

Study on the preparation of luminescent material BaCaSiO₄ by combustion method and its luminescent properties

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The blue phosphor material in trichromatic phosphors for white light emitting diodes (WLED) has a great application prospect. Therefore, the silicate blue luminescent material BaCaSiO₄:Eu²⁺, Gd³⁺ for WLED was prepared by combustion method. Using urea as combustion agent, the optimum sintering temperature and sintering time of primary sintering and secondary sintering were studied. The main emission peak of the luminescent material is located at 499nm, which was the transition emission peak of 4f⁶5d¹→4f⁷ of Eu²⁺, and the luminescence properties of silicate luminescent material could be enhanced by doping a certain amount of Gd³⁺. The color of light emitted from the luminescent material was pure blue according to the color coordinates obtained from the emission spectrum.

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1. Introduction

Now, white light-emitting diode (WLED) has the advantages of superior optical performance, easier to manufacture and environmental protection, and has a great application prospect in the field of lighting and display, so it has attracted more and more attention [1-2]. For the preparation of white light emitting diodes, BaMgAl₁₀O₁₇:Eu²⁺ is the most widely used blue phosphor in tricolor phosphors. However, the ultraviolet light below 365nm has higher luminous efficiency, but when the excitation wavelength increases, the luminous efficiency will decrease obviously [4]. In recent years, silicate-based luminescent materials have attracted much attention because of their high luminous efficiency, rich luminous colors, high chemical stability and thermal stability. Silicate matrix luminescent materials are mainly synthesized by high temperature solid state method [5]. The traditional high temperature solid state synthesis method has the advantages of high temperature, long time and high energy consumption. Another method for the synthesis of silicate matrix luminescent materials is combustion method [6]. In the combustion synthesis, the synthesis time is short, but the crystallinity of the prepared sample is poor, and the

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morphology and luminescent properties of the particles will be greatly affected, so it is necessary to carry out the post-treatment of secondary sintering at a certain temperature. even silicate luminescent materials are prepared by secondary sintering. Rare earth ions have been widely studied as doping activators because of their unique multi-level structure and various transition types. Eu^{2+} is the most widely used in all kinds of doped rare earth ions. Its luminescence is mainly due to the $4f^65d \rightarrow 4f^7$ broadband allowable transition in silicate. The emission wavelength of luminescent materials can be seen in the ultraviolet region with different substrates, so a new type of phosphors with specific wavelengths can be prepared by selecting the chemical composition of the matrix [7]. In recent years, some researchers have doped Ce^{3+} [8], Tb^{3+} [9] and Dy^{3+} [10] into silicate luminescent materials, and studied the luminescent properties of different rare earth ions [11]. For rare earth ions Gd^{3+} , Gd^{3+} is a very good activation ion, its emission light is located in the ultraviolet region, while the general rare earth ions have very good absorption in the ultraviolet region, so it is often used as a sensitizer. In many compounds, it acts as an intermediary of energy transfer to enhance the luminescence of other ions [12]. Among the silicate matrix luminescent materials used in blue phosphors studied in recent years. The thermal quenching of blue luminescence of $\text{Sr}_{0.25}\text{Ba}_{0.75}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ oxynitride silicate phosphors is only above 450K, which makes this material an interesting candidate material for LED conversion phosphors [13]. However, the quantum efficiency of the synthesized powder of the luminescent material is relatively low. Therefore, it is urgent to synthesize blue luminescent materials for WLED with good fluorescence properties and simple preparation of rare earth ions doped silicate.

In this paper, the blue luminescent material for WLED doped with rare earth ions was studied. By analyzing the effects of various process parameters and other factors on the surface morphology, crystal structure and fluorescence properties of the luminescent material, the best preparation process of silicate blue fluorescent material was obtained, and the color of the luminescent material was obtained by color coordinate.

