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High-brightness Eu^{3+}-doped $Ca_9Gd(PO_4)_7$ red phosphor for NUV light-emitting diodes application

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ABSTRACT

A novel red-emitting phosphor $Ca_9Gd(PO_4)_7$:Eu^{3+} has been synthesized by a high-temperature solid-state reaction. X-ray powder diffraction (XRD) analysis confirmed the phase formation of $Ca_9Gd(PO_4)_7$:Eu^{3+} materials. The photoluminescence excitation and emission spectra, the concentration dependence of the emission intensity, and decay curves of the phosphor were investigated. The results showed that the phosphor could be efficiently excited by the near ultraviolet (NUV) light and blue light, and it exhibited red light emission. The intensity of $Ca_9Gd_{0.1}(PO_4)_7$:$0.90Eu^{3+}$ phosphors is 4.13 times than that of commercial phosphors Y_2O_3:$0.05Eu^{3+}$. The decay time was also determined for various concentrations of Eu^{3+} in $Ca_9Gd(PO_4)_7$. The calculated color coordinates lies in the red region. Therefore, these obtained results suggest that the prepared phosphors exhibit great potential for use as red emitting phosphor for near ultraviolet white light emitting diodes (NUV WLEDs).

1. Introduction

Phosphor-converted white light emitting diodes (pc-WLEDs) are promising light sources due to the high electro-optical conversion efficiency, stability and reliability. There is a huge demand for novel phosphor materials with superior luminescence properties to improve the luminous efficiency [1,2]. An LED-based light is fabricated using the combination of a blue-emitting LED chip with a yellow-emitting $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) phosphor; this combination is widely used due to an unsurpassed efficiency (> 30 lm W^{-1}). Although a blue-emitting LED chip with a yellow-emitting YAG:Ce^{3+} phosphor has a high efficiency, it has a poor color-rendering index because YAG:Ce^{3+} phosphors have a relatively weak emission in the red spectral region, and it is difficult to obtain good color rendering as measured by the index (Ra). Currently, Y_2O_2S:Eu^{3+} has been the main commercial red-emitting phosphor for near UV InGaN-based white LED, However, it has a few shortcomings, such as low efficiency short working lifetime under UV irradiation, and air sensitive [3]. To overcome these problems, it is urgently needed to develop novel red phosphors to meet the requirements for solid state lighting.

Phosphates as the hosts for the phosphor materials have the advantages of low synthetic cost, relatively simple tech-process, outstanding thermal stability and the strong adsorption band in the (near) ultraviolet region. The whitlockite-type β-$Ca_3(PO_4)_2$ compound, as a typical phosphate, has six metal sites (M1–6) in the crystal lattice: the M1–M2 sites are coordinated by eight oxygen atoms, the M3 and M5 sites are surrounded by nine and six oxygen atoms, and the M4, M6 sites is vacant. The presence of this particular structure suggests a possible method by which the lattice can accommodate other cations with similar radii and charges without significant changes to the structural frame. So far, some $Ca_3(PO_4)_2$-type luminescence materials, such as $Ca_8MgBi(PO_4)_7$:Eu^{3+} [4], $Ca_9Gd(PO_4)_7$:Eu^{2+}, Mn^{2+} [5] have been studied by many researchers.

In this study, whitlockite-type $Ca_9Gd(PO_4)_7$:Eu^{3+} phosphor has been prepared, and the photoluminescence (PL) properties were investigated for the first time.

2. Experimental section

$Ca_9Gd_{1-x}(PO_4)_7$:xEu^{3+} (x=0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, and 1.00) phosphors were synthesized using a solid state reaction method. Highly pure $CaCO_3$ (99.9%), $(NH_4)_2HPO_4$ (99.9%), Gd_2O_3(99.99%) and Eu_2O_3 (99.99%) supplied by Sinopharm Chemical Reagent, Co. Ltd., Shanghai China, were used as starting materials. Stoichiometrical amounts of these reagents were mixed thoroughly in alcohol by ball milling in an agate mortar. They were

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pre-sinter at 900 °C for 6 h in air, and re-sintered at 1250 °C for 6 h. Finally, the samples were ground into powder for characterization. Phase purities were analyzed by using a D/MAX2500TC powder diffractometer. Excitation spectra, emission spectra and luminescence decay times were measured using a steady state and transient state fluorescence spectrometer (FLS920).

