Photoluminescence Properties of Eu^{3+}-Activated $YCa_3(GaO)_3(BO_3)_4$ phosphor

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Abstract

A borate compound was adopted as new host material for Eu^{3+} activator. The Eu^{3+}-doped $YCa_3(GaO)_3(BO_3)_4$ (YCGB) phosphors were successfully synthesized. Also, their photoluminescence properties under the excitation of UV ray were measured. In the XRD patterns of the synthesized powders, most peaks were well-matched to a gaudefroyite phase. The emission of Eu^{3+} in YCGB consists of a strong peak centered at 622 nm, which is attributed to $^5D_0$– $^7F_2$ transition of Eu^{3+} and several weak peaks at near the wavelength. Optimum Eu^{3+} concentration of the red phosphor under the excitation with the wavelength of 395 nm was about 75 mol%. This indicates that the red phosphor has a relatively higher critical concentration than that of the other Eu^{3+}-doped phosphors. The dominant interaction character of Eu^{3+} might be dipole-dipole interaction.

1. Introduction

Within the last several years, much progress has been made in the art of high-brightness LEDs with various colors. In recent, the white light emission using the LED is under examination for application to displays as a light source such as LCD backlight. Nowadays, a white LED device has been commendably realized using YAG:Ce as a broad band yellow phosphor coated on the blue LED chip. However, there exist at least two drawbacks in this combination. Firstly, the overall efficiency decreases rapidly when lowering the correlated color temperature of the device. Secondly, a concern with this device is that the " White" output light has an undesirable color balance for a true color rendition, viz., the output light is deficient in the red region of the visible light spectrum (above 600 nm). So, a separate red light source may have to be used to compensate LED for the red deficiency of the output light. On the other hand, for UV LED chip coated by red, green and blue phosphors, a promising white light generation way, it also desiderates a kind of efficient and stable red phosphor.

In this work, the Eu^{3+}-activated YCGB red phosphor was prepared by conventional solid-state reaction and found that this phosphor has a very high critical concentration. To obtain insight into the mechanism responsible for the concentration quenching of the Eu^{3+} emission, in this case, we have investigated YCGB:Eu^{3+} phosphor over a wide concentration range.

2. Experimental

$YCa_3(GaO)_3(BO_3)_4$:Eu phosphors were prepared from analytically pure starting materials of Y_2O_3, $CaCO_3$, Ga_2O_3, H_3BO_3 and Eu_2O_3 by a solid-state reaction. The mixture of the starting compounds was heated at 500℃ for 4 h and then sintered at the

temperature of 1000-1100℃. Since the reaction proceeds very slowly, it is important to maintain the long reaction time for about 60 h at 1000- 1100℃. The resulting powders were identified using a Rigaku D/MAX-33 X-ray diffraction (XRD) system with Cu Kα radiation. The excitation and emission spectra of the fired samples were measured using a Perkin-Elmer LS-50 luminescence spectrometer with a xenon flash lamp ($\Delta\ \nu^{1/2}$ = 10 μs). The decay measurement was performed at 622 nm emission for $^5D_0 \rightarrow {}^7F_2$ transition. All the measurements were accomplished at room temperature.

3. Results and Discussion

The XRD pattern of the Eu^{3+}-doped YCGB sample is presented in Fig. 1. In the XRD patterns of the powders heat-treated with different amounts of Eu^{3+}, most peaks correspond to the gaudefroyite phase with a hexagonal space group, *P6₃/m*.

