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Yellow-emitting $(Ca_2Lu_{1-x}Ce_x)(ScMg)Si_3O_{12}$ phosphor and its application for white LEDs

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ABSTRACT

Luminescence properties of the yellow-emitting $(Ca_2Lu_{1-x}Ce_x)(ScMg)Si_3O_{12}$ (CLSM:$x$$Ce^{3+}$ x = 0.01–0.15) phosphor are investigated for various Ce^{3+} concentrations. Different Ce^{3+} emission sites and energy transfers between them are observed, resulting in a red shift of the emission spectra from 530 to 575 nm with increasing x from 0.01 to 0.15. Combining with blue (460 nm) InGaN LEDs, CLSM:Ce^{3+} shows excellent performances for phosphor-converted white LEDs with higher color rendering index R_a of 87.4–87.9 and lower color temperature T_C of 5034–5814 K, especially for warm pcWLEDs with a high color rendering ($R_a > 80$) and a low color temperature ($T_C < 4000$ K). Thermal quenching behaviors depending on Ce^{3+} concentrations and temperatures are discussed.

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1. Introduction

Phosphor-converted white light emitting diode (pcWLED) is regarded as a new lighting source for the next generation [1,2]. The most current pcWLEDs employ yellow emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) garnet phosphors combined with blue InGaN LEDs [3,4]. The YAG:Ce^{3+} emits a band peaking at 530 nm with a width of about 100 nm due to $5d \rightarrow {}^2F_{7/2}, {}^2F_{5/2}$ transition [5,6]. However, the deficient red emission leads to a low color rendering index ($R_a < 80$) and a high color temperature ($T_C > 6500$ K) of the pcWLED. In addition to Al-based garnets, Si-based garnets, such as the green-emitting phosphor $Ca_3Sc_2Si_3O_{12}:Ce^{3+}$ (CSS:Ce^{3+}) [7] and the red-emitting phosphor $Lu_2CaMg_2Si_3O_{12}:Ce^{3+}$ [8], have been studied in recent years, but none of them can singly generate white light under blue light excitation. Shimomura et al. [9] obtained a yellow-emitting phosphor $Ca_3(Sc_{2-b}Mg_b)Si_3O_{12}:Ce^{3+}$ ($0 \leq b \leq 1$) by the partial Mg substitution for Sc but with a relatively weak emission intensity for the large amount of $Ca_2MgSi_2O_7$ by-product. In our previous work, we provided an effective way to improve the color quality by eliminating the by-product through the addition of Lu^{3+} ions as charge compensators [10]. In this paper, furthermore, we investigate the luminescence properties of $(Ca_2Lu_{1-x}Ce_x)(ScMg)Si_3O_{12}$ (CLSM:$x$$Ce^{3+}$, $0.01 \leq x \leq 0.15$) with various Ce^{3+} concentrations and demonstrate the performances of the CLSM:Ce^{3+} phosphors in pcWLEDs with high R_a of 82.3–87.9 and lower T_C of 3970–5814 K.

2. Experimental

Samples with the nominal compositions of $(Ca_2Lu_{1-x}Ce_x)(ScMg)Si_3O_{12}$ (CLSM:$x$$Ce^{3+}$, $0.01 \leq x \leq 0.15$) were prepared by a solid-state reaction from high purity raw materials of $CaCO_3$, Lu_2O_3, CeO_2, Sc_2O_3, MgO and SiO_2 at 1250 °C for 4 h in a reducing atmosphere (5% H_2 + 95% N_2 mixed flowing gas). Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Advance diffractometer in the range of $15^\circ \leq 2\theta \leq 75^\circ$ with a step of 0.02°. Photoluminescence (PL), photoluminescence excitation (PLE) and diffuse reflectance (DR) spectra were measured using a Hitachi F-4500 fluorescence spectrometer. Fluorescence decay curves of Ce^{3+} were measured by FL920 Fluorescence Lifetime Spectrometer (Edinburgh Instruments, Livingston, UK). PcWLEDs were fabricated with various ratios (14–18%) by weight of the CLSM:Ce^{3+} phosphors and the transparent silicone resin on blue (460 nm) InGaN LED chips. The color rendering index (R_a), color temperature (T_C), color coordinates (x, y) and luminous efficiency of the pcWLEDs were measured by an Ocean Optics USB4000 Spectrometer.

