

Optical properties of novel blue-emitting phosphor

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A novel blue-emitting phosphor, $0.15\text{K}_5\text{B}_{19}\text{O}_{31}\cdot\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$, was synthesized by solid state reaction in N_2/H_2 reductive atmosphere, and X-ray powder diffraction (XRD) analysis confirmed containing $\text{K}_5\text{B}_{19}\text{O}_{31}$ and SrB_2O_4 . The phosphor can be efficiently excited by UV-visible light from 220 to 430 nm, and exhibited bright blue emission. Photoluminescence of $0.15\text{K}_5\text{B}_{19}\text{O}_{31}\cdot\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$, $\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ and $\text{K}_5\text{B}_{19}\text{O}_{31}\text{:Eu}^{2+}$ were investigated in detail, and the results showed that $0.15\text{K}_5\text{B}_{19}\text{O}_{31}\cdot\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ expands excitation wavelength range of $\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ and emission, and excitation intensity is stronger 200 times than that of $\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ but the positions of emission peaks have no shift. We conclude that the experiment is a new method to research high brightness and wide excitation band phosphors.

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Keywords: New method, Blue-emitting phosphor, Ultraviolet light emitting diode

1. Introduction

During the past two decades, with the white light-emitting diodes (LEDs) applications, the design and synthesis corresponding phosphor has become the new hot spot because of their high luminous efficiency, energy-saving, maintenance and environmental protection. Therefore, they are called replacement of conventional incandescent and fluorescent lamps [1]. A white LED device has been commendably realized using YAG:Ce as yellow phosphor coated on the blue LED chip. However, it is hard to improve power of blue-emitting GaN chip and find other suitable phosphors excited at 460 nm efficiently. To solve these problems, white LEDs have been fabricated employing blue, green and red emitting multiphase phosphors excited by an ultraviolet (350-410 nm) In GaN chip [2]. Researchers worldwide have investigated many other chemical compounds as suitable phosphors for solid-state lighting. This Eu^{2+} ion is particularly unique because its broad and intense band luminescence $4f^65d \rightarrow 4f^7$ are strongly host dependent. Thus, researching emission wavelength extending from the UV to the red range of Eu^{2+} , we must seek out appropriate host and study the property of host [3-5]. Alkaline earth borate is an important luminescent material because of its excellent chemistry and thermal stabilization, facile synthesis and cheap raw material, so it has been extensively applied to phosphor for lamps [6]. We report in detail the synthesis and photoluminescence properties of Eu^{2+} doped $0.15\text{K}_5\text{B}_{19}\text{O}_{31}\cdot\text{SrB}_2\text{O}_4$ phosphor which has potential applications in ultraviolet LED region.

Many scientists have studied many methods to

enhance the emission intensity of phosphor. For example, doping rare earth ions Eu^{2+} in $\text{BaMgAl}_{10}\text{O}_{17}$: Mn, La^{3+} and Y^{3+} co-doped the Ba_2SiO_4 : Eu [7-8], and doping the same value ions Ba^{2+} in Sr_3SiO_5 : Eu [9]. Moreover, doping flux is frequently used method, for instance, borate is doped BaMgSiO_4 : Eu phosphor [10]. In this paper, we research a novel method which can yield high luminescence intensity and expand wavelength range by doping another matrix.

2. Experimental

2.1. Sample synthesis

SrCO_3 (AR), H_3BO_3 (AR), KHCO_3 (AR) and Eu_2O_3 (powders, 99.99%, High Purity Chemicals) were as raw materials. After the individual materials had been mixed in the requisite proportions sufficiently, the powders were prepared by conventional solid state reaction technique at 900 °C, 620 °C or 800 °C in N_2/H_2 reducing atmosphere for 2h. The phosphors of $0.15\text{K}_5\text{B}_{19}\text{O}_{31}\cdot\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ were prepared at 800 °C but $\text{SrB}_2\text{O}_4\text{:Eu}^{2+}$ must be heated up to 900 °C due to influence of $\text{K}_5\text{B}_{19}\text{O}_{31}$.