2. Experiment

$\text{Ba}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{CO}(\text{NH}_2)_2$, $\text{Eu}(\text{NO}_3)_3$, $\text{Gd}(\text{NO}_3)_3$ powders and tetraethyl orthosilicate were ground for 30 minutes to get the materials to be sintered. The muffle furnace is heated to the ignition temperature, and then the material to be sintered in the crucible is pushed into the muffle furnace. After burning in 12 minutes, the once-sintered luminescent material is obtained. By burying carbon, the luminescent material was placed in a high temperature resistance furnace for secondary sintering, and the final blue luminescent material $\text{BaCaSiO}_4:\text{Eu}^{2+}$, Gd^{3+} was obtained.

The phase structure of the product was analyzed by HT100 X-ray diffraction analyzer of Elite Technology Co. Ltd. The morphology of the product was obtained by scanning electron microscope of Sirion 200 made by Philippe Company of the Netherlands. The fluorescence spectrum of luminescent materials was measured by RF- 5301PC fluorescence spectrophotometer made by Shimadzu Company in Japan.

3. Results and discussion

3.1. Research on process parameters

In order to obtain better particle uniformity and better luminous intensity, urea was selected as the combustion agent [14]. As can be seen from figure 1, with the increase of the amount of urea, the interface between the particles becomes clear gradually, from the initial adhesion to uniform and complete particles. The optimal particle size of the prepared luminescent material is when the molar ratio of urea to metal ions is 3: 1. With the increase of the amount of urea, the particles become fine and agglomerated. The main reason for this phenomenon is that urea releases a lot of heat during combustion, as well as a large amount of NO_2 , CO_2 , H_2O and other gases. At the same time of synthesizing luminescent materials, the reactants can be expanded and loose foam products can be obtained. With the increase of the amount of urea, urea combustion produces high temperature exothermic heat, which can synthesize better and better

luminescent materials with better particle size. When the content of urea is too much, the heat released is more than that needed by the luminescent materials, resulting in the phenomenon of overheating and the agglomeration between the particles, which affects the preparation of the luminescent materials.

