Analysis of Ce^{3+} luminescence quenching in solid solutions between $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ by temperature dependence of photoconductivity measurement

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Photocurrent excitation spectra were measured to investigate the quenching in the garnet solid solutions. Intense photocurrent excitation bands attributed to the lowest $5d_1$ and the second lowest $5d_2$ levels were observed in the Ce-doped $\text{Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (Ce:YAGG) and $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (Ce:YGG). Based on the results of temperature dependence of photoconductivity, the $5d_1$ and $5d_2$ levels in the Ce:YAGG are found to be located below and within the conduction band, respectively, while both levels in the Ce:YGG are found to be located within its conduction band located at lower energy levels. In addition, the threshold of photoionization from the $4f$ level of Ce^{3+} to the conduction band in the Ce:YAGG and Ce:YGG were estimated to be 3.2, and 2.8 eV, respectively. We conclude that the main quenching process in the Ce:YAGG is caused by the thermally stimulated ionization process with activation energy of 90 meV from the $5d_1$ to the conduction band, and that in the Ce:YGG is caused by the direct ionization process from the $5d$ levels to the conduction band.

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I. INTRODUCTION

Recently, the Ce^{3+} -doped garnet phosphors are attracting a great deal of attention in the application for white light emitting diodes (LEDs). Most white LEDs are composed of blue LEDs and yellow phosphors ($\text{Ce}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$), which have many advantages such as strong absorption at the blue LED wavelength (~ 450 nm), broad yellow luminescence, and high quantum efficiency ($\sim 90\%$).¹ The garnet crystals can be formed in wide ranges of solid solutions with various crystal field strengths of Ce^{3+} ion. Therefore, tuning of $5d$ energy levels of Ce^{3+} ion by tailoring the host garnet crystals is possible. However, some garnet phosphors doped with Ce^{3+} show low quantum efficiency and large thermal quenching.

For instance, $\text{Ce}^{3+}:\text{Gd}_3\text{Al}_5\text{O}_{12}$ (Ce:GAG) is a good candidate of orange phosphors for warm white LEDs.² However, the thermal quenching of the Ce:GAG is much higher than that of the $\text{Ce}^{3+}:\text{Y}_3\text{Al}_5\text{O}_{12}$ (Ce:YAG). Chiang *et al.* investigated the differences in the thermal quenching in the Ce:YAG, Ce: $\text{Tb}_3\text{Al}_5\text{O}_{12}$ (Ce:TAG), and Ce:GAG.³ They explained that the strong thermal quenching is caused by the difference of activation energies in the nonradiative relaxation process from the excited $5d$ level to the ground $4f$ level. Because the excited $5d$ states have largely extended orbitals, the offset of the potential curve of the $5d$ excited state (U_e) is shifted from the bottom of $4f$ ground state (U_g) in the configuration coordinate diagram as shown in Fig. 1. The electrons in the excited $5d$ levels are thermally activated from the lowest position of $5d$ level to the crossing point at the intersection of U_e and U_g , where the excited electron and ground

states are intermixed. The thermal quenching can be promoted with decreasing energy gap (ΔE) between the bottom of the excited $5d$ level and the cross point of U_e and U_g . In general, the $5d$ energy level of Ce^{3+} ion is red shifted with increasing crystal field in garnet crystals, such as $\text{Y}_3\text{Al}_5\text{O}_{12}$ ($\lambda_{\text{em}} \sim 540$ nm), $\text{Tb}_3\text{Al}_5\text{O}_{12}$ ($\lambda_{\text{em}} \sim 555$ nm), and $\text{Gd}_3\text{Al}_5\text{O}_{12}$ ($\lambda_{\text{em}} \sim 560$ nm), and thus the activation energy decreases in the order of $\Delta E_{\text{YAG}} > \Delta E_{\text{TAG}} > \Delta E_{\text{GAG}}$. Therefore, the thermal quenching of Ce:GAG is the strongest among these garnet phosphors.

