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Temperature-dependent photoluminescence studies on $Y_{2.93-x}Ln_xAl_5O_{12}:Ce_{0.07}$ (Ln = Gd, La) phosphors for white LEDs application

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ABSTRACT

Gd^{3+}-doped, La^{3+}-doped and Gd^{3+}/La^{3+} co-doped $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce^{3+}) phosphors were prepared by high-temperature solid-state reaction. Their crystal structure and photoluminescence properties at various temperatures (25–200 °C) were investigated. By increasing the substitution concentration of Gd^{3+} in YAG:Ce^{3+} phosphor, the Ce^{3+} emission band shifts toward longer wavelength but shows a stronger thermal quenching. Addition with small amount of La^{3+} can improve the thermal stability of YAG:Ce^{3+} phosphors without leading to evident shifts of Ce^{3+} emission band. The La^{3+} and Gd^{3+} doping can complement each other. The Gd^{3+}/La^{3+} co-doped YAG:Ce^{3+} phosphors have longer wavelength emission and furthermore exhibit good thermal stability, which is especially favorable for high power white LEDs aiming at general illumination.

1. Introduction

White light emitting diodes (w-LEDs), the so-called next generation solid-state lighting sources, are gaining lots of attentions because of their numerous advantages over the existing incandescent and fluorescent lamps in energy saving, reliability, lifetime and environment-amity [1]. Although the white radiation can be generated from many methods, the combination of a GaN-based blue LED and a cerium-activated yttrium aluminum garnet (YAG:Ce^{3+}) phosphor is the most popular and sophisticated method at present [2]. However, this strategy suffers from low color-rendering index (CRI) and high color-temperature due to the weak emission intensity in red spectral region. Using a large rare earth ion, such as Gd^{3+} and Tb^{3+}, to substitute the dodecahedral site of the garnet structure can shift the Ce^{3+} emission band to a longer wavelength because of the larger crystal splitting of the 5d energy level of Ce^{3+} ions [3,4]. It is beneficial to improve the color-temperature and color-rendering properties of w-LEDs based on YAG:Ce^{3+} phosphor [4].

For w-LEDs application, phosphors are coated on a chip which excites them. The heat generated by the LED chip will result in serious problems not only to the chip itself but also to the phosphors [5,6]. The emission intensity of luminescent materials is decreased with increasing the operation temperature, and this behavior is well known as thermal quenching. It is obvious that the thermal quenching behavior of phosphors has important effects on the efficiency and chromatic properties of w-LEDs. Therefore, the thermal quenching property is also one of the most important technological parameters for phosphors applied in white LEDs [7,8], especially in high power white LED devices. The promising phosphors should perform well and retain their luminance and chromatic properties at the elevated temperatures of the LED junction (>100 °C) [9]. Setlur et al. have investigated the temperature-dependent photoluminescence properties of Ga^{3+}-doped and Tb^{3+}-doped YAG:Ce^{3+} phosphors, and found that Ga^{3+} and Tb^{3+} substitution will lead to stronger thermal quenching [10]. Chiang et al. have reported Gd^{3+} substituting Y^{3+} in $Tb_3Al_5O_{12}:Ce^{3+}$ phosphors can induce the redshifts of emission wavelength and unfortunately worsen their thermal quenching properties [5]. An efficient way to improve the temperature stability of YAG:Ce^{3+} phosphor is absent, and further studies are still needed. In this paper, Gd^{3+}-doped, La^{3+}-doped and Gd^{3+}/La^{3+} co-doped YAG:Ce^{3+} phosphors were synthesized by the high-temperature solid-state reaction method. The luminescent properties of these phosphors at elevated temperature were studied.

2. Experimental

Gd^{3+}-doped, La^{3+}-doped and Gd^{3+}/La^{3+} co-doped YAG:Ce^{3+} phosphors were synthesized by high-temperature solid-state reaction. The Ce^{3+} concentration of these samples remained constant at 7 mol%. Our early studies indicated that YAG:Ce^{3+} phosphor with 7 mol% Ce^{3+} had maximum emission intensity [11]. The starting materials of Y_2O_3 (99.99%), Al_2O_3 (99.99%), CeO_2 (99.99%), La_2O_3 (99.99%) and Gd_2O_3 (99.99%) were weighted with a certain stoichiometric ratio, and mixed thoroughly along with a certain amount of H_3BO_3 and BaF_2 as flux. These homogeneous mixtures were placed in an alumina crucible with a lid and then calcined at 1550 °C for 6 h in a reducing atmosphere (75% H_2, 25% N_2).

