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The room temperature photoluminescence properties of Eu^{3+}-doped bi-phase calcium phosphate under visible light

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Abstract The Eu-doped bi-phase calcium phosphate (BCP) phosphors with (Eu + Ca)/P = 1.1, 1.3, 1.5, and 1.6 were synthesized for the first time by the precipitation method. The BCP phosphors were investigated by the X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Photoluminescence (PL) spectra. The XRD and FTIR results indicated that BCP consisted of β-tricalcium phosphate and hydroxyapatite phases. The PL results showed the BCP phosphors fluoresced under three visible light bands (396, 463, and 535 nm) and the strongest emission spectrum was obtained at (Eu + Ca)/P = 1.3. The PL excitated at 463 nm showed the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} mainly generated three emission bands due to the $^7F_2$ energy level splitting.

Introduction

Apatites, with the general formula $M_5(PO_4)_3X$, where M = Ca, Sr, Ba, and Pb and X = F, Cl, Br, and OH, have been extensively studied for their technological applications such as phosphors [1], laser hosts [2], and biomaterials [3]. Among the apatites, hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) have received considerable interest as a bone graft substitute [3–5]. However, there are little reports on the photoluminescence (PL) property of stoichiometric HA [6–9].

β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$) is a host for the PL phosphors and several colors have been produced by using activators such as Cu^{+}, Ce^{3+}, Mn^{2+}, Sn^{2+}, and Eu^{2+} [1, 10, 11]. The solid solution in $Ca_3(PO_4)_2$–$EuPO_4$ system has been studied and the PL spectrum of Eu^{3+}-doped TCP was also reported at 90 K [12].

Both of Eu:HA and Eu:TCP emit intense red light. If they were compounded, their luminescence intensity would enhance and the scale of application would expand. The Ca-deficient hydroxyapatiter is a bi-phase ceramic with HA and TCP. When the Ca-deficient hydroxyapatiters of different ratio Ca/P have been calcined, the bi-phase ceramics including HA and TCP which are different ratio are gained [13].Thus, it is interesting to investigate the emission properties of Eu^{3+} in the bi-phase calcium phosphate (BCP). In this study, the phosphor of Eu^{3+}-doped bi-phase calcium phosphate was prepared by the precipitation method, and the luminescence properties were investigated, particularly focusing on the effects of (Eu + Ca)/P value on the PL characteristics at room temperature.

Experimental

All the reagents for synthesis including Eu_2O_3 (99.99%, Sinopharm Chemical Reagent Co., Ltd), H_3PO_4 (85%, Sinopharm Chemical Reagent Co., Ltd), HNO_3 (65%, Sinopharm Chemical Reagent Co., Ltd), ammonia (25%, Sinopharm Chemical Reagent Co., Ltd), anhydrous ethanol (99.7%, Sinopharm Chemical Reagent Co., Ltd), $(NH_4)_2HPO_4$ (98.5%, Sinopharm Chemical Reagent Co., Ltd), and $Ca(NO_3)_2{\cdot}4H_2O$ (AR, Bodi Co., Ltd). The doping concentration of Eu^{3+} was 1 mol% to Ca^{2+} in Eu^{3+}-doped bi-phase calcium phosphate, and was obtained by dissolving stoichiometrical Eu_2O_3 in dilute HNO_3 with vigorous stirring at 90 °C. An aqueous $Ca(NO_3)_2$ solution was slowly added to Eu $(NO_3)_3$ solutions. The H_3PO_3 was added to the mixed solutions containing Ca and Eu cations ((Eu + Ca)/P = 1.1, 1.3, 1.5, 1.6, 1.67). The pH value of

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the solution was adjusted to 10.6 using ammonia, and the solution was stirred intensely for 20 min at room temperature. Then, the solution was aged in a water bath of 95 °C for 24 h. The precipitate was filtered, washed with distilled water and anhydrous ethanol once, respectively, dried in an oven at 90 °C for 3 h, and calcined at 950 °C for 2 h.

For the preparation of TCP, the precipitation conditions were (Ca + Eu)/P = 1.5, Eu:Ca = 1:99, and pH = 6.5. The solutions were aged in a water bath of 40 °C for 24 h. The precipitate was filtered, washed with distilled water, dried in an oven at 80 °C for 24 h, and then calcined at 950 °C for 2 h.

The phase of the calcined powders was examined by X-ray diffraction(XRD, Rigaku Vtima II,Japan) using Cu K_α radiation($\lambda = 1.54056$ Å) at 40 kV and 40 mA between 2θ values of 20° and 60° with a step size of 0.02°. FT-IR spectra were recorded on a Nicolet Impact 420 Fourier transform infrared spectrometer (MIR, spectral rang 4000–400 cm^{-1}). PL spectra were measured at room temperature using a fluorescence spectrometer (970CRT, Shanghai Precision & Scientific Instrument Co., Ltd) equipped with a 150 W xenon lamp at a scanning speed of 600 nm/min and a sampling interval of 0.1 nm.

Results and discussion

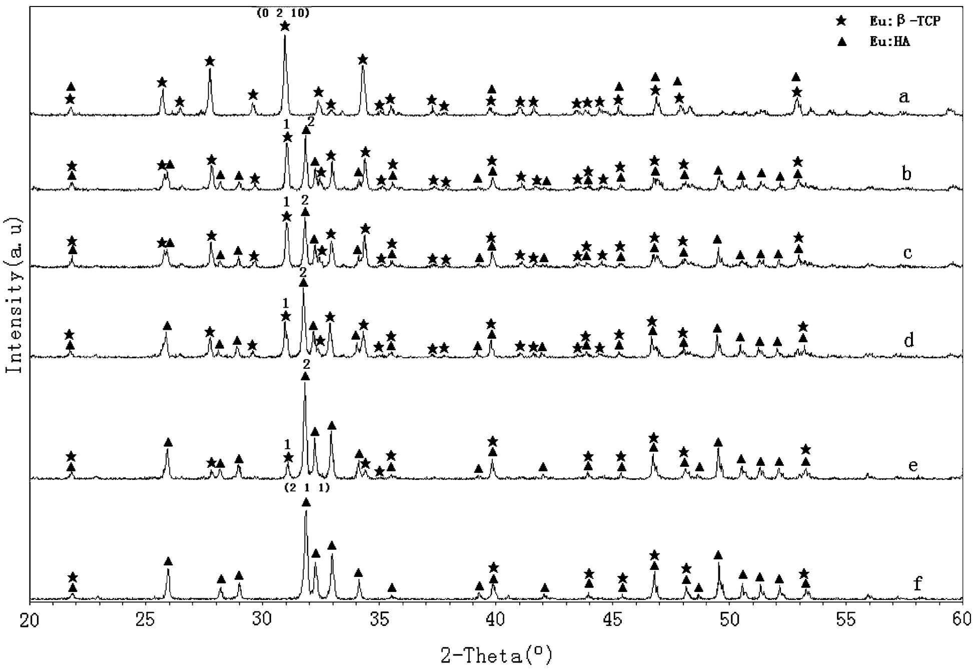
Chemical composition analysis of the products

Figure 1 showed the XRD patterns of Eu:β-TCP, Eu:BCP ((Eu + Ca)/P = 1.1, 1.3, 1.5, 1.6) and Eu:HA. As for Eu:β-TCP (Fig. 1a), the diffraction peaks could be well indexed to the trigonal β-$Ca_3(PO_4)_2$ in *R-3c* space group (Compared with the JCPDS cared No.09-0169. The peaks are marked by ★). In addition, as shown in Fig. 1f (Eu:HA), the diffraction peaks were assigned to HA, which was the hexagonal system in $P6_3m$ space group (Compared with the JCPDS card No.09-0432. The peaks are marked by ▲). In the case of the Eu^{3+}-doped BCP, there were two obvious characteristic peaks (which was marked by 1 and 2 in Fig. 1b–e), which represented (0 2 10) in TCP and (211) in HA, respectively. It implied different photoluminescence properties.

Figure 2 showed that the approximate ratio of the β-TCP/HAP was got via comparing the intensity of “1” and “2” characteristic peaks. With the increased value of (Eu + Ca)/P, the BCP phase transformed the HA phase gradually. When (Eu + Ca)/P = 1.3, the content of TCP phase was the most.

FTIR spectra of Eu:β-TCP, Eu:BCP ((Eu + Ca)/P = 1.1, 1.3, 1.5, 1.6) and Eu:HA were shown in Fig. 3. The bands at 3420 and 1641 cm^{-1} (H–O–H bond bending) showed the presence of surface water molecules, and the band at 3576 cm^{-1} indicated the existence of M–OH group [14]. In addition, the bands at 1094 and 1050 cm^{-1} could be attributed to P–O band. The 961 cm^{-1} band could be due to v_1 non-degenerated symmetric stretching of P–O bond [15]. The bands at 604 and 568 cm^{-1} were associated with the triply degenerated v_4 vibration of O–P–O bond [16]. Furthermore, with the value of (Eu + Ca)/P adding, the band intensity at 3576 cm^{-1} became high,which illuminated that the content of Eu:HAP added.

