

Luminescence of Eu³⁺-doped GdCa₄B₃O₁₀ phosphor under UV and VUV irradiation

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Abstract

Due to its efficient red emission, Eu^{3+} ion has been doped in various host materials. $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphor for red emission has been prepared by solid state reaction. Photoluminescence properties for the phosphor under UV and VUV excitation were investigated. The $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphor under both excitation conditions shows typical red emission spectrum centered at 611 nm with several weak peaks due to energy transfer from $^5\text{D}_0$ to $^7\text{F}_j (j=1,2,3,4)$ of Eu^{3+} ion. On the other hand, the activator content exhibiting the concentration quenching under UV and VUV irradiation is 10 mole% and 2.5 mole%, respectively.

1. Introduction

The luminescence of the rare earth ions doped in inorganic hosts has been extensively investigated during the last decades. Especially, the development of phosphors excited by vacuum ultraviolet (VUV) radiation has attracted far attention with their potential industrial application for plasma display panels (PDP) [1-2]. The Eu^{3+} ion has interested great attraction due to the application as red phosphors. The $(\text{Y,Gd})\text{BO}_3:\text{Eu}^{3+}$ phosphor, which is known as the commercial red component for PDP, has three sharp emissions peaked at 593, 612, and 627 nm and its color purity is not satisfied [3]. On the other hand, the

phosphors of borate compound are expected to have strong absorption in the VUV region and to exhibit good color purity.

We are searching for red phosphors that can be applied as novel materials for emissive displays. Here we report the synthesis of Eu^{3+} -doped $\text{GdCa}_4\text{B}_3\text{O}_{10}$ powder by solid state reaction and their luminescence properties. The $\text{GdCa}_4\text{B}_3\text{O}_{10}$, in which a portion of the Gd^{3+} ions easily substituted by Eu^{3+} ions due to similar ionic radii of Gd^{3+} (0.94 Å) and Eu^{3+} (0.95 Å), has been adopted as a host material for red emission. Syntheses of $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphors were performed by a conventional solid state method. Some characterizations for the synthesized phosphors have been measured by using XRD, PL, and VUV-PL.

2. Experimental

The $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphors with the variation of activator content were prepared by the solid state reaction method. For the preparation of these phosphors, ultra pure gadolinium oxide (99.99%), europium oxide (99.99%), calcium carbonate (99.99%) and boric acid (99.99%) were taken as the starting materials. The resulting powders calcined for 24 h at 1400°C were identified using a powder X-ray diffraction system (Rigaku DMAX-33) with Cu K α radiation and Ni filter. Photoluminescence spectra were obtained by scanning the wavelength region from 560 nm to 720 nm at room temperature

under an excitation of a 147 nm vacuum ultraviolet (VUV) ray with D₂ lamp and Perkin Elmer LS-50B (UV), respectively.

3. Results and Discussion

Phosphors for PDP are required to have good quantum efficiency under VUV excitation. Some oxides such as borates, aluminates and silicates exhibit a strong absorption property in the VUV region. Thus, borate compounds are good candidates for PDP application. It is known that the host compound forms monoclinic crystal belonging to the space group *Cm*. Fig. 1 shows X-ray diffraction patterns of the GdCa₄B₃O₁₀:Eu³⁺ phosphor powder calcined for 24 h at 1400°C with the JCPDS file (50-390). In the XRD pattern, it can be confirmed that most characteristic peaks without impurity phase are well-matched with those of GdCa₄B₃O₁₀ phase that has a monoclinic structure.

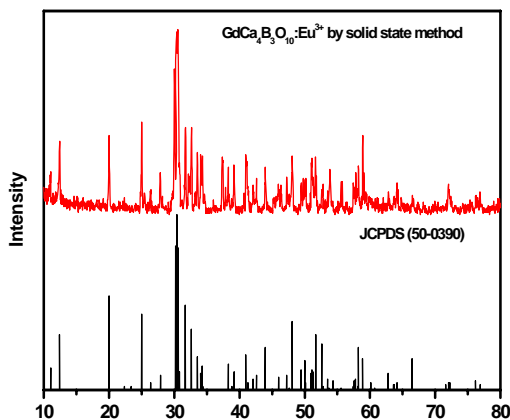


Fig. 1. XRD patterns of GdCa₄B₃O₁₀:0.025Eu³⁺ and JCPDS file.

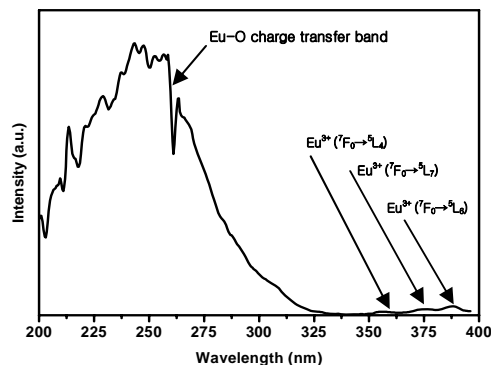


Fig. 2. UV excitation spectrum of Gd_{0.975}Ca₄B₃O₁₀:0.025Eu³⁺ phosphor with 611 nm emission.