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3. Results and discussion

3.1. Crystal structure

In our previous work, we provided an effective way to eliminate the $Ca_2MgSi_2O_7$ by-product through adding Lu^{3+} ions into $Ca_3(Sc,Mg)Si_3O_{12}$ as charge compensators, and demonstrated the formation of a pure garnet-type structure when the charge reach a balance [10]. Basing on charge balance, furthermore, we investigate the phase characteristics of CLSM:$x$$Ce^{3+}$ phosphors with various Ce^{3+} contents. As Fig. 1 shows, each sample exhibits a pure phase of garnet-type structure. The garnet is more similar to the type of $Y_3Al_5O_{12}$ (PDF No. 73–1370) while not to the type of CSS (PDF No. 72–1969). This change should be related with the addition of Lu^{3+} and Mg^{2+} cations that cause the disorder of the CSS structure.

3.2. Optical properties

Fig. 2(a) and (b) shows the normalized PL and PLE spectra of CLSM:$x$$Ce^{3+}$ with $x = 0.01–0.15$. Under 460 nm excitation, each sample exhibits a broad yellow emission with a band width more than 120 nm due to the transition of Ce^{3+} from the 5d excited state to the $^2F_{5/2}$ and $^2F_{7/2}$ ground state. With increasing x, the PL spectra shift to the longer wavelength from 530 nm for $x = 0.01$ to 575 nm for $x = 0.15$. On the other hand, the PLE spectra exhibit an intense blue excitation band and some weak bands in the ultraviolet region, accounting for the transitions from $^2F_{5/2}$ state to the energy levels of Ce^{3+} 5d orbits. The blue excitation band also exhibits a red shift and broadens from 60 nm for $x = 0.01$ to 82 nm for $x = 0.15$. The relative integrated PL intensity depending on Ce^{3+} contents is displayed in Fig. 2(c), which exhibits a maximum at $x = 0.09$. In our previous report, we have demonstrated that the emission intensity was directly related with the absorbance of the CLSM:Ce^{3+} phosphor when the content of Lu^{3+} changed [10]. In this work, the absorbance of the CLSM:$x$$Ce^{3+}$ phosphor for various Ce^{3+} contents was also measured and shown in Fig. 2(d). It can be seen that the change of the absorbance almost keeps consistent with that of the emission intensity, further demonstrating the close relationship between the emission intensity and the absorbance in CLSM:Ce^{3+} phosphor.

To understand the redshift and broadens of the spectra in Fig. 2(a) and (b), PL and PLE spectra for various excitation and emission wavelengths were carried out. As Fig. 3 presents, for the optimum Ce^{3+} concentration, one can observe that the emission spectra obviously shift toward red sides with tuning the excitation from short wavelengths to the longer wavelengths. Correspondingly, the excitation spectra for the longer wavelengths are also shifted to the lower energy. These results indicate that there are different Ce^{3+} emission centers in CLSM:Ce^{3+} phosphor. Among the phases present in these samples, only the garnet phase is observed. Therefore, the different Ce^{3+} emission centers should arise from different Ce^{3+} sites in the garnet. Shimomura et al. [7] have demonstrated that Ce^{3+} presented at the dodecahedral site in the CSS silicate garnet by the EXAFS analysis. In CLSM, both Ca^{2+} and Lu^{3+} are in the dodecahedral site, therefore, Ce^{3+} will be randomly distributed over the Ca^{2+} and the Lu^{3+} sites when Ce^{3+} ions are incorporated into the CLSM garnet. Thus, different Ce^{3+} sites are induced for the different crystal field environment surrounding Ca^{2+} and Lu^{3+}.