It is known that $\text{Ce}^{3+}:\text{Y}_3\text{Ga}_5\text{O}_{12}$ (Ce:YGG) shows no luminescence from the $5d$ to the $4f$ level at room temperature.⁴⁻⁶ Hansel *et al.* explained the quenching in the Ce:YGG by the nonradiative relaxation process from the $5d$ excited state to the $4f$ ground state using a configuration coordinate diagram.⁶ However, the $5d$ state of Ce^{3+} in the Ce:YGG has higher energy compared with that in the Ce:YAG. The nonradiative relaxation through the cross points between $5d$ and $4f$ levels are usually suppressed with increasing $5d$ energy levels as shown in Fig. 1. Therefore, it is not conceivable to explain the quenching in the Ce:YGG by the nonradiative relaxation process through the cross point.

Generally, quenching of Ce^{3+} in Ce: Lu_2O_3 and Ce: Y_2O_3 , which are known as nonluminescent materials, are explained by the photoionization process from the $5d$ level to the conduction band.⁷⁻⁹ It is possible that the quenching of the Ce:YGG is also a result of the photoionization. In this study, therefore, solid solutions between the Ce:YAG and the Ce:YGG were prepared, and the photoluminescence (PL), photoluminescence excitation (PLE) spectra, and photocurrent excitation (PCE) spectra were measured to investigate the quenching process.

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FIG. 1. (Color online) Configuration coordinate diagram in Ce:YAGG, Ce:YAG, Ce:TAG, and Ce:GAG.

II. EXPERIMENTAL METHODS

Polycrystalline ceramics of $(Y_{0.995}Ce_{0.005})_3Al_5O_{12}$ (Ce:YAG), $(Y_{0.995}Ce_{0.005})_3Al_2Ga_3O_{12}$ (Ce:YAGG), and $(Y_{0.995}Ce_{0.005})_3Ga_5O_{12}$ (Ce:YGG) were synthesized by the solid-state reaction. Commercial powders of Y_2O_3 (99.99%), Al_2O_3 (99.99%), Ga_2O_3 (99.99%), and CeO_2 (99.99%) were used as starting materials. The powders were mixed, grained, and pressed into a pellet of 10-mm diameter and sintered at 1400°C–1600°C for 6 h in air. The grinding and sintering processes were performed 2–3 times to obtain a single phase of the garnet crystal. PL and PLE spectra were measured by using a fluorescence spectrophotometer (Shimadzu, RF-5000). For the photoconductivity measurement, gold electrodes were deposited on the sample, which was partially masked by a tape of 1-mm width to separate the electrodes. The sample connected with two copper wires was mounted into a cryostat (Iwatani industrial gases Co., Ministat) to control the sample temperature between 20 K and 300 K. In addition, a sample chamber was always kept in a vacuum to suppress surface current of the sample. The sample was excited by a combination of a 300-W Xe lamp (Asahi Spectra Co., Ltd, MAX-302) and a monochromator (Nikon, G250). Direct voltage of 300 V was applied to the sample, and photocurrents were measured with a digital electrometer (ADVANTEST, 8240).

III. RESULTS AND DISCUSSION

A. XRD of Ce^{3+} -doped garnet crystals

Figure 2 shows XRD patterns of the Ce:YAG, Ce:YAGG, and Ce:YGG ceramics. Each XRD pattern of the Ce:YAG, Ce:YAGG, and Ce:YGG ceramic corresponds to that in reference data ICSD No. 082-05756, 089-6660, and 073-1374, respectively. All samples are identified as a single phase of the garnet crystals. From the obtained peak in XRD patterns, a lattice constant of the garnet crystal was estimated by using a formula of

FIG. 2. (Color online) XRD patterns of Ce:YAG, Ce:YAGG, and Ce:YGG ceramics.

$$a = \frac{\lambda \sqrt{h^2 + k^2 + l^2}}{2 \sin \theta},$$

where λ is Cu K_α x-ray wavelength; h , k , and l are Miller's indices; and θ is the diffraction angle. The calculated lattice constant of garnet crystals are 12.00 Å for Ce:YAG, 12.19 Å for Ce:YAGG, and 12.27 Å for Ce:YGG, following the Vegard's law against Ga content.

