

Fluorescence and preparation of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ phosphate by co-precipitation method

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Abstract The micron-sized $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ green phosphors were prepared by being annealed at different temperatures with its precursors synthesized by co-precipitates of $(\text{NH}_4)_2\text{HPO}_4$ at ambient temperature. The phase structure, grain size, surface morphology, and luminescent properties of phosphors were investigated by X-ray diffraction, scanning electron microscope, transmission electron microscope, and fluorescence spectrum. The results show that the product of precursor annealed at 1,100 °C is $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$, which belongs to orthorhombic phase. The powder is spherical and the size distribution is in micron grade. The sample with the molar ratio of Sr/Tb/Ce of 100.0:0.4:0.6 shows the best fluorescence effect annealed at 1,100 °C for 3 h. The phosphors produce green fluorescence by being excited with ultraviolet radiation of 254 nm wavelength, and the main emission peak is at 547 nm. The $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ phosphors synthesized by co-precipitation method of precursors at ambient temperature is a kind of efficient green-emitting phosphors.

Keywords Phosphors; Co-precipitation method; Rare earth phosphate; Phosphorescence

1 Introduction

Fluorescent lamp possesses outstanding features for its good fluorescence efficiency with high light intensity, saving energy, long life time, low heat productivity, and is

the most widely used in daily life for the common people [1–4]. The key component of fluorescent lamp is the luminescent materials, which has the important influence on the light intensity of fluorescent lamp [5–7]. The phosphate phosphors have a long history of development in luminescent materials. It is easily synthesized with low cost raw material and exhibits high fluorescence performance, so it is applied in fluorescent lamp with these advantages [8, 9]. In recent years, special attention has been drawn on the synthesis and potential applications of certain luminescent phosphor materials doped with rare earth ions sensitizing agent to form active centers [10–13]. Structural details and processes involving in the excitation multiplication for some 4f–4f and 5d–4f transitions of doped optical systems were investigated [14, 15]. The main methods to prepare the luminescent materials are high temperature solid state, sol–gel, combustion, hydrothermal, and co-precipitation, etc. The industrial production of luminescent materials is high temperature solid phase method; however, it is highly energy-consuming due to the high reaction temperature and long reacting time. The co-precipitation does not have these shortcomings, which is the most economical method. In this paper, the micron-sized $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ green phosphors were prepared by being annealed at different temperatures with its precursors synthesized by co-precipitates of $(\text{NH}_4)_2\text{HPO}_4$ at ambient temperature. The phase structure, size, morphology, and luminescent properties of phosphors were investigated.

2 Experimental

In a typical synthesis process, $\text{Ce}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ was added to the solution of $\text{Sr}(\text{NO}_3)_2$ to make a mixed solution with the concentration of $0.5 \text{ mol}\cdot\text{L}^{-1}$. The molar ratio of

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Sr(NO₃)₂/Ce(NO₃)₃ and Tb(NO₃)₃ is 100:1, and the molar ratio of Ce(NO₃)₃/Tb(NO₃)₃ are 1:1, 2:3, or 3:2, respectively. The transparent precursor solution was magnetically stirred for 5 h at room temperature. The solution of (NH₄)₂HPO₄ was slowly added into the former solution with the vigorous stirring, and then the transparent precursor solution became turbid. The solution of NH₃·H₂O was slowly added in vigorous stirring to adjust pH value to 7. After being aged at room temperature for about 2 h, the white precipitate was separated by centrifuging and washing several times with de-ionized water. After drying the samples at room temperature, they were annealed at different temperatures of 900, 1000, 1100, and 1200 °C in weak reducing atmospheres for 2, 3, and 4 h, respectively.

The product phase was identified by X-ray diffraction (XRD, Model D/max-2200PC, Rigaku, Tokyo, Japan) using Cu K α radiation. A FEI Sirion200 scanning electron microscope (SEM) was used for morphological analysis of the samples. The photoluminescence spectra of the powder phosphor were measured by a fluorescence spectrophotometer (Model RF-5301, Shimadzu, Japan) at room temperature.

3 Results and discussion

3.1 Phase characterization

Figure 1 shows the XRD pattern of the synthesized Sr₂(P₂O₇):Ce,Tb (molar ratio of Ce/Tb = 2:3) sample. The XRD pattern agrees well with JCPDF 12-362, which shows the product is a single phase of Sr₂(P₂O₇) and belongs to orthorhombic crystal system. The sharp diffraction peaks imply that the particles are highly crystalline. The lattice

parameters calculated from the XRD measurement are $a = 89.10$ nm, $b = 54.04$ nm, and $c = 131.00$ nm.

3.2 SEM characterization

Figure 2 shows the SEM images of the Sr₂(P₂O₇):Ce,Tb (molar ratio of Ce/Tb = 2:3) powder phosphor by annealed at different temperatures. The powder consists of spherical crystals with a uniform size of 2 μ m in length annealed at 900 and 1,000 °C. Spherical crystals have a uniform size of 3–4 μ m in length annealed at 1,100 °C, but the shape of crystals changes and grain sizes increase obviously annealed at 1,200 °C. At high temperature, overburning may occur and leads to liquefy the crystals and recrystallize.

3.3 Fluorescence performance

Figure 3 presents the excitation spectrum of Sr₂(P₂O₇):Ce,Tb (molar ratio of Ce/Tb = 2:3) phosphor annealed at 1,100 °C with an excitation band at 254 nm. The emission bands of 486, 542, 584, and 625 nm are attributed to ⁵D₄ → ⁷F₆, ⁵D₄ → ⁷F₅, ⁵D₄ → ⁷F₄, ⁵D₄ → ⁷F₃ of transition of 4d⁵ level of Tb³⁺, respectively. The energy level transition of ⁵D₄ → ⁷F₆ leads to energy level splitting, which is attributed to outermost electrons of Tb³⁺ being influenced by the crystalline field shown in Fig. 3. The emission band of Ce³⁺ does not appear, because that Ce³⁺ undertake the sensitization, which can enhance the luminescent intensity of Tb³⁺.

Figure 4 presents the excitation spectrum of Sr₂(P₂O₇):Ce,Tb (molar ratio of Ce/Tb = 2:3) phosphor annealed at different temperatures (between 900 and 1,200 °C) for 4 h with an excitation band at 254 nm. From

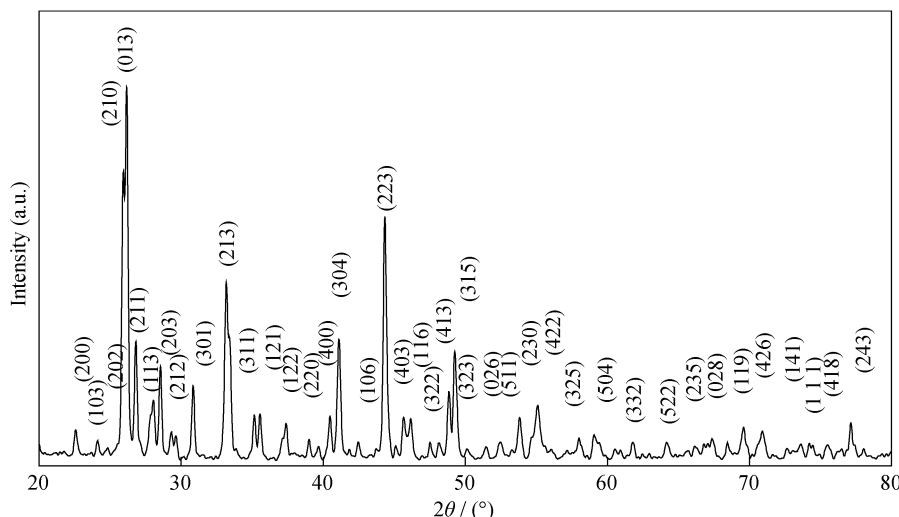


Fig. 1 XRD pattern of Sr₂(P₂O₇):Ce,Tb powder

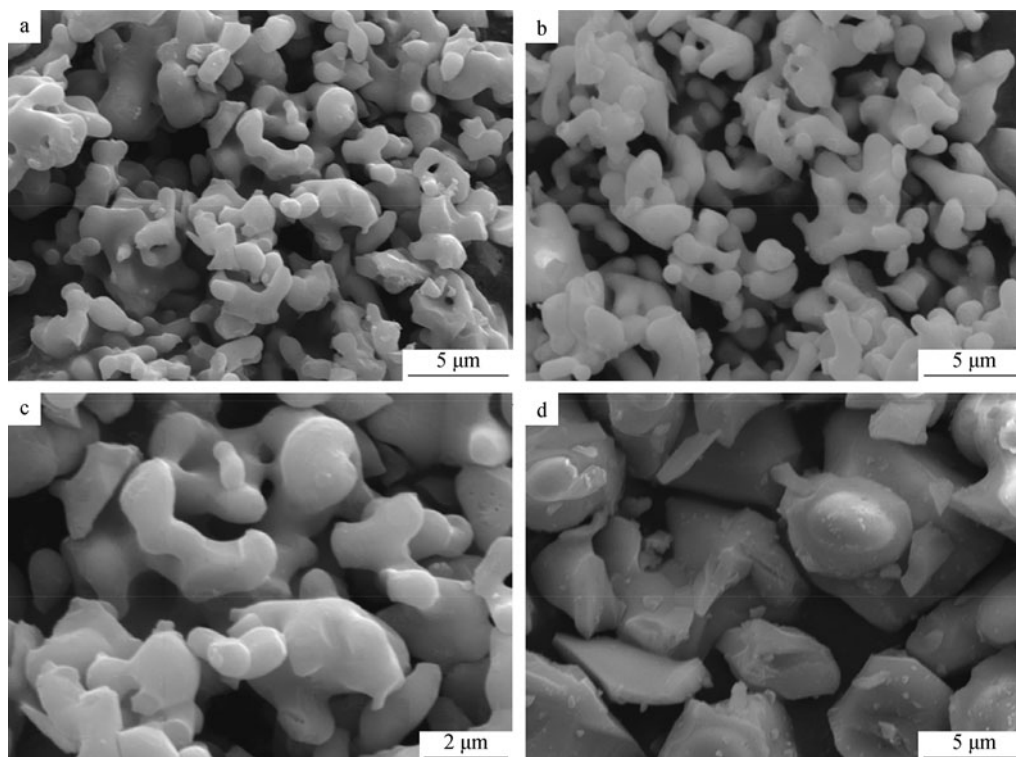


Fig. 2 SEM images of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ annealed at different temperatures for 4 h: **a** 900 °C, **b** 1,000 °C, **c** 1,100 °C, and **d** 1,200 °C

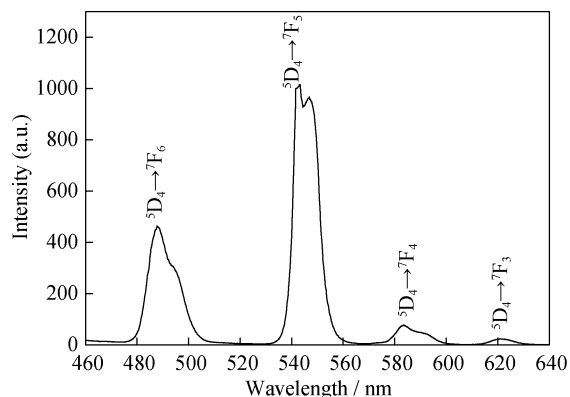


Fig. 3 Excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ powder phosphor

Fig. 4, we find that the sample prepared at 1,100 °C exists the maximum green emission intensity. Fluorescence intensity of samples improves with annealed temperature in the sintering temperature range. But overburning can lead to the crack of crystal lattice, liquefy the crystalline phase and the imperfection escalation on the high temperature, which result in decreased fluorescent strength.

The excitation spectra were measured with the samples annealed for different time (2, 3, and 4 h, respectively). Figure 5 presents the excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ (molar ratio of $\text{Ce}/\text{Tb} = 2:3$) phosphor prepared at 1,100 °C for different time. According to Fig. 5, luminous

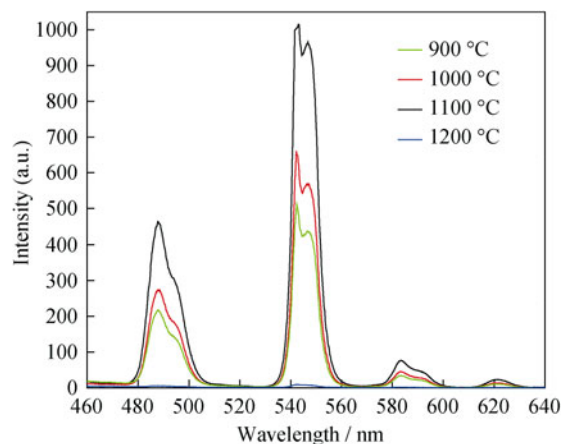


Fig. 4 Excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ phosphor annealed at different temperatures

intensity increases with the increase of annealing time. The luminous performance can be influenced by the crystalline degree of sample. At high annealing temperature, the crystalline degree enhances with the annealed time.