2.2. Measurements

X-Ray powder diffraction (XRD) measurements were carried out on a D8 Focus diffractometer (Bruker) at 40 kV and 20 mA with Cu K α radiation ($\lambda = 0.15405$ nm). The photoluminescence (PL) measurements were performed on a Hitachi F-4500 spectrophotometer equipped with a 150 W xenon lamp as the excitation

source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. X-ray diffraction analysis

$\text{Sr}_{1-n}\text{B}_2\text{O}_4 \cdot n\text{Eu}^{2+}$ phosphors XRD patterns are shown in Fig. 1, which indicated that doped Eu^{2+} ions have no obvious influence on the structure of the host and all the peaks can be indexed to the phases of SrB_2O_4 (JCPDS No. 84-2175). Fig. 2 shows XRD pattern of $\text{K}_{5-m}\text{B}_{19}\text{O}_{31} \cdot m\text{Eu}^{2+}$ phosphors. As can be seen, pure diffraction peaks of $\text{K}_5\text{B}_{19}\text{O}_{31}$ are predominant in the XRD patterns, which are in excellent agreement with the standard card (JCPDS No. 70-1038), and Fig. 3 presents XRD pattern of $0.15\text{K}_5\text{B}_{19}\text{O}_{31} \cdot \text{SrB}_2\text{O}_4 \cdot \text{Eu}^{2+}$ phosphors, and the diffraction patterns consist of $\text{K}_5\text{B}_{19}\text{O}_{31}$ and SrB_2O_4 . No other product or starting material was observed, implying that the phase composition of the samples has no obvious influence on the structure of the host.

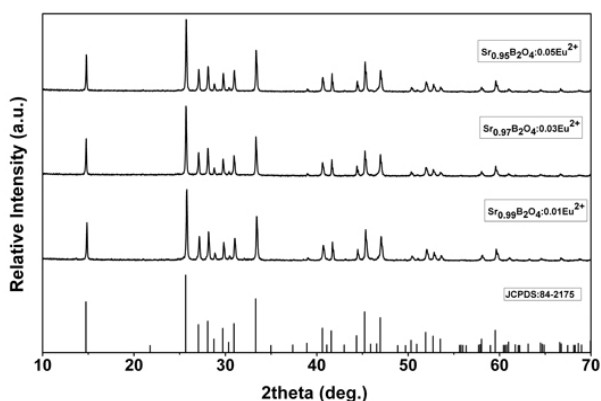


Fig. 1. XRD patterns of $\text{Sr}_{1-n}\text{B}_2\text{O}_4 \cdot n\text{Eu}^{2+}$ Phosphors and SrB_2O_4 (JCPDS No. 84-2175).

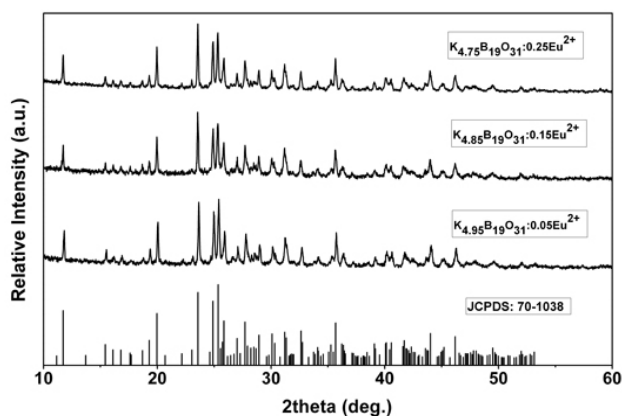


Fig. 2. XRD patterns of $\text{K}_{5-m}\text{B}_{19}\text{O}_{31} \cdot m\text{Eu}^{2+}$ Phosphors and $\text{K}_5\text{B}_{19}\text{O}_{31}$ (JCPDS No. 70-1038).