Fig. 2 exhibits the excitation spectrum measured in the range of 200 nm to 400 nm for the synthesized GdCa₄B₃O₁₀:0.025Eu³⁺ phosphor, when the detection wavelength is monitored at 611 nm. The excitation spectrum consists of a strong absorption band in the range below 300 nm and some weak peaks between 350 nm and 400 nm. The strong absorption is assigned the Eu-O charge transfer band [4] and very weak peaks are due to the transitions of ⁷F₀-⁵D₄, ⁷F₀-⁵L₁ and ⁷F₀-⁵L₆ of 4f⁶. This indicates that the high quantum efficiency of Eu³⁺ excitation originates from the charge transfer transition of an electron from the 2p state of O²⁻ to a 4f state of Eu³⁺. The luminescence spectrum corresponds to direct excitation of the Eu³⁺ ground state to higher levels of the 4f-manifold and their assignments are marked in the figure in terms of the previous work [5]. Also, the weak peak by the ⁸S_{7/2}-⁶P_{5/2} transition of Gd³⁺ is observed at 310 nm.

The emission spectrum of the prepared GdCa₄B₃O₁₀:Eu³⁺ phosphor under VUV excitation is exhibited in Fig. 3, which is the

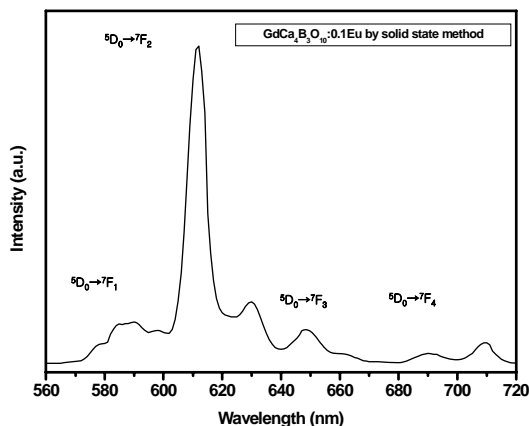


Fig. 3. Emission spectrum of $\text{Gd}_{0.975}\text{Ca}_4\text{B}_3\text{O}_{10}:0.025\text{Eu}^{3+}$ phosphor by 147 nm excitation.

same as the emission spectrum by UV (250 nm) excitation. $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphor has the typical red emission corresponding to the $f-f$ transition of Eu^{3+} . The emission spectrum consists of a strong peak at 611 nm and several weak emission peaks at the vicinity. This spectrum is interpreted by $^5\text{D}_0 \rightarrow ^7\text{F}_0$ line emissions of the Eu^{3+} ions with the strong emission $J=2$ at 611 nm ($^5\text{D}_0 \rightarrow ^7\text{F}_2$). It is known that the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transitions depend strongly on the local symmetry of the Eu^{3+} ions [6-7]. In case that Eu^{3+} occupies the site with inversion symmetry, the optical transitions are strictly forbidden as the electric dipole transition and can only occur as magnetic dipole transition. On the other hand, in case there is no inversion symmetry at the Eu^{3+} site, both dipole transitions exist and the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is observed. In the emission spectrum, the electric dipole $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 611 nm is stronger than the magnetic dipole $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition around 590 nm. This indicates that Eu^{3+} ions doped in $\text{GdCa}_4\text{B}_3\text{O}_{10}$ host material occupy the non-inversion symmetric sites. Eu^{3+} ions occupy the Gd^{3+} sites due to the same

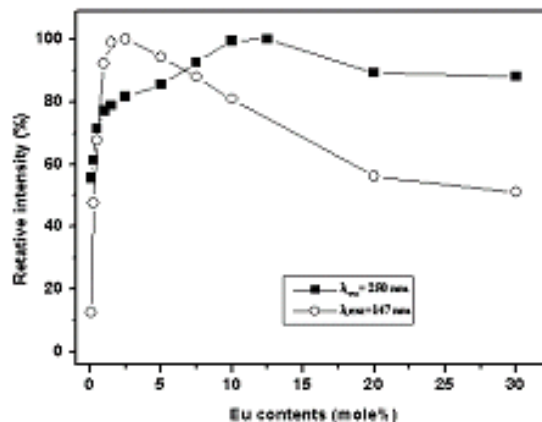


Fig. 4. The concentration quenching behavior for $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission of Eu^{3+} in $(\text{Gd}_{1-x}\text{Eu}_x)\text{Ca}_4\text{B}_3\text{O}_{10}$ on the excitation wavelength.

valence state and small difference in ion sizes.

To investigate the concentration dependence for the luminescence in $(\text{Gd}_{1-x}\text{Eu}_x)\text{Ca}_4\text{B}_3\text{O}_{10}$, the emission intensities by the 147 nm and 250 nm excitations, respectively, were measured as a function of x value at room temperature. As shown in Fig. 4, the concentration quenching of $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphor under the UV excitation takes place at the Eu concentration of 12.5 mole%. On the other hand, the emission intensity of the phosphor under VUV excitation reaches a maximum at Eu concentration of 2.5 mole%.

4. Conclusions

For effective red emission by UV and VUV excitations, $\text{GdCa}_4\text{B}_3\text{O}_{10}$ was adopted as a host material for Eu^{3+} activator. Thus, the red phosphor with the chemical formula of $\text{Gd}_{(1-x)}\text{Ca}_4\text{B}_3\text{O}_{10}:x\text{Eu}^{3+}$ has been synthesized by the conventional method. The monoclinic

phase of $\text{GdCa}_4\text{B}_3\text{O}_{10}:\text{Eu}^{3+}$ phosphor was formed by firing at 1400°C in air ambience. The typical red emission peaks of Eu^{3+} were observed in emission spectra. The optimum concentration of Eu^{3+} showing the maximum emission intensity by UV-excitation was 12.5 mole%, while by VUV excitation 2.5 mole%.

5. Acknowledgement

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6. References

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