Figure 6 presents the excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7):\text{Ce},\text{Tb}$ phosphor at different doping molar ratios of Ce/Tb . From Fig. 6, the relative fluorescence intensity increases with the Tb^{3+} doping content. It can be concluded that more doping content of Tb^{3+} can increase the fluorescence performance.

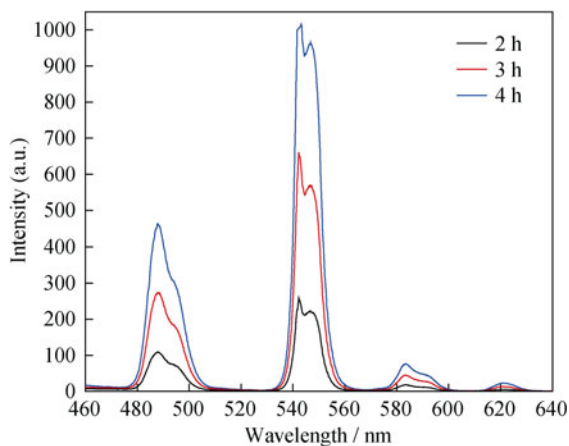


Fig. 5 Excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphor annealed at $1,100^\circ\text{C}$ for different time

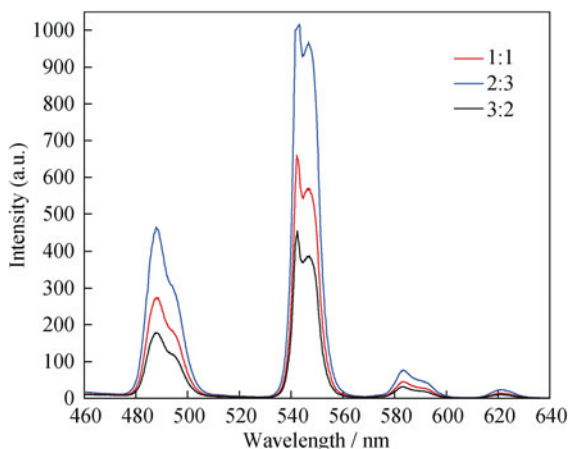


Fig. 6 Excitation spectrum of $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphor at different doping molar ratio of Ce/Tb

3.4 Chromaticity coordinates

Figure 7 shows the commission international del'eclairage (CIE) chromaticity coordinates of the $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphor (molar ratio of Ce/Tb = 2:3). The chromaticity coordinates of the phosphor are $x = 0.253$ and $y = 0.588$. In the PL spectra, $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphor exists a strong green emission with the UV light excitation (254 nm) at 7,114 K. It means the $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphor could be a good green phosphor candidate for creating white light in phosphor-converted white light.

4 Conclusion

$\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphors were prepared with co-precipitation method. The product is a single orthorhombic phase of $\text{Sr}_2(\text{P}_2\text{O}_7)$ and free of secondary phases. The powders are spherical and the size distribution is micron grade. The

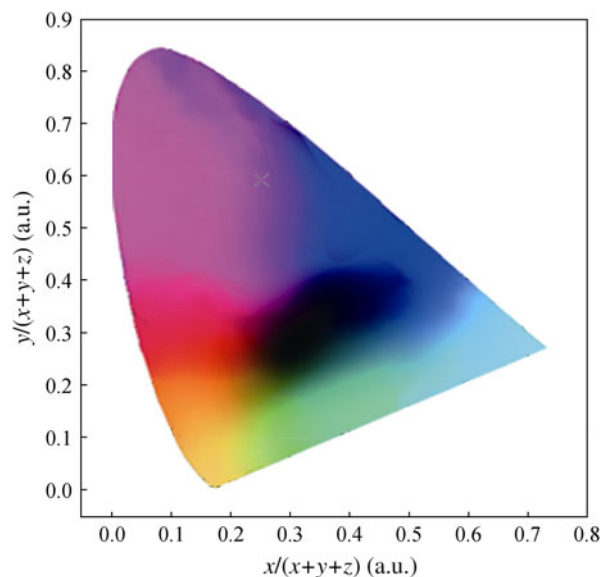


Fig. 7 Chromaticity coordinates of $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphors

phosphors produce green fluoresce when excited by ultraviolet radiation of 254 nm wavelength. The emission peak is at 547 nm. $\text{Sr}_2(\text{P}_2\text{O}_7)\text{:Ce,Tb}$ phosphors synthesized by co-precipitation method of precursors at ambient temperature is an efficient green-emitting fluorescer.

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