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Letter

Photoluminescence properties of red phosphor $Gd_3PO_7:Eu^{3+}$ for UV-pumped light-emitting diodes

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ABSTRACT

A red-emitting Gd_3PO_7:5% Eu^{3+} phosphor is reported. Through transitions of 5d → 4f ($^7F_1$ and $^7F_2$) in Eu^{3+}, the phosphor shows a bright red emission under ultraviolet (UV) light excitation. The emission intensity at 615 nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ion depending on irradiation time under 394 nm excitation increases firstly and then small reduces. After 20 min for UV-light irradiation, it decreases by about 0.5% suggesting that the photostability of the red phosphor $Gd_3PO_7:Eu^{3+}$ is excellent. Under 325 nm excitation, the emission intensities grow rapidly as the temperature increases from 75 K to 285 K and then it keeps on growing slowly until 475 K, revealing the excellent thermostability of the red phosphor $Gd_3PO_7:Eu^{3+}$. Decay time and time-resolved luminescence measurements have also been studied. All the results reveal that $Gd_3PO_7:Eu^{3+}$ is a promising red-emitting phosphor for UV LED applications.

1. Introduction

White-light-emitting diodes (LEDs) have been considered to be important solid-state light sources for the advantages of high brightness, low power consumption, and long working time [1,2]. The conventional way involves combining a blue-emitting LED with a yellow-emitting $Y_3Al_5O_{12}:Ce^{3+}$ (YAG: Ce^{3+}) phosphor [3]. Although the white LED based on YAG: Ce^{3+} phosphor has high efficiency (>100 lm W^{-1}), it exhibits a poor color rendering index (CRI ≅ 70–80) and a high correlated color temperature (CCT ≅ 7750 K) [4,5] because of lacking red component, [6] which is not suitable for applications requiring high CRI properties. In order to achieve white light with high CRI and suitable CCT, the alternative way is the combination of blue or short UV LED chips with tri-color phosphors. Therefore, red emitting phosphors with good quality can be pumped by blue or near-UV emitting LEDs gain a lot of attention [7,8]. Rare earth ions doped phosphates exhibit excellent luminescence properties in the UV region [9,11,12]. The Eu^{3+} ion as an activator have been investigated frequently for its excellent fluorescent properties, particularly in which the Eu^{3+} occupies a non-centrosymmetric site due to the exhibited characteristic red emission corresponding to $^5D_0 \rightarrow {}^7F_2$ transition and the intense charge-transfer band (CTB) absorption in UV region [10]. Compound Gd_3PO_7 adopts a monoclinic structure, and the Eu^{3+} ion in this host lattice have no inversion symmetry, which is in favor of the red emission ($^5D_0 \rightarrow {}^7F_2$) transition of Eu^{3+} [11,12].

In this paper, red phosphor $Gd_3PO_7:Eu^{3+}$ has been prepared by solid-state method. This phosphor demonstrates strong red fluorescence, originating from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} upon near-UV excitation into the $^5L_6$ state of Eu^{3+} at 394 nm. The photoluminescence (PL) emission intensity area of Eu^{3+} ion depending on irradiation time under 394 nm excitation has been studied, suggesting that the photostability of the red phosphor $Gd_3PO_7:Eu^{3+}$ is excellent as a potential red phosphor for LED. Under 325 nm excitation, the dependence of emission intensities on temperature and decay time and time-resolved luminescence were measured. All the results reveal that $Gd_3PO_7:Eu^{3+}$ is a promising red-emitting phosphor for UV LED applications.

2. Experimental section

Red phosphor $Gd_3PO_7:Eu^{3+}$ was synthesized at high temperature by solid state reaction using Gd_2O_3, $(NH_4)_2HPO_4$ and Eu_2O_3. All starting materials were of analytical grade and they were used without any further purification. Stoichiometric proportion Gd_2O_3, $(NH_4)_2HPO_4$ and Eu_2O_3 were measured, mixed and ground in an agate mortar homogeneously. Then, the mixture was placed in a capped alumina crucible, which was heated to 1000 °C and maintained for 2 h. After cooling to room temperature, the product was grounded to fine powder in an agate mortar.

