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Luminescence properties of red-emitting $Ca_9Y(PO_4)_7$: Eu^{3+} phosphor for NUV white-LEDs

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ABSTRACT

$Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors have been prepared by solid state reaction. X-ray diffractometer, spectrofluorometer and UV–Vis spectrometer were used to characterize structural and optical properties of the samples. The results indicate that single-phase trigonal $Ca_9Y(PO_4)_7:Eu^{3+}$ can be obtained when the calcination temperature is higher than 1100 °C. The optimum concentration of Eu^{3+}-doped in the $Ca_9Y(PO_4)_7$ is 13 mol%. The CIE chromaticity coordinate of $Ca_9Y(PO_4)_7:0.13Eu^{3+}$ phosphor (0.650, 0.349) is close to National Television Standard Committee (NTSC) standard value for red phosphor (0.670, 0.330).

1. Introduction

White light-emitting diodes (LEDs) are considered to be potential lighting devices which would replace traditional fluorescence or incandescence lamps due to energy preservation. One of the most promising approaches to generate white light in w-LEDs is to combine an UV chip with tricolor (red, green and blue) phosphors. However, commercially red phosphors for w-LEDs such as $Y_2O_2S:Eu^{3+}$ show chemical instability and lower efficiency under NUV or blue light excitations. [1] Therefore, it is necessary to develop new red phosphor to meet demand. It is well known that hosts of red phosphors widely studied are based on borates, phosphates, aluminates, silicates, vanadates, etc. [2–7] Among them, phosphates are better luminescence materials because of their low annealing temperature, high brightness, excellent thermal stability, stable physical and chemical properties. The trivalent europium (Eu^{3+}) ion is good for strong red and orange photoluminescence of *f–f* transitions and is widely used in lighting and display fields. To the best of our knowledge, the synthesis and luminescence properties of $Ca_9Y(PO_4)_7:Eu^{3+}$ red phosphors have not been reported. In this paper, the influences of annealing temperature and Eu^{3+} ion concentration on PL intensities of $Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors are investigated. The CIE chromaticity coordinates of $Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors are also characterized.

2. Experimental

2.1. Synthesis of $Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors

$Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors were prepared by a solid state reaction technique at high temperature. Stoichiometric amounts of $CaCO_3$ (AR), $(NH_4)_2HPO_4$ (AR), Y_2O_3 (99.99%) and Eu_2O_3 (99.99%) were mixed and ground thoroughly. Then the resultant mixtures were sintered at different temperatures for 5 h in air atmosphere. The final products were cooled down to room temperature and ground again. The doping concentrations of Eu^{3+} ions were 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 mol%, respectively.

2.2. Characterizations of $Ca_9Y(PO_4)_7:Eu^{3+}$ phosphors

The phase purity of the as-prepared phosphors was checked by a Thermo ARL XTRA automatic X-ray diffractometer using Cu Kα radiation at 40 kV and 30 mA with a graphite monochromator. The 2θ ranges of all the data are from 10° to 90°with a step size of 0.02°. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with a FL3-211-P spectrofluorometer equipped with a Xe flash lamp. The measurement of reflectance spectra was performed by using a Shimadzu UV-2450 UV–vis spectrometer.

3. Results and discussion

3.1. X-ray diffraction analysis

The XRD profiles of $Ca_9Y(PO_4)_7:0.13\ Eu^{3+}$ phosphors sintered at different temperatures are shown in Fig. 1. Samples sintered above 1300 °C were not prepared because of limited experimental conditions. All diffraction peaks of $Ca_9Y(PO_4)_7$ crystal appeared when the calcination temperature was higher than 1100 °C according to the standard card (JCPDS card No. 46-0402), which suggests that a pure structure phase was synthesized, and the doped Eu^{3+} ions

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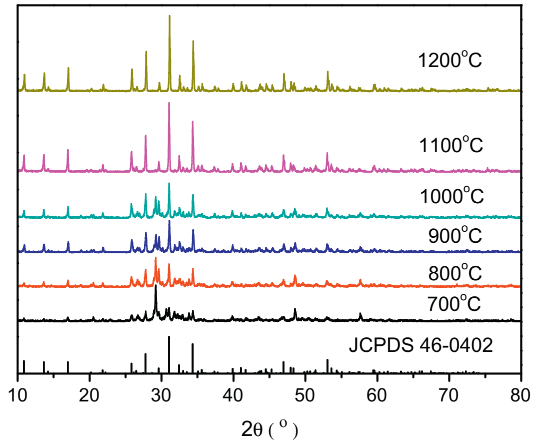

Fig. 1. X-ray diffraction patterns of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphor sintered at different temperatures.

did not cause any significant change in the host structure. The higher intensity of the diffraction peaks of the sample sintered at 1200 °C was ascribed to the enhanced crystallinity. The radius of Y^{3+} ion (0.090 nm) is similar to that of Eu^{3+} ion (0.095 nm), so Eu^{3+} ions can be easily doped into $Ca_9Y(PO_4)_7$ and prefer to locate in Y^{3+} sites. On the other hand, Y^{3+} and Eu^{3+} ions are both trivalent cations, no charge compensation is required and, as a consequence, no further point symmetry lowering can be caused by charge compensating defects. The prepared sample has trigonal system with cell parameters $a = b = 1.0444$ nm, $c = 3.7324$ nm, $Z = 6$. In the range of 700–1000 °C, obviously, the oxides have not entirely formed into $Ca_9Y(PO_4)_7$ crystal.

