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Tunable single-host full-color-emitting $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb phosphor via Eu^{2+}/Eu^{3+} dual-emitting

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ABSTRACT

A series of $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb phosphors were prepared by solid-state reaction method under reductive atmosphere. The crystal structure and morphology of the phosphors were characterized by the X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The results showed that the phosphors were pure and the doped ions did not change the structure of phosphors. Photoluminescence results indicated that $Ca_9Zn_{1.5}(PO_4)_7$: Eu shows a sharp blue emission peaking at 420 nm that was produced by 4f-5d transition of Eu^{2+}, and accompanied by the emission of Eu^{3+} under UV excitation. The phosphor of $Ca_9Zn_{1.5}(PO_4)_7$: Tb shows that peaks within 370–380 nm correspond to the $^7F_6 \rightarrow {}^5D_3$, $^5G_6$, and $^5L_{10}$ transitions. Additionally, the corresponding CIE color coordinate of $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb changes from (0.2548, 0.087) to (0.3365, 0.3117) due to the energy transfer of $Eu^{2+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$, which covering the purple to white region. Based on these summary, $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb is a potential single-host white light emitting phosphor applied in WLEDs.

1. Introduction

White light-emitting diodes (WLEDs) are considered as the most promising solid-state light sources because of their outstanding properties of high energy efficiency, long lifetime, light stability and environmental friendliness, and they are used extensively in displays, flashlights, machine vision, etc [1–3]. The formation of phosphors with single phase is one of the important factors because of their excellent color rendering indexes and the electro-optical design being simple to control the different colors in comparison to mixed phosphors [4].

In recent years, whitlockite β-$Ca_3(PO_4)_2$ host has been studied due to its versatile structural as well as the tunable luminescence behaviors doped with rare earth [5,6]. For the β-$Ca_3(PO_4)_2$ phase, five kinds of cationic sites are conventionally labeled by Ca(1), Ca(2), Ca(3), Ca(4) and Ca(5), and the coordination numbers are seven for Ca1, eight for Ca2 and Ca3, three for Ca4, and six for Ca5, respectively [7,8]. Accordingly, the five kinds of Ca sites are completely filled, but Ca(4) is occupied by 50% Ca^{2+} ions and 50% vacancies [9]. Herein, β-$Ca_3(PO_4)_2$ can be also written as β-$Ca_{21}(PO_4)_{14}$, and through different ion substitutions into the initial β-$Ca_3(PO_4)_2$, many new phase with β-$Ca_3(PO_4)_2$-type structure can be constructed [7,10]. For example, when two univalent metal M^+ ions are substituted for one divalent Ca^{2+} ion, the β-$Ca_{20}M_2(PO_4)_{14}$ host can be obtained, namely, $Ca_{10}M(PO_4)_7$. Furthermore, two trivalent metal R^{3+} ions can replace three divalent Ca^{2+} ions with final composition β-$Ca_{18}R_2(PO_4)_{14}$, namely, $Ca_9R(PO_4)_7$ [11]. The substitution algorithm yielded a large number of new phosphors with β-$Ca_3(PO_4)_2$-type structure, such as the reports on $Ca_{10}M(PO_4)_7$:Eu^{2+} (M = Li, Na, and K) [12,13], color-tunable $Ca_9R(PO_4)_7$:Eu^{2+}, Mn^{2+} (R = La, Gd, Lu and Y) [14–18], red-emitting $Ca_8MgLa(PO_4)_7$:Ce^{3+}, Mn^{2+} [19], yellow-emitting $Sr_{1.75}Ca_{1.75}(PO_4)_2$ phosphors [20], and so on.

