Photoluminescence properties of $Gd_{1-x}Ln_xCa_3(GaO)_3(BO_3)_4$ (Ln=Eu, Tb, Tm) under UV excitation

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Abstract

A borate compound was adopted as new host material for Eu^{3+}, Tb^{3+} and Tm^{3+} activators. The phosphor samples, $Gd_{1-x}Eu_xCa_3(GaO)_3(BO_3)_4$, $Gd_{1-x}Tb_xCa_3(GaO)_3(BO_3)_4$ and $Gd_{1-x}Tm_xCa_3(GaO)_3(BO_3)_4$ have been synthesized by conventional solid-state reaction. The crystalline phase for the resulting powders was identified using an X-ray diffraction system.[1] Their photoluminescence properties under the excitation of UV ray were investigated. The Eu, Tb or Tm-doped $GdCa_3(GaO)_3(BO_3)_4$ emits efficient red, green or blue light, respectively. It was observed that the optimum concentration of Eu or Tb activator for the borate host was much higher than other Eu^{3+} or Tb^{3+}-doped phosphors.

1. Introduction

The phosphors for PDP in practical use have some problems such as thermal degradation from the blue phosphor, high discharge voltage from the green one and bad color purity from the red one.[3,4] In case of cold cathode fluorescent lamps (CCFLs) and light emitting diode lamps (LEDLs), which have been developed for use in back light unit (BLU) for liquid crystal displays (LCDs), color purity problem originated from phosphors is also being addressed. In this regard, it is important to search for novel and efficient phosphors for displays and lamps.[2] Therefore, many investigations about the luminescence properties of the compounds doped with rare-earth ions have been performed. On the other hand, it was recently reported that two new borates with the compositions of $YCa_3(MO)_3(BO_3)_4$ (M=Al, Ga) were prepared by solid-state reaction and their structures were determined from the X-ray powder diffraction data. In these borate compounds, the Y^{3+} and M^{3+} sites are substituted by most rare-earth and Cr, Mn ions, respectively. Therefore, Y^{3+} site can be replaced with Gd^{3+} ion and other rare-earth activators can be substituted into a portion of Gd^{3+} sites. These novel compounds could have efficient luminescent properties.

In this study, the Eu, Tb or Tm-doped $GdCa_3(GaO)_3(BO_3)_4$ phosphors were synthesized using conventional solid-state reaction. Their photoluminescence properties under UV excitation were characterized. In the emission spectra of the Eu or Tb-doped $GdCa_3(GaO)_3(BO_3)_4$ phosphors, it was found that these phosphors have a very high critical concentration. To obtain insight into the mechanism responsible for the concentration quenching of the Eu^{3+} or Tb^{3+} emission, the properties of $Gd_{1-x}Eu_xCa_3(GaO)_3(BO_3)_4$ and $Gd_{1-x}Tb_xCa_3(GaO)_3(BO_3)_4$ over a wide concentration range were measured.

2. Experimental

Phosphor samples of $Gd_{1-x}Ln_xCa_3(GaO)_3(BO_3)_4$, Ln=Eu, Tb, Tm ($0 \leq x \leq 1$), were prepared by firing the stoichiometric mixtures of Gd_2O_3, $CaCO_3$, Ga_2O_3, H_3BO_3 with Eu_2O_3 for Eu^{3+}-doped sample, Tb_4O_7 for Tb^{3+}-doped one or Tm_2O_3 for Tm^{3+}-doped one. The mixture was put into an alumina crucible with cover. That crucible with the mixture was pre-fired at 500℃ for 4 h and then fired at 1000℃ for 60 h. After firing, samples were gradually cooled to room temperature in the furnace. The phase identifications of samples were