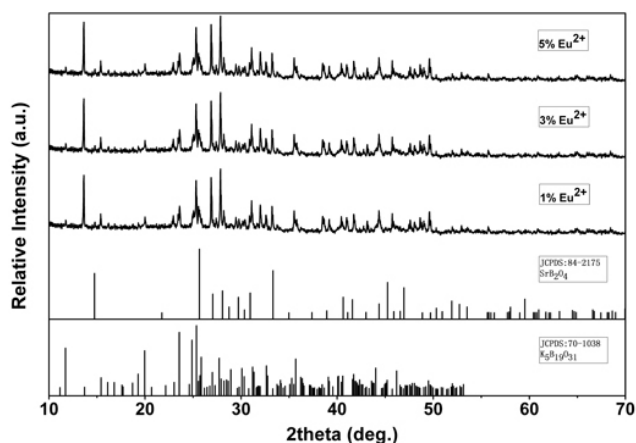


Fig. 3. XRD patterns of $0.15\text{K}_5\text{B}_{19}\text{O}_{31} \cdot \text{SrB}_2\text{O}_4 \cdot \text{Eu}^{2+}$ Phosphors and SrB_2O_4 (JCPDS No. 84-2175) and $\text{K}_5\text{B}_{19}\text{O}_{31}$ (JCPDS No. 70-1038).

3.2. Emission spectra characteristics

Fig. 4 shows the emission spectra of $\text{Sr}_{1-n}\text{B}_2\text{O}_4 \cdot n\text{Eu}^{2+}$ phosphors. Under the excitation of 315 nm, the emission spectrum exhibits blue emission bands at 450 nm, which are originated from the $4f^65d^1 \rightarrow 4f^7$ ($5d-4f$) typical transitions of Eu^{2+} . And the Eu^{2+} concentration is from 1 mol% to 5 mol%. As can be seen from these figures, the emission intensity initially increases with Eu^{2+} concentration, and reaches a maximum at 3 mol% Eu^{2+} . A decrease in the emission intensity is observed beyond the optimum concentrations, and this shows the occurrence of energy migration between Eu^{2+} in the lattice, resulting in concentration quenching [11]. At low concentration, Eu^{2+} ions can easily be accommodated into the Sr^{2+} site in the phosphors, however, the difference of the ionic radius of Eu^{2+} and Sr^{2+} lead to the solubility of Eu^{2+} become saturated. With further increase of Eu^{2+} ions, the distance of the Eu^{2+} ions becomes smaller, which lead to the energy transfer between the Eu^{2+} centers in the host lattice.

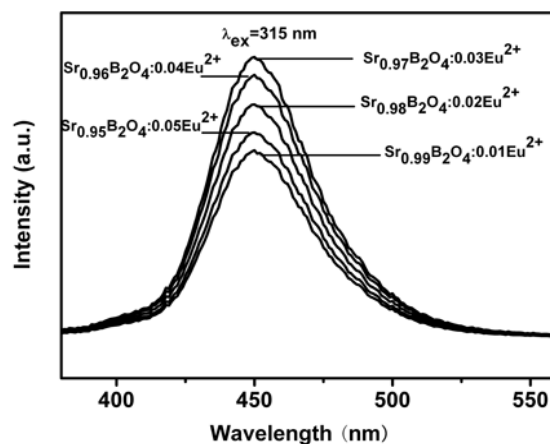


Fig. 4. Emission intensity of $\text{Sr}_{1-n}\text{B}_2\text{O}_4 \cdot n\text{Eu}^{2+}$ phosphors as function of Eu^{2+} concentration ($\lambda_{\text{ex}} = 315 \text{ nm}$).

Fig. 5 is the emission spectra of the obtained $K_{5-m}B_{19}O_{31}:mEu^{2+}$ phosphors. Under 315nm excitation, the emission spectra exhibit emission bands centered at about 396 nm, which are attributed to the $4f^65d^1 \rightarrow 4f^7$ ($5d-4f$) typical transitions of Eu^{2+} ions. The $5d$ state of Eu^{2+} is greatly affected by the crystal field and can be spitted by different crystal field, this makes Eu^{2+} emit different light when the crystal filed change. With increasing of Eu^{2+} ions concentration, emission intensity of $K_{5-m}B_{19}O_{31}:mEu^{2+}$ increases up to 3 mol%. Because a nonradiative energy transfer from one Eu^{2+} ion to another Eu^{2+} ion takes place, a decrease of the emission intensities has been observed after a maximum intensity is reached.