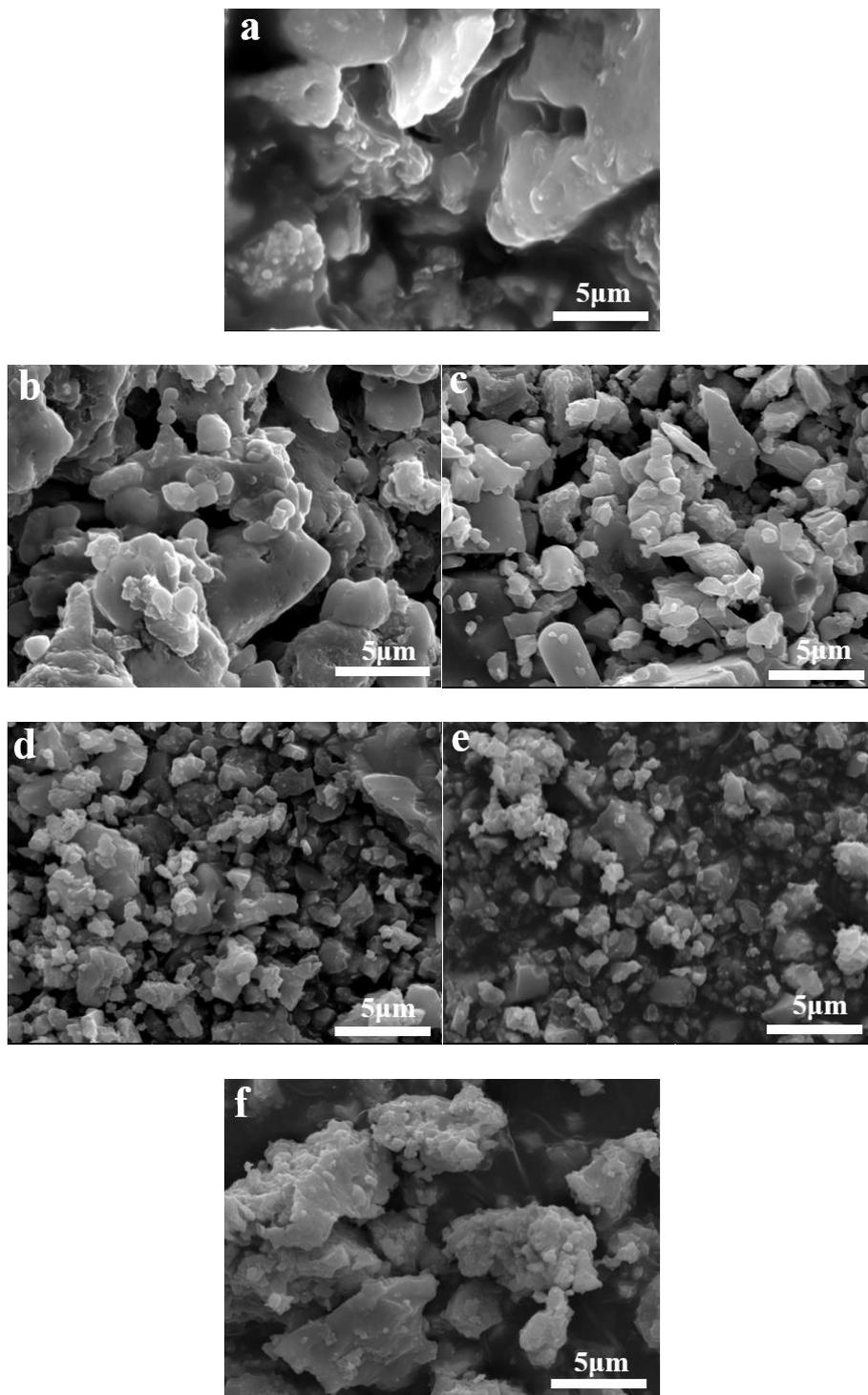
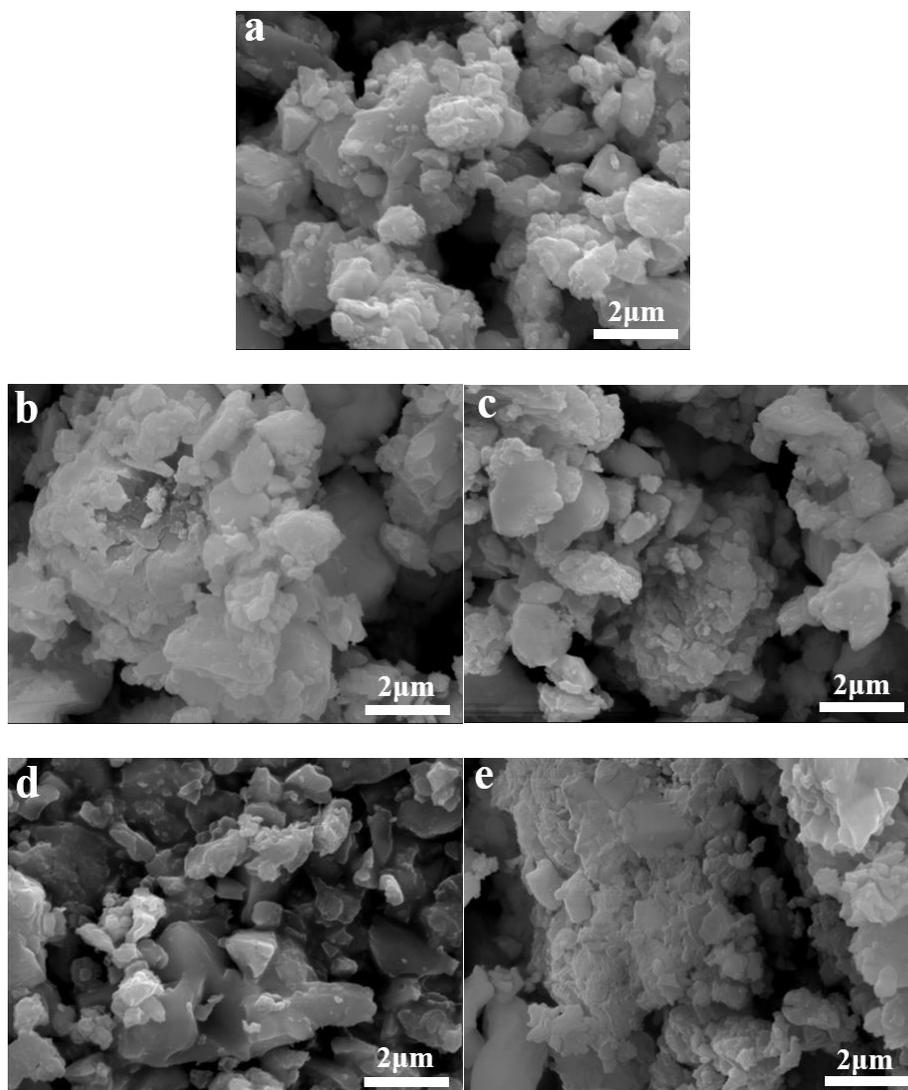


