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# Luminescence properties of $Ce^{3+}$ and $Tb^{3+}$ ions codoped strontium borate phosphate phosphors

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## ABSTRACT

The $Ce^{3+}$-activated, $Tb^{3+}$-activated, and $Ce^{3+}$ and $Tb^{3+}$ co-activated phosphors $2SrO–nB_2O_3–(1-n)P_2O_5$ were synthesized by the solid-state reaction. The structures, photoluminescent spectra and dynamics of them were systemically studied. The results demonstrate that the structure of the samples with $n = 0.10$–$0.50$ belongs to the hexagonal phase. When $n$ is beyond this range, the structures are the mixed phases of $\alpha$-$Sr_2P_2O_7$ and $Sr_2B_2O_5$. The optimum composition is determined to be $n = 0.25$ for the $2SrO–nB_2O_3–(1-n)P_2O_5$ phosphors. As $n$ varies from 0.01 to 0.50, the lifetime of $Ce^{3+}$ ion increases gradually, while the lifetime of $Tb^{3+}$ ion decreases, indicating that the energy transfer efficiency decreases with the increase of $n$. The ET efficiency between $Ce^{3+}$ and $Tb^{3+}$ in the optimum composition reaches to 70%. The present results demonstrate that the $Ce^{3+}$ and $Tb^{3+}$ co-activated hexagonal $2SrO–0.25B_2O_3–0.75P_2O_5$ powders can possibly be applied as the newly developed green efficient phosphors in the field of lighting and display.

## 1. Introduction

The rare earth ions activated materials are widely used as lamp phosphors, cathode ray tube phosphors and scintillator phosphors, because of their unique spectroscopic properties [1,2]. New hosts doped with rare earth ions are getting much attention owing to their potential applications. Recently, the considerable variety in crystal structure of the borophosphate compounds provides a great deal of objects for the study aiming at exploring new functional materials. As far as luminescence is concerned, attention has been brought to alkaline earth borophosphate lattices doped with rare earth ions, because it has high luminescence, moderately synthetical temperature, great X color coordinate and low thermal degradation. Generally, the alkaline earth borophosphates are reported to be isostructural with mineral stillwellite, which are built up with $BO_4$ and $PO_4$ tetrahedra. The ions are coordinated with nine oxygen ions with $C_2$ symmetry [3,4]. The basic anionic constituents of these compounds are recommended to be interpreted in terms of $BPO_4$ groups, i.e. $PO_4^+$–$BO_4^-$, where B and P are four-coordinated [5,6]. The alkaline earth borophosphates are built up with $BO_4$ and $PO_4$ tetrahedra, which formed three-dimensional net-like structures. The structures of these borophosphates can keep rare earth ions from oxidation because of their stable structures. Blasse first reported the UV-excited blue emission of $Eu^{2+}$ in $MBPO_5:Eu^{2+}$ (M = Ca, Sr, Ba) [7]. Verwey et al. studied the luminescence properties of divalent europium in crystalline and glass modification of calcium borophosphate [8]. Karthikeyani and Jagannathan prepared the X-ray storage phosphor $SrBPO_5:Eu^{2+}$ [4]. Previously, the studies on luminescence properties of rare earth ions in the $MBPO_5$ host were mainly focused on divalent $Eu^{2+}$ and $Sm^{2+}$ [4,9–11], which mainly based on the 4f–5d transitions of the rare earths.

$Ce^{3+}$ and $Tb^{3+}$ ions are important trivalent RE ions, which have been applied in blue and green phosphors. Cerium and terbium ions doped materials are of great importance because of their practical application in lighting and display. The energy transfer (ET) processes between $Ce^{3+}$ and $Tb^{3+}$ in different hosts, such as lanthanum oxybromide [12], aluminate [13], alkaline earth sulfate [14] and so on, are intensively investigated. However, the studies on luminescence dynamics, ET processes between $Ce^{3+}$ and $Tb^{3+}$ in these alkaline earth borophosphate systems have not been investigated. In this paper, we systemically synthesize the green-emitting phosphors $2SrO–nB_2O_3–(1-n)P_2O_5:Ce^{3+},Tb^{3+}$ by the solid-state reaction and systemically study on their photoluminescence properties.