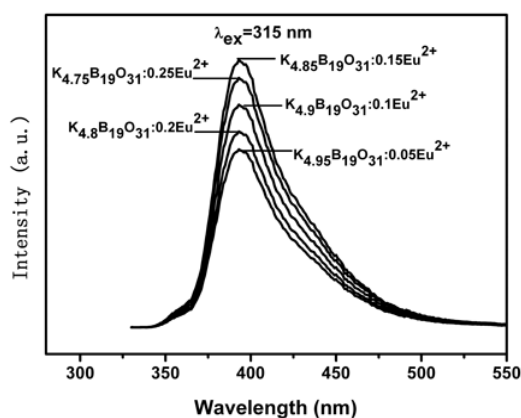


Fig. 5. Emission spectra of the obtained $K_{5-m}B_{19}O_{31}:mEu^{2+}$ phosphors ($\lambda_{ex} = 315$ nm).

The emission intensities for the $0.15K_5B_{19}O_{31}:SrB_2O_4:Eu^{2+}$ phosphors have been investigated as a function of the Eu^{2+} concentration as shown in Fig. 6, the optimum concentration is 3 mol%. Eu^{2+} ions show characteristic emission bands between 390 and 520 nm and emission intensity is stronger 200 times than that of $SrB_2O_4:Eu^{2+}$ or $K_5B_{19}O_{31}:Eu^{2+}$ (Fig. 7), which can indicate an interaction between the host and the activator corresponding to the $4f^65d-4f^7$ transition of Eu^{2+} ions.

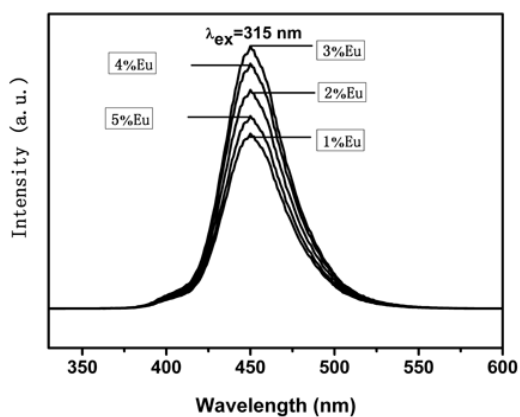


Fig. 6. Emission spectra of $0.15K_5B_{19}O_{31}:SrB_2O_4:Eu^{2+}$ phosphors ($\lambda_{ex} = 315$ nm).

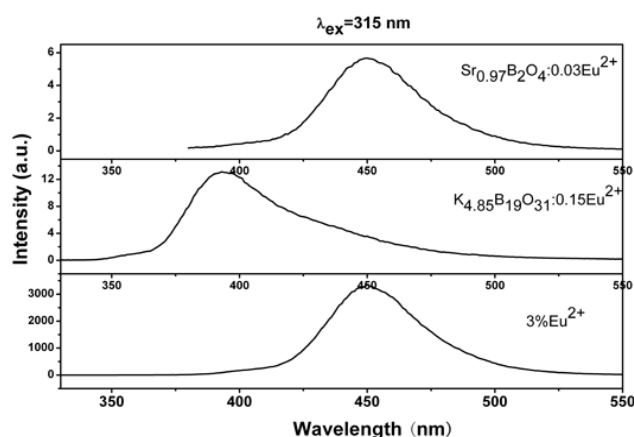


Fig. 7. The relative emission spectra of $Sr_{0.97}B_2O_4:0.03Eu^{2+}$, $K_{4.85}B_{19}O_{31}:0.15Eu^{2+}$ and 3 mol% Eu^{2+} doped $0.15K_5B_{19}O_{31}:SrB_2O_4$ phosphors ($\lambda_{ex} = 315$ nm).