B. Variation of PL and PLE of Ce^{3+} luminescence in garnet crystals with Ga content

Figure 3 shows PLE spectra monitoring at 550 nm and PL spectra by 440 nm excitation in the Ce:YAG and Ce:YAGG. No luminescence was observed in Ce:YGG at room temperature, so that the PL and PLE spectra are not shown in Fig. 3. PLE bands at around 450 nm and 350 nm were observed in the Ce:YAG and Ce:YAGG. The longer wavelength band and the shorter wavelength band are ascribed to the transitions from the ground 4f level to the 5d₁ and 5d₂, which are the lowest and the second lowest 5d levels, respectively. In addition, a broad PL band at around 550 nm was observed in the Ce:YAG and Ce:YAGG. This band is attributed to the 5d₁–4f transition. The peak wavelengths of the PL (5d₁–4f) and PLE (4f–5d₁) bands in the Ce:YAGG were blue-shifted compared with that in the Ce:YAG, while the peak wavelength of the PLE (4f–5d₂) was red-shifted. This is because the crystal field of Ce^{3+} in the YAGG crystal is weaker than that in the YAG crystal. The energy level of the 5d₁ level and 5d₂ level of Ce^{3+} increase and decrease,

FIG. 3. (Color online) PL and PLE spectra of Ce:YAG, Ce:YAGG, and Ce:YGG ceramics. Spectra of Ce:YGG are not shown because luminescence was not observed.

respectively, with increasing ionic radius in the octahedral and tetrahedral sites in the garnet crystals.^{5,10,11} In addition, the PL and PLE intensity decreased with increasing Ga concentration. We also observed the quenching of Ce^{3+} luminescence caused by Ga-substitution for Al in the garnet crystals.

C. Photoconductivity of Ce^{3+} in garnet crystals

No photocurrent was observed in the Ce:YAG, whereas intense photocurrent excitation bands were observed at around 420 and 350 nm in the Ce:YGG and Ce:YAGG at 300 K as shown in Fig. 4. Peak wavelengths of these two bands correspond to the results in the PLE spectra in the Ce:YAGG and the absorption spectra reported elsewhere for Ce:YAGG and Ce:YGG.^{4,5} Therefore, the PCE bands at around 420 and 350 nm are identified as the $4f-5d_1$ and $4f-5d_2$ transitions. These results of the photocurrent excitation spectra show that the excited $5d_1$ and $5d_2$ levels promote carriers into the conduction band. In addition, the PCE intensity increased with increasing Ga concentration. This is completely in contrast to the results of Ga concentration

FIG. 4. (Color online) Photocurrent excitation spectra of Ce:YAG, Ce:YAGG, and Ce:YGG ceramics.

FIG. 5. (Color online) Temperature variation of the photocurrent excitation spectra in the Ce:YAGG ceramics.

dependence of PL and PLE intensities. Therefore, the photocurrent from the $5d$ levels to the conduction bands is strongly correlated to cause of the luminescence quenching of Ce^{3+} in the Ga-substituted garnet crystals.

D. Location of $5d$ levels in garnet crystals

Figures 5 and 6 show temperature variation of the PCE spectra in the Ce:YAGG and Ce:YGG. In the Ce:YAGG, at low temperature, photocurrent was observed only by the $5d_2$ excitation at low temperature, but not by the $5d_1$ excitation. However, the excited $5d_1$ level of Ce^{3+} gradually induced the photocurrent with increasing temperature. On the other hand, in the Ce:YGG, a significant photocurrent was observed by both $5d_1$ and $5d_2$ excitations even at low temperature. These phenomena can be understood on the basis of the relative position between the $5d$ levels and the conduction band. The $5d_1$ level in the Ce:YAGG can be located just below the bottom of the conduction band, so that the photoconductivity from the $5d_1$ level to the conduction band can be induced by a thermally stimulated process. The fact that the PCE band of the $5d_2$ level in the Ce:YAGG was observed at low temperature shows that the $5d_2$ level is located within

FIG. 6. (Color online) Temperature variation of the photocurrent excitation spectra in the Ce:YGG ceramics.

