Microwave synthesis and properties studies of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} yellow phosphor

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The $Sr_{2.93}B_2O_6$:0.07Eu^{2+} yellow phosphor samples were synthesized by a rapid microwave heating method. The structure, luminescent properties and the effects on structure and luminescence of heating temperature were studied through a systematic research. The excitation and emission spectra indicate that this phosphor can be effectively excited by blue light of 460nm, and exhibit bright yellow emission peaking at 555nm. The main excitation peak is at 468nm, which is very suitable for blue chip excitation. The structure of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor is a hexagonal system with a R*c(167) space group. The high pure phase $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor can be obtained at 1150℃ by a microwave heating method. Similarly, the heating temperature of optimum luminescent phosphor is also at 1150℃.

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1. Introduction

In order to deal with the global energy crisis and the developing requirements of the environment, white light-emitting diodes (LEDs) have been the subject of increasing interest due to their advantages of low electric consumption, high efficiency, long lifetime, reiteration on-off, lack of pollutants and so on. In many synthesis methods of White LEDs, the phosphor conversion method, since it has the advantages of low-cost, easy preparation etc, has spontaneously become very important in our daily life. Phosphor conversion method is a way available to make the blue LED chip covered with yellow phosphor or UV chip covered with three color phosphors [1,2]. Therefore, the yellow phosphor excited by blue light chip becomes a hotspot in white LEDs study. There are many kinds of yellow phosphor materials excited by blue chip, such as YAG[3,4], sulfide [5,6], silicate [7-10], borate [11-15], nitride [16-18] et al. Borate-based matrix is considered to be a practical value luminescence material due to their simple preparation process, low calcinations temperature and high luminous efficiency. In 2007, Chun-Kuei Chang and Teng-Ming Chen [19] firstly worked on the studies of $Sr_3B_2O_6$: Ce^{3+}, Eu^{2+} phosphor and pointed out the phosphor can be used for white LEDs excited by ultraviolet light. In 2009, Woo-Seuk Song et al [20] reported the $Sr_3B_2O_6$: Eu^{2+} phosphor used in white light-emitting diodes, which can create warm white light excited by 450 nm blue LED. Therefore, $Sr_3B_2O_6$ host phosphor used for white LEDs has turned into a current hotspot. Microwave heating method has aroused wide public concern in synthesis of non-organic materials as a new innovative method. The method has many advantages, such as saving energy, non-pollution, rapid heating speed, short synthetic time, easy control and so on. Although many inorganic luminescence materials have been synthesized by microwave heating method, yet, as we have seen, the studies about $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor microwave synthesis method have not been reported before. Therefore, we carried out the studies of microwave heating synthesis $Sr_{2.93}B_2O_6$:0.07Eu^{2+} yellow phosphor. Additionally, we have discussed the effect of microwave heating temperature on the structure and luminescent properties. The optimum heating temperature was also found.

2. Experimental

2.1 Preparation of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphors

The $Sr_3B_2O_6$: Eu^{2+} yellow phosphor for warm white LED was synthesized by a microwave synthesis method. The starting materials used in the preparation of the $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphors were $SrCO_3$(AR), H_3BO_3 (AR), and Eu_2O_3 (99.99%). Graphite powder was used as the microwave absorptionor and reductor placed on mixes upon and down side. The starting materials were weighed by the stoichiometric amounts of $Sr_{2.93}B_2O_6$:0.07Eu^{2+}. Then, the individual materials have been mixed sufficiently in the agate mortar for 30 minutes. Finally, put the graphite and mix raw material into corundum crucible calcined at 1000℃, 1050℃, 1100℃, 1150℃ and 1200℃ for

30 minutes and the heating up time is only about 10 minutes. The $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphors samples heated at various temperatures were obtained.

2.2 Sample characterization

The crystal structural characteristics of samples were characterized by a Japanese Rigaku Ultima IV powder X-ray diffraction (XRD) (D/max-rA, Cu K_α 40 kV, 20 mA, λ= 1.5406Å). The photoluminescence emission and excitation spectra were measured by a Japanese RF5301PC fluorescence spectrophotometer equipped with a150W Xe lamp which is made by Shimadzu Company. All the measurements were carried on room temperature.

3. Results and discussion

3.1 Structure of $Sr_3B_2O_6$: Eu^{2+} phosphor

Fig. 1 shows the XRD pattern of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor sample heated at 1150°C. The diffraction pattern of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor sample is consistent with PDF card (No.31-1343). The results indicate that $Sr_{2.93}B_2O_6$:0.07Eu^{2+} is a hexagonal system with a R*c(167) space group and the values of the lattice parameters are a=b=9.046Å, c=12.566Å. There is no marked about diffraction of Eu^{2+} ion compound meaning that the $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor sample is highly pure $Sr_3B_2O_6$ structure in spite of Eu^{2+}ion-doping. The XRD pattern indicates that high pure $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor can be synthesized by microwave heating method.

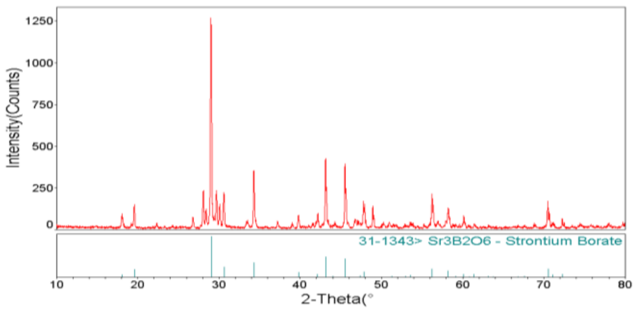


Fig. 1. XRD pattern of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor sample.

3.2 The luminescent properties of the samples

The excitation and emission spectra of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor sample heated at 1150°C are shown in Fig. 2.While, (a) is the emission spectrum of $Sr_{2.93}B_2O_6$:0.07Eu^{2+}, (b) is the excitation spectrum of $Sr_{2.93}B_2O_6$:0.07Eu^{2+}. With excitation wavelength of 460, the emission peak was at 555nm. As we can see, the spectrum shows a good symmetry under the peaking center and the shape of spectrum is nearby gauss curve. The phosphor excited by blue light can create warm white light. The yellow emission peaking at 555nm corresponds to the allowed transition from excitation state of $4f^6$ (^7F) 5d (^2e_g) to the ground state of $^8S_{7/2}$ ($4f^7$) of Eu^{2+} ion. The 5d energy levels of Eu^{2+} have lower energy than that of 4f, therefore, it is quite common for the electron transit from $4f^6$ (^7F) 5d (^2e_g) to the ground state $^8S_{7/2}$ ($4f^7$) . However, 5d level is very susceptible to different crystal field effects. So, the transition of 5d to 4f is also possible to be realized. Under detection the emission of 555nm, the excitation spectrum shows a broad asymmetric excitation band centering at 468 nm, extends from 400nm to 500nm, which indicate that the phosphor is quite suitable for a phosphor conversion white LED excited blue light chip. The novel yellow phosphor synthesized by microwave heated method is suitable for warm white LEDs.

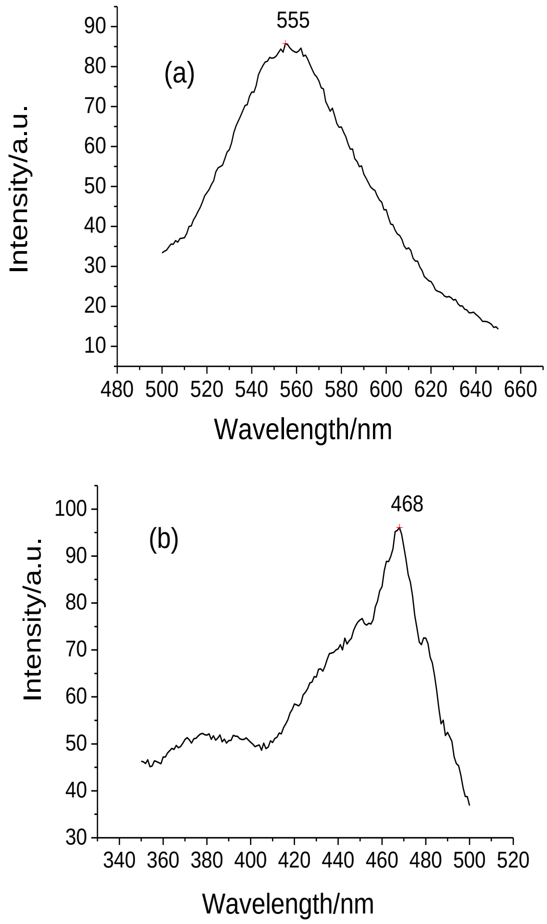


Fig. 2. The excitation and emission spectra of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} (a) Emission spectrum (b)Excitation spectrum.

3.3 The effects on crystal structure of calcined temperature

Fig. 3 shows the XRD patterns of $Sr_{2.93}B_2O_6$:0.07Eu^{2+} phosphor samples with various synthetic temperatures, from (a) to (e), the heated temperature is 1000℃, 1050℃, 1100℃, 1150℃ and

1200°C respectively. It is shown in Fig. 3 that the diffraction intensity first increases then decreases and the pure of diffraction peak first simplify then intermix with the increase of heating temperature. While the heating temperature is at 1150°C, the diffraction intensity is the strongest and the diffraction phase is the purest. It indicates that the optimization heating temperature of $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phosphor sample is 1150°C. Excepting 1150°C, other samples come forth the diffraction of $Sr_2B_2O_5$ phase. While the heating temperature is lower than 1150°C, the appearance of $Sr_2B_2O_5$ phase contributed to the lower synthetic temperature of $Sr_2B_2O_5$ phase, because of the high B context. Especially, the sample synthesized at 1000°C is basically the $Sr_2B_2O_5$:Eu^{2+}phosphor. While the heating temperature is higher than 1150°C, the existence of $Sr_2B_2O_5$ phase owes to decomposing of $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phase.