3. Results and discussion

Fig. 1 shows the XRD patterns of $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ powders. All the diffraction peaks of the as-synthesized samples were consistent with those of $Ca_9Y(PO_4)_7$ JCPDS No. 46-0402 database. XRD results indicate that the structure of $Ca_9Gd(PO_4)_7$ host lattice was unchanged upon the doping of Eu^{3+} ions co-doping. The $Ca_9Gd(PO_4)_7$ sample exhibited the same crystal structure as the $Ca_9Y(PO_4)_7$.

The fluorescence excitation spectra of typical sample $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ (x=0.20, 0.50, 0.70, and 1.00) monitoring at the $^5D_0 \rightarrow {}^7F_2$ emission (615 nm) were shown in Fig. 2(a). The excitation spectra of Eu^{3+}-doped $Ca_9Gd(PO_4)_7$ clearly indicate a broad absorption from 225 to 315 nm (with a maximum at about 265 nm) and several excitation peaks located at 319 nm ($^7F_{0,1} \rightarrow {}^5H_{3,6}$), 362 nm ($^7F_{0,1} \rightarrow {}^5D_4$), 382 nm ($^7F_{0,1} \rightarrow {}^5L_7$), 394 nm ($^7F_0 \rightarrow {}^5L_6$), 414 nm ($^7F_1 \rightarrow {}^5D_3$), 465 nm ($^7F_0 \rightarrow {}^5D_2$), respectively [4]. The broad absorption from 225 to 315 nm can be attributed to charge-transfer transition from negative oxygen ion ($2p^6$) to the empty state of $4f^7$ of Eu^{3+} ion [ligand-to-metal charge-transfer band (CTB)]. The strongest absorption peaks at 395 nm and 465 nm match well with the output wavelength of near-UV and blue chips, respectively.

Fig. 2(b) illustrates the PL spectra of $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ (x=0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, and 1.00) phosphors excited at 395 nm. The peaks with the maxima at 579, 591, 612, 652 and 700 nm of $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ phosphor are assigned to the $^5D_0 \rightarrow {}^7F_J$ (J=0, 1, 2, 3, 4) transition of Eu^{3+}, respectively [4]. The electric dipole transition $^5D_0$–$^7F_2$ (615 nm) is hypersensitive to distortion of the inversion symmetry, whereas the magnetic dipole transition $^5D_0$–$^7F_1$ (591 nm) is insensitive to it. The ($^5D_0$–$^7F_2$)/($^5D_0$–$^7F_1$) intensity ratio, namely, the asymmetry ratio, which suggests the degree of distortion, with respect to inversion symmetry, of the local Eu^{3+} ion environments in the lattice. The R/O values calculated for samples are between 4.28 and 4.43, which is strong evidence that Eu^{3+} ions mainly occupy the lattice site without inversion symmetry.

The inset of Fig. 2(b) shows relation between the integral intensity of $^5D_0 \rightarrow {}^7F_2$ transition and concentration of Eu^{3+}. As shown in the inset of Fig. 2(b), as the concentration increases, the emission intensity increases, and it reaches to maximum at x=0.90, which was taken as the optimum concentration. After that, the concentration quenching effect occurs. Obviously, the quenching concentration of Eu^{3+} in $Ca_9Gd(PO_4)_7$ is seemly larger than that in other host. It can be explained by the specific of the crystal structure of the host. The $Ca_9Gd(PO_4)_7$ belongs to the typical whitlockite structure with space group of R3c. In the structure of $Ca_9Gd(PO_4)_7$, there are six different sites for Ca^{2+}, named as Ca(1)–Ca(6). Among the six sites, Ca(6) and Ca(4) site are completely empty. The empty Ca(4) and Ca(6) sites can dilute the concentration of Eu^{3+}. Fig. 2(c) shows the PLE and PL spectra of the commercial Y_2O_3:0.05Eu^{3+} phosphors which produced by Changshu Xinlian phosphors Co. Ltd. Compared with the commercial phosphors Y_2O_3:0.05Eu^{3+}, the intensity of $Ca_9Gd_{0.1}(PO_4)_7$:0.90Eu^{3+} phosphors is 4.13 times than that of Y_2O_3:0.05Eu^{3+}. Herein, Eu^{3+}-doped $Ca_9Gd(PO_4)_7$ is a potential commercial phosphor.