Fig. 1 XRD patterns of Eu:β-TCP (*a*), Eu:BCP ((Eu + Ca)/P = 1.1 (*b*), 1.3 (*c*), 1.5 (*d*), 1.6 (*e*)), and Eu:HA (*f*)



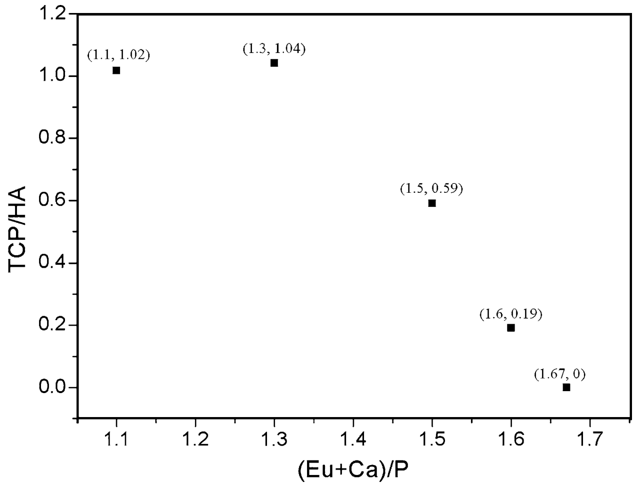


Fig. 2 The approximate ratio of the β-TCP/HAP in the DCP

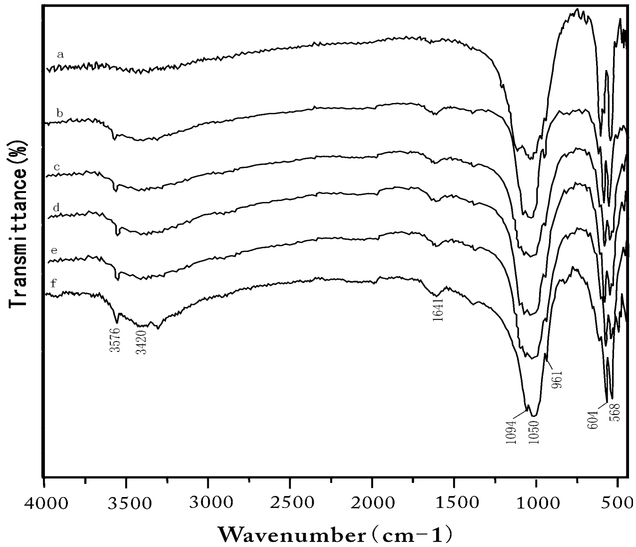


Fig. 3 FTIR spectra of Eu:β-TCP (*a*), Eu:BCP ((Eu + Ca)/P = 1.1 (*b*), 1.3 (*c*), 1.5 (*d*), 1.6 (*e*)), and Eu:HA (*f*)

Photoluminescence properties analysis of the products

Excitation spectra of Eu:TCP, Eu:BCP, and Eu:HAP were shown in the Fig. 4. These were obtained by monitoring to emission connected with Eu(III) $^5D_0 \rightarrow {}^7F_2$ transition at 614 nm. An intense broad band was noticed in the interval range of 350–430 nm. The maximum at 396 nm could be assigned to the charge transfer transition between Eu^{3+} and O^{2-} and the weak lines arise from f–f transitions within the Eu^{3+} $4f_6$ electron configuration. These peaks corresponded to the direct excitation of the Eu^{3+} ground state into higher levels of the 4f-manifold, which could be ascribed to $^7F_0 \rightarrow {}^5L_6$ (396 nm), $^7F_0 \rightarrow {}^5D_2$(463 nm), $^7F_0 \rightarrow {}^5D_1$(535 nm), respectively [17].