3.3 Excitation spectra characteristics

Fig. 8 is excitation spectra of $Sr_{1-n}B_2O_4:nEu^{2+}$ phosphors. We can be concluded from the spectra that the wavelength range is 220–360 nm and excitation intensity at 3 mol% is stronger than other excitation intensity of any concentration, and the spectrum is attributed to transitions of Eu^{2+} from $4f^7$ ground state to the excited state $4f^65d^1$. Excitation spectra of $K_{5-m}B_{19}O_{31}:mEu^{2+}$ phosphors are showed in Fig. 9. We observed two main excitation bands in the excitation spectra of Eu^{2+} doped $K_5B_{19}O_{31}$ phosphors. One was located at around 260–300nm and the other at around 300–330 nm, which is absolutely caused by the replacement of K^+ by Eu^{2+} . The quenching concentration of the Eu^{2+} ions is 3 mol% at the maximum excitation intensity of the phosphor.

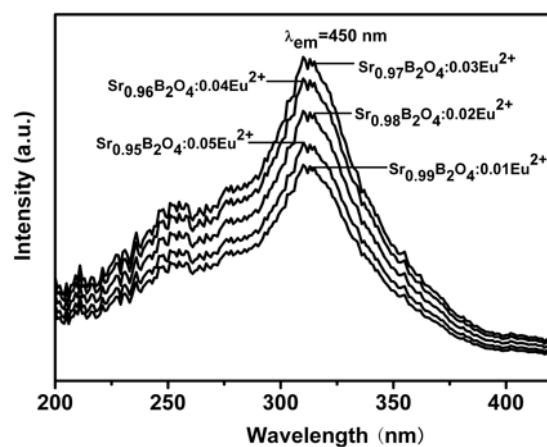


Fig. 8. Excitation spectra of $Sr_{1-n}B_2O_4:nEu^{2+}$ phosphors ($\lambda_{em} = 450$ nm).

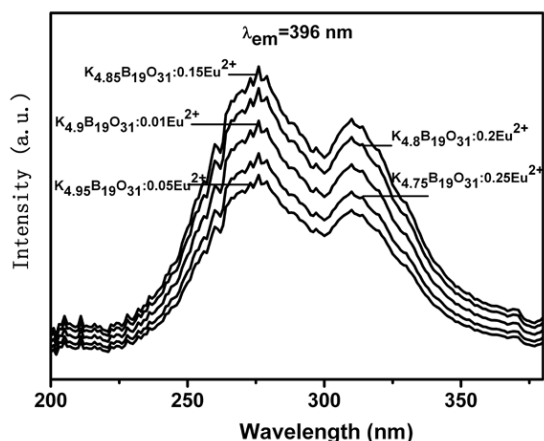


Fig. 9. Excitation spectra of $K_{5-m}B_{19}O_{31}:mEu^{2+}$ phosphors ($\lambda_{em} = 396$ nm).

The optimum concentration of the $0.15K_5B_{19}O_{31}\cdot SrB_2O_4:Eu^{2+}$ phosphors is 3 mol%, which is described in Fig. 10. The excitation spectrum range is from 220 to 430 nm and excitation intensity is stronger at least 200 times than that of Eu^{2+} doped SrB_2O_4 (Fig. 11). Matrix of $n(K_5B_{19}O_{31}):n(SrB_2O_4) = 0.15:1$ owns both $K_5B_{19}O_{31}$ advantages of lower temperature synthesis and SrB_2O_4 blue-emitting properties, and it not only retains the original nature of the two but also enhances emission intensity and expands the range of excitation spectrum of $SrB_2O_4:Eu^{2+}$. The emission of the divalent lanthanide ions originates either from an intra-configurational $4f^n$ transition or from inter-configurational $4f^{n-1}5d \rightarrow 4f^n$ transition, former has line emission but the latter has band. Among divalent lanthanides, Eu^{2+} ion may present some stability because of its $4f^7$ configuration [12].

