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Investigation of Luminescence and Photoacoustic Properties in Ce$^{3+}$-Doped Ln$_3$Al$_5$O$_{12}$ ($Ln = Lu, Y, Gd$) Garnet

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Optical and photoacoustic properties of Ce$^{3+}$-doped lanthanide (Lu, Y, Gd) aluminum garnet were investigated. In the photoacoustic (PA) spectra, the $5d_1$ (lowest $5d$ level) band of Ce$^{3+}$ was observed at around 450 nm in the obtained Ce$^{3+}$-doped garnet samples. This result shows that a part of the excited energy is converted to thermal energy, which is generated by some nonradiative processes. In Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$, the $5d_1$ PA peak wavelength is shorter than the $5d_1$ photoluminescence excitation peak wavelength, which indicates that part of the heat generation is caused by the phonon relaxation process within $5d_1$ state. The PA intensity and luminescence quantum efficiency of the Ce$^{3+}$-doped gadolinium yttrium aluminum garnets ((Gd$_0.5$Y$_0.5$)$_3$Al$_5$O$_{12}$, (Gd$_0.75$Y$_0.25$)$_3$Al$_5$O$_{12}$) are much stronger and smaller, respectively, than those of Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$. Based on these results and the persistent luminescence excitation spectra, we conclude that (Gd$_0.5$Y$_0.5$)$_3$Al$_5$O$_{12}$:Ce$^{3+}$ and (Gd$_0.75$Y$_0.25$)$_3$Al$_5$O$_{12}$:Ce$^{3+}$ possess the additional heat generation process explained by the thermal ionization.

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Ce$^{3+}$-doped garnet materials have attracted a great deal of attention in w-LEDs and scintillators applications because of their intense broad absorption in a blue region, high quantum efficiency, and luminescence in various colors. These absorption and luminescence properties of the Ce$^{3+}$ ion are derived from the $4f$-$5d$ allowed transitions. The luminescence color variation is caused by the shift of $5d$ excited level by the nephelauxetic effect (centroid shift caused by covalency) and the crystal field splitting. 1-4 The chemical formula of general garnet crystals can be expressed as [A]$_3$[B]$_2$(C)$_3$O$_{12}$, where [A], [B] and (C) represent the cations at the dodecahedral, octahedral and tetrahedral sites, respectively. The dodecahedral site to which Ce$^{3+}$ occupies the distorted square anti-prism structure with D$_2$ point-group symmetry, which results in the large crystal field splitting of $5d$ state. The split $5d$ levels are referred as $5d_1$, $5d_2$, $5d_3$, $5d_4$, $5d_5$ from the lowest $5d$ energy level. The crystal field strength and $5d$ splitting can be changed by varying the garnet component ions. So far, the optical properties of Ce$^{3+}$ in many garnet host compositions have been studied. 1-11

When the dodecahedral site in Ln$_3$Al$_5$O$_{12}$ are changed from the smaller lanthanide, Ln$_3$ to the larger Ln$_5$ ion, for instance in the order of Lu, Y, Tb to Gd, the $5d_1$ energy shifts to the lower energy and quenching temperature becomes much lower. 1,5,16 Therefore, the luminescence quantum efficiency of Ce$^{3+}$:$5d_1$ is much lower. In the PLE spectra, two PLE bands at room temperature can be increased with increasing ionic radius of the dodecahedral site. The decrease of quantum efficiency should cause excess heat generation through some nonradiative relaxation processes.

Photoacoustic (PA) spectroscopy is one of the measurements to get information of heat generation after photon absorption. The heat flux generated by excitation light is transported in a sample and changes the surface temperature. As a result, the gas pressure in the photoacoustic chamber will be changed and the formed sound can be detected by a microphone. Grinberg et al. reported the PA spectrum of Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ in a wide wavelength range between 265 nm and 570 nm and discussed the results with configuration diagrams and the hot luminescence from $5d_2$ to $4f$. 1,2 However, the PA spectroscopy of other Ce$^{3+}$-doped garnet phosphors has not been reported. In this study, the PA properties of Ce$^{3+}$-doped multi lanthanide (Lu, Y, Gd) component aluminum garnet were investigated as a function of excitation wavelengths, and the heat generation process was discussed.
to the 4f-5d₂ and 4f-5d₁, respectively. According to the PL and PLE, the 5d₁ energy level shifts to longer wavelength (lower energy) with increasing average ionic radius of Ln ion in the dodecahedral site in the order of Lu (0.977 Å), Y (1.019 Å) and Gd (1.053 Å) while the 5d₂ levels shifts to higher energy (shorter wavelength). These results are in good agreement with the previous report.²¹

Figure 2 shows photoacoustic (PA) excitation spectra of Ln₃Al₅O₁₂:Ce³⁺ (Ln = Y, Gd, Lu) in the range between 370 nm and 600 nm. A broad PA band was observed at around 450 nm in all the samples. This PA band can be attributed to the 4f-5d₁ transition of Ce³⁺. The observation of 5d₁ PA band indicates that the heat is generated after the 4f-5d₁ photon absorption. The intensity of 5d₁ PA band in Ln₃Al₅O₁₂:Ce³⁺ becomes much stronger with increasing average ionic radius of Ln site. The PA intensity can be compared in the series of Ln₃Al₅O₁₂ because the sample sizes of the ceramics are exactly the same.

Compared with the PLE spectra, the PA peak of 5d₁ slightly shifts to shorter wavelength (higher energy) in the LuAG, LuYAG and YAG samples. Figure 3a shows the comparison between PLE and PA spectra in YAG:Ce³⁺. The 5d₁ PA peak is located at 450 nm while the 5d₁ PLE band is at 464 nm. This mismatch of PA peak position from PLE can be explained by the wavelength dependence of the heat generation process. The heat generation can be caused by two processes. One is the nonradiative relaxation (such as thermally activated crossover and through the thermal ionization processes) from the 5d state to the 4f ground state as shown in process 2 of Figure 4, the other is the phonon relaxation within 5d₁ state from the higher vibronic state of 5d₁ to the zero phonon state of 5d₁ as shown in the red arrow (process 1) of Figure 4. The phonon relaxation also occurs within 4f state (process 1')
of Figure 4). For the nonradiative relaxation from the 5d\textsubscript{1} to the 4f, the heat generation as a function of wavelength should be the same as the absorption spectrum. For the phonon relaxation within 5d\textsubscript{1} state, the heat generation process should have the excitation wavelength dependence, which should be distinguished from the absorption spectrum. In the case of the excitation on the zero phonon line (ZPL), there is no heat generation within the 5d potential curve while in the excitation on higher vibronic modes in 5d potential curve, the heat flux is generated and increased with increasing excitation energy. Figure 3b shows a simple simulation of the wavelength dependence of heat generation by the phonon relaxation within 5d\textsubscript{1} state. For the simulation, the Gaussian type absorption band (in the energy scale) peaked at 465 nm and the ZPL energy of 488 nm were assumed. The simulated absorption curve was converted to the wavelength scale as shown in red line of Figure 3b. The generating heat flux within 5d\textsubscript{1} state increases with increasing excitation photon energy as the heat generation is zero at ZPL energy as shown in the black line of Figure 3b. By multiplying the generating heat flux to absorption spectra, we can roughly estimate the wavelength dependence of heat generation (PA spectrum) by the phonon relaxation within 5d\textsubscript{1} state as shown in the blue line of Figure 3b. From the simulation, it is found that the peak wavelength in PA spectrum shifts to shorter wavelength compared with the absorption peak. Based on these results, the PA band of 5d\textsubscript{1} in YAG:Ce\textsuperscript{3+} can be mainly caused by the phonon relaxation within 5d\textsubscript{1} state. If the heat generation occurs by the phonon relaxation within 5d\textsubscript{1} state in all the samples, the PA intensity is not different from each other because all the Ce\textsuperscript{3+}-doped garnet samples undergo the similar phonon relaxation within 5d\textsubscript{1} state. However, with increasing average Ln ionic radius the integrated PA intensity increases especially from the Gd substitution as shown in Figure 5. For the integrated PA intensity, because the rising of PA intensity was observed below 450 nm, the PA spectra in Figure 6 shows a weak persistent luminescence excitation (PersLE) spectra at room temperature in LuYAG:Ce, YAG, GdYAG and Gd75YAG doped with Ce\textsuperscript{3+} and PersLE spectrum at 100 °C in Gd75 YAG.

These results show that the increase of PA intensity is caused by some additional heat generation by nonradiative process. In general, two main nonradiative processes by thermally activated crossover and thermal ionization have been reported for the 5d-4f transition. Thermally activated crossover is the nonradiative relaxation process from the excited 5d potential curve to the lower 4f potential curve through the crossing point in a configuration coordinate diagram.\textsuperscript{22} Thermal ionization is the thermally activated electron transfer process from the 5d state to the conduction band (CB).\textsuperscript{23} We already demonstrated the thermal ionization quenching process in YAG:Ce\textsuperscript{3+} at 300 °C from the thermoluminescence excitation spectroscopy.\textsuperscript{24} The band gap decreases with increasing lattice constant of host garnet in the order of LuAG, YAG and GdAG (Gd\textsubscript{3}Al\textsubscript{5}O\textsubscript{12}), which results in the decrease of energy gap between the 5d\textsubscript{1} and CB (\(\Delta E_{5d-CB}\)) because of the energy shift of 5d\textsubscript{1} by crystal field splitting is much smaller than the that of CB.\textsuperscript{21} The \(\Delta E_{5d-CB}\) of LuAG, YAG and GdAG were estimated to be 1.05 eV, 1.07 eV and 0.6 eV, respectively.\textsuperscript{21} Assuming that the quenching is caused by thermal ionization, it is expected that the QE at room becomes much lower and the PA intensity becomes much stronger with increasing Gd content in the garnet composition. In order to check the thermal ionization process, persistent luminescence excitation (PersLE) spectra were measured as shown in Figure 6. Persistent luminescence can be caused by detrapping of charges that were previously trapped followed by recombination on a luminescent center. Charge trapping occurs when electrons in the excited state of luminescence centers are transferred to the CB (e.g., through thermal ionization) and then captured by traps in the host. From the PersLE spectra, the threshold energy that causes the thermal ionization can be discussed. Although the obtained samples are not persistent phosphors, very weak persistent luminescence due to the Ce\textsuperscript{3+}:5d-4f was detected by high sensitivity photomultiplier tube. The normalized integrated intensity of persistent luminescence 2 min after ceasing excitation light was plotted as a function of excitation wavelength as shown in Figure 6. The PersLE of LuAG:Ce is not shown because the S/N ratio is very low due to the weak persistent heat flux caused by nonradiative process from the 5d level compared with LuAG:Ce, LuYAG:Ce, YAG:Ce. The absