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Investigation of luminescence quenching and persistent luminescence in Ce^{3+} doped $(Gd,Y)_3(Al,Ga)_5O_{12}$ garnet using vacuum referred binding energy diagram

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ABSTRACT

Optical properties of Ce^{3+}:$5d-4f$ luminescence in garnet compounds are strongly related to the energy locations of the excited 5*d* levels and the host conduction band (*CB*). By constructing the vacuum referred binding energy (*VRBE*) diagram including information on these energy location for $Gd_yY_{3-y}Al_{5-x}Ga_xO_{12}$ garnet (GYAG*G*) from the measured spectroscopic data, the luminescence quenching and persistent luminescence properties of GYAG*G*:Ce^{3+}(-Cr^{3+}) were discussed. The quantum yield (QY) of Ce^{3+}:$5d-4f$ in GYAG*G*:Ce^{3+} is clearly related to the energy gap, ΔE_{5d_1-CB}, between the lowest 5*d* level and the bottom of conduction band in the constructed *VRBE* diagram. This result indicates that the luminescence quenching of GYA*GG*:Ce^{3+} is caused by the thermal ionization. For GYA*GG*:Ce^{3+}-Cr^{3+} persistent phosphors, the depth of the electron trap formed by Cr^{3+} was remarkably changed from 0.27 to 0.69 eV by varying the Gd and Ga contents. The estimated *VRBE* value of Cr^{2+} in GYA*GG* can be used as effective value to predict the electron trap depth by Cr^{3+} in other oxide compounds as well as garnet hosts.

1. Introduction

Ce^{3+} doped garnet phosphors are attracting much attention in the application for white light emitting diodes (w-LEDs), scintillators and also luminous paints [1]. This is due to some excellent optical properties such as strong absorption at blue-LED wavelength, broad luminescence, high quantum efficiency, luminescence color tuning by crystal field (CF) splitting, fast decay time, large emission cross section of radiation and so on [2–4].

The oxide garnet composition is generally expressed as $\{A\}_3[B]_2(C)_3O_{12}$, where {A}, [B] and (C) mean dodecahedral, octahedral and tetrahedral cation sites, respectively. The garnet structure belongs to the cubic crystal structure with $Ia\bar{3}d$ space group and generates strong CF strength on {A} site where the Ce^{3+} ion occupies. As a result, the energy of Ce^{3+}:$4f-5d_1$ (the lowest in 5*d* levels) transition is generally located in the visible range. The CF strength can be changed by types of cations for {A}, [B] and (C) site. Empirically, when the ionic radius of {A} site cation becomes larger, the CF strength becomes larger and the luminescence peak wavelength becomes longer [5–7]. The increase of CF strength of Ce^{3+}: 5*d* level is known as specific phenomenon in garnet host [5–7]. It has reported that an increase of the radius of the cation at the dodecahedral site induces a ligand field distortion of eight oxide anions, leading to an increased splitting of the Ce^{3+} :5*d* levels and resulting in a red shift of the emission [1,8]. On the other hand, when the ionic radius of [B],(C) site cation becomes larger, for instance from Al to Ga, the CF becomes weaker and the luminescence peak wavelength becomes shorter [5–7].

In addition to the CF strength, the edges of the conduction band (*CB*) and the valence band (*VB*) also determine the optical properties in Ce^{3+}-doped phosphors [9–11]. Our group previously investigated the luminescence quenching in Ce doped YA*G*, $Y_3Al_2Ga_3O_{12}$ (YA_2G_3G) and $Y_3Ga_5O_{12}$ (YG*G*) phosphors. From the results of temperature dependence of photocurrent excitation spectra in YA*G*-YG*G* phosphors, we considered that the bottom of *CB* moves to downward and the $5d_1$ level moves to upward by substitution of Ga^3 for Al^{3+} in [B], (C) sites. Consequently, the energy gap, ΔE_{5d_1-CB}, between the $5d_1$ and the bottom of *CB* becomes smaller with increasing Ga content and the quenching processes of Ce^{3+} in the YA_2G_3G and YG*G* hosts were found to be thermal ionization and auto ionization, respectively [10]. Based on the thermal ionization process in YA_2G_3G:Ce^{3+} and the electron trap formation by Cr^{3+}-codoping, the bright green persistent phosphors of Ce^{3+}-Cr^{3+} codoped $Y_3Al_{5-x}Ga_xO_{12}$ (YAG*G*:Ce-Cr) have also been developed by our group [12,13]. The blue light charging efficiency and the electron trap depth in YAG*G*:Ce-Cr persistent phosphors were found