Fig. 1. SEM images of different content of urea. The values of a~f were 0, 1:1, 2:1, 3:1, 4:1 and 5:1, respectively.

As can be seen from figure 2, with the increase of furnace temperature, the particle integrity of the prepared luminescent materials increases, the difference of particle size decreases, the regularity of morphology increases, and the interface between particles becomes clearer and

clearer. When the furnace temperature is 550°C, the agglomeration and adhesion between particles become more and more serious when the furnace temperature is increased. As can be seen from Table 1, with the increase of furnace temperature, the time t_1 for the appearance of white smoke in the muffle furnace and the time t_2 for the explosion in the muffle furnace are getting faster and faster. On the other hand, the time difference between Δt_1 and Δt_2 for the preparation of luminescent materials at pre-and post-furnace temperature decreased at first and then increased, and the difference was the smallest at 500°C~600°C. The synthesis of figure 2 and Table 1 shows that when the furnace temperature is lower than 550 °C, the prepared luminescent material particles are fine and agglomerated, the reaction time is longer, and the temperature difference between the front and rear furnace tends to decrease. The main reason for this is that the furnace temperature is too low, the water in the raw material evaporates slowly, and the reaction starts later. When the furnace temperature is higher than 550 °C, the prepared luminescent materials exhibit agglomeration and the reaction time is short. The main reason for this phenomenon is that the reaction starts quickly, the raw material heats up quickly, the water evaporates incompletely, the residual water wraps the raw material, and urea decomposes at high temperature to form a basic compound with -OH group, which affects the quality of luminescent materials.



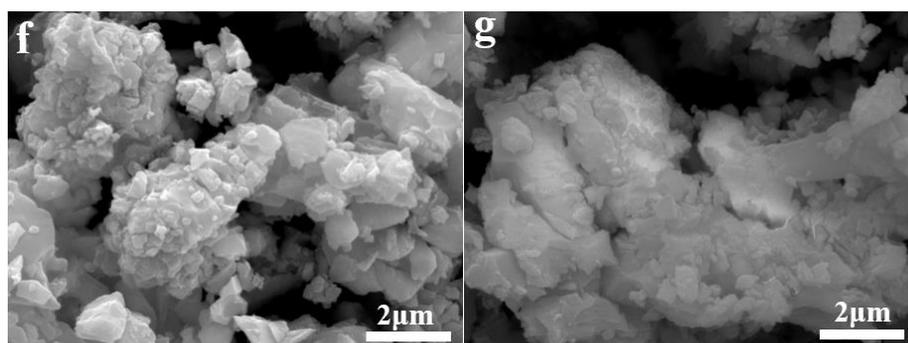


Fig. 2. SEM images of different furnace temperature (The furnace temperature of a~g is 400 °C 450 °C 500 °C 550 °C 600 °C 650 °C and 700 °C respectively.)

Table 1. The reaction time at different furnace temperature (t_1 is the time when the raw materials are put into the muffle furnace at different furnace temperatures to see the appearance of white smoke; t_2 is the time when the raw materials are put into the muffle furnace at different furnace temperatures until the explosion occurs. t_1 and t_2 are the time difference for the preparation of luminescent materials at the front and back furnace temperature.)

Furnace temperature (°C)	400	450	500	550	600	650	700
t_1 (s)	240	210	185	180	165	122	115
t_2 (s)	890	721	576	448	428	389	328
Δt_1 (s)	-	30	15	5	15	43	15
Δt_2 (s)	-	169	145	128	20	39	61

In the primary synthesis of combustion method, the synthesis time is short, the crystallinity of the prepared sample is poor, and the morphology and luminescent properties of the particles will be greatly affected, so it is necessary to carry out post-treatment of secondary sintering at a certain temperature. in order to achieve the required luminescent materials.