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2.1. Measurements

The structures were characterized by X-ray diffraction (XRD) (Rigaku D/max-rA powder diffractometer with Cu target radiation resource (λ = 1.54078 Å)). Fluorescence spectra were recorded at room temperature using a Hitachi F-4500 spectrophotometer equipped with a 150 W Xe-arc lamp. The PL spectra were excited by the 325 nm of a continuous-wave He–Cd laser and detected by a cooled charge-coupled device. The temperature was controlled by a closed-cycle helium cryostat system with a programmable temperature controller. Luminescent decay curves were recorded by an oscillograph (Tektronix, TDS 3052, 500 MHz, 5 Gs/s), with a 266 nm light as excitation source. It was generated from the fourth harmonic generator pumped by the pulsed Nd-YAG laser, with a line width of 1.0 cm^{-1}, pulse duration of 10 ns, and repetition frequency of 10 Hz.

3. Results and discussion

Fig. 1 shows the XRD pattern of the product $Gd_3PO_7:Eu^{3+}$, in which all of the peaks were agreed well with the monoclinic phase Gd_3PO_7, the JCPDF 34–1066 with the unit cell parameters a_0 = 12.02 Å, b_0 = 15.60 Å, c_0 = 13.886 Å. No excessive traces of Eu^{3+} ion were observed, indicating that the dopant ion did not change the structure of the host.

Room-temperature photoluminescence excitation spectrum (PLE) by monitoring the emission wavelength at 615 nm depicted in Fig. 2 (left part). The PLE spectra revealed a broad band and some sharp peaks. The band extending from 220 to 330 nm is due to the charge transfer from the completely filled $2p^6$ orbital of the O^{2-} ion to the partially filled 4f orbital of Eu^{3+} ion [13]. The weaker band around 210 nm is attributed to Gd-O absorption [11]. The sharp lines are assigned to the *f–f* transitions of Eu^{3+} ion corresponding to $^7F_0 \rightarrow {}^5H_3$ at 318 nm, $^7F_0 \rightarrow {}^5D_4$ at 362 nm, $^7F_0 \rightarrow {}^5G_4$ at 383 nm, $^7F_0 \rightarrow {}^5L_6$ at 394 nm, $^7F_0 \rightarrow {}^5D_3$ at 413 nm, $^7F_0 \rightarrow {}^5D_2$ at 465 nm and $^7F_0 \rightarrow {}^5D_1$ at 533 nm. Among the observed *f–f* transitions the $^7F_0 \rightarrow {}^5L_6$ transition at 394 nm was an intense one. These peaks indicate that Eu^{3+} ion can be excited by UV, violet and blue light source including LED and LD.

The PL emission spectrum under 394 nm is also shown in Fig. 2 (right part). The spectrum consists of sharp peaks ranging from 560 to 700 nm associated with the transitions from the excited $^5D_0$ level to ^7F_J (J = 1, 2, 3 and 4) of the Eu^{3+} activator. The major emissions at 591 nm corresponding to $^5D_0 \rightarrow {}^7F_1$ transitions are magnetic dipole and at 615 nm corresponding to $^5D_0 \rightarrow {}^7F_2$ transitions are a hypersensitive electric dipole, revealing orange and red emission, respectively. The emission transitions besides $^5D_0 \rightarrow {}^7F_1$ are found to be further split into two, mainly due to the interaction of the local environment. The intensity distributions of the $^5D_0 \rightarrow {}^7F_J$ transitions among different J levels depends mainly on the symmetry of the local environment around Eu^{3+} ion described by Judd–Ofelt theory [14,15]. According to the selection rules, magnetic dipole transitions are permitted and electric dipole transitions are forbidden. However, some cases the local symmetry of the activator is without an inversion center, the parity forbidden is partially permitted. When Eu^{3+} ion occupies the site with inversion centers, the $^5D_0 \rightarrow {}^7F_1$ transition would be relatively strong, while the $^5D_0 \rightarrow {}^7F_2$ transition is parity forbidden and should be very weak. As shown in Fig. 2, the $^5D_0 \rightarrow {}^7F_2$ transition is prominent in all the transitions, suggesting that Eu^{3+} ion occupied at the sites without inversion symmetry.