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## 2. Experimental

### 2.1. Sample preparation

$2SrO–nB_2O_3–(1-n)P_2O_5$:1%$Ce^{3+}$,2.5%$Tb^{3+}$ phosphors were prepared by the solid-state reaction at high temperature. The starting materials were analytical grade $Sr(NO_3)_2$, $Tb(NO_3)_3 \cdot 5H_2O$ (purity 99.99%), $Ce(NO_3)_3 \cdot 5H_2O$ (purity 99.99%), $H_3BO_3$ (excess 3 mol% to compensate the evaporation) and $(NH_4)_2HPO_4$ with different proportion between $(NH_4)_2HPO_4$ and $H_3BO_3$. Two annealing steps were necessary for synthesizing the samples. First, stoichiometeric amount of the starting materials were thoroughly mixed and annealed at 400 °C for 4 h, and subsequently annealed in air at 1000 °C for another 4 h in a covered aluminum oxide crucible. After these steps, the temperature was slowly reduced to room temperature. Finally, the white powders of $2SrO–nB_2O_3–(1-n)P_2O_5$:1%$Ce^{3+}$,2.5%$Tb^{3+}$ were obtained.

To obtain the optimum composition, which was doped with different ($Ce^{3+}$or $Tb^{3+}$) concentration and study the dependence of ET processes between $Ce^{3+}$ and $Tb^{3+}$ on concentration, the amount of $Ce(NO_3)_3 \cdot 5H_2O$ or $Tb(NO_3)_3 \cdot 5H_2O$ was adjusted in the preparation.

### 2.2. Measurements

The crystal structures were obtained by X-ray diffraction (XRD) using a Cu target radiation resource ($\lambda = 1.54078$ Å). The excitation and emission spectra at room temperature were measured with a Hitachi F-4500 fluorescence spectrometer. In the measurements of fluorescence dynamics of $Tb^{3+}$, a 355 nm light generated from the Fourth-Harmonic-Generator pumped by the pulsed Nd:YAG laser was used as excitation source. It is with a line width of 1.0 $cm^{-1}$, pulse duration of 10 ns and repetition frequency of 10 Hz. The spectra were recorded by a Spex-1403 spectrometer, a photomultiplier and a boxcar integrator and processed by a computer. The fluorescence dynamics of $Ce^{3+}$ were measured with a FL920 single-photon spectrometer using a nanosecond flash-lamp as the excitation source, which is with a pulse width of 1 ns and a repetition rate of 40 kHz.

## 3. Results and discussion

### 3.1. Structure of the $2SrO–nB_2O_3–(1-n)P_2O_5$ powders

Fig. 1 shows the X-ray diffraction patterns (XRD) of different $2SrO–nB_2O_3–(1-n)P_2O_5$:1%$Ce^{3+}$,2.5%$Tb^{3+}$ samples in contrast to the standard card of orthorhombic α-$Sr_2P_2O_7$ (JCPDS no. 24-1011), monoclinic $Sr_2B_2O_5$ (JCPDS no. 73-1930) and strontium borate phosphate (JCPDS no. 18-1270). For the α-$Sr_2P_2O_7$ sample ($n = 0$), all the XRD lines match the lines given in no. 24-1011 of JCPDS data files. It can be found that the structure of the powder is in pure orthorhombic phase (α-$Sr_2P_2O_7$). The unit cell parameters obtained are $a = 8.917$ Å, $b = 13.16$ Å, $c = 5.400$ Å, respectively. The structure of $Sr_2B_2O_5$ ($n = 1$) is in pure monoclinic phase, which is similar to that reported for the compound strontium borate (JCPDS no. 73-1930). As for the $n = 0.01$ and 0.90 samples, the results indicate that there exist the mixed phases of the α-$Sr_2P_2O_7$ and $Sr_2B_2O_5$ in both the two samples, as shown in Fig. 1. As $n$ varies from 0.10 to 0.50, the XRD patterns are similar to that reported for the compound strontium borate phosphate (JCPDS no. 18-1270). As the value of $n$ varies from 0.10 to 0.50, the crystal structure of the samples can be indexed to the hexagonal space groups. In contrast to the standard cards, the XRD patterns in the present samples become broader to different degree. It may be attributed to the different structure between $BO_4^-$ and $PO_4^-$, which leads to the inhomogeneous structure distribution. Therefore, there is considerable line broadening, indicating lattice strain, in the diffraction patterns of the mixed borate and phosphate compounds [15].