It can be seen from figure 3 that when the secondary sintering temperature is lower than 1000 °C, the prepared luminescent materials have uniform particle size, good surface morphology and uniform dispersion, and the effect of secondary sintering temperature is the best. When the secondary sintering temperature is higher than 1000 °C, the agglomeration and adhesion between the particles are serious, the interface between the particles is fuzzy and the morphology is irregular. The reason for this phenomenon is that when the secondary sintering temperature is too high, the grains of the primary products will grow too much, which will lead to the agglomeration between the particles, and the uniformity of the particles and the regularity of the surface morphology will be reduced, which is not conducive to the preparation of luminescent materials.

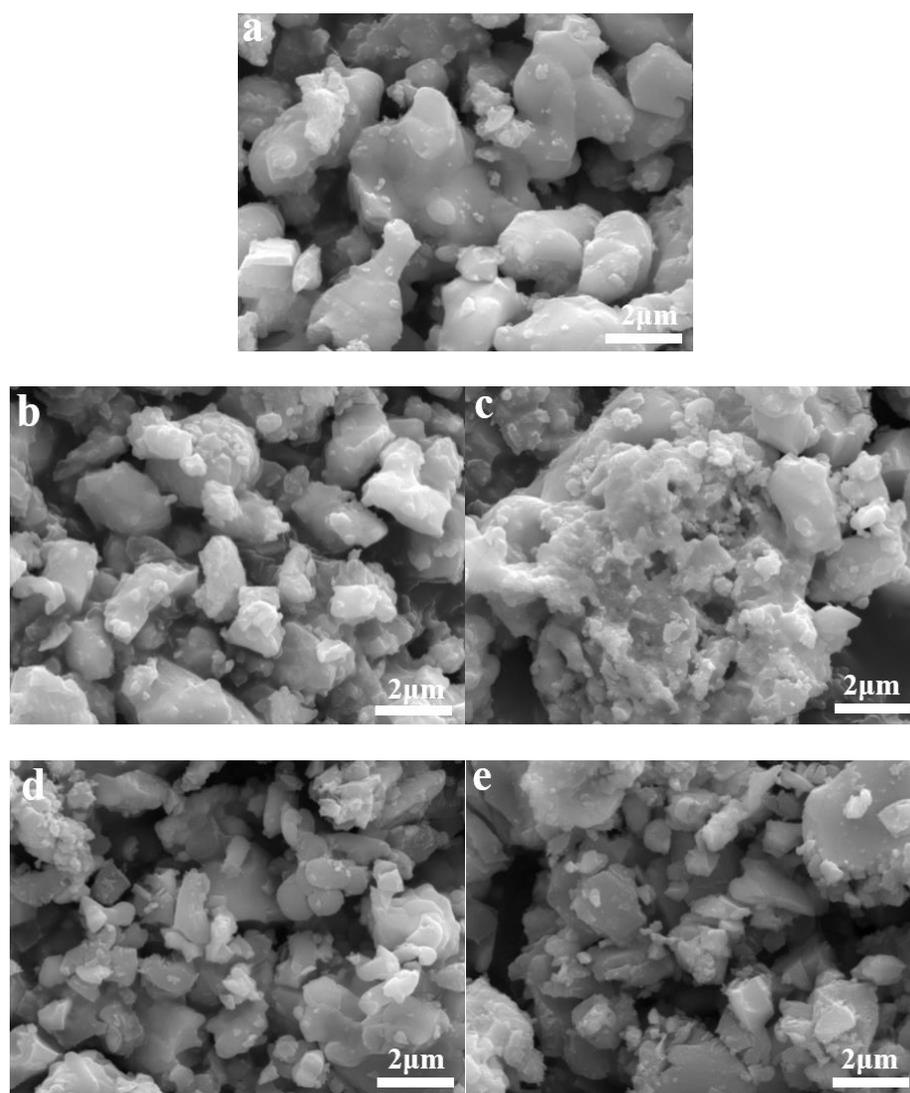


Fig. 3. SEM images of the different secondary sintering temperature (The secondary sintering temperature of a-e is 800 °C, 900 °C, 1000 °C, 1100 °C and 1200 °C respectively.)

