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Photoluminescence properties of blue light excited $Ca_8La_2(PO_4)_6O_2$:Eu^{3+} red phosphors

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ABSTRACT

A series of red emitting $Ca_8La_2(PO_4)_6O_2$:xEu^{3+} ($0 \le x \le 0.4$) phosphors were synthesized by the conventional solid state reaction, and their photoluminescence properties were investigated in this work. Upon excitation of blue light, the $Ca_8La_2(PO_4)_6O_2$:xEu^{3+} phosphors exhibit strong red emission at 616 nm, which corresponds to the dominant transition of Eu^{3+} ions in $Ca_8La_2(PO_4)_6O_2$ host, originating from the electric dipole transition $^5D_0$–$^7F_2$. Moreover, $Ca_8La_2(PO_4)_6O_2$:0.3Eu^{3+} phosphor shows more intense photoluminescence than that of other phosphors, where the concentration of Eu^{3+} ion is not equal to 0.3. The CIE chromaticity coordinate (0.657, 0.343) of $Ca_8La_2(PO_4)_6O_2$:0.3Eu^{3+} phosphor is close to National Television Standard Committee standard value (0.670, 0.330) of red phosphors, which indicates $Ca_8La_2(PO_4)_6O_2$:0.3Eu^{3+} is potential to apply in white light-emitting diodes as an excellent red emitting phosphor.

1. Introduction

Phosphor-based white light-emitting diodes (WLEDs) have been considered as an indispensable solid light source and display systems for the next generation lighting industry, because of their merits of being environmentally friendly and exhibiting energy savings, high brightness, high luminous efficiency and a long lifetime [1,2]. Currently, most of the commercially available LED-based white light sources rely on the phosphor (YAG:Ce^{3+}) converted emission method (pc-LEDs). However, there are low color rendering index and high correlated color temperature (CCT) for commercial WLEDs due to the deficiency of red component [3,4]. Consequently, it is necessary to exploit efficient red phosphors for application in white light-emitting diodes. Among numerous red phosphors, Eu^{3+} activating hosts was one of the most popular methods to obtain high-performance red light-emitting phosphors due to intense red light range emission deriving from Eu^{3+} ion [5,6]. Therefore, red light-emitting phosphors, which are prepared by doping Eu^{3+} in different hosts, are extensively studied in the fields of luminescence materials.

Besides rare earth doped ions, the hosts are also the key factor for obtaining efficient red emitting phosphors. However, some hosts of red phosphors are not stable, for example, sulfides and oxysulfides (Ca, Sr)S Y_2O_2S [7,8], or have rigorous synthesis conditions, such as nitrides $CaAlSiN_3$, $Sr_2Si_5N_8$ [9,10]. Therefore, it is urgent to develop novel hosts of phosphors with stable physical and chemical properties. Phosphates are a type of promising materials due to their high stability, various crystal structures, and relatively facile preparation method, which have been widely investigated as hosts of phosphors. Among these phosphates, the ternary metal oxyapatite family is a potential host material of efficient phosphors by doping of various rare earth ions. In the lattice of oxyapatite, there are two cationic sites, that is, the 9-fold coordinated 4f sites with C_3 point symmetry and 7-fold coordinated 6h sites with C_S point symmetry. Both sites are suitable and easily accommodate a great variety of RE^{3+}. Therefore, excellent photoluminescence is expected when Eu^{3+} ion doping into the oxyapatite hosts. It is well known that some red phosphors by Eu^{3+} doping phosphates have fairly good luminescence properties, such as $LiEu(PO_3)_4$:Eu^{3+}, $Sr_3Y(PO_4)_3$:Eu^{3+} and $Ca_9Y(PO_4)_7$:Eu^{3+} [11–13].