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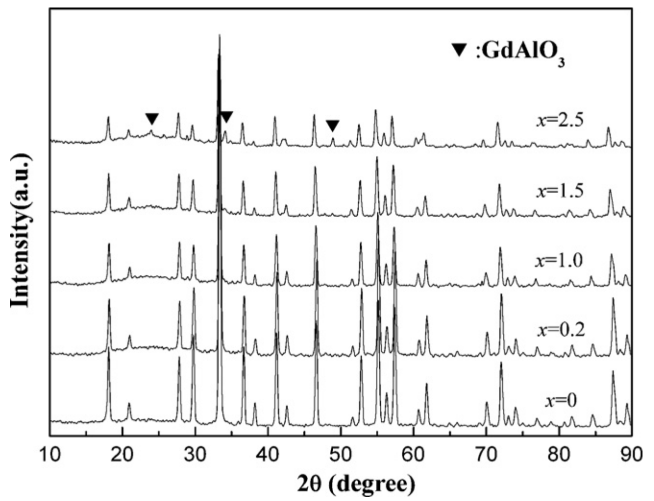

Fig. 1. XRD patterns of $Y_{2.93-x}Gd_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with different x values.

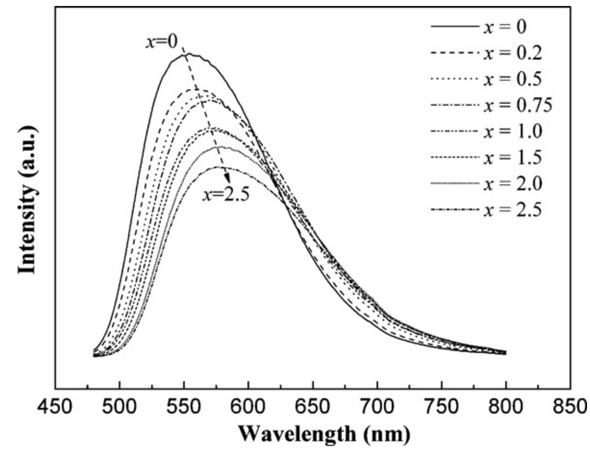

Fig. 2. Photoluminescence emission spectra of $Y_{2.93-x}Gd_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with varying x values at room temperature (λ_{ex} = 460 nm).

The crystal structure of the final products was identified by powder X-ray diffraction (Shimadzu XD-3A) with Cu Kα radiation generated at 40 kV/30 mA. The photoluminescence spectra of the samples were analyzed by a Hitachi F-7000 fluorescence spectrophotometer (with an R928F PMT) at room temperature. The temperature-dependent luminance of the phosphors was recorded by a self-made measuring system, which includes a temperature-controlled heating part and a fluo-brightness meter (Zhejiang University Sensing Instruments Co., Ltd., China). The heating part consists of a resistance-heating plate and a temperature controller. The thermocouple directly embeds within the phosphors to assure the accuracy of temperature measurement. The relative luminance of a certain phosphor at elevated temperature was tested by setting its luminance at room temperature as 100%. A blue LED (λ_{em} = 460 nm) was used as excitation source for temperature-dependent luminance measurements.

3. Results and discussion

3.1. Gd^{3+}-doped YAG:Ce^{3+} phosphors

Fig. 1 shows the XRD patterns of $Y_{2.93-x}Gd_xAl_5O_{12}$:$Ce_{0.07}$ phosphors (x = 0, 0.2, 1.0, 1.5, and 2.5). As $x \leq 1.0$, the products completely phase transform to a pure garnet structure. The Gd^{3+}-doped phosphor with x = 1.5 presents a minor intermediate phase, gadolinium aluminum pervoskite ($GdAlO_3$). As the x value increases to 2.5, the diffraction intensity of $GdAlO_3$ phase increases too. In the Gd_2O_3–Al_2O_3 system, the garnet structure does not seem to be a stable phase [5]. Gd^{3+} substituting Y^{3+} with higher concentration will lead to the formation of secondary phase ($GdAlO_3$).

Fig. 2 represents the emission spectra of $Y_{2.93-x}Gd_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with various x values. At the same activator concentration and excitation light (λ_{ex} = 460 nm), the emission wavelength is shifted to the red by increasing the Gd^{3+} content in the YAG lattice. As the x value varies from 0 to 2.5, the emission wavelength shifts from ∼550 nm to ∼580 nm. Longer emission wavelength of Ce^{3+}-activated garnet phosphor is favorable for improving the color-temperature and color-rendering properties of w-LEDs. However, it should be noted that the emission intensity of Gd^{3+}-doped YAG:Ce^{3+} phosphors is also decreased remarkably with the increase of Gd^{3+} content.