3.3. Energy transfers

Since there is spectral overlap between the emission of the high-energy site and the excitation of the low-energy site, energy

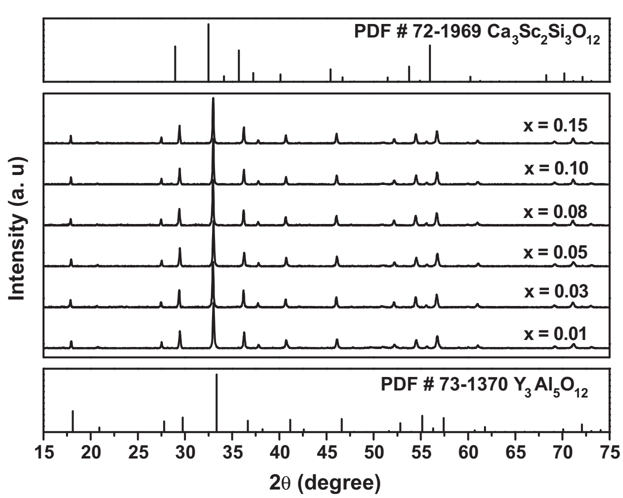

Fig. 1. XRD patterns of CLSM:$x$$Ce^{3+}$ phosphors with different x.

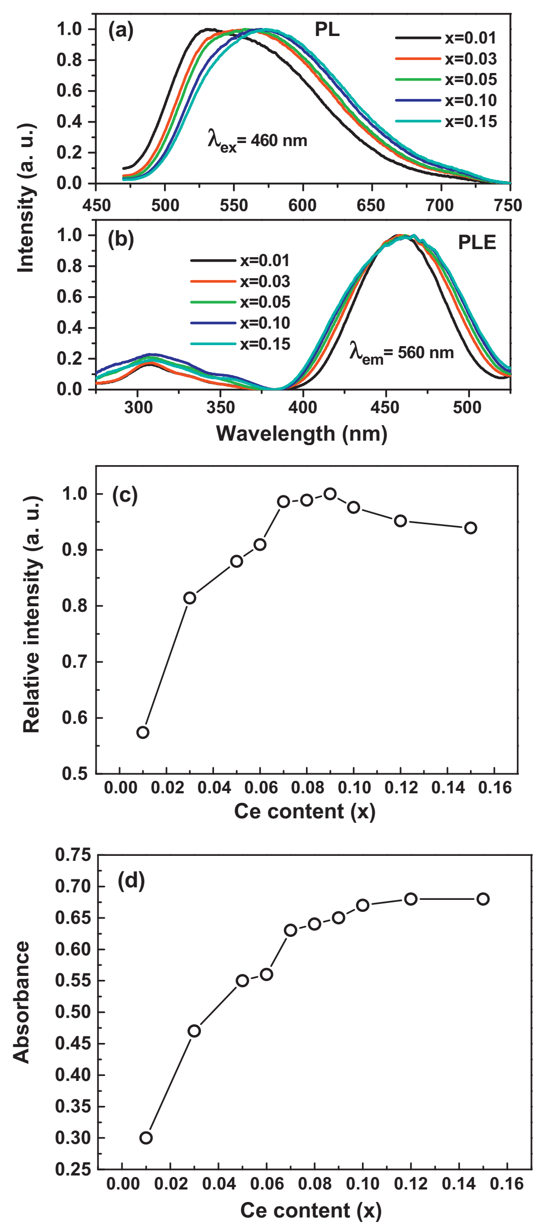

Fig. 2. (a) and (b), normalized PL (λ_{ex} = 460 nm) and PLE (λ_{em} = 560 nm) spectra; (c) and (d), relative integrated emission intensity and absorbance for CLSM:$x$$Ce^{3+}$ with $x = 0.01–0.15$.

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