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Synthesis and photoluminescence properties of high-$Ba_3P_4O_{13}$:Eu^{2+}—A broadband yellow-emitting phosphor for near ultraviolet white light-emitting diodes

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ABSTRACT

We have synthesized and investigated a series of yellow-emitting high-$Ba_3P_4O_{13}$:Eu^{2+} phosphors, showing an extreme broad band at around 587 nm, with a full width at half maximum of about 175 nm, which is attributed to the 5d-4f transition of Eu^{2+} under near ultraviolet excitation. This phosphor shows good absorption in the near ultraviolet range and nearly no absorption in the blue region. The concentration quenching and the fluorescence lifetime of Eu^{2+}, as well as the temperature-dependent photoluminescence have also been studied. Moreover, a white light with chromaticity coordinates of (0.364, 0.357) and color temperature of 4354 K was obtained by blending the yellow-emitting high-$Ba_3P_4O_{13}$:Eu^{2+} and the commercial blue-emitting $BaMgAl_{10}O_{17}$:Eu^{2+} phosphor. These results indicate that high-$Ba_3P_4O_{13}$:Eu^{2+} has potential applications in the dual-color-phosphor-converted white light-emitting diodes.

1. Introduction

Phosphor-converted white light-emitting diodes (pc-WLEDs) have attracted much attention due to their great advantages compared with traditional fluorescent lamps and incandescent bulbs, such as long life time, high energy efficiency, and they are mercury free [1–5]. Generally, two different configurations are possible for WLEDs. One is to integrate blue LEDs and yellow-emitting phosphors (YAG:Ce^{3+}) [6,7], and another one is to combine tricolor phosphors with near ultraviolet (NUV) LED chips [8]. The former one suffers from poor color rendition because of the weak luminescence in the red spectral region [9]. The latter one often induces some problems like energy loss induced by color balance and reabsorption [10,11]. Using binary color phosphors complementary to each other for NUV LED chips has been put forward to overcome these shortcomings, since this method can reduce the energy loss in the reabsorption process to a certain degree and make the fabrication processes of WLEDs simplified meanwhile [11–13]. In this regard, on one hand, the yellow-emitting phosphor is required to exhibit a broadband emission with an enriched red component, and on the other hand, the phosphor itself should show little absorption of the blue light [12]. Therefore, it is very urgent to develop novel suitable yellow-emitting phosphors.

The CaO-BaO-P_2O_5 phase diagram is well understood and includes many complex phases such as $(Ca,Ba)_2P_2O_7$, $Ca_2Ba(PO_4)_2$, $(Ca,Ba)_3(PO_4)_2$, $Ca_{10}(PO_4)_6O$, $Ca_4(PO_4)_2O$ and $Ca_6Ba(PO_4)_4O$ [14–17]. The system has been explored for phosphors applications in combination with UV or blue LEDs. Deng et al. have reported $Ca_4(PO_4)_2O$:Eu^{2+} as a red phosphor [18] and Komuro et al. reported $Ca_6Ba(PO_4)_4O$:Eu^{2+} as a yellow phosphor [17] for blue LEDs. Lagos reported the behavior of $(Ca,Ba)_2P_2O_7$:Eu^{2+} as a blue phosphor and $(Ca,Ba)_3(PO_4)_2$:Eu^{2+} as a yellow phosphor for UV excitation [19]. Millet et al. reported that $Ba_3P_4O_{13}$ has two polymorphic forms. Low-$Ba_3P_4O_{13}$ transforms at 870 °C into high-$Ba_3P_4O_{13}$, which crystallizes in the orthorhombic system, space group Pbcm (No. 57) (or Pbc2, No. 29) with unit-cell dimensions a = 7.107, b = 13.883, c = 19.219 Å, [20]. But the detailed structure of high-$Ba_3P_4O_{13}$ is still unclear. Zhang et al. reported the luminescence properties of Eu^{2+} in low-$Ba_3P_4O_{13}$ [21], which emits a blue light under UV irradiation. Our group have reported Eu^{2+} doped low- and high- $Ba_3P_4O_{13}$ [22,23] as the long-lasting phosphors. However, there is no report on the detailed luminescence properties of Eu^{2+} doped high-$Ba_3P_4O_{13}$ and its application for WLEDs. In this article, we report the phosphor,

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Eu^{2+} doped high-$Ba_3P_4O_{13}$, which emits yellow luminescence upon NUV excitation, with a full width at half maximum (FWHM) of about 175 nm and nearly no absorption in the blue wavelength region. Moreover, the white light can be obtained by using the yellow-emitting high-$Ba_3P_4O_{13}$:Eu^{2+} phosphor, and the commercial blue-emitting $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM:Eu^{2+}) under NUV irradiation.

2. Experimental section

Samples of high-$Ba_{3-x}P_4O_{13}$:xEu^{2+} ($0.01 \le x \le 0.09$) investigated in this work were synthesized through solid state reactions. $BaCO_3$ (A. R.), $NH_4H_2PO_4$ (A. R.) and Eu_2O_3 (99.99%) were employed as raw materials. These raw materials in the desired ratio were mixed in an agate mortar by adding an amount of ethanol and then ground for 30 min. Finally, the mixture was fired at 900 °C under H_2/N_2 atmosphere for 8 h in an electric furnace. After firing, the samples were cooled to room temperature in the furnace and ground again into powders for subsequent use.