Fig. 3(a) shows the relative luminance of the pure and Gd^{3+}-doped YAG:Ce^{3+} phosphor ($Y_{0.43}Gd_{2.5}Al_5O_{12}$:$Ce_{0.07}$) varying with temperature (25–200 °C). The luminance of the samples at elevated temperature is normalized to that at 25 °C. The pure YAG:Ce^{3+} exhibits a remarkable thermal quenching behavior. Its luminance falls by 12% at 150 °C, and by 20% at 200 °C. The introduction of Gd^{3+} significantly increases the temperature sensitivity of YAG:Ce^{3+}. The relative luminance of $Y_{0.43}Gd_{2.5}Al_5O_{12}$:$Ce_{0.07}$ falls by 70% at 150 °C, and by 87% at 200 °C. The thermal quenching property of phosphors with various Gd^{3+} contents was characterized by the ratio of their luminance at 150 °C to that at 25 °C, notated as L_{150}/L_{25}. Fig. 3(b) shows the ratios of L_{150}/L_{25} of Gd^{3+}-doped phosphors as a function of Gd^{3+} concentration. The thermal quenching behavior of Ce^{3+} luminescence is very sensitive to the Gd^{3+} doping, and increasing the Gd^{3+} concentration in YAG:Ce^{3+} leads to enhanced thermal quenching. It is well known that luminescent materials with higher quenching temperature have a stiff structure [12]. Kanke and Navrotsky noted that the distance of Gd–O at the dodecahedral site of garnet is lager than that of Y–O [13]. This implies that the garnet structure becomes soft with the introduction of Gd^{3+}. Therefore, the thermal quenching behavior of Gd^{3+}-doped phosphor becomes stronger.

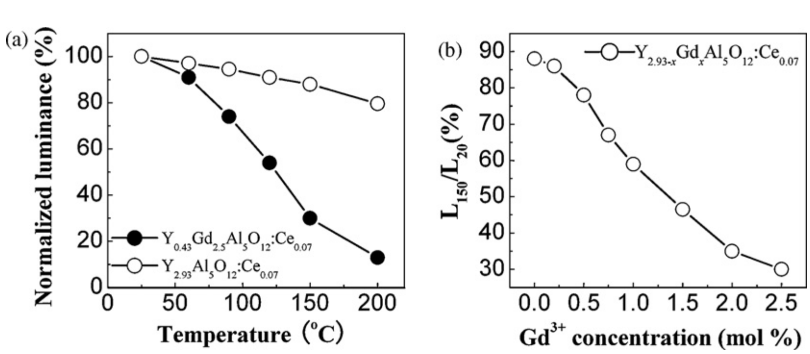

Fig. 3. (a) Normalized luminance of $Y_{2.93}Al_5O_{12}$:$Ce_{0.07}$ and $Y_{0.43}Gd_{2.5}Al_5O_{12}$:$Ce_{0.07}$ phosphors at various temperatures. (b) The ratios of luminance at 150 °C to that at 25 °C (L_{150}/L_{20}) of $Y_{2.93-x}Gd_xAl_5O_{12}$:$Ce_{0.07}$ phosphors as a function of Gd^{3+} concentration.

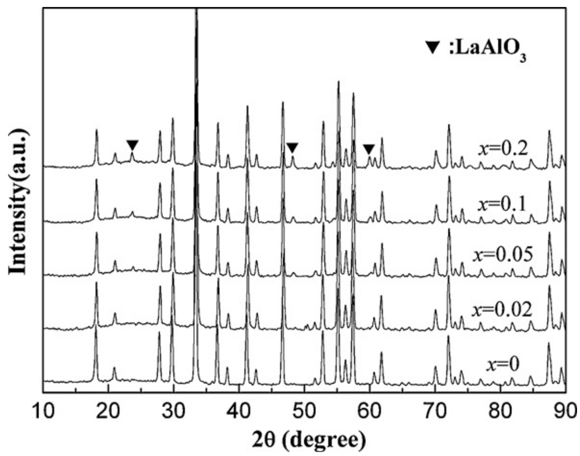

Fig. 4. XRD patterns of $Y_{2.93-x}La_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with different x values.