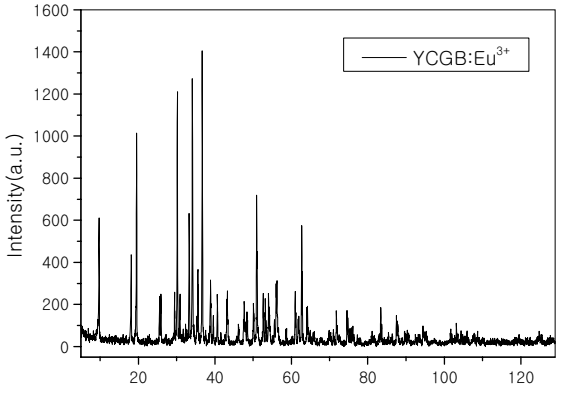

Fig. 1. XRD pattern of YCGB:Eu

Fig. 2 is excitation and emission spectra of YCGB:0.75Eu^{3+} phosphor. The excitation data of the main red fluorescence (λ_{em} = 622 nm) was recorded in the region from 200 to 500 nm. The broad band centered at 287 nm is attributed to a charge-transfer transition, which occurs by electron delocalization from the filled 2p shell of the O^{2-} to the partially filled 4f shell of Eu^{3+}. Several intense and sharp lines by Eu^{3+} ion are exhibited in the range of 300- 500 nm. The emission spectrum of YCGB:Eu has several characteristic peaks located in the wavelength range from 575 to 725 nm, which is typical emission spectrum due to the f-f transition of Eu^{3+} ion occupied Y^{3+} sites in $YCa_3(GaO)_3(BO_3)_4$ with inversion symmetry. It is observed in the emission spectrum that the YCGB:Eu phosphor exhibits a sharp band spectrum.

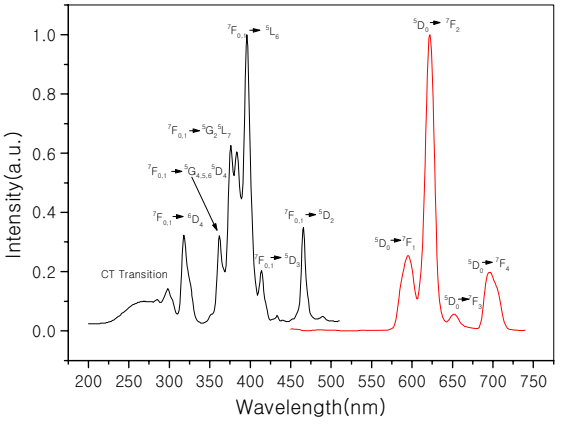

Fig. 2. Excitation and emission spectra of YCGB:Eu^{3+}.

In general, the luminescent intensity is proportional to the concentration of activators which could be excited by incident photons. As increasing the concentration of the activator, however, the emission intensity is saturated and begins to decrease at over a critical quenching concentration. To investigate the concentration dependence of the emission in YCGB:Eu, the emission

intensity under the 395 nm excitation was measured as a function of x at room temperature. Fig. 3 shows the concentration quenching curve of Eu^{3+} ions doped in $YCa_3(GaO)_3(BO_3)_4$. This phosphor invites the strongest red emission when the doping concentration of Eu^{3+} ion is 75 mol% (x=0.75). This result indicates that YCGB:Eu^{3+} phosphor has a relatively much higher quenching concentration compared with the other Eu^{3+}-doped phosphors.

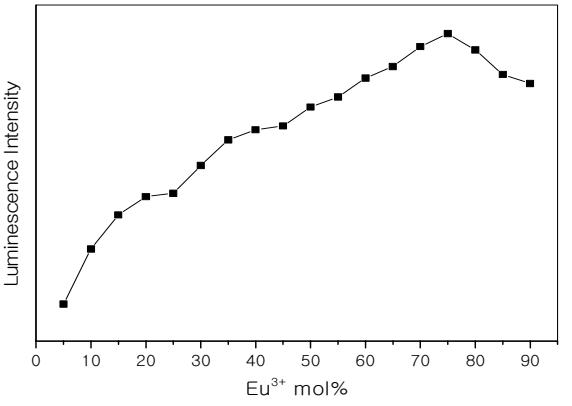

Fig. 3. Concentration quenching curve of YCGB:Eu^{3+} phosphor

As a new red phosphor, the present synthesized phosphor has higher emission intensity compared with a conventional sulfide phosphor (CaS:Eu) used as red phosphor in white LEDs under the excitation by blue light, as shown in Fig. 4. The sulfide phosphor is activated by Eu^{2+} ion and exhibits broad band emission with the highest peak at the vicinity of 650 nm. On the other hand, the emission of YCGB:Eu is caused by the f-f transition of Eu^{3+}, which conducts sharp band emission with the highest peak. It can be noted that the emission intensity of YCGB:Eu phosphor is higher by 226% (by peak height) than that of the sulfide phosphor.