TABLE I. Lattice constant, band gap energy, and threshold energy of photoionization in Ce^{3+} -doped garnet crystals.

Samples	Measured lattice constant (Å)	Band gap energy, E_g (eV)	Threshold energy of photoionization, E_{PI} (eV)
$\text{Ce:Y}_3\text{Al}_5\text{O}_{12}$	12.00	6.5	3.8
$\text{Ce:Y}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$	12.19	5.9	3.2
$\text{Ce:Y}_3\text{Ga}_3\text{O}_{12}$	12.27	5.5	2.8

the conduction band and can cause the photoconductivity directly. On the other hand, the peak intensity ratio of the PCE bands of $5d_1$ and $5d_2$ were not changed in the Ce:YGG at various temperatures. This is because both of the $5d_1$ and $5d_2$ levels in the Ce:YGG are located within the conduction band and the photocurrent occurs directly from the $5d$ levels to the conduction band.

Based on these energy relationships between the $5d$ state and the conduction band, the threshold energy of photoionization (E_{PI}) from the $4f$ ground state of Ce^{3+} to the conduction band is estimated. Table I shows the lattice constant, bandgap energy, E_g and E_{PI} in the Ce-doped garnet crystals. The E_{PI} in the Ce:YAGG and Ce:YGG is about 3.2 eV and 2.8 eV, respectively, because the photocurrents at low temperature were observed below about 390 nm (3.2 eV) excitation in the Ce:YAGG and below 450 nm (2.8 eV) excitation in the Ce:YGG. The E_{PI} in the Ce:YAG can be above 3.8 eV because the PCE band of $5d_2$ (330 nm) was not observed completely, even at room temperature. According to the result of photoconductivity of the Ce:YAG by Pedrini *et al.*,¹² the threshold of photoionization in the Ce:YAG is 3.8 eV. In addition, You *et al.*¹³ estimated that the threshold of photoionization in the Ce:YAG is 3.9 eV by thermoluminescence excitation spectra. The E_{PI} estimated by our results of the photoconductivity in the Ce:YAG is in reasonable agreement with the E_{PI} reported in the Ce:YAG.^{12,13}

The origin of the decrease of E_{PI} with increasing Ga concentration can be explained as follows. It has been reported that the E_g of the YAG and YGG crystals are about 6.5 eV and 5.5 eV.^{14,15} The E_g of the YAGG crystal has not been reported. However, the lattice constants between the YAG and YGG crystals follow the Vegard's law (Table I). Assuming that the E_g also changes by the Vegard's law, the E_g of the YAGG is expected to be about 5.9 eV. Application of the Vegard's law to the E_g is often used in the solid solutions of various III-V semiconductors. Therefore, this assumption is not a bad approximation to estimate E_g . The monotonic decrease of the E_{PI} and the E_g with increasing Ga concentration shows that the change of the E_{PI} is caused mainly by the shift of the conduction band to lower energy side.

E. Activation energy from $5d$ state to conduction band

To estimate the activation energy from the $5d$ state to the conduction band, we plot a natural-logarithmic integrated PCE band intensity as a function of $1/kT$, where k is Boltzmann constant and T is temperature as shown in Figs. 7 and 8. The photocurrent intensities of $5d_1$ and $5d_2$ decreased with decreasing temperature in both samples. However, the

FIG. 7. (Color online) Temperature dependence of the integrated area of the individual photocurrent bands in Ce:YAGG.

temperature dependences are not linear and not fitted by the Arrhenius equation. The similar temperature dependence of the photocurrent to that in the present Ce:YAGG have been reported in the Ce^{3+} -doped Lu_2SiO_5 .^{16,17} In that material, the lowest $5d$ level of Ce^{3+} is located within the bandgap and the second and third lowest $5d$ levels are located within the conduction band. According to these reports, temperature dependence of the PCE band ($5d_1$), which is located within bandgap, is described by

$$I = C_1 + C_2 \exp\left(-\frac{\Delta E_1}{kT}\right), \quad (1)$$

where C_1 is a temperature-independent contribution by an electron-tunneling process to adjacent Ce^{4+} and the exponential term $C_2 \exp(-\Delta E_1/kT)$ is a result of a thermally stimulated ionization process from the $5d_1$ to conduction band.^{16,17} From fitting of the data of $5d_1$ in the Ce:YAGG, the activation energy was estimated to be $\Delta E_1 = 90$ meV. This activation energy corresponds to the energy gap from the $5d_1$ level to the conduction band.

FIG. 8. (Color online) Temperature dependence of the integrated area of the individual photocurrent bands in Ce:YGG.

FIG. 9. Energy level scheme of Ce^{3+} in YAG, YAGG, and YGG.

In addition, they also reported that the temperature dependence of the PCE band ($5d_2$), which is located within the conduction band can be fitted to

$$I = C_3 + C_2 \exp\left(-\frac{\Delta E_1}{kT}\right) + C_4 \exp\left(-\frac{\Delta E_2}{kT}\right), \quad (2)$$

where C_3 is also a temperature-independent contribution and equal to the sum of C_1 and C_1' , which is a result of a direct ionization process from the $5d_2$ to the conduction band; $C_4 \exp(-\Delta E_2/kT)$ is the second thermally stimulated process.^{16,17} The excitation of the $5d_2$ level results in the fast population of the lowest $5d$ level; thus, the photocurrent by the $5d_2$ level excitation includes the contribution from the $5d_1$ level by the thermally stimulated process. Therefore, Equation (2) includes the term $C_2 \exp(-\Delta E_1/kT)$. From fitting to our present results, the small activation energy of ΔE_2 was calculated to be 43 meV. This activation energy can be explained by a thermally stimulated process from electron traps, which can be either Ce-bound exciton, oxygen vacancies, or anti-site defects.^{16,18,19}

We consider the temperature dependence of the PCE bands ($5d_1$ and $5d_2$) in the Ce:YGG. In this material, the $5d_1$ and $5d_2$ levels are located within the conduction band, where the electron in the $5d$ levels are transferred to the conduction band directly without any thermally activated passes. The observed temperature dependences of the PCE bands ($5d_1$ and $5d_2$) can be caused by the thermally stimulated process from electron traps to the conduction band and fitted to

$$I = C_3 + C_4 \exp\left(-\frac{\Delta E_2}{kT}\right). \quad (3)$$

The activation energy from the $5d_1$ and $5d_2$ bands estimated by the temperature dependence of PCE spectra was 56 and 38 meV, respectively. These activation energies are similar to each other and also almost the same values in Ce:YAGG. Therefore, the electrons are caught by the same electron traps upon both $5d_1$ and $5d_2$ excitations.

Based on these results, Fig. 9 summarizes a band model including the $5d$ state and the conduction band in three garnet crystals with different Ga concentration. With increasing Ga content in the solid solutions between the Ce:YAG and the Ce:YGG, the crystal field strength, the conduction band energy, and threshold of photoionization decreased, resulting in the change of the relative position between the $5d$ state of Ce^{3+} and the conduction band. The $5d_1$ and $5d_2$ levels in the Ce:YAGG are located below and within the conduction band, respectively, while both those levels in the Ce:YGG are located within the conduction band. Therefore, the main quenching process in the Ce:YAGG is caused by the thermally stimulated ionization process from the $5d_1$ to the conduction band, and that in the Ce:YGG is caused by the direct ionization process from the $5d$ levels to the conduction band.

IV. CONCLUSION

The location of the $5d$ levels of Ce^{3+} relative to the energy bands and luminescence quenching mechanism was proposed based on the PL, PLE, and PCE spectra. The main quenching process in the Ce:YAGG is caused by the thermally stimulated ionization process from the $5d_1$ to the conduction band whereas that in the Ce:YGG is caused by the direct ionization process from the $5d$ levels to the conduction band.

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