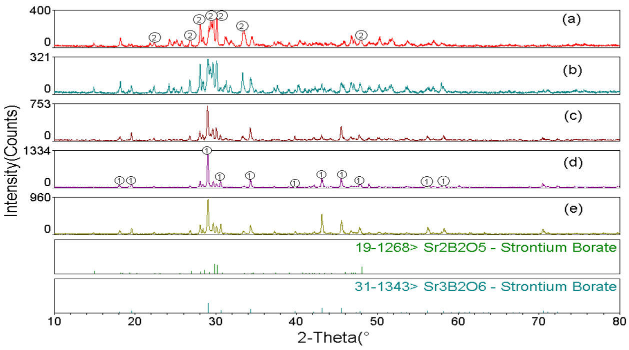
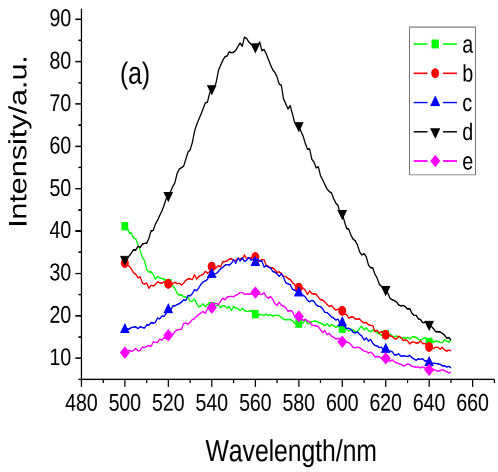


Fig. 3. The XRD patterns of $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ samples heated at various temperatures (a) 1000 ℃(b) 1050 ℃(c) 1100 ℃(d) 1150 ℃ (e) 1200 ℃.

3.4 The effects on luminescence properties of calcined temperature

Fig. 4 shows the spectra of $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phosphor sample with various synthetic temperatures, pattern (a) is the emission spectra and pattern (b) is the excitation spectra, the heated temperature of curves from a to e is 1000°C, 1050°C, 1100°C, 1150°C and 1200°C respectively. As can be seen from the pattern (a), the luminescence intensity of peaks at 555nm firstly increases with the rise of the heating temperature, when the heating temperature reach 1150°C, the luminescence intensity is the highest. Continuing rise temperature, the luminescence intensity begins to fall. Otherwise, there is no luminescent peak at 555nm for the phosphor sample of heating temperature at 1000°C, which is consistent with XRD pattern, indicating no yellow light emission of $Sr_2B_2O_5$:Eu^{2+} phosphor. Seeing from pattern (b), we can draw the uniform change rule, the excitation intensity first increase then decrease with the rise of heating temperature. Since the heating temperature arrives to 1150°C, the excitation intensity is the highest. We can get the conclusion that the optimization heating temperature is also 1150°C from the luminescent properties.



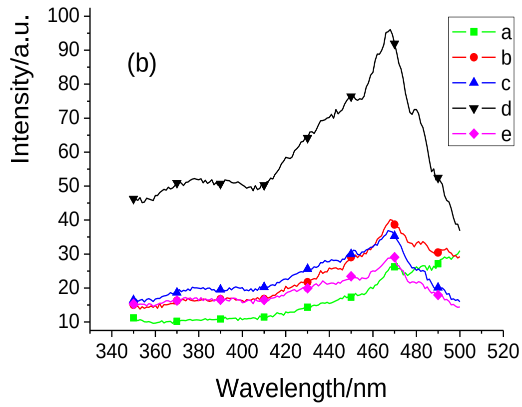


Fig. 4. The excitation and emission spectra of $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ with different temperatures (a) Emission spectra (λex=460nm) (b) Excitation spectra (λem=555nm).

4. Conclusions

In the present work, the $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$: phosphors have been synthesized by a rapid microwave heating method. The structure of $Sr_3B_2O_6$:Eu^{2+} phosphor is a hexagonal system with a R*c(167) space group. The luminescence spectrum of the $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phosphor is a broad band spectrum peaking at 555nm, and its excitation spectrum is also a broad asymmetric excitation band centering at 468 nm, extends from 400nm to 500nm. The optimum heating temperature is 1150°C.The $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phosphor is quite suitable for a phosphor conversion white LED excited by blue chip. The pure $Sr_{2.93}B_2O_6$:$0.07Eu^{2+}$ phosphor can be synthesized by microwave heating method.

Acknowledgments

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