$Ca_8RE_2(PO_4)_6O_2$, a typical metal oxyapatite compound, has been an excellent host of efficient luminescence phosphors [14–18]. For instance, Silva et al. reported the study of structural and photoluminescent properties of $Ca_8Eu_2(PO_4)_6O_2$ prepared by the

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mechanical alloying technique [14]. $Ca_8La_2(PO_4)_6O_2$ (abbreviated as CLPO) as a host of phosphor is investigated by doping Yb^{3+}, Ce^{3+} and Eu^{2+} ions [16,18]. However, up to now, there is no research on Eu^{3+}-doped CLPO phosphors. In this paper, red emitting phosphors CLPO:xEu^{3+} ($0 \le x \le 0.4$) were synthesized by the conventional solid-state reaction. The structure, composition and photoluminescence properties of CLPO:Eu^{3+} phosphors were investigated. In addition, the effects of Eu^{3+} concentration on the photoluminescence spectra were demonstrated in detail. The CIE chromaticity coordinate of CLPO:0.3Eu^{3+} phosphor (0.657, 0.343) is close to National Television Standard Committee standard (0.670, 0.330) for red phosphors, which indicates the phosphor is potential to apply in WLEDs as an excellent red phosphor.

2. Experimental section

A series of CLPO:xEu^{3+} ($0 \le x \le 0.4$) were prepared by a typical solid-state reactions in air. The stoichiometric amounts of raw materials, $CaCO_3$, La_2O_3, $NH_4H_2PO_4$ and Eu_2O_3 were weighed and mixed in an agate mortar, and 10 ml of acetone was added during the grindings becoming homogenous mixtures. In order to obtain the target compounds with pure phase, two firing steps are necessary. The mixture was first conducted at 600 °C for 2 h in a covered alumina crucible, then reground thoroughly after cooled down to the room temperature. The second firing was heated at 1300 °C for 6 h. Finally, the samples were ground into powders for characterizations. In addition, the high quality commercially available phosphors Y_2O_3:0.05Eu^{3+} was purchased from Xinchangji Luminate Material Co., Ltd. as the reference in the work.

The crystal structure of phosphors were characterized for phase formation by using powder X-ray diffraction (XRD) analysis with a Bruker AXS D8 advanced automatic diffractometer with Cu Kα radiation (λ=1.5418 Å). The morphology of the phosphors were measured using a scanning electron microscope (SEM, JEOL JSM-6510) and the elemental analysis of the synthesized products were carried out on an Oxford EDAX equipment (INCA-Penta Fet X3) attached to the SEM system. UV–visible spectra were obtained by a diffuse reflection method with a Spectrophotometer (Hitachi U-3010) by $BaSO_4$ as a reflectance standard. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the samples were analyzed using a FluoroMax-4 fluorescence spectrometer at room temperature. Commission International de L'Eclairage (CIE) coordinates were measured by the integrating sphere (F-3018) attached to the spectrofluorometer.

3. Results and discussion

3.1. The morphology and compositional analysis of CLPO host

The grain size of phosphors is important for their applications in commercial WLEDs. In general, for practical bepowdering applications, the phosphors with micron particles can feed well the commercial demand for WLEDs. Therefore, morphology of CLPO host is first presented in the typical SEM image as shown in Fig. 2(A). Crystallization granules and agglomeration of particles are observed in the presented sample. It can be seen that CLPO is made up of fine sip distributed uniformly particles with 2–5 μm diameters. Moreover, the morphology and size of CLPO:xEu^{3+} did not obviously change after doping Eu^{3+} ions in CLPO host. A selected area of CLPO sample was performed under energy dispersive spectrometer (EDS), characterizing the compositions of the sample in Fig. 2(B). The EDS analysis revealed that the sample consisted of mainly four elements Ca, La, P and O. The approximately atomic ratio is 4.10:1.04:2.61:12.2, approaching to the stoichiometric ratio of each elements in $Ca_8La_2(PO_4)_6O_2$ formula.