As can be seen from figure 4, the diffraction peaks of the five prepared luminescent materials are all sharp and the half-width of the peak is narrow. The results show that the change of holding time within 5 h has little effect on the sharpness and half width of the diffraction peak of luminescent materials. In other words, changing the holding time of secondary sintering has little effect on the change of grain size and crystallinity of luminescent materials prepared by combustion method. The main reason for this phenomenon is that the required crystal phase has been basically synthesized during the primary combustion synthesis of luminescent materials, and the temperature of secondary sintering is relatively low. The heat provided by the holding time within 5 hours cannot achieve the purpose of grain growth and crystallinity of silicate luminescent materials. Therefore, in the XRD spectrum, we can see that the diffraction peak position, peak sharpness and half peak width of each curve are basically the same. Under the premise of comprehensive energy saving and the sharpness of the diffraction peak, the best holding time of secondary sintering in this experiment is 2 hours.

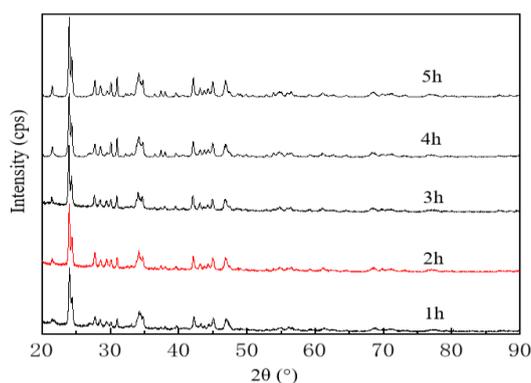


Fig. 4. The XRD patterns of the different secondary sintering holding time.
(The holding time was 1h, 2h, 3h, 4h and 5h respectively.)

As can be seen from figure 5, the main emission peak is located at 499nm, which is the transition emission peak of $4f^65d^1 \rightarrow 4f^7$ of ion Eu^{2+} . The change of Eu^{2+} doping concentration does not change the position of the emission peak of the luminescent material, only the intensity of the emission peak changes. The intensity of the emission peak increases with the increase of doping concentration. The optimum value of this experiment is reached when the molar ratio of metal ion to Eu^{2+} is 100:3 respectively. With the increase of the amount of Eu^{2+} , the intensity of the emission peak begins to decrease, which increases at first and then decreases. For the reason, we think that the excited energy states of the same activated ions in the luminescent materials are the same. With the increase of the concentration of the activator, these energy states will be close to each other, and the energy transfer between the energy states is easy to occur. The result is that the energy is consumed in the matrix lattice vibration through the quenching impurity center, which leads to the quenching of luminescence.

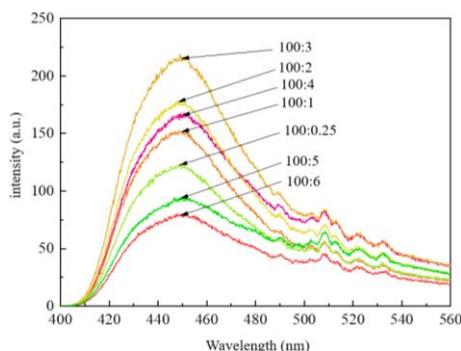


Fig. 5. The emission spectra of different amount of Eu^{2+} added (Emission spectrum with excitation wavelength of 385nm. The molar ratios of metal ions to Eu^{2+} are 100:0.25, 100:1, 100:2, 100:3, 100:4, 100:5, 100:6 respectively.)