Generally, a solid state compound involving two or more sites, which luminescent center ions (such as Eu^{2+}, Eu^{3+}, Tb^{3+}) can occupy, will be challenging for photoluminescence tuning [21]. The Eu^{2+} usually generates strong emission from blue to green region due to the dipole allowed 4f-5d electronic transition, and Eu^{3+} has characteristic transition emission from orange to red region because of the 4–4f parity-forbidden transition [22–24]. The Tb^{3+} is well known as a green emitting activator due to its predominant $^5D_4$-$^7F_5$ transition [25]. Moreover, Eu^{2+} ion can cause small energy difference between the $4f^65d^1$ and $4f^7$ states and it is considered to be a good candidate to transfer its energy to Tb^{3+} [26–29]. In addition, Tb^{3+} ion is considered to be an appropriate candidate due to the matched energy levels between the $^5D_4$ state of Tb^{3+} and the $^5D_{1,2}$ state of Eu^{3+} [30]. So, Eu and Tb co-doped single-host phosphors can realize full-color-emitting tuning from blue to red [31,32]. To the best of our knowledge, a great deal of work has been done on the partial reduction of Eu^{3+} and stabilization of both Eu^{3+} and Eu^{2+} in a single-host lattice. Therefore, in analogy to the $Eu^{2+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is of great interest by the introduction of a mixed valence of Eu elements [33]. Direct

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Table 1
All the prepared composition parameter of $Ca_{9-x-y}Zn_{1.5}(PO_4)_7$: xEu, yTb.

Sample Number	$Ca_{9-x-y}Zn_{1.5}(PO_4)_7$: xEu, yTb (x, y)/mol
1	x = 0, y = 0
2	x = 0.02, y = 0
3	x = 0.04, y = 0
4	x = 0.06, y = 0
5	x = 0.08, y = 0
6	x = 0.10, y = 0
7	x = 0.12, y = 0
8	x = 0.14, y = 0
9	x = 0, y = 0.05
10	x = 0, y = 0.10
11	x = 0, y = 0.15
12	x = 0, y = 0.20
13	x = 0, y = 0.25
14	x = 0, y = 0.30
15	x = 0, y = 0.35
16	x = 0.08, y = 0.05
17	x = 0.08, y = 0.10
18	x = 0.08, y = 0.15
19	x = 0.08, y = 0.20
20	x = 0.08, y = 0.25
21	x = 0.08, y = 0.30

sensitization of Eu^{3+} luminescence by Eu^{2+} is inefficient due to the metal-metal charge transfer (MMCT) quenching [33].

Based on these reasons, in our present paper, we have prepared a series of Eu and Tb single-doped or co-doped $Ca_9Zn_{1.5}(PO_4)_7$ phosphors with β-$Ca_3(PO_4)_2$-type structure, which have many good properties, such as stability, easy method, cheap raw materials, etc. The emission color of $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb varies from purple to white by changing the relative doped ratio of Eu/Tb. Moreover, the crystal structure, photoluminescence properties and energy transfer mechanism of phosphors are investigated.

2. Experimental

A series of $Ca_9Zn_{1.5}(PO_4)_7$: Eu, Tb phosphors were prepared by conventional solid-state reaction method under reductive atmosphere. The parameters of all prepared composition are summarized in the Table 1. The raw materials were $CaHPO_4$ (A.R.), $CaCO_3$ (A.R.), ZnO (A.R.), Eu_2O_3 (99.99%) and Tb_4O_7 (99.99%). Stoichiometric amounts of staring materials were thoroughly mixed in an agate mortar by grinding and sintered at 1400 °C in reductive atmosphere (5%H_2/95% N_2) for 2 h. The heating rate was controlled at 6–7 °C/min. Finally, all of the as-synthesized samples were ground into powders and collected for further measurements.

The X-ray diffraction (XRD) pattern was collected on an X-ray diffraction (Bruker Axs D2 PHASER diffractometer) with Cu K_α radiation (λ = 1.5405 Å) ranging from 10° to 80°. The chemical composition was examined by X-ray photoelectron spectroscopy (XPS). The morphology and elemental analysis were characterized by scanning electronic microscopy (SEM). The interplanar crystal spacing was carried out by transmission electron microscope (TEM, HitachiH-9500). The diffuse reflectance spectra were analyzed with a Shimadzu UV-3600 UV–Vis spectrometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were examined by a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source. The luminescence decay was measured using a spectral LED (370 nm) of a pulsed Nd: YAG laser. The thermal stability of luminescence was recorded on an EX 1000 spectrometer (EVERFINE PHOTO).

