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# Luminescent Properties of $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ Green Phosphor

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**Abstract** The  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$  green phosphor was synthesized by the general high temperature solid-state reaction and its luminescence properties were investigated. It shows four major emission peaks locating at 495, 548, 598 and 625 nm corresponding to the  $^5\text{D}_4 \rightarrow ^7\text{F}_6$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_5$ ,  $^5\text{D}_4 \rightarrow ^7\text{F}_4$  and  $^5\text{D}_4 \rightarrow ^7\text{F}_3$  typical transitions of  $\text{Tb}^{3+}$ , respectively, and the strongest one appears at 548 nm. The excitation spectrum contains a broad band extending from 200 nm to 400 nm, which is coupled well with the emission of ultraviolet light-emitting diodes (UVLEDs). The influences of doped- $\text{Tb}^{3+}$  concentration and charge compensation of  $\text{Li}^+$  on the emission intensity were also investigated. The  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  is a kind of potential green-emitting phosphor for white light emitting diode (w-LED).

**Key words**  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ ; luminescence

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## 1 Introduction

Recent years, white light-emitting diodes (LEDs) have been widely utilized for backlight of the liquid crystal display (LCD), traffic signals, and especially for solid-state lighting. In comparison with the incandescent and fluorescent lamps, white LEDs have a number of advantages in terms of high luminous efficiency, energy-saving, maintenance, and environmental protection<sup>[1]</sup>.

Up to now, the most common and the easiest way to generate white light is the combination of the yellow-emitting phosphor made of cerium doped yttrium aluminum garnet ( $\text{YAG}:\text{Ce}^{3+}$ ) and blue-emitting GaN chips<sup>[2~4]</sup>.

However, white LEDs made by this way have some problems: white emitting color changes with input power and low color rendering index due to two-color mixing. A novel approach has been sug-

gested to utilize tricolor (red/green/blue) phosphors excited by ultraviolet (UV) or near UV LED to generate white light<sup>[5~8]</sup>. Compared with the commercial white LEDs fabricated with a blue chip and yellow phosphor  $\text{YAG}:\text{Ce}^{3+}$ , the white LEDs made by near UV chip and tricolor phosphors have two main advantages: excellent color rendering index and white color almost generated by phosphors.

Because of stability and long luminescence time, borate-based phosphors have been firstly choiced for high definition television and projection television luminescent material<sup>[9]</sup>. Here, the  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  green-emitting phosphor was synthesized and its luminescent properties were also investigated.

## 2 Experiments

### 2.1 Preparation of $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$ Phosphor

The samples  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  were prepared with a solid-state reaction technique at high temperature.

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The starting materials used in the preparation of this phosphor were analytic reagents  $\text{SrCO}_3$ ,  $\text{H}_3\text{BO}_3$ , and  $\text{Tb}_4\text{O}_7$  (99.99%).  $\text{Tb}^{3+}$  ion replaces  $\text{Sr}^{2+}$  ion in host. Because trivalent Tb ions are located on divalent Sr ion sites and some charge-compensating defect is built into the lattices, we use  $\text{Li}_2\text{CO}_3$  to introduce  $\text{Li}^+$  for the charge compensation. After the individual materials were mixed in the requisite proportions sufficiently, the powder was sintered at 800 °C for 2 h in an alumina crucible. After cooled to room temperature, the samples were re-ground again and finally calcined at 1000 °C for 2 h in  $\text{CO}$  atmosphere to reduce to  $\text{Tb}^{3+}$  ions. The obtained products are crystalline  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$  phosphors.

## 2.2 Measurement Procedure

The lattice phase of as-prepared samples were characterized by powder X-ray diffraction (XRD, D/max-rA,  $\text{Cu K}\alpha$ , 40 kV, 100 mA). The excitation spectrum was measured by a SHIMADZU RF-540 ultraviolet spectrophotometer. The emission spectrum was measured by a SPEX 1404 spectrophotometer. All the photoluminescence properties of the phosphors were measured at room temperature.

## 3 Results and Discussion

### 3.1 XRD Analysis of $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$

Fig. 1 shows the XRD patterns of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ . It can be seen that the XRD pattern agrees well with Joint Committee on Powder Diffraction Standards (JCPDS No. 31-1343), indicating that the doped  $\text{Tb}^{3+}$  ions do not cause any obvious change in the host structure.  $\text{Sr}_3\text{B}_2\text{O}_6$  has a rhombohedral crystal

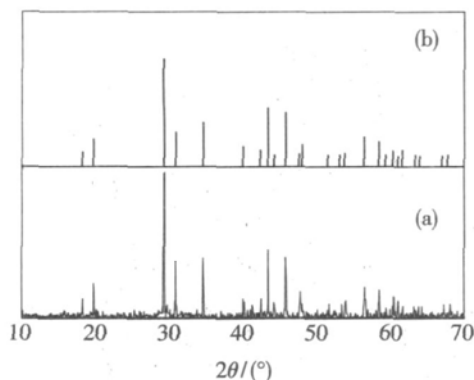


Fig. 1 (a) XRD pattern of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ ; (b)  $\text{Sr}_3\text{B}_2\text{O}_6$  (JCPDS 31-1343).