3.2. Crystal structure analysis of CLPO:xEu^{3+} phosphors

Though, CLPO host is consisted of mainly four elements Ca, La, P and O. Structure and purity of CLPO, especially for Eu^{3+} doped-CLPO simples, are still unknown. XRD patterns of CLPO and Eu^{3+} ions activated CLPO phosphors are measured as shown in Fig. 1. $Ca_8La_2(PO_4)_6O_2$ is isostructural to natural oxyapatite $Ca_{10}(PO_4)_6F_2$, crystallizes in a hexagonal phase with the space group P63/m (No. 176) and unit-cell dimensions of a=9.4868 Å, c=6.9335 Å, V=540.41 Å^3, and Z=1 [18]. It is obvious that all the diffraction peaks of as-prepared phosphors can be exactly assigned to the hexagonal phase of CLPO according to JCPDS no. 33-0287, indicating that the Eu^{3+} ions were completely incorporated into the CLPO host without inducing significant impurities of the crystal structure. Owing to the similar radii and the same electrovalence for Eu^{3+} ions (1.01 Å, coordination number (CN)=7) and La^{3+} (1.1 Å, CN=7) [18,19], Eu^{3+} ions can substitute for La^{3+} ions in the host. Moreover, it can be seen that the major diffraction peaks are shifted slightly to the higher angle side with the increase of Eu^{3+} ions concentration, attributing to the replacement of the larger La^{3+} ions by relatively smaller Eu^{3+} ions. In addition, the average size of 100 CLPO granules is calculated by Scherrer equation:

$$D = K\lambda/\beta \cos\theta \quad (1)$$

where D is the crystalline size; K is the Scherrer constant, 0.89; λ is the wavelength of X-ray, β is the full width at half-maximum of diffraction peak; and θ is the diffraction angle. The average size of 100 crystalline granules is 4.63 μm, which are consistent with the calculated result from FESEM.

3.3. Luminescence properties of Eu^{3+}-doped CLPO phosphors

After the pure and good crystalline Eu^{3+}-doped CLPO phosphors are obtained, their optical properties are investigated. The diffuse reflection spectra of the CLPO:xEu^{3+} (x=0, 0.1, 0.3) are first presented as shown in Fig. 3. The diffuse reflection spectra of CLPO:xEu^{3+} exhibit a strong absorption band below 400 nm, attributing to the charge transfer absorption between the valance band and the empty conduction band in the host crystal lattice [20]. The obvious peaks located at 394 and 465 nm in CLPO:0.1Eu^{3+} and CLPO:0.3Eu^{3+} samples are associated with typical intra-4f forbidden transitions of the Eu^{3+} ions, and the peak intensity of CLPO:0.3Eu^{3+} is obviously stronger than that of CLPO:0.1Eu^{3+} due to the high doping concentration of Eu^{3+}. The optical bandgap of sample usually can be calculated from diffuse reflection spectrum by using Kubelka–Munk function

$$F(R) = (1-R)^2 2/R = K/S \quad (2)$$

where R, K, and S are the reflection, the absorption coefficient and the scattering coefficient, respectively. The optical bandgap of CLPO:0.3Eu^{3+} is about 3.16 eV by extrapolating the Kubelka–Munk function to K/S=0 [21], which was shown in the inset of Fig. 3.

In addition, the excitation spectrum (λ_{em}=616 nm) and emission spectrum (λ_{ex}=465 nm) of CLPO:0.3Eu^{3+} phosphors are shown in Fig. 4A. There is a broad absorption band in the wavelength range from 250 to 300 nm, which originates from the charge-transfer transition from the filled 2p shell of O^{2-} to the partially filled 4f shell of Eu^{3+}. Several main sharp bands in the excitation spectrum are due to the f–f transitions of Eu^{3+} ions from the ground state $^7F_0$ to the excitation levels ^{5}L6 (394 nm), $^5D_2$ (465 nm), $^5D_1$ (532 nm), respectively. It is noted that the $^7F_0$–$^5D_2$ transition at 465 nm is the strongest excitation band, which