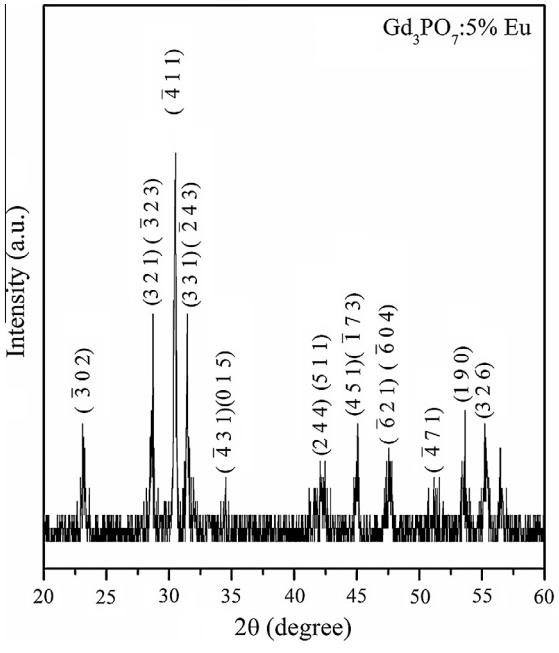

Fig. 1. The XRD pattern of the product Gd_3PO_7:5% Eu^{3+}.

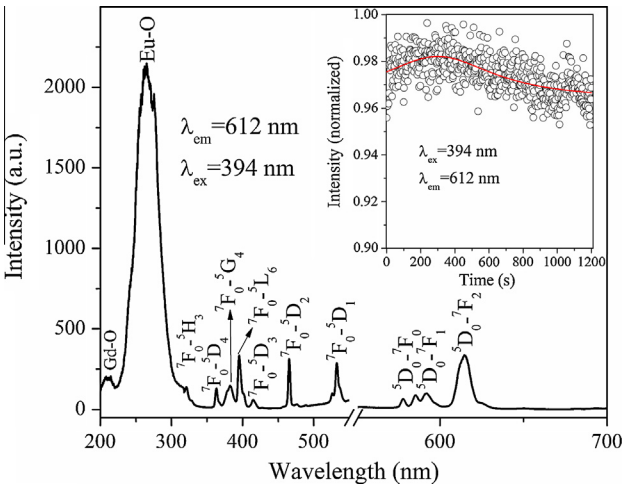

Fig. 2. Room-temperature photoluminescence excitation spectrum (PLE) (λ_{em} = 615 nm) and emission spectum (λ_{ex} = 394 nm). Inset: Dependence of normalized intensity at 615 nm on irradiation time for UV lights.

Emission intensity at 615 nm of Eu^{3+} ion depending on irradiation time under 394 nm excitation was measured, as shown in insert of Fig. 2. The emission intensity increases firstly and then small reduction gradually. At beginning, the normalized intensity is 0.975 and after 20 min for UV-light irradiation, the normalized intensity is 0.97. That is to say, it decreases by 0.005 about 0.5% after 20 min for UV-light irradiation. It suggests that the photostability of the red phosphor $Gd_3PO_7:Eu^{3+}$ is excellent as a potential red phosphor.