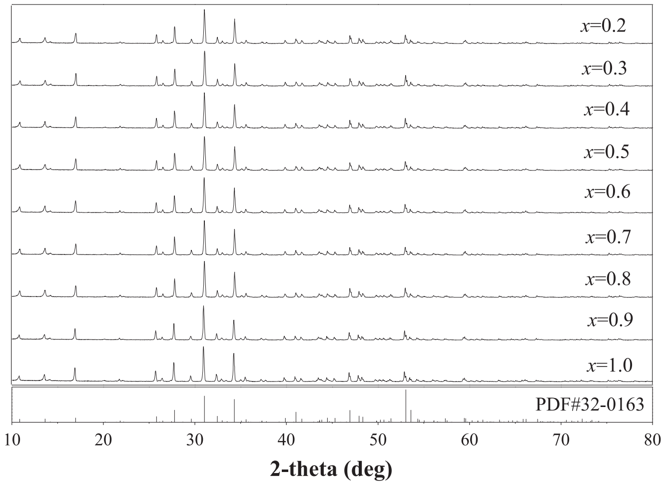

Fig. 1. XRD patterns of the as-prepared samples.

The decay curves of $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ (x=0.30, 0.60, and 0.90) phosphors were measured, and the results are shown in Fig. 3. The corresponding luminescence decay times can be best fitted to a third-order exponential equation as follows [6]:

$$I = A_1\exp(-t/\tau_1) + A_2\exp(-t/\tau_2) + A_3\exp(-t/\tau_3) \tag{1}$$

where I is the luminescence intensity; A_1, A_2, and A_3 are the weight constants; t is the time; and τ_1, τ_2, and τ_3 are the lifetimes for the exponential components. There are three lifetimes for Eu^{3+} ions, indicating that the Eu^{3+} ions mainly occupy the three different sites in the $Ca_9Gd(PO_4)_7$ host, namely, Ca1, Ca2, and Ca3. Using these parameters, the average decay times (t) can be determined by the following formula [6]:

$$\tau^* = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3) \tag{2}$$

The average decay times (τ^*) were calculated to be 1.803, 1.799, and 1.754 ms, corresponding to x=0.30, 0.60, and 0.90, respectively. The lifetime decreases with increased concentration due to the concentration quenching effect.

The International Commission on Illumination (CIE) chromaticity coordinates of $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ phosphors are shown in Fig. 4. The symbol * in CIE-1931 chromaticity diagram (Fig. 4) shows the ideal white light chromaticity coordinates with x=0.333 and y=0.333 [7,8]. The CIE chromaticity coordinates for these phosphors were all located in the red region at (x=0.657, y=0.342), and hardly change with increasing Eu^{3+} contents. The inset of Fig. 4 shows the luminescence photograph of $Ca_9Gd_{0.1}(PO_4)_7$:0.90Eu^{3+} phosphor excited at 365 nm. Under NUV excitation, $Ca_9Gd_{0.1}(PO_4)_7$:0.90Eu^{3+} phosphor emitted a bright red light.

4. Conclusions

In summary, $Ca_9Gd_{1-x}(PO_4)_7$:$x$$Eu^{3+}$ phosphors were synthesized by a solid-state reaction. The phase analysis, luminescence properties, decay times, and CIE coordinates on the emission were investigated. The excitation spectra show that $Ca_9Gd(PO_4)_7$:Eu^{3+} can be effectively excited under excitation of 395 and 465 nm which is in good agreement with the Near-UV and blue LEDs chips, respectively. The intense red emission corresponding to the transition of $^5D_2$–$^7F_0$ at 615 nm is dominant in the emission spectra, and the intensity ratio of R/O are between 4.28 and 4.43, which indicates that Eu^{3+} ions mainly occupy the lattice site without inversion symmetry. Luminescence decay times can be best fitted