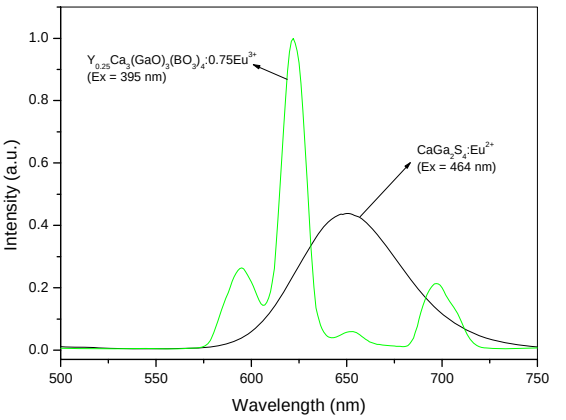

Fig. 4. Emission spectra of YCGB:Eu and CaS:Eu phosphors.

The decay curves for $^5D_0 \rightarrow {}^7F_2$ (622 nm) of Eu^{3+} in $Y_{1-x}Ca_3(GaO)_3(BO_3)_4$:$x$Eu are presented in Fig. 5. They are all well-fitted with a single-exponential function, and the lifetime τ values for x = 0.05, 0.75 and 0.85 are 0.87 ms, 2.65 ms and 2.51 ms, respectively. In the Eu^{3+} concentration between 0.05 and 0.75 mol, the lifetime τ of samples increase gradually with increasing Eu content.

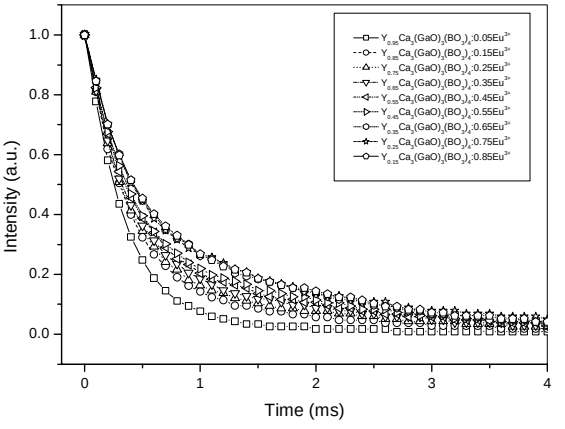

Fig. 5. Decay curves of the Eu^{3+} emission in YCGB:Eu ; λ_{ex} = 395 nm; λ_{em} = 622 nm.

4. Conclusions

The $YCa_3(GaO)_3(BO_3)_4$:Eu phosphor was synthesized by solid-state reaction. It was confirmed that the phosphor has a hexagonal structure by its XRD pattern. In the excitation spectrum, the most intense peak at about 395 nm corresponded to the ${}^7F_{0,1} \rightarrow {}^5L_6$ transition and a wide band around 287 nm attributed to a CT transition. The predominating emission peak was centered at 622 nm, which indicates that the local environments of Eu^{3+} ions in YCGB crystal have no inversion symmetry. The maximum doping concentration of Eu^{3+} measured under UV excitation with 395 nm wavelength was about 75 mole%. The dominant interaction character of Eu^{3+} in this case might be dipole-dipole interaction. Compared with the CaS:Eu phosphor used as red phosphors in white LEDs, this novel phosphor exhibits stronger emission intensity under the excitation of 464 nm blue light, but shows much stronger emission intensity under the excitation by the UV light of 395 nm. Most importantly, it is known that the oxide phosphor is much more stable than sulfide phosphor. Accordingly, we expect that this phosphor can be applied as a red component for white light emission by combination of tricolor phosphors with UV LED chip.

5. Acknowledgement

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6. References

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