wavelengths.

of Eu^{3+} by resonance between the two energy levels. The energy transfer from Sm^{3+} to Eu^{3+} is almost irreversible because the $^4G_{5/2}$ level in Sm^{3+} is higher than the $^5D_0$ level in Eu^{3+} by 600 cm^{-1}, and the probability of emitting phonons for the $^4G_{5/2}$ (Sm^{3+}) $\rightarrow{}^5D$ (Eu^{3+}) process is much higher than that of capturing phonons for the $^5D_0$ (Eu^{3+}) $\rightarrow{}^4G_{5/2}$ (Sm^{3+}) process. Hence, the $^5D_0 \rightarrow{}^7F_2$ transition of Eu^{3+} is enhanced by the efficient energy transfer from Sm^{3+} to Eu^{3+}.[33,34]

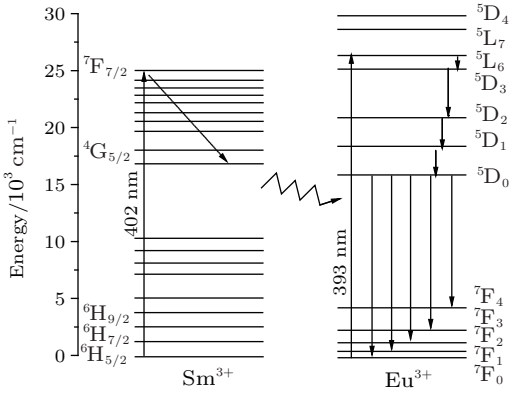


Fig. 6. Energy level diagrams of Sm^{3+} and Eu^{3+}.

4. Conclusion

The $CaYAl_3O_7$: Eu^{3+}, Sm^{3+} phosphor, a novel red-emitting phosphor for near-UV LED chips based WLED applications, is synthesized by a fast and economical viable combustion method at a low temperature (850 °C) for the first time. The critical concentrations of Eu^{3+} ions (0.04) and Sm^{3+} ions (0.01) are confirmed by observing the concentration quenching. And the critical distance between Eu^{3+} ions for energy transfer, R_c, is calculated to be about 19 Å. In addition, making comparison of the excitation and emission spectra between $CaYAl_3O_7$: Eu^{3+} and $CaYAl_3O_7$: Eu^{3+}, Sm^{3+} phosphors, we affirm that the $Sm^{3+} \rightarrow Eu^{3+}$ energy transfer process takes place in the $CaYAl_3O_7$ host matrix, thereby enhancing the red emission of Eu^{3+}. Moreover, owing to the efficient energy transfer, a strong excitation line at 402 nm (monitored at 617 nm of Eu^{3+}), originating from the $^6H_{5/2} \rightarrow{}^4F_{7/2}$ transition of Sm^{3+}, is detected, which extends the excitation region of this phosphor for better matching the near-ultraviolet LED chips. So it provides a special and crucial way to not only enhance photoluminescence intensity and expand the excitation region, but also reduce the production cost.

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