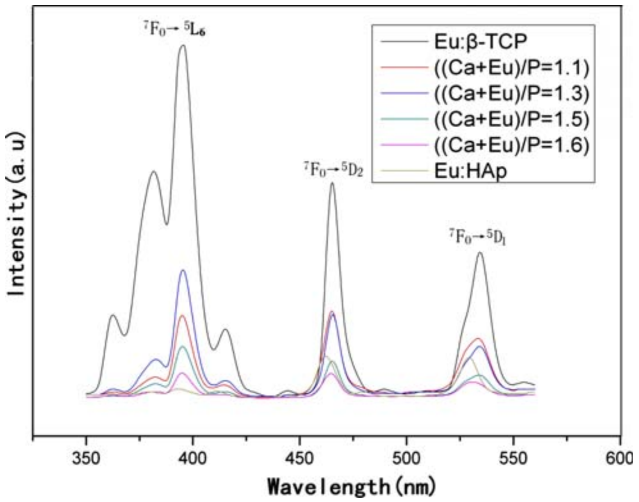


Fig. 4 Excitation spectra for Eu:TCP, Eu:BCP ((Eu + Ca)/P = 1.1, 1.3, 1.5, and 1.6), and Eu:HAP

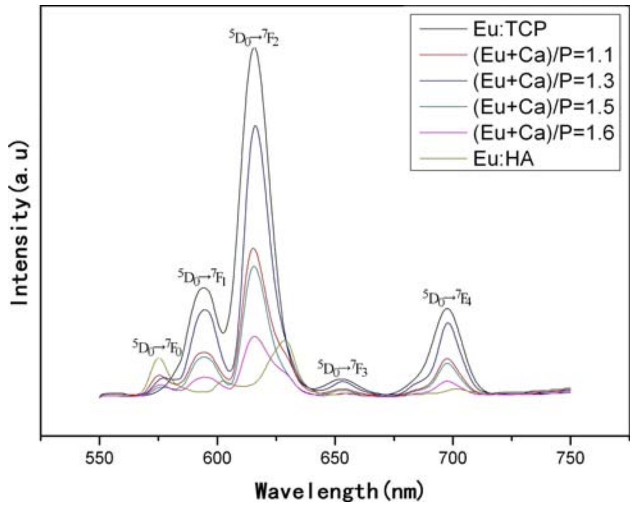


Fig. 5 Emission spectra of Eu:TCP, Eu:BCP, and Eu:HAP under 396 nm excitation

Figure 5 presented the emission spectra of Eu:TCP, Eu:BCP, and Eu:HAP under 396 nm excitation. Comparing Eu:BCP with Eu:TCP and Eu:HA, the emission spectra of Eu:BCP resembled the spectra of Eu:TCP. It was illuminated that the emission of Eu:BCP basically was the emission of Eu:TCP under near UV, which was reported by Lazoriak et al. [12]. The spectra were dominated by a bond at 614 nm, which attributed the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+}. Other weak band at 575 nm ($^5D_0 \rightarrow {}^7F_0$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), 655 nm ($^5D_0 \rightarrow {}^7F_3$), and 697 nm ($^5D_0 \rightarrow {}^7F_4$) were ascribed to f–f transitions of Eu(III) ions.

The spectra of Eu:TCP, Eu:BCP, and Eu:HAP under the excitation of $\lambda_{exc} = 463$ nm were shown in Fig. 6. Generally, the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} is partial