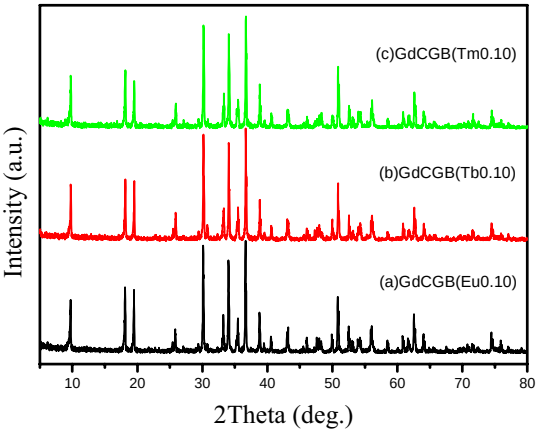

Fig. 1. The XRD patterns of $GdCa_3(GaO)_3(BO_3)_4$:Ln (Ln=Eu, Tb, Tm)

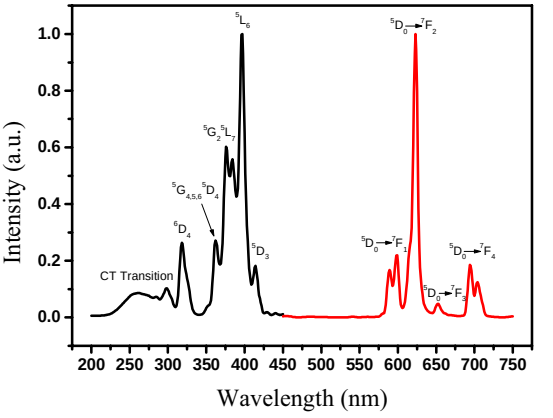

Fig. 2. The excitation and emission spectra of $Gd_{0.25}Eu_{0.75}Ca_3(GaO)_3(BO_3)_4$ (λ_{em}=623 nm, λ_{ex}=397 nm)

performed by a Rigaku D/MAX-33 X-ray diffraction system with Cu Kα (λ=1.5406 Å) radiation. The operation voltage and current were maintained at 40 kV and 40 mA, respectively. The excitation and emission spectra were measured using a luminescence spectrometer. The excitation spectra were measured in the wavelength range of 200-450 nm. All the measurements were performed at room temperature.

3. Results and discussion

According to the powder XRD patterns of the phosphor samples as can be seen in Fig. 1, it was confirmed for all samples to be obtained as a single phase, which are isostructure to $YCa_3(GaO)_3(BO_3)_4$ with heat treatment about 1000-1100℃ by solid-state technique.[1] Therefore, all the samples were fired at the same condition as above.

2-1. $GdCa_3(GaO)_3(BO_3)_4$:Eu^{3+} red phosphor

Fig.2 shows the excitation and emission spectra of the Eu-doped $GdCa_3(GaO)_3(BO_3)_4$ phosphor. As can be seen, the excitation spectrum of this phosphor consists of a broad band with the maximum at about 298 nm and a series of intense and sharp lines in the region 310-450 nm. The broad absorption band 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+}. In emission spectrum under UV irradiation, the $Gd_{1-x}Eu_xCa_3(GaO)_3(BO_3)_4$ ($0\leq x\leq 1$) phosphor exhibits a sharp band spectrum centered at around 623nm. Also, the phosphor has several characteristic peaks in the

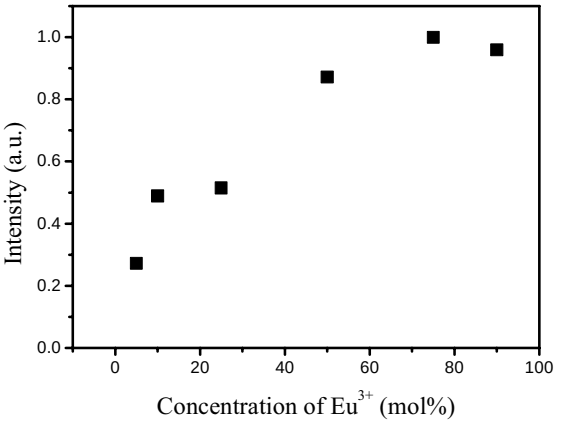

Fig. 3. Eu^{3+} concentration dependency in luminescence intensity of $Gd_{1-x}Eu_xCa_3(GaO)_3(BO_3)_4$ ($0\leq x\leq 1$) (Emission intensity at 623 nm)

region from 570 to 730 nm, which result from transitions between the energy levels of the $4f^6$ configuration of Eu^{3+}.

