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Concentration induced site symmetry transformation of Eu^{3+} luminescence center in β-$Ca_2P_2O_7$

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ABSTRACT

A series of high brightness orange-red phosphors β-$Ca_{2-x}P_2O_7$:xEu^{3+} (x = 0.02, 0.04, 0.06, 0.08, 0.10, 0.12) were synthesized via solid state reaction in air atmosphere. The phase, morphology, photoluminescence properties and fluorescent thermal stability of the obtained phosphors were investigated. The chromaticity coordinates of the samples were calculated and located in the orange-red region. The intense emissions at 585, 591 nm ($^5D_0 \rightarrow {}^7F_1$), 610 nm ($^5D_0 \rightarrow {}^7F_2$) were observed under NUV excitation. Furthermore, the ratio of the emission of $^5D_0 \rightarrow {}^7F_2$ transition to that of $^5D_0 \rightarrow {}^7F_1$ transition changed dramatically with varied Eu^{3+} concentration, indicating the existence of the site symmetry transformation of Eu^{3+} luminescence center in the matrix. The phosphors performed excellent properties at 423 K with temperature quenching at 473–573 K, and may be potential orange-red phosphor in lighting field.

1. Introduction

Alkaline earth pyrophosphates with general formula $M_2P_2O_7$ (M = Ca, Sr, Ba) containing rare earth ions are considered to be one of the most desirable phosphate phosphors because of their excellent properties, such as low synthesis temperature (compared with other matrix), chemical and thermal stabilities, low cost as well as environmental friendliness, and are therefore regarded as important luminescence materials [1]. In recent years, much research has been done to explore the luminescence properties and potential applications of those phosphors. Xu et al. [2] synthesized $Sr_2P_2O_7$:Eu^{3+} orange-red phosphors by introducing Gd^{3+} at 1100 °C, which was demonstrated to play an important role in improving the luminescence properties of Eu^{3+} in the system. Pang et al. [3] investigated the long-lasting phosphorescence (LLP) blue phosphors α-$Ca_2P_2O_7$:Eu^{2+},Y^{3+}, which was calcined at 1250 °C, the co-doping of Y^{3+} was suggested to be electron traps to improve the performance of the blue phosphorescence of Eu^{2+} such as intensity and persistent time, while the emission intensity slightly decreased on the luminescence spectrum. Ta and Chen [4] synthesized β-$Ca_2P_2O_7$:Eu^{2+} blue phosphors by combustion method at different temperature ranging from 700–1050 °C, the morphology and luminescence properties of the obtained phosphors were studied in detail. Ye et al. [5] successfully synthesized $Sr_2P_2O_7$:Eu^{2+},Mn^{2+} at 1050 °C, which was thought to have potential applications in white light-emitting diodes (W-LEDs) owing to its simultaneous bright blue and orange-red emissions.

Nowadays, many attentions are paid on the W-LEDs for their high luminous efficiency, energy-saving, environmental friendliness, long life, good color rendering, low temperature-rising and convenience using. There are basically three ways to generate W-LEDs. The first approach is to combine blue, green, red LED chips. The second approach is to combine a blue LED chip with a yellow phosphor yttrium aluminum gamet (YaG:Ce^{3+}), which has been widely used in business. However, this kind of W-LED cannot generate warm white light due to the absence of the red light component. The problem can be solved by the third approach, which is to combine a UV chip with blue, green, red phosphors. Of course, the third approach is considered to be the most promising one because of simple apparatus, high color rendering index and energy efficiency [6].

The luminescence behavior of phosphors not only depends on the luminescence center (the rare earth ions), but also influenced a lot by the chemical composition of the matrix and the crystal field environment. Among the rare earth ions species, Eu^{3+} ion is well known for its red emission at 590 nm and 610 nm due to the

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magnetic dipole transition of $^5D_0 \rightarrow {}^7F_1$ and electric dipole transition of $^5D_0 \rightarrow {}^7F_2$, respectively [7]. It can be efficiently excited under near ultraviolet (NUV) light in various hosts, such as Y_2O_2S:Eu^{3+} [8], Sr_3WO_6:K^+,Eu^{3+} [9], $LaBWO_6$:Eu^{3+} [10], $CaMoO_4$:Eu^{3+} [11], $CaSrAl_2SiO_7$:Eu^{3+} [12], $Ba_2B_2O_5$:Eu^{3+} [13], $Ca_3(PO_4)_2$:Eu^{3+} [14], etc., where Y_2O_2S:Eu^{3+} as the commercial red phosphors, holds comparatively high luminescence efficiency but poor chemical stability. Thus, finding novel red phosphors that exhibit excellent performance is imperative. Based on the great interest of rare earth pyrophosphate red phosphors, the traditional high-temperature solid-state method was applied to prepare $Ca_{2-x}P_2O_7$:xEu^{3+}. The phase, morphology, photoluminescence and fluorescent thermal stability were systematically investigated. And the emission spectra of $Ca_{2-x}P_2O_7$:xEu^{3+} shows a unique phenomenon that the predominant peak changes while the Eu^{3+} concentration varies, indicating the existence of the site symmetry transformation of Eu^{3+} luminescence center in $Ca_2P_2O_7$, compared with that of $Sr_2P_2O_7$ and $Ba_2P_2O_7$.