The temperature-dependent photoluminescence properties of $Gd_3PO_7:Eu^{3+}$ under 325 nm He–Cd laser excitation were investigated. The emission spectra at different temperatures under 325 nm He–Cd laser excitation are shown in Fig. 3a. The emissions corresponding to the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2, 3, 4) transitions are all observed. In the measured range (75 K–475 K), the emission intensities are all increasing with the temperature raising and no temperature quenching is observed. Fig. 3b shows further the dependence of integrated intensities of the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transition on temperature. Under 325 nm excitation, the emission intensities grows rapidly as the temperature increases from 75 to 285 K and it approaches a shoulder at 285 K. Then it keeps on growing slowly. It reveals the stronger luminescence intensity with the elevated temperatures roughly, suggesting that the thermostability of $Gd_3PO_7:Eu^{3+}$ is excellent as a potential red phosphor for LED.

Fig. 4a shows time-resolved emission spectra for the $^5D_0 \rightarrow {}^7F_J$ (J = 0, 1, 2) transitions under 266 nm excitation. As we can see, from shorter delay time (5 and 10 μs) to longer delay times (50 μs) the luminescence intensity corresponding to $^5D_0 \rightarrow {}^7F_1$

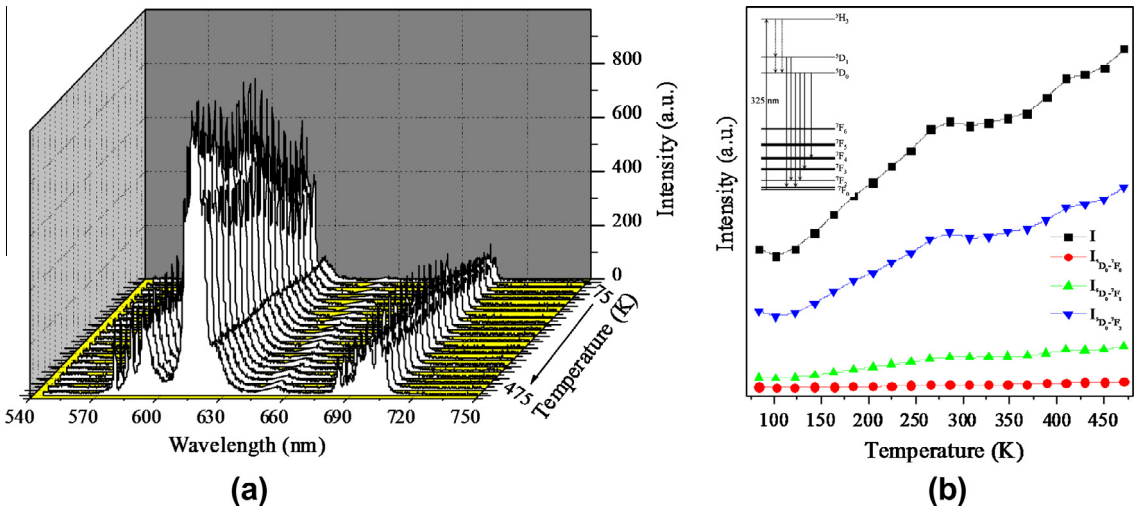

Fig. 3. (a) Emission spectra at various temperatures under 325 nm He–Cd laser excitation; (b) temperature-dependent emission intensity of Eu^{3+} under 325 nm excitation. Inset: Schematic diagram for the luminescent processes of $Gd_3PO_7:Eu^{3+}$ under 325 nm excitation.

