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Luminescence characteristics of Eu^{3+} activated borate phosphor for white light emitting diode*

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In this paper, the $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor was synthesized by high temperature solid-state reaction method and the luminescence characteristics were investigated. The emission spectrum exhibits one strong red emission at 613 nm corresponding to the electric dipole $^5D_0$–$^7F_2$ transition of Eu^{3+} under 365 nm excitation, this is because Eu^{3+} substituted for Y^{3+} occupied the non-centrosymmetric position in the crystal structure of $Sr_3Y_2(BO_3)_4$. The excitation spectrum indicates that the phosphor can be effectively excited by ultraviolet (254 nm, 365 nm and 400 nm) and blue (470 nm) light. The effect of Eu^{3+} concentration on the red emission of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ was measured, the result shows that the emission intensities increase with increasing Eu^{3+} concentration, then decrease. The Commission Internationale del'Eclairage chromaticity (x, y) of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor is (0.640, 0.355) at 15 mol% Eu^{3+}.

Keywords: white light emitting diode, $Sr_3Y_2(BO_3)_4:Eu^{3+}$, luminescence characteristics
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1. Introduction

Within the last several years, a white light emitting diode (LED) device has been commendably realized by using YAG:Ce as a broad band yellow phosphor coated on the blue LED chip due to their applications,[1–5] such as backlighting for liquid crystal displays and incandescent lamps. However, there exist at least three drawbacks in this combination. Firstly, there are few yellow phosphors that efficiently emit under the 450–470 nm excitation range, i.e., the YAG:Ce phosphor and the organic luminescent materials.[6–8] Secondly, the overall efficiency rapidly decreases when lowering the correlated colour temperature of the device. Thirdly, a concern with this device is that the 'white' output light has an undesirable colour balance for a true colour rendition, viz., the output light is deficient in the region of the visible light spectrum (above 600 nm). So, a separate red light source may be used to compensate LED for the red deficiency of the output light. On the other hand, a promising white LED can be fabricated by employing red, green and blue emitting phosphors which are excited by ultraviolet (UV) LED chip. So a kind of efficient and stable red phosphor is desired. The red light emitting phosphor for white LED is commercially still limited to divalent Eu ion activated sulfide. However, the sulfide phosphors are chemically unstable, so the new and stable red phosphors which can be used for white LED are desired. Recently, the borate was obtained attention because of their chemical stability.[9] Hence, we have attempted to make the borate develop a red phosphor which can efficiently emit under the UV and blue light excitation. In the present work, we have synthesized an Eu^{3+} activated $Sr_3Y_2(BO_3)_4$ red phosphor and investigated the luminescence characteristics, the results can help the development of white LED.

2. Experimental

The phosphor was synthesized by high temperature solid-state reaction method in air. $SrCO_3$ (99.5%), H_3BO_3 (99.5%), Y_2O_3 (99.99%), and Eu_2O_3 (99.99%) were used as starting materials. The mol ratio of $SrCO_3$ to H_3BO_3 and Y_2O_3 is 1.5 : 2 : 0.5 in this experiment. After the individual materials have been sufficiently mixed, the $Sr_3Y_2(BO_3)_4:Eu^{3+}$ red phosphor was synthesized by firing twice at 800°C and 1125°C for 4 h and 4 h, respectively.

The phase purity of the as-prepared phosphor was

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investigated by x-ray powder diffraction spectroscopy (XRD) (D/max-rA, Cu Kα, 40 kV, 100 mA).[10] The excitation spectrum was measured by a SHIMADZU RF-540 UV spectrophotometer. The emission spectrum was measured by a SPEX1404 spectrophotometer. All the luminescence characteristics of the phosphors were investigated at room temperature.

3. Results and discussion

3.1. The structure of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor

$Sr_3Y_2(BO_3)_4$ has a orthorhombic structure with $Pc21n$ space group, and its lattice parameter is $a = 0.87011$ nm, $b = 1.59848$ nm, $c = 0.73812$ nm (DICVOL91 program). The XRD pattern of the $Sr_3Y_2(BO_3)_4:Eu^{3+}$ with 15 mol% Eu^{3+} is presented in Fig.1. It can be observed that most peaks can be indexed to the $Sr_3Y_2(BO_3)_4$ phase. It indicates that the doping Eu^{3+} ions do not form new phases in the synthesis process.

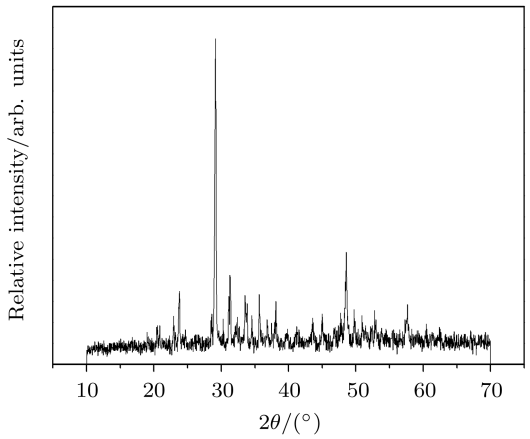


Fig.1. XRD pattern of $Sr_3Y_2(BO_3)_4:Eu^{3+}$.