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to be controlled by the relationship between the bottom of *CB*, Ce^{3+}:5d_1 and electron trap level of (Cr^{3+} + e^-) [14]. In scintillation material, it has been reported that substitution of Ga enables the improvement of light yield and the decrease of afterglow component in Ce^{3+} doped $Gd_3(Al,Ga)_5O_{12}$ (GAG*G*) series [15]. The Ga doping makes the density higher and CB energy lower, so that the absorption coefficient for radiation is increased the shallow trap level formed by anti-site defects are buried by *CB* [15].

Because optical properties of Ce^{3+}-doped garnets are influenced by the 5d_1 level of Ce^{3+}, the host *CB* and electron trapping centers as mentioned above, it is important to predict the *CB* and *VB* and energy states (4*f* and 5*d* levels) of Ce^{3+}. The vacuum referred binding energy (*VRBE*) diagram proposed by Dorenbos summarizes these information, which helps comparison of optical properties among different compounds and understanding of electron transfer such as luminescence quenching by ionization and charging and de-trapping process for persistent luminescence [16,17].

Gd_yY_{3-y} $Al_{5-x}Ga_xO_{12}$ garnet (GYAG*G*) system is one of the attracting hosts for Ce^{3+}. From the *VRBE* diagram of $RE_3(Al, Ga)_5O_{12}$ (*RE* = Gd, Y, Lu), the substitution of Gd for Y at {A} site could affect the CF splitting, but not the band gap energy strongly, while the substitution of Al with Ga could affect both of the CF and the band gap energy efficiently [16]. Thus, GYAG*G*: Ce^{3+} has the possibility to vary the luminescence and persistent luminescence properties as desired. Although the *VRBE* diagram of $RE_3(Al, Ga)_5O_{12}$ (*RE* = Gd, Y, Lu) was already reported, the *VRBE* of GYAG*G* is not [16]. In this study, we constructed the *VRBE* diagram in GYAG*G* host and discussed the quantum yield (QY) of Ce^{3+} emission and the electron trap depth by Cr^{3+} in GYAG*G*:Ce^{3+}-Cr^{3+} with changing the Gd/Y ratio at {A} site and the Ga/Al ratio at [B] and (C) sites.

2. Experimental

Ceramic phosphors of (Gd_yY_{3-y}) ($Al_{5-x}Ga_x$)O_{12} (Ga content, x = 0, 1, 2, 2.5, 3, 4 and 5; Gd content, y = 1, 2 and 3) doped with 0.2 mol% Ce^{3+}, 0.2 mol% Eu^{3+} were fabricated by a solid-state reaction method. Metal oxides powders, Gd_2O_3, Y_2O_3, Al_2O_3, Ga_2O_3, CeO_2 and Eu_2O_3 were used as starting materials. These powders were homogeneously mixed by using a ball milling system (Premium Line P-7, Fritsch) with addition of ethanol. The obtained slurry was dried, pulverized, and then compacted to form a ceramic tablet (ϕ10 mm × 2 mm thickness) under uniaxial pressing of 50 MPa. The tablets were pre-sintered at 800 °C for 60 h and sintered at 1600 °C for 10 h in air. According to the phase diagram of Al_2O_3-Gd_2O_3 binary system [18], the garnet sample of $Gd_3Al_5O_{12}$ (x, y) = (0, 3) cannot be fabricated by a solid-state reaction method [19,20]. Ce-Cr codoped (Gd_yY_{3-y}) ($Al_{5-x}Ga_x$)O_{12} samples were also prepared in the same way, excess 0.05 mol% Cr^{3+} (Cr_2O_3) were added to the starting powder mixture. The crystal phases of samples obtained were analyzed by an X-ray diffraction measurement system (Rigaku, Ultima IV). The X-ray source is Cu Kα and the accelerative voltage and current were 40 kV and 40 mA, respectively.