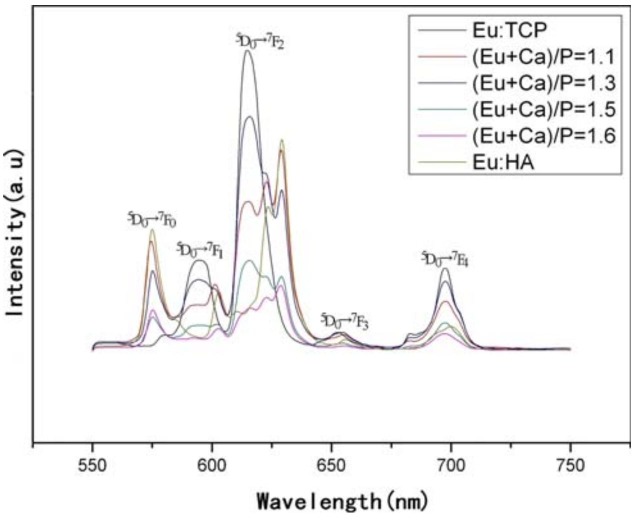


Fig. 6 Emission spectra of Eu:TCP, Eu:BCP, and Eu:HAP under 463 nm excitation

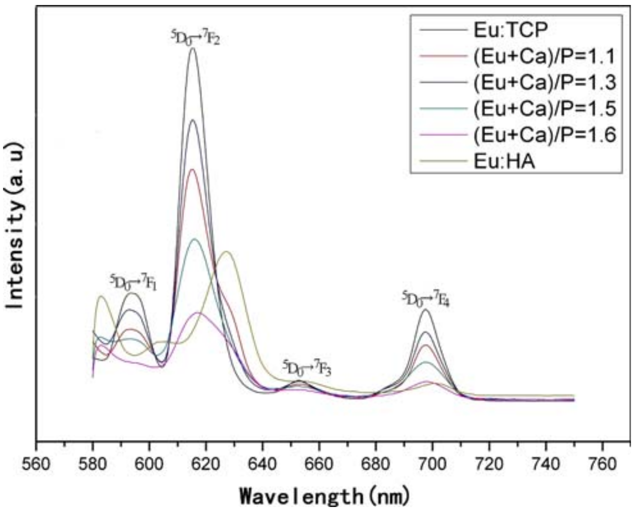


Fig. 7 Emission spectra of Eu:TCP, Eu:BCP, and Eu:HAP under 535 nm excitation

forbidden, but when Eu^{3+} ions occupy one of the C_s, C_n ($n = 1$, 2, 3, 4, and 6) and C_{nv} ($n = 2$, 3, and 6) sites, the partial forbidden will partially permitted. Thus, a $^5D_0 \rightarrow {}^7F_2$ transition could be observed [18]. Therefore, the site and the number of $^5D_0 \rightarrow {}^7F_2$ transition peaks would correspond to the C_s or C_n or C_{nv} site in luminescent material [19–22]. In case of Eu:BCP, the $^5D_0 \rightarrow {}^7F_2$ emission spectra showed three peaks at 615, 623, and 629 nm. The peak of 615 nm was existed because the Ca^{2+} site is occupied by the Eu^{3+} ions in TCP. The other two peaks were associated with the $^5D_0 \rightarrow {}^7F_2$ transition emission of Eu^{3+} ions in Ca(II) and Ca(I) sites of HA, respectively. More interestingly, superficial red shifts of this $^5D_0 \rightarrow {}^7F_2$ transition were observed with the HAP phase increasing in BCP.

Figure 7 showed the emission spectra of Eu:TCP, Eu:BCP, and Eu:HAP under 535 nm excitation. There were 4 emission bands in Eu:BCP, which were 595, 615, 655, and 698 nm, respectively. They attributed the emission transition of $^5D_0 \rightarrow {}^7F_j$ ($j = 1$, 2, 3 and 4). With the value of (Eu + Ca)/P increasing, the band of $^5D_0 \rightarrow {}^7F_2$ became broad because of the emission peak of Eu:HAP existing.

Via investigating the three emission spectra of Eu:BCP, it was observed that the emission of Eu:BCP changed with the value of (Eu + Ca)/P changing. When (Eu + Ca)/P = 1.3, the emission intensity of Eu:TCP was the maximum, because the content of Eu:TCP was the most in Eu:BCP, which accorded with the result of XRD in Eu:BCP. As the value of (Eu + Ca)/P becoming high, the emission spectra transformed from Eu:BCP to Eu:HAP. In Fig. 6, when (Eu + Ca)/P < 1.3, the content of Eu:HAP increased and the content of Ca(I), Ca(II) vacancy increased [13], so the content of Eu^{3+} occupying the Ca(I) vacancy increased. There was intensive emission spectra under 463 nm excitation in Eu:HAP, thus, when (Eu + Ca)/P = 1.1, the emission intensity of 629 nm became high.

Conclusion

Novel Eu-doped BCP phosphors composed of Eu:β-TCP and Eu:HA were successfully prepared by a co-precipitation method. XRD results displayed that Eu:BCP included a β-tricalcium phosphate phase and a hydroxyapatite phase. The analysis of PL showed that Eu:BCP could fluoresce under three visible light bands which were 396, 463, and 535 nm, respectively. The spectra under the excitation of 463 nm showed the main $^5D_0 \rightarrow {}^7F_2$ transition engender three emission peaks due to the $^7F_2$ energy level splitting many levels. Two bands at 629 and 623 nm were resulted from the Eu^{3+} substitution at Ca(I) and Ca(II) sites of HA, respectively, however, another band at 615 nm was arose from the Eu^{3+} substitution at Ca^{2+} sites of TCP. The different ratios of (Eu + Ca)/P were investigated, and it was found that the emission intensities of Eu:BCP during $^5D_0 \rightarrow {}^7F_2$ transition increased with the increase of the contents of Eu:TCP, and in the case of (Eu + Ca)/P = 1.3, both the content of the β-TCP phase and the emission intensity reached the maxima. Rich fluorescence bands and strong fluorescence intensity within the scope of visible light imply a potential prospect in the photoluminescence field.

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