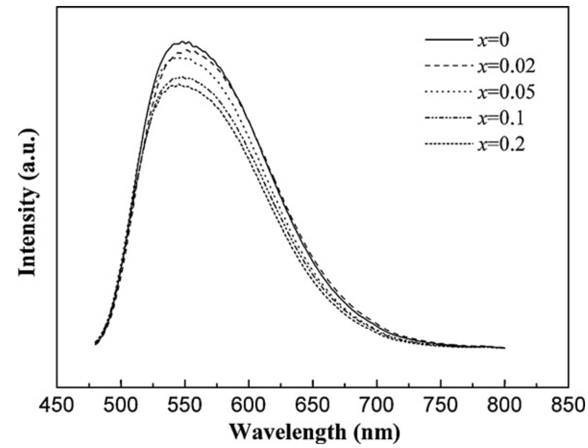

Fig. 5. Photoluminescence emission spectra of $Y_{2.93-x}La_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with varying x values at room temperature.

3.2. La^{3+}-doped YAG:Ce^{3+} phosphors

The ion radii of La^{3+} (0.116 nm) is much bigger than that of Y^{3+} (0.102 nm) [14], and therefore only small amount of La^{3+} was introduced to investigate its effects on the luminescence property and thermal quenching behavior of YAG:Ce^{3+}. Fig. 4 shows the XRD patterns of $Y_{2.93-x}La_xAl_5O_{12}$:$Ce_{0.07}$ phosphors (x = 0, 0.02, 0.05, 0.1, and 0.2). It can be found that as x = 0.05–0.2, an obvious intermediate phase ($LaAlO_3$) can be detected except for the dominant garnet structure. There is a competition between perovskite ($LaAlO_3$) and garnet formation, which limits the solubility of larger La^{3+} ions.

Fig. 5 shows the emission spectra of $Y_{2.93-x}La_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with varying x values at room temperature. As only small amount of La^{3+} was introduced, the emission bands of La^{3+}-doped YAG:Ce^{3+} phosphors have no evident shifts in comparison with the un-doped sample. The emission intensity of La^{3+}-doped samples descends slightly with La^{3+} concentration increasing, which is coincides with previous reports [3]. Fig. 6(a) shows the normalized luminance of the pure and La^{3+}-doped YAG:Ce^{3+} phosphor varying with temperature (25–200 °C). The luminance of $Y_{2.88}La_{0.05}Al_5O_{12}$:$Ce_{0.07}$ falls by 8% at 150 °C and by 13% at 200 °C, better than that of the pure YAG:Ce^{3+} (12% at 150 °C, 20% at 200 °C). Fig. 6(b) shows the ratios of luminance at 150 °C to that at 25 °C of $Y_{2.93-x}La_xAl_5O_{12}$:$Ce_{0.07}$ phosphors with various x values. It indicates that addition by small amount of La^{3+} (x = 0.02–0.1) is favorable to improve the thermal quenching property of YAG:Ce^{3+} phosphor.

The ion radii of La^{3+} is larger than that of Y^{3+} and Gd^{3+} (0.106 nm) [14], and therefore the structure of La^{3+}-doped YAG:Ce^{3+} should become much softer. In contrast, the YAG:Ce^{3+} doped with small amount of La^{3+} exhibits weaker thermal quenching. In addition, there does not appear to be significant changes in Ce^{3+}excitation (not shown) and emission spectra and in the Stokes shift. Bachmann et al. have reported that thermally activated concentration quenching makes a main contribution to the thermal quenching behavior of highly Ce^{3+}-doped YAG phosphors (x > 1%) [15]. One possible reason for weaker thermal quenching of La^{3+}-doped samples is that secondary phases ($LaAlO_3$) formed due to La^{3+} addition have a preferentially large amount of Ce^{3+} ions and therefore reduce the Ce^{3+} content in garnet phases. It could lead to an improved thermal quenching behavior in La^{3+}-doped samples.

3.3. Gd^{3+}/La^{3+} co-doped YAG:Ce^{3+} phosphors

Substituting Y^{3+} with Gd^{3+} can shifts the emission band of YAG:Ce^{3+} to the long wavelength side, which can improve the color-temperature and color-rendering properties of the w-LEDs due to the enhanced emission intensity in red spectral region. However, the thermal quenching property of YAG:Ce^{3+} is unfortunately worsened with increasing the Gd^{3+} concentration. In contrast, adding La^{3+} in YAG:Ce^{3+} can improve the thermal stability of Ce^{3+} emission without inducing evident emission shifts. It can be expected that the La^{3+} and Gd^{3+} doping can complement each other to produce the garnet phosphor with desirable emission spectrum and good thermal stability.