To investigate the Eu concentration dependence in the luminescence of $Gd_{1-x}Eu_xCa_3(GaO)_3(BO_3)_4$, the emission intensities under 379 nm excitation were measured between 5 mol% and 90 mol% of Eu^{3+}. The luminescence quenching behavior of $GdCa_3(GaO)_3(BO_3)_4$ with the changes of Eu^{3+} content is shown in Fig. 3. The phosphor exhibits the strongest emission intensity when the concentration of Eu^{3+} ion is 75 mol%. This indicates that this red phosphor has a relatively much higher quenching concentration compared to the other Eu^{3+}-doped phosphors. The

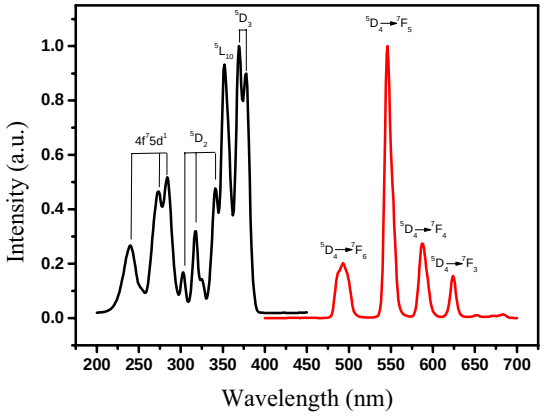

Fig. 4. The excitation and emission spectra of $Gd_{0.20}Tb_{0.80}Ca_3(GaO)_3(BO_3)_4$ (λ_{em}=546 nm, λ_{ex}= 369 nm)

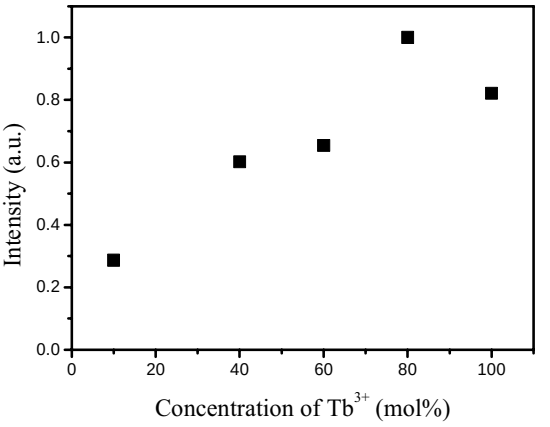

Fig. 5. Tb^{3+} concentration dependency in luminescence intensity of $Gd_{1-x}Tb_xCa_3(GaO)_3(BO_3)_4$ ($0 \le x \le 1$) (Emission intensity at 546 nm)

dominant interaction character of Eu^{3+} is dipole-dipole interaction in this case. The probabilities of those interactions were decreasing with increase in the distance between Eu^{3+} ions. The energy migration to quenching sites resulting in concentration quenching was restricted by the long distance. As concentration quenching is obviously not possible by a simple multipolar transfer process due to the energy gap between the $^5D_0$ level and the top of the $^7F_{0\text{-}6}$ multiplet, it is assumed that the quenching of Eu^{3+} in this system could be associated with a migration effect. [5]

2-2. $GdCa_3(GaO)_3(BO_3)_4$:Tb^{3+} green phosphor

The excitation and emission spectra of the $GdCa_3(GaO)_3(BO_3)_4$ doped with 80 mol% Tb^{3+} is presented in Fig. 4. The excitation spectrum is composed of some broad bands and several sharp peaks in the region 300-400 nm. The broad bands are attributed to the transition between the $4f^8$ and $4f^75d^1$ states of Tb^{3+} and the absorption lines result from transitions between the $4f^8$ configurations. In the emission spectrum, several characteristic lines which are originated from typical emission of Tb^{3+} are observed in the wide range of 470-650 nm. The strongest emission spectrum of the $Gd_{1-x}Tb_xCa_3(GaO)_3(BO_3)_4$ ($0 \le x \le 1$) green phosphor is centered at the wavelength of 546 nm, indicating the emission of green light.