2. Experimental

2.1. Sample synthesis

The phosphors $Ca_{2-x}P_2O_7$:xEu^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12), $Sr_{2-x}P_2O_7$:xEu^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10) and $Ba_{2-x}P_2O_7$:xEu^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10) were prepared through high-temperature solid-state reaction. Raw materials are $CaCO_3$, $SrCO_3$, $BaCO_3$, $(NH_4)_2HPO_4$ (analytical grade), Eu_2O_3 (99.99%). Stoichiometric mixtures of the starting materials are homogeneously ground in an agate mortar, and then sintered at 1050 °C for 2 h in air atmosphere. After cooling down to room temperature, the mixtures were regrind and the final samples were obtained for subsequent use.

2.2. Characterization

X-ray powder diffraction (XRD) measurements were performed on a Rigaku D/Max-3c X-ray Powder Diffractometer in the 2θ range from 10–60°, with Cu K_α radiation (λ = 1.5418 Å) at 40 kV, 40 mA. Transmission electronic microscopy (TEM) analysis was taken on a FEI Technai G2F20 device transmission electron microscopy using an accelerating voltage of 200 kV. The excitation and emission spectra were recorded on a HORIBA Fluoromax-4 Spectrofluorometer equipped with a 150 W xenon lamp as the excitation source. And the fluorescent thermal stability was also analyzed on the Spectrofluorometer with a TAP-02 high temperature fluorescence controller.

3. Results and discussion

3.1. Phase analysis

Fig. 1a shows the XRD patterns of $Ca_{2-x}P_2O_7$:xEu^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12) sintered at 1050 °C for 2 h. It is observed that the main diffraction peaks of the samples match well with the phase of β-$Ca_2P_2O_7$ registered in JCPDS file 09-0346, which crystallizes in tetragonal space group of $P4_1$, indicating that these samples are single phase when the doping concentration of Eu^{3+} is low. The Eu^{3+} ion is expected to substitute Ca^{2+} site according to the fact that the radius of Eu^{3+}(9) (0.1120 nm) is close to that of Ca^{2+}(9) (0.118 nm) instead of P^{5+}(4) (0.017).

The magnified XRD patterns in the 2θ range from 29.2–29.8° are illustrated in Fig. 1b. It is observed that the dominant peaks corresponding to (0 0 8) slightly shift between 0–6% (mol fraction) Eu^{3+}-doped $Ca_2P_2O_7$ (line 1–7). Because the radius of Eu^{3+} is smaller than that of Ca^{2+}, the substitution of Ca^{2+} by Eu^{3+} will result in a peak shift to higher angle. For 1% Eu^{3+}-doped $Ca_2P_2O_7$ (line 2), the shift of (0 0 8) peak to higher angle is almost imperceptible. It is considered that 1% doping ion of Eu^{3+} makes no significant change

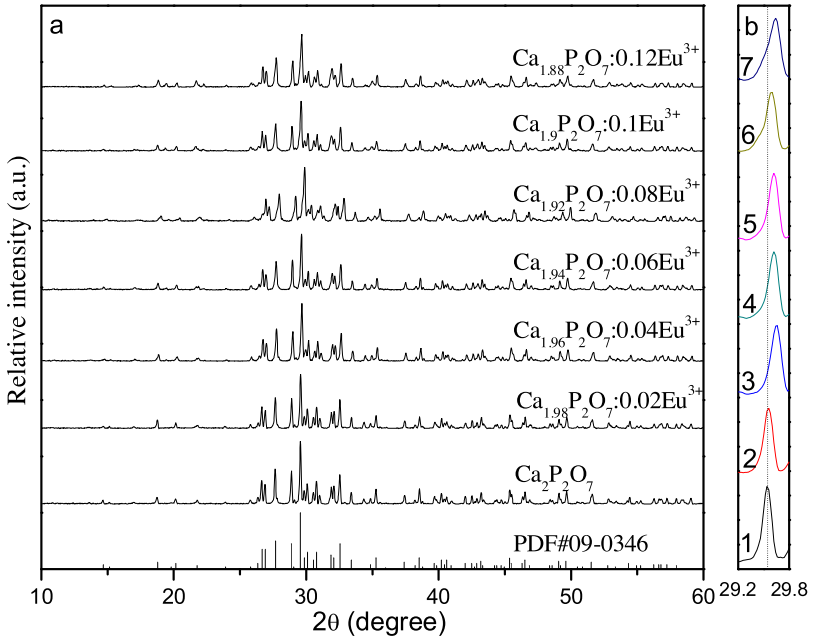

Fig. 1. (a) XRD patterns of $Ca_{2-x}P_2O_7$:xEu^{3+} (x = 0, 0.02, 0.04, 0.06, 0.08, 0.10, 0.12) sintered at 1050 °C for 2 h; (b) magnified XRD patterns in the 2θ range from 29.2–29.8° of 0–6% Eu^{3+}-doped $Ca_2P_2O_7$ (line1–7).