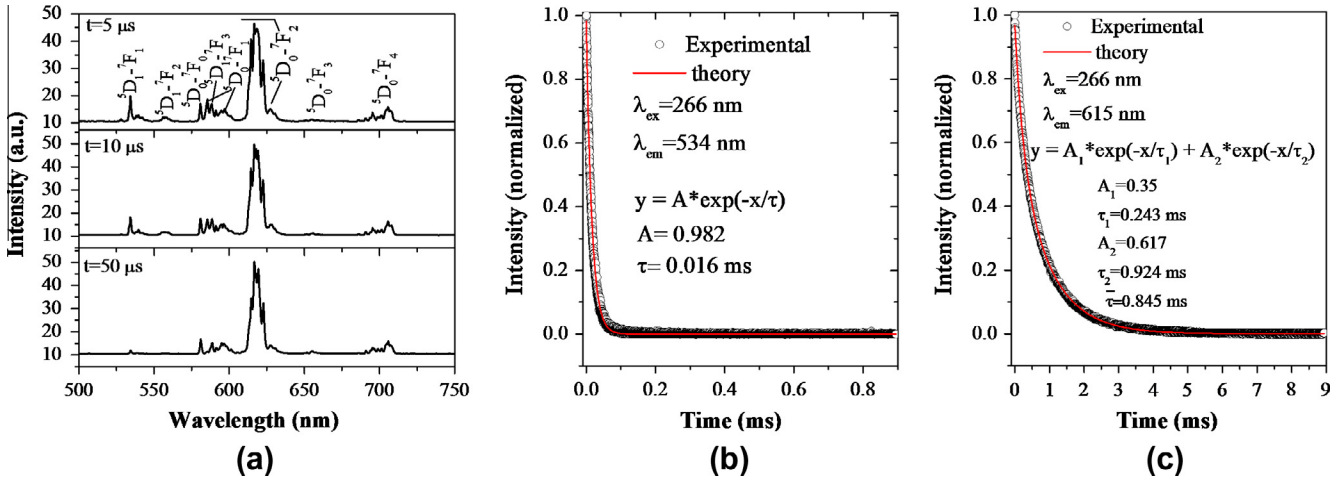

Fig. 4. (a) Time-resolved emission spectra for the $Gd_3PO_7:Eu^{3+}$ powders under 266 nm excitation; (b and c) the decay curves for the $^5D_1 \rightarrow {}^7F_1$ (534 nm) and $^5D_0 \rightarrow {}^7F_2$ (617 nm) emission of Eu^{3+} in the $Gd_3PO_7:Eu^{3+}$ sample (λ_{ex} = 266 nm).

transition is dropped rapidly and the luminescence intensity corresponding to $^5D_0 \rightarrow {}^7F_2$ transition is almost unchanged.

The kinetic curves for the representative emission of Eu^{3+} $^5D_1 \rightarrow {}^7F_1$ (534 nm) and $^5D_0 \rightarrow {}^7F_2$ (615 nm) were measured, as shown in parts b and c of Fig. 4, respectively. The decay curve for $^5D_1 \rightarrow {}^7F_1$ (534 nm) of Eu^{3+} (Fig. 4b) can be well fitted into single-exponential function as $I = A \exp(-t/\tau)$, and the fitting parameters are shown inside the figure. A lifetime τ value of 0.016 ms, 16 μs is obtained for $^5D_1 \rightarrow {}^7F_1$ emission of Eu^{3+}. However, the decay curve for $^5D_0 \rightarrow {}^7F_2$ (615 nm) of Eu^{3+} (Fig. 4c) cannot be fit into the single exponential function but can be well fit into a double-exponential function as $I = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, and the fitting results are shown inside Fig. 4c. Two lifetimes, τ_1 = 243 μs and τ_2 = 924 μs, have been obtained for $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+}. The average lifetime of Eu^{3+} $^5D_0 \rightarrow {}^7F_2$ emission, defined as $\langle\tau\rangle = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$ [16], can be determined to be 845 μs.

4. Conclusion

Red phosphor $Gd_3PO_7:Eu^{3+}$ has been synthesized by solid-state method. In the system, the Eu^{3+} ion occupied at the sites without inversion symmetry and it will emit intense red light in the region of 590–750 nm while it is excited by UV light. The thermostability and the photostability of the red phosphor $Gd_3PO_7:Eu^{3+}$ are both excellent which have been proved by the temperature-dependent photoluminescence and photostability test. Through further optimizations, it is believed that the photoluminescence properties of this composite can be further improved and can be an ideal candidate red phosphor for LEDs.

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