Fig. 5 exhibits the concentration dependence of the Tb^{3+}-doped $GdCa_3(GaO)_3(BO_3)_4$. On the basis of the emission intensity with the changes of Tb^{3+} content, optimum concentration of activator is 80 mol%. This result also indicates that the Tb^{3+}-doped $GdCa_3(GaO)_3(BO_3)_4$ phosphor has a relatively higher quenching concentration than the others.

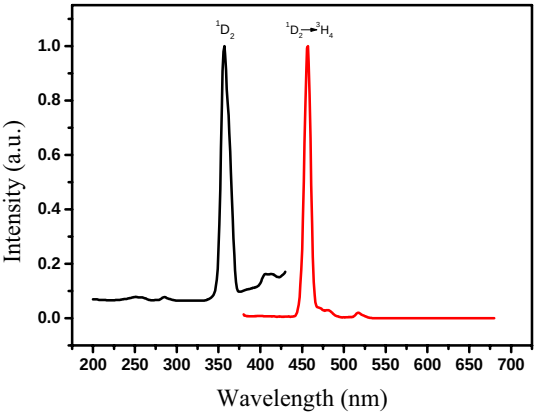

Fig. 6. The excitation and emission spectra of $Gd_{0.95}Tm_{0.05}Ca_3(GaO)_3(BO_3)_4$ (λ_{em}=456 nm, λ_{ex}= 356 nm)

2-3. $GdCa_3(GaO)_3(BO_3)_4$:Tm^{3+} blue phosphor

The excitation and emission spectra of $GdCa_3(GaO)_3(BO_3)_4$ doped with 5 mol% Tm^{3+} is shown in Fig. 6. In both excitation and emission spectra of this blue phosphor, an intense peak and some very weak peaks in the vicinity are observed. A intense peak shown in the excitation spectrum results from the transition between the excited level and the ground state of the $4f^{12}$ configuration of Tm^{3+}. In the

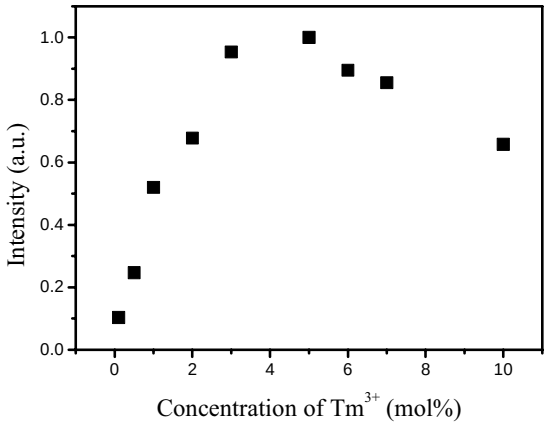

Fig. 7. Tm^{3+} concentration dependency in luminescence intensity of $Gd_{1-x}Tm_xCa_3(GaO)_3(BO_3)_4$ ($0 \leq x \leq 0.1$) (Emission intensity at 456 nm)

emission spectrum, on the other hand, the maximum peak centered at 456 nm is identified as the $^1D_2 \rightarrow {}^3H_4$ transition, which is originated from a typical blue emission by Tm.

In Fig. 7, the concentration dependence of the Tm^{3+}-doped $GdCa_3(GaO)_3(BO_3)_4$ phosphor is observed. In the concentration ranges from 0.1 mol% to 10 mol% of Tm^{3+}, the strongest emission intensity is accomplished at 5 mol%. Consequently, this composition could be applied as a blue component for white emission using an UV LED.

4. Summary

New borate phosphors, $Gd_{1-x}Ln_xCa_3(GaO)_3(BO_3)_4$ doped with Eu, Tb and Tm, were synthesized by conventional solid state reaction. In their XRD patterns, it was confirmed that the phosphor has single phases. Under UV irradiation, the phosphor samples doped with Eu, Tb or Tm emit efficient red, green or blue light, which predominating emission peak was at 623 nm, 546 nm, 456 nm, respectively. Optimum concentration of Eu or Tb activator for $GdCa_3(GaO)_3(BO_3)_4$ host is relatively high compared with other Eu^{3+} or Tb^{3+}-doped phosphors. We expect that these phosphors could be applied for white light emission by combination of tricolor phosphors with UV LED.

5. Acknowledgements

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