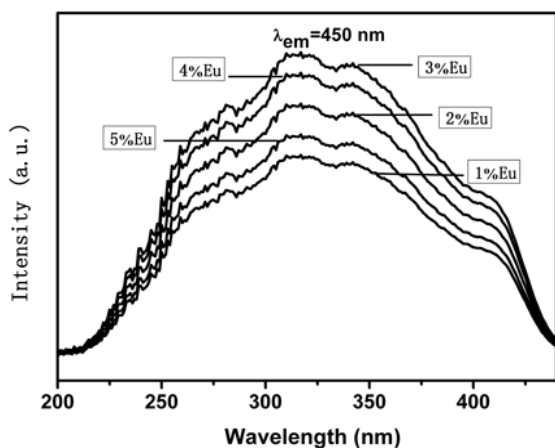


Fig. 10. Excitation spectra of $0.15K_5B_{19}O_{31}\cdot SrB_2O_4:Eu^{2+}$ phosphors ($\lambda_{em} = 450$ nm).

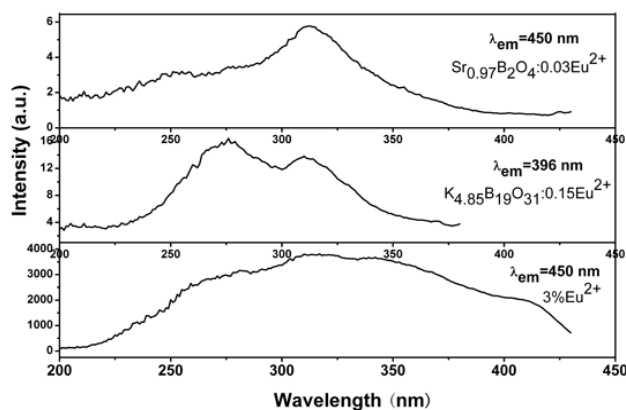


Fig. 11. The relative excitation spectra of $Sr_{0.97}B_2O_4:0.03Eu^{2+}$, $K_{4.85}B_{19}O_{31}:0.15Eu^{2+}$ and 3 mol% Eu^{2+} doped $0.15K_5B_{19}O_{31}\cdot SrB_2O_4$ phosphors.

All of the samples did not measure excitation spectrum by 464 nm light corresponds to intraconfigurational ${}^7F_0 \rightarrow {}^5D_2$ transitions due to Eu^{3+} ion, which proves no Eu^{3+} characteristic transition [13]. K^+ ions have flux effects on decreasing the melting point of the components and preventing the oxidation of Eu^{2+} ions, and K^+ ions may exist in the interstitials of the lattice due to its very small radius and distort the surroundings. For the 5d electron of Eu^{2+} ions lies in external layer in a naked and unshielded state, the splitting of energy level is strongly affected by the crystal field, and it makes the $4f^65d-4f^7$ transition broad. Furthermore, this can expand the scope of application of blue light phosphor. The result of properties is energy transfer between the matrix of $K_5B_{19}O_{31}$ and SrB_2O_4 .

4. Conclusion

All of the phosphors were prepared by solid state reaction in N_2/H_2 reducing atmosphere for 2h. Photoluminescence spectra of $0.15K_5B_{19}O_{31}\cdot SrB_2O_4:Eu^{2+}$ show that this phosphor can be excited efficiently by UV-visible light from 220 to 430 nm and emits intensely blue light with center at about 450 nm for the application of ultraviolet LEDs. The emission intensity of all of the phosphor increases with increasing Eu^{2+} concentration, then reaches the maximal value at 3 mol%. The phosphors of $0.15K_5B_{19}O_{31}\cdot SrB_2O_4:Eu^{2+}$ enhances emission intensity at least 200 times than that of Eu^{2+} doped SrB_2O_4 without any change in the peak position, and expands the range of excitation spectrum of $SrB_2O_4:Eu^{2+}$.

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