The Gd^{3+}/La^{3+} co-doped phosphors ($Y_{2.43-y}Gd_{0.5}La_yAl_5O_{12}$:$Ce_{0.07}$) were prepared by the same process. The Gd^{3+} concentration of these samples remains constant, and the La^{3+} concentration y varies from 0 to 0.2. XRD data (not shown) indicate that as $y \geq 0.05$, a minor intermediate phase ($LaAlO_3$) can be detected, and no $GdAlO_3$ phase has formed. Independent of La^{3+} content, these Gd^{3+}/La^{3+} co-doped samples have a longer emission

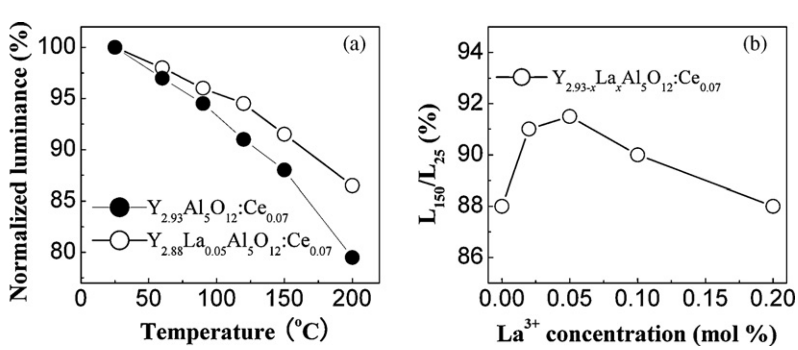

Fig. 6. (a) Normalized luminance of $Y_{2.93}Al_5O_{12}$:$Ce_{0.07}$ and $Y_{2.88}La_{0.05}Al_5O_{12}$:$Ce_{0.07}$ phosphors at various temperatures. (b) The ratios of luminance at 150 °C to that at 25 °C (L_{150}/L_{20}) of La^{3+}-doped phosphors as a function of La^{3+} concentration.

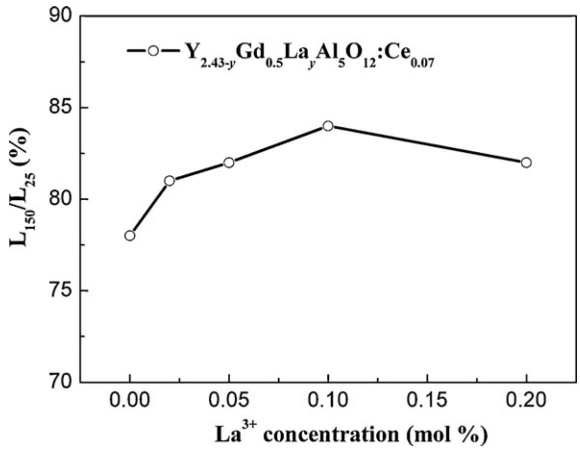

Fig. 7. The ratios of luminance at 150 °C to that at 25 °C of $Y_{2.43-y}Gd_{0.5}La_yAl_5O_{12}:Ce_{0.07}$ phosphors with various La^{3+} content.

wavelength (λ_{em} = ~560 nm), in comparison with pure YAG:Ce^{3+} (λ_{em} = ~550 nm). Fig. 7 shows the ratios of luminance at 150 °C to that at 25 °C of $Y_{2.43-y}Gd_{0.5}La_yAl_5O_{12}:Ce_{0.07}$ phosphors with various La^{3+} content. The $Y_{2.43}Gd_{0.5}Al_5O_{12}:Ce_{0.07}$ phosphor (no La^{3+} doping) exhibits a significant thermal quenching behavior, as mentioned above. At 150 °C it only can retain 78% of its luminance at 25 °C. Gd^{3+}/La^{3+} co-doped YAG:Ce^{3+} phosphors have a better thermal stability than singly Gd^{3+}-doped phosphor. For example, at 150 °C the $Y_{2.33}Gd_{0.5}La_{0.1}Al_5O_{12}:Ce_{0.07}$ phosphor can retain 84% of its luminance at 25 °C. These results prove that there is a possibility to develop such garnet phosphor that has a longer wavelength emission and better thermal stability at elevated temperature.

4. Conclusions

In this paper, Gd^{3+}-doped, La^{3+}-doped, Gd^{3+}–La^{3+} co-doped YAG:Ce^{3+} phosphors were prepared by solid-state reaction. Their photoluminescence properties at elevated temperature were studied. Gd^{3+} substitution shifts the Ce^{3+} emission to the red, at the expense of decreasing the emission intensity and deteriorating the thermal quenching. Adding small amount of La^{3+} does not lead to significant shifts of Ce^{3+} emission band, and can improve the thermal quenching property of YAG:Ce^{3+}. The Gd^{3+}/La^{3+} co-doped phosphors exhibit a better thermal stability and an emission redshift, suitable for high power w-LEDs applied in general illumination field.

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