All measurements were made on finely ground powders. The phase purity of the samples was analyzed by X-ray diffraction (XRD) using a D2 PHASER X-ray diffractometer with Ni-filtered Cu Kα radiation. Diffuse reflectance spectra (DRS) of the samples were collected on finely ground samples by a UV–vis spectrophotometer (PE lambda950) using $BaSO_4$ as a reference in the range of 200–700 nm. Photoluminescence (PL) and PL excitation (PLE) spectra were measured at room temperature using an FLS-920T fluorescence spectrophotometer equipped with a 450 W Xe light source and double excitation monochromators. The PL decay curves were measured using an FLS-920T fluorescence spectrophotometer equipped with an nF900 nanosecond flash lamp as the light source. The quantum efficiency (QE) was measured by a Fluorlog-3 spectrofluorometer equipped with a 450 W xenon lamp (Horiba Jobin Yvon). High temperature luminescence intensity measurements were carried out by using an aluminium plaque with cartridge heaters; the temperature was measured by thermocouples inside the plaque and controlled by using a standard TAP-02 high temperature fluorescence controller.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-synthesized high-$Ba_{3-x}P_4O_{13}$:xEu^{2+} ($0.01 \le x \le 0.09$) samples, which match well with JCPDS file No. 12-0689, and no phase transformation, except for a small amount of impurities (*$Ba_2P_2O_7$ (JCPDS#30-0144) and #$Ba(PO_3)_2$ (JCPDS#43-0518)), which emit blue light when Eu^{2+} was doped [17,24]. It is also observed that the increase of x results in a high angle shift in the XRD patterns, due to smaller sized Eu^{2+} (1.09 Å) for larger Ba^{2+} (1.34 Å) [25], which strongly indicates that Eu^{2+} substituted Ba^{2+} sites.

Fig. 2 depicts the reflectance spectra of the undoped high-$Ba_3P_4O_{13}$ and Eu-doped high-$Ba_3P_4O_{13}$. Undoped high-$Ba_3P_4O_{13}$ shows high reflection in the visible range and a drop around 320 nm, which corresponds to the band transition of the host lattice. The intense reflection in the visible range is consistent with the observed white body color of the host sample. The Eu^{2+} doping introduces a strong absorption in the NUV range associated to its $4f^7$–$4f^65d^1$ transition. What's more, high-$Ba_3P_4O_{13}$:Eu^{2+} shows nearly no absorption in the blue region and this will avoid the reabsorption of the blue phosphor by the yellow phosphor in the LEDs.

Fig. 3 exhibits the excitation and emission spectra for various Eu^{2+} activator contents. The excitation spectra show a broad absorption from 300 to 420 nm, which corresponds to the $4f^7$-$4f^65d^1$ transition of the Eu^{2+} ions. As the concentration of Eu^{2+} increases, the excitation band in the NUV range becomes stronger than the UV range, indicating the application of the phosphors for

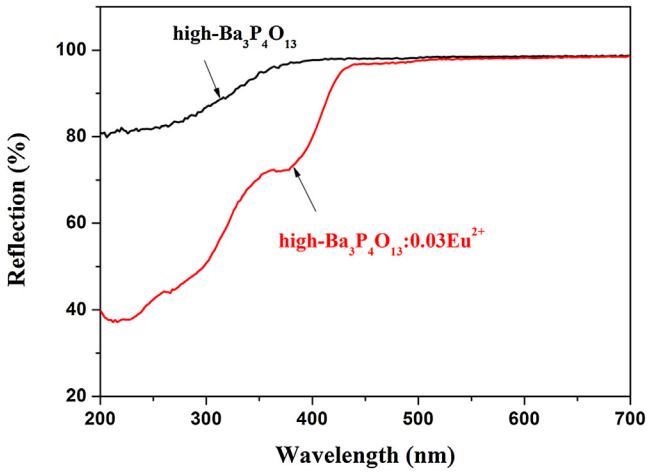

Fig. 2. DRS of doped and undoped high-$Ba_3P_4O_{13}$.

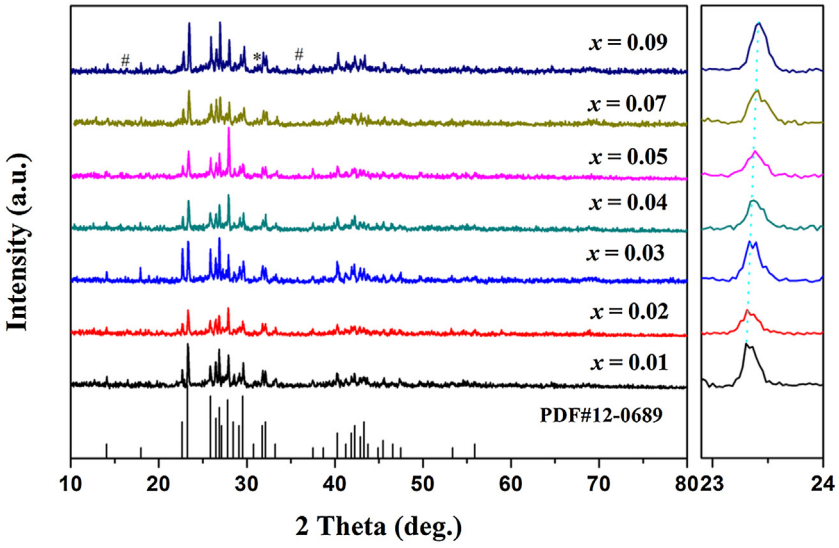

Fig. 1. XRD patterns of high-$Ba_{3-x}P_4O_{13}$:xEu^{2+} ($0.01 \le x \le 0.09$) samples.