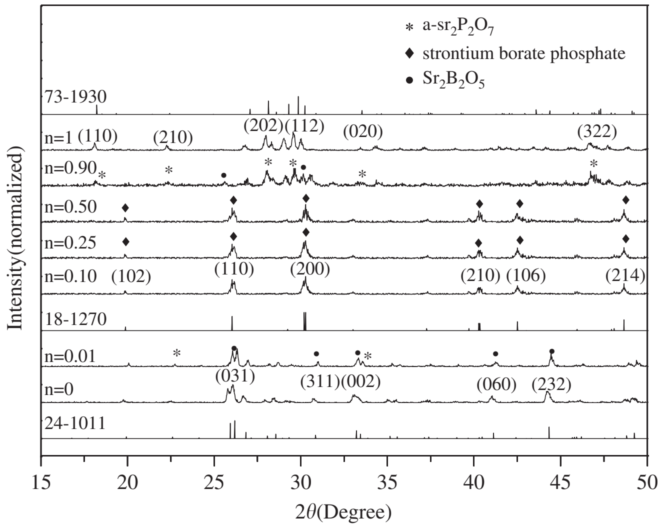

**Fig. 1.** The X-ray diffraction patterns (XRD) in different $2SrO–nB_2O_3–(1-n)P_2O_5$: 1%$Ce^{3+}$,2.5%$Tb^{3+}$ samples and the JCPDS card 24-1011 for α-$Sr_2P_2O_7$, the JCPDS card 18-1270 for compound strontium borate phosphate and the JCPDS card 73-1930 for $Sr_2B_2O_5$.

### 3.2. The luminescence properties of $2SrO–nB_2O_3–(1-n)P_2O_5$:1%$Ce^{3+}$,2.5%$Tb^3$

Fig. 2(a) gives the excitation (left) and emission spectra (right) of $Ce^{3+}$-activated $2SrO–0.25B_2O_3–0.75P_2O_5$ powders. It can be seen that the excitation spectrum consists of three components, having peaks at 258, 266 and 286 nm (the strongest), respectively, which corresponds to the transitions from the ground-state $^2F_{5/2}$ of $Ce^{3+}$ to different crystal-field components of the excited $Ce^{3+}$5d states. The emission band of $Ce^{3+}$ consists of a broadband with a maximum at 326 nm and a shoulder at 340 nm, which are the characteristic splitting of the emission bands of $Ce^{3+}$due to the spin–orbit split of the ground state. These bands should correspond to the 5d–$^2F_J$ ($J = 7/2$, 5/2) transitions of $Ce^{3+}$. The energy difference between the two peaks is ~1263 $cm^{-1}$, which is basically in accordance with the ground state splitting of $Ce^{3+}$ (2000 $cm^{-1}$, i.e., energy difference between $^2F_{5/2}$ and $^2F_{7/2}$ doublets in the $4f^1$ configuration of the $Ce^{3+}$ ion) [16].

The rare earth ions were reported to occupy the crystal lattice sites with $C_2$ symmetry in iso-structural host $MBPO_5$ (M = Ca, Sr) [10,17,18]. Berezovskaya et al. reported the UV excitation spectrum of $Ce^{3+}$ in the $SrBPO_5$ host recently. They observed that the 5d orbits split into sublevels in the range of 230–290 nm and the crystal-field components of the excited 5d configuration located at 241, 258 and 277 nm, respectively [19]. Compared with their result, the excitation spectrum of $Ce^{3+}$ in the present sample shifts to red, which points to a stronger relaxation in the 5d excited state of $Ce^{3+}$ in the $2SrO–0.25B_2O_3–0.75P_2O_5$ host.

Fig. 2(b) exhibits the excitation (left) and emission spectra (right) in $Tb^{3+}$-activated $2SrO–0.25B_2O_3–0.75P_2O_5$ powders. A number of excitation lines of $Tb^{3+}$ ions exist in UV range, which is associated with $^7F_6$–$^5D_3$, $^7F_6$–$^5G_J$ and $^7F_6$–$^5L_6$ transitions of $Tb^{3+}$. The emission lines from 480 to 650 nm are associated with the $^5D_4$–$^7F_J$ ($J = 3$–6) transitions. Among them, the green $^5D_4$–$^7F_5$ emission at 541 nm is the strongest.