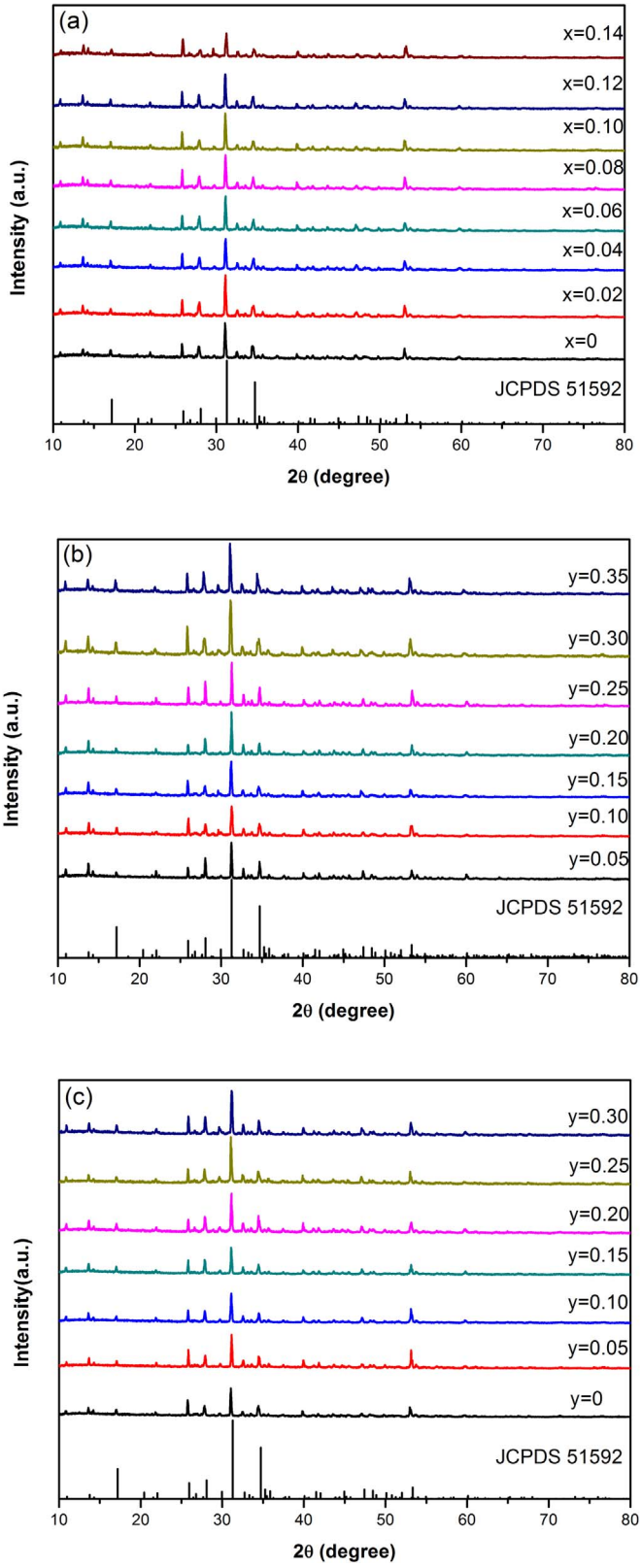

Fig. 1. (a) Representative powder XRD profiles of $Ca_{9-x}Zn_{1.5}(PO_4)_7$: *x*Eu (*x* = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12 and 0.14) together with the standard data of $Ca_9Cu_{1.5}(PO_4)_7$ (JCPDS card No.51592); (b) Representative powder XRD profiles of $Ca_{9-y}Zn_{1.5}(PO_4)_7$: *y*Tb (*y* = 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 and 0.35) together with the standard data of $Ca_9Cu_{1.5}(PO_4)_7$ (JCPDS card No.51592); (c) Representative powder XRD profiles of $Ca_{8.92-y}Zn_{1.5}(PO_4)_7$: 0.08Eu, *y*Tb (*y* = 0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.30) together with the standard data of $Ca_9Cu_{1.5}(PO_4)_7$ (JCPDS card No.51592).