The structure of $Sr_3Y_2(BO_3)_4$ is formed by isolated BO_3 triangles, strontium-oxygen polyhedra, and yttrium-oxygen polyhedra. The trivalent yttrium ions occupy two different crystallographic sites (Y1 and Y2), and every Y^{3+} has an eight-fold coordination to form YO_8 polyhedra. The bond valence of Y1 is stronger than that of Y2, so the Eu^{3+} prefers to occupy the Y2 site. Y_2O_8 polyhedra columns are built by sharing edges along the c-axis.[11] The distance between Y1 and Y2 equals to the value of the c-constant, and the environment around Y^{3+} is not centrosymmetric. The structure of $Sr_3Y_2(BO_3)_4$ indicated that the long distance between the rare-earth ions could result in a higher doping concentration, and the imperfection symmetry of Eu^{3+} will induce the pure red emission.[11]

3.2. The excitation and emission spectra of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor

Figure 2 shows the emission spectrum of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor under 254 nm excitation with 15 mol% Eu^{3+}. It shows that several narrow bands were observed between 580 nm and 700 nm. The main peak was observed at 613 nm, which is due to the electric dipole transition of $^5D_0$–$^7F_2$ of Eu^{3+}. This is because the Eu^{3+} did not occupy the centrosymmetric position in the crystal structure of $Sr_3Y_2(BO_3)_4$. Other peaks correspond to transitions of $^5D_0$–^7F_j ($j = 1, 2, 3$), such as the peaks at 599 nm, 632 nm and 654 nm being due to $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, $^5D_0$–$^7F_3$ transitions of Eu^{3+}, respectively.

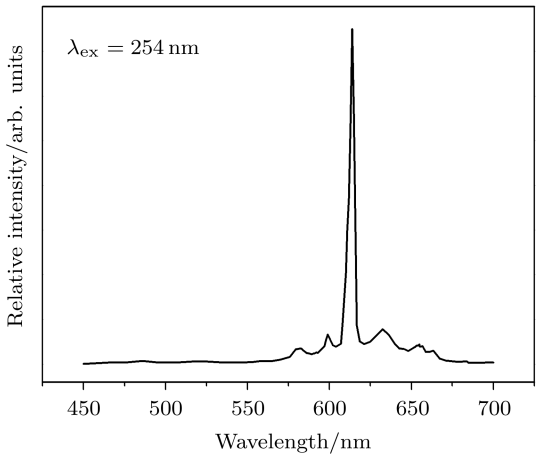


Fig.2. The emission spectrum of $Sr_3Y_2(BO3)_4:Eu^{3+}$ ($\lambda_{ex} = 254$ nm).

Figure 3 shows the emission spectrum of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor under the 365 nm excitation. It can be observed that the emission spectrum exhibits one strong red emission at 613 nm corresponding to the electric dipole $^5D_0$–$^7F_2$ transition of Eu^{3+}. And the Commission Internationale del'Eclairage (CIE) chromaticity (x, y) of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ is (0.640, 0.355).

The excitation spectrum of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor was shown in Fig.4. It shows that the broad

band at 254 nm was observed, which is due to the charge transition band of O^{2-}–Eu^{3+}. The band between 325 nm and 425 nm was detected, which means that the $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor can exhibit a satisfactory red performance under UV–vis excitation. And one band centred at 470 nm was observed in the excitation spectrum. It means that the phosphor has a sufficient absorption at the emission wavelength of the blue diodes. Consequently, $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor can compensate the red deficiency of the output light of white LED which was combined by blue InGaN chip based on the yellow phosphor materials.

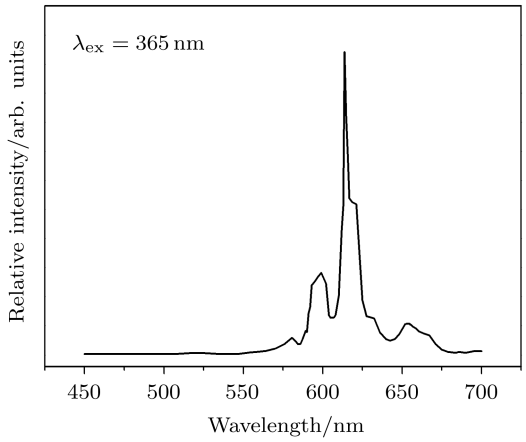


Fig.3. The emission spectrum of $Sr_3Y_2(BO3)_4:Eu^{3+}$ (λ_{ex} = 365 nm).

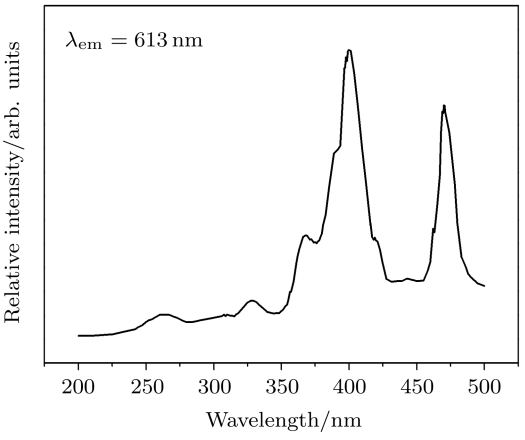


Fig.4. The excitation spectrum of $Sr_3Y_2(BO3)_4:Eu^{3+}$ (λ_{em} = 613 nm).