Fig. 2 represents the effect of calcination temperatures on the PL spectra of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphors. The inset is the relative PL intensity (615 nm) as function of the calcination temperature. It can be seen that no distinct diversifications of PL spectra shapes and positions occurred when the samples sintered at different temperatures. The PL intensity increased gradually in the range of 700–1000 °C, and then increased remarkably during the temperature of 1000–1200 °C. Therefore, the purity of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} sample had an impact on not only the peak intensity in the diffraction pattern, but also the brightness of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphor.

From the above data analysis, we choose 1200 °C as the final sintering temperature.

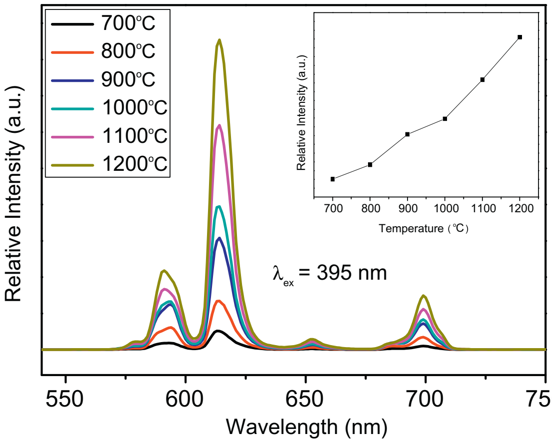

Fig. 2. Effect of calcination temperature on the emission spectra of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphors.

3.2. Photoluminescence emission and excitation analysis

The excitation and emission spectra of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphor are shown in Fig. 3. In the excitation spectrum, the broad band between 200 nm and 290 nm is ascribed to the charge transfer band (CTB) of $O^{2-} \rightarrow Eu^{3+}$. There are several sharp peaks located at 362 nm($^7F_0 \rightarrow {}^5D_4$), 376 nm, 382 nm ($^7F_0 \rightarrow {}^5L_7$), 395 nm ($^7F_0 \rightarrow {}^5L_6$), 416 nm($^7F_0 \rightarrow {}^5D_3$), 465 nm($^7F_0 \rightarrow {}^5D_2$), respectively. The strongest excitation peak located at 395 nm matches well with the emission wavelength of near-UVchips. The emission spectrum of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphor excited at 395 nm includes five typical emission bands assigned to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0,1,2,3,4$) transitions of Eu^{3+} ions, in which the dominant red emission band at 615 nm is attributed to the $^5D_0 \rightarrow {}^7F_2$ transition.

According to Ref. [8], $^5D_0 \rightarrow {}^7F_2$ (615 nm) electronic dipole transition is hypersensitive, while $^5D_0 \rightarrow {}^7F_1$ (590 nm) magnetic dipole transition is insensitive to the symmetry of occupied site. Thus, the PL intensity ratio of the transitions $^5D_0 \rightarrow {}^7F_2$ to $^5D_0 \rightarrow {}^7F_1$, $R = I_2/I_1$, is a good way to detect the symmetry of crystal field environment around Eu^{3+} ion. A low symmetry leads to a high value of R (>1), the opposite will lead to a low value ($1 > R > 0$). In this work, the R value of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphor is 4.065, which strongly indicates that Eu^{3+} ions occupy the sites with no inversion symmetry.

Fig. 4 presents the reflection spectra of $Ca_9Y(PO_4)_7$:x Eu^{3+} phosphors. All samples possess high reflectance (>90%) between 370 nm and 600 nm. Strong absorption bands at 200–290 nm were found, which correspond to the charge transfer bands (CTB) of $O^{2-} \rightarrow Eu^{3+}$, and the absorption intensity increases with the enhancement of Eu^{3+} ion concentration. However, with the increase of Eu^{3+} ion concentration, there is no obvious red-shift of the absorption wavelength. It suggests that the energy bands of the phosphors were not changed because of Eu^{3+} ion doping. The sharp peaks located at 395 nm, 465 nm are due to the 4*f*–4*f* inner shell transitions of Eu^{3+} ions.

The influence of Eu^{3+} ion concentration on the PL intensity of $Ca_9Y(PO_4)_7$:$x$$Eu^{3+}$ phosphors (x = 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.12, 0.13, 0.14, 0.15) is shown in Fig. 5. The emission intensity of the dominant peak located at 615 nm increases with the increasing of Eu^{3+} ion concentration and reaches the maximum when the molar fraction is 0.13, then it decreases because of the concentration quenching. According to Dexter' theory, the relation between emission intensity (I) and activator concentration (x) can be expressed by Eq. (1) [9] :

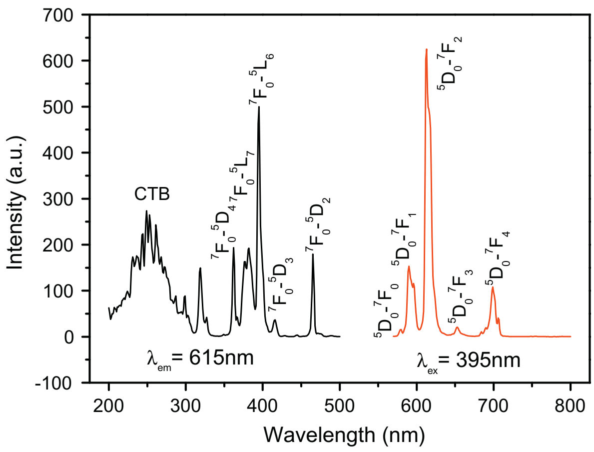

Fig. 3. Excitation and emission spectra of $Ca_9Y(PO_4)_7$:0.13 Eu^{3+} phosphors.