Photoluminescence excitation (PLE) spectra in the vacuum ultraviolet (VUV) and visible region (100–500 nm) were measured at the BL3B beamline of the UVSOR facility (Institute for Molecular Science, Okazaki, Japan). This beamline consists of a 2.5 m off-plane Eagle type normal incidence monochromator, which covers the VUV, UV and visible regions. In the present experiments a spherical grating with a groove density of 300 lines/mm optimized at a photon energy of ~12 eV was used [21]. High-order light from the normal incidence monochromator was removed using lithium fluoride and quartz plates, and color-glass filters. PLE spectra observed were corrected for the spectral distribution of the excitation light source.

Spectral power distribution of photoluminescence was measured by a commercial 450 nm LED in an integrating sphere (Labsphere, LMS-100), which is connected to a CCD detector (Ocean Optics, USB2000) with an optical fiber. A standard halogen lamp (Labsphere, CLS-600)

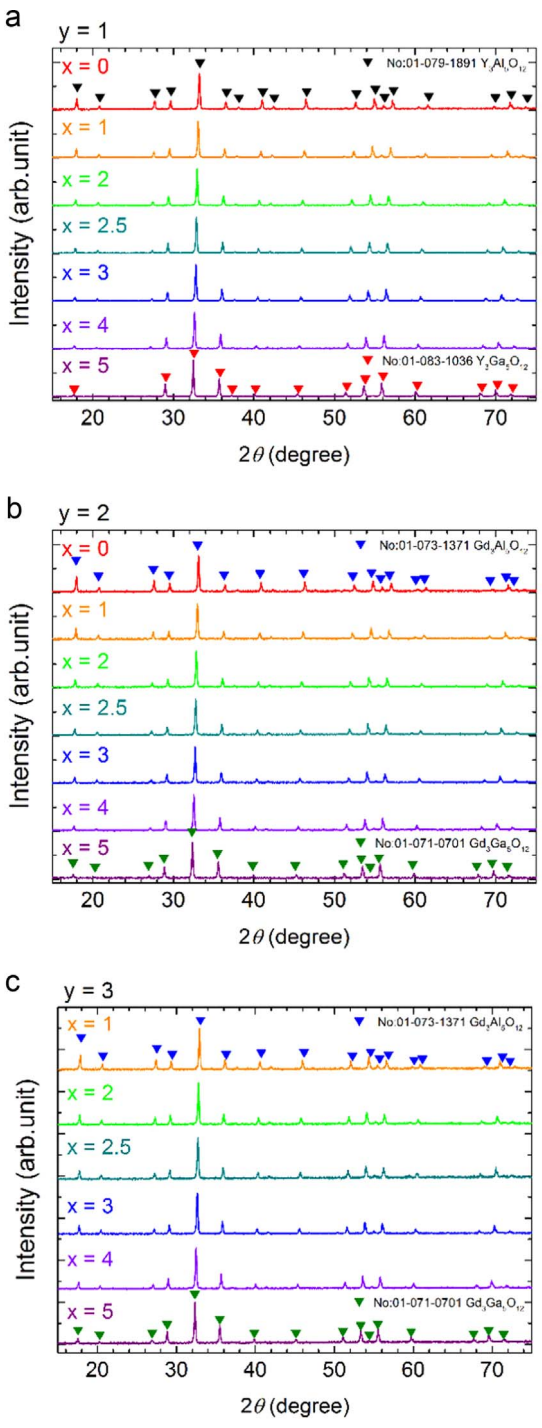

Fig. 1. XRD patterns of GYAG*G*: Ce^{3+} samples. (a) Gd content, y = 1, (b) y = 2, (c) y = 3.

Table 1
Host lattice constants of GYAGG:Ce samples.

Ga content, x	Gd content, y		
	y = 1	y = 2	y = 3
x = 0	12.04	12.08	–
x = 1	12.09	12.13	12.17
x = 2	12.15	12.18	12.22
x = 2.5	12.17	12.21	12.24
x = 3	12.20	12.23	12.27
x = 4	12.26	12.29	12.32
x = 5	12.31	12.35	12.38