As can be seen from figure 6, with the increase of the amount of Gd^{3+} , the luminous intensity of luminescent materials increases gradually. The emission peak intensity of the luminescent material is the highest when the molar ratio of Eu^{2+} : Gd^{3+} is 1: 1.5. Finally, with the increase of the amount of Gd^{3+} , the luminous intensity decreases, showing a trend of increasing at

first and then decreasing. The addition of Gd^{3+} can play a good sensitizing effect and enhance the luminous intensity of luminescent materials. This is because the $6P_{7/2}$ energy level of Gd^{3+} is above the ground state energy level $8S_{7/2}$, which is about 32113 cm^{-1} , which matches the $4f^65d$ excited state energy level of Eu^{2+} . Under external light stimulation, Gd^{3+} electrons are excited to a high energy level. Then the energy is rapidly relaxed to the $6P_{7/2}$ level, and the energy is transferred to the $4f^65d$ level of Eu^{2+} in a non-radiative manner, and then relaxed to the lower level of Eu^{2+} , emitting the characteristic light of Eu^{2+} . When the amount of Gd^{3+} is too much, the luminous intensity will decrease, which is because the amount of sensitizer will have a critical value. Concentration quenching occurs when the critical value is exceeded. The internal reason is that when there are too many sensitizers, there is a large amount of energy that can be absorbed by external energy and converted into activators, which is prone to energy transfer and rapid and extensive energy transmission. The energy entering the quenching center increases, which leads to the decrease of the luminous intensity of the luminescent materials.

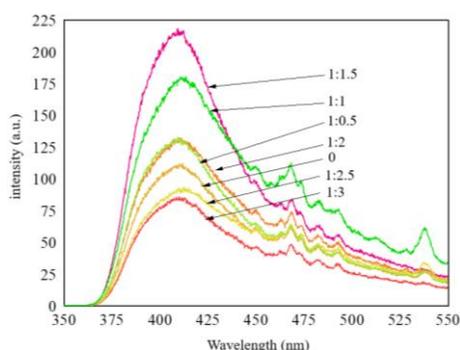


Fig. 6. The emission spectra of different amount of Gd^{3+} added. (The mole ratio of Eu^{2+} : Gd^{3+} was 0,0.5,1:1, 1.5,1:2, 2.5,1:3 respectively.)

Through the calculation of the formula, the emission spectrum data of the silicate luminescent material synthesized under the optimum preparation conditions in the experiment are transformed into the color coordinates of the material. Point B ($X=0.143$, $Y=0.065$) marked in Fig. 7. As can be seen from the color coordinate diagram, the color of the light emitted by $BaCaSiO_4:Eu^{2+}$, Gd^{3+} luminescent materials is pure blue.

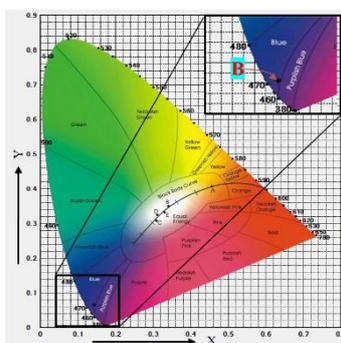


Fig. 7. The color coordinates (The coordinates of point B are $X=0.143$, $Y=0.065$).

4. Conclusion

The silicate blue luminescent material $\text{BaCaSiO}_4:\text{Eu}^{2+}, \text{Gd}^{3+}$ for WLED was successfully prepared by combustion method. The molar ratio of combustion agent urea to metal ions is 3:1. The optimum furnace temperature for the first sintering of luminescent materials is 550 °C. In the primary synthesis of combustion method, the synthesis time is short, the crystallinity of the prepared sample is poor, and secondary sintering is needed. The temperature of secondary sintering is 900 °C and the holding time is 2h. The main emission peak is located at 499nm, which is the transition emission peak of $4f^65d^1 \rightarrow 4f^7$ of ion Eu^{2+} . Eu^{2+} doping concentration can change the intensity of emission peak. The emission peak intensity is the strongest when the molar ratio of metal ion to Eu^{2+} is 100: 3. The addition of Gd^{3+} can play a good sensitizing effect, and the luminous intensity of luminescent materials increases gradually with the increase of the amount of Gd^{3+} . The emission peak intensity of the luminescent material is the highest when the molar ratio of $\text{Eu}^{2+}:\text{Gd}^{3+}$ is 1: 1.5. The color coordinates of luminescent materials are $X=0.143$, $Y=0.065$, and the color of the light emitted is pure blue.

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