From the excitation and emission spectra, we can obtain that $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor is a promising red phosphor which can be used to compensate LED for the red deficiency of the output light or a separate red light source being excited by UV LED chip.

3.3. The effect of Eu^{3+} concentration on the red emission of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor

The effect of Eu^{3+} concentration on the emission intensity of $^5D_0$–$^7F_2$ (613 nm) transition was shown in Fig.5, and the Eu^{3+} concentration is from 5 mol% to 25 mol%. It can be observed that the emission intensities increase with increasing Eu^{3+} concentration, then decrease because of the concentration quenching, and reach the peak value at x = 15 mol%. However, The emission intensities of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor is higher under 365 nm excitation than 254 nm excitation at the same Eu^{3+} doped concentration, for example, the peak value is 5.58 under the 365 nm excitation, and 3.75 under the 254 nm excitation.

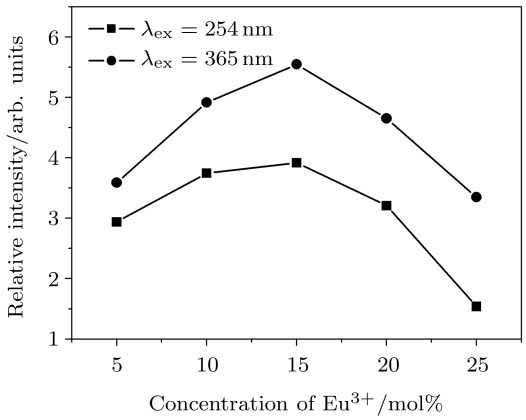


Fig.5. Luminescence intensity of $Sr_3Y_2(BO3)_4:Eu^{3+}$ as function of Eu^{3+} concentration.

Huang and Lou[12] proposed that the interaction type between sensitizers or sensitizer and activator can be determined by the slope of the curve ($\lg(I/x)$–$\lg x$) of the emission intensity and the composition in the double logarithm coordinates when the concentration is high enough. Among the concentration quenching caused by the electric multipole interaction, the slopes of dipole–dipole (d–d), dipole–quadrupole (d–q) and quadrupole–quadrupole (q–q) are located in [−2, −1], [−8/3, −5/3] and [−10/3, −7/3], respectively. According to the above mentioned method, we used the 365 nm to excite the sample of $Sr_3Y_2(BO_3)_4:Eu^{3+}$ phosphor and measured the emission intensities (I) of $^5D_0$–$^7F_2$ transition and plotted the concentration dependence curves ($\lg(I/x)$–$\lg x$) as shown in Fig.6.

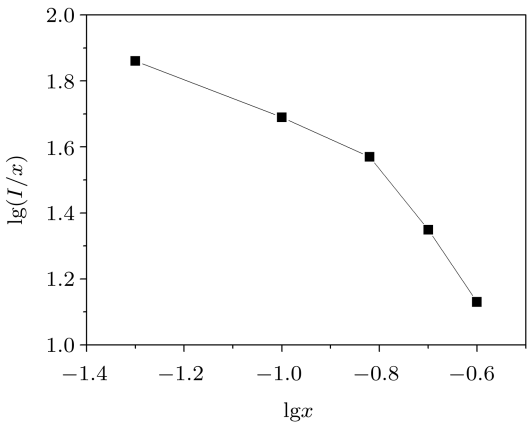


Fig.6. Relation between the $\lg(I/x)$ and $\lg x$ of Eu^{3+} for $Sr_3Y_2(BO_3)_4$ ($\lambda_{ex} = 365$ nm).

From the slope of the linear section of the concentration quenching, we have found that the slope is -1.09, and it located in $[-2, -1]$. This indicates that the concentration self-quenching mechanisms of Eu^{3+} $^5D_0$–$^7F_2$ transition in $Sr_3Y_2(BO_3)_4$ are both the d–d interaction. This result is consistent with Dexter theory,[13] which also shows that it is feasible to determine the concentration selfquenching of the activator by Ref.[12].

4. Conclusions

In summary, the $Sr_3Y_2(BO_3)_4 : Eu^{3+}$ red phosphor was synthesized and the luminescence characteristics was investigated. The phosphor can be effectively excited by UV and blue light, and the intense pure red emission due to the $^5D_0$–$^7F_2$ transition of Eu^{3+} is observed in $Sr_3Y_2(BO_3)_4 : Eu^{3+}$ under 254 nm or 365 nm excitation. And the CIE chromaticity (x, y) of $Sr_3Y_2(BO_3)_4 : Eu^{3+}$ is (0.640, 0.355). It can be concluded that $Sr_3Y_2(BO_3)_4 : Eu^{3+}$ is a promising red phosphor for white LED.

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