structure, and its lattice parameters values are  $a = 0.9046 \text{ nm}$ ,  $b = 0.9046 \text{ nm}$ ,  $c = 1.2566 \text{ nm}$ . Since the ionic radius of  $\text{Tb}^{3+}$  (0.092 nm) and  $\text{Sr}^{2+}$  (0.121 nm) are similar,  $\text{Tb}^{3+}$  is expected to occupy the  $\text{Sr}^{2+}$  site preferably.

### 3.2 Excitation and Emission Spectra of $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$

The excitation spectrum of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$  phosphor is depicted in Fig. 2. The overall excitation spectrum can be divided into two parts: one is in the range from 220 nm to 300 nm, representing the spin-allowed  $4f^8 \rightarrow 4f^7 5d^1$  transition of  $\text{Tb}^{3+}$ ; the other is in the range from 300 nm to 400 nm, representing the  $4f \rightarrow 4f$  transition of  $\text{Tb}^{3+}$ . The main excitation peak is located at 385 nm, which matches well with the emission of UVLED chip.

The emission spectrum of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$  phosphor is depicted in Fig. 3. The emission spectrum under 365 nm excitation consists of four emission peaks located at 495, 548, 598, and 625 nm, which are ascribed to the  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_6$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_5$ ,  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_4$  and  ${}^5\text{D}_4 \rightarrow {}^7\text{F}_3$  transitions of  $\text{Tb}^{3+}$  respectively, indicating that this phosphor can generate excellent

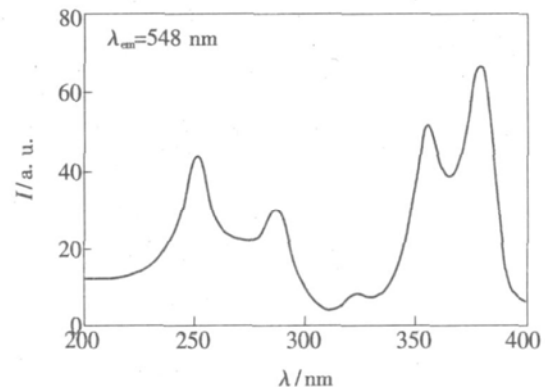


Fig. 2 The excitation spectrum of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ .

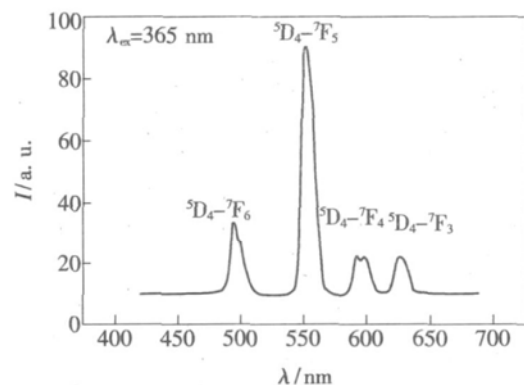


Fig. 3 The emission spectrum of  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ .

green light. The emission from  $^5\text{D}_3$  level isn't observed, suggesting the cross-relaxation ( $^5\text{D}_3 \rightarrow ^5\text{D}_4$ ) of  $\text{Tb}^{3+}$  occurs in the concentration range we investigated.

### 3.3 Effect of $\text{Tb}^{3+}$ Content on $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}, \text{Li}^+$ Luminescence Intensity

The effect of doped- $\text{Tb}^{3+}$  concentration on the emission intensity of  $\text{Sr}_{3-2x}\text{B}_2\text{O}_6:x\text{Tb}^{3+}, x\text{Li}^+$  phosphor was also investigated. The variations of emission intensity with different  $\text{Tb}^{3+}$  content are illustrated in Fig. 4. The emission intensity increases with  $\text{Tb}^{3+}$  content increasing. The maximum intensity occurs when the  $x$  is equal to 0.6, then decreases slowly. But we didn't find concentration quenching in the experiments. The reason is probably that the crystal structure of host is unique. For example,  $\text{Tb}^{3+}$  ions are one-dimensional or two-dimensional array in host which leads to migration of excitation energy arising from resonance delivery being suppressed. The concentration quench phenomenon does not appear nearly. This kind of phenomenon has also appeared in other fluorescence materials<sup>[10]</sup>.

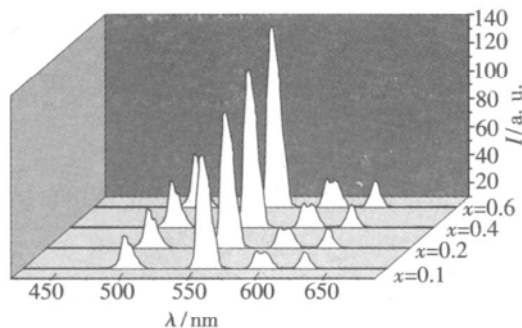


Fig. 4 The emission intensity of  $\text{Sr}_{3-2x}\text{B}_2\text{O}_6:x\text{Tb}^{3+}, x\text{Li}^+$  as function of  $\text{Tb}^{3+}$  concentration ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ).

### 3.4 Effect of Charge Compensator $\text{Li}^+$ on $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$ Luminescence Intensity

A series of  $\text{Sr}_{3-2x}\text{B}_2\text{O}_6:x\text{Tb}^{3+}, x\text{Li}^+$  and  $\text{Sr}_{3-x}\text{B}_2\text{O}_6:x\text{Tb}^{3+}$  specimens were prepared. Their emission spectra under excitation of 365 nm, are shown in

Fig. 5. In the  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  crystallite, one  $\text{Tb}^{3+}$  is expected to replace one  $\text{Sr}^{2+}$  site. It was difficult to keep charge balance, so  $\text{Tb}^{3+}$  may not be fully introduced into  $\text{Sr}^{2+}$  site. We use  $\text{Li}_2\text{CO}_3$  to introduce  $\text{Li}^+$  for the charge compensation. As charge compensation and co-activator,  $\text{Li}^+$  ion can enhance luminescence intensity of rare earths fluorescence materials strongly<sup>[11]</sup>. Since  $\text{Li}^+$  (0.059 nm) has the minimal radius, it can be doped in matrix most easily and help  $\text{Tb}^{3+}$  enter into host material more effectively. Therefore, the samples co-doped by  $\text{Li}^+$  and  $\text{Tb}^{3+}$  have stronger emission intensity.

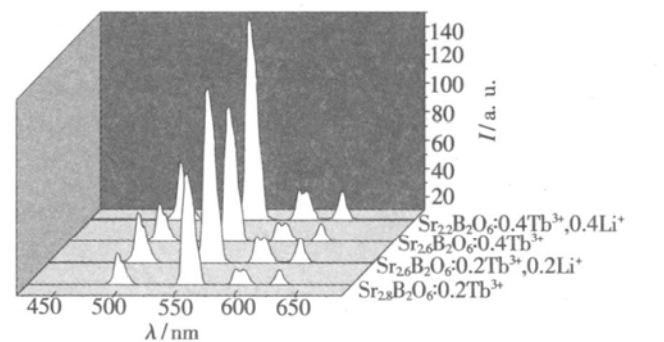


Fig. 5 Effect of  $\text{Li}^+$  charge-compensator on emission intensity ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ).

## 4 Conclusion

In conclusion, the  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  phosphor was synthesized by conventional high temperature solid-state method. The emission spectrum shows the strongest peak at 548 nm corresponding to the  $^5\text{D}_4 \rightarrow ^7\text{F}_5$  transition of  $\text{Tb}^{3+}$  in  $\text{Sr}_3\text{B}_2\text{O}_6$ . It was shown that the optimum doping content of  $\text{Tb}^{3+}$  in  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  phosphor under 365 nm excitation is 20%. The introduction of charge compensator  $\text{Li}^+$  can lead to the strongly enhanced emission intensity of  $\text{Tb}^{3+}$ . The  $\text{Sr}_3\text{B}_2\text{O}_6:\text{Tb}^{3+}$  is a kind of potential green-emitting phosphor for UVLED due to the efficient excitation by 385 nm.

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## $Sr_3B_2O_6:Tb^{3+}, Li^+$ 绿色荧光粉的发光特性

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**摘要:** 用高温固相法合成了  $Sr_3B_2O_6:Tb^{3+}, Li^+$  绿色荧光粉, 并研究粉体的发光性质。发射光谱由位于黄绿区的 4 个主要荧光发射峰组成, 峰值分别位于 495, 548, 598, 625 nm, 对应了  $Tb^{3+}$  的  $^5D_4 \rightarrow ^7F_6$ ,  $^5D_4 \rightarrow ^7F_5$ ,  $^5D_4 \rightarrow ^7F_4$  和  $^5D_4 \rightarrow ^7F_3$  特征跃迁发射。548 nm 的发射最强。激发光谱表现从 200~400 nm 的宽带, 可以被近紫外光辐射二极管 (near-ultraviolet light-emitting diodes, UVLED) 管芯产生的 350~410 nm 辐射有效激发。研究了  $Tb^{3+}$  掺杂和电荷补偿剂对样品发光亮度的影响。 $Sr_3B_2O_6:Tb^{3+}, Li^+$  是一种适用于白光 LED 的绿色荧光粉。

**关键词:**  $Sr_3B_2O_6:Tb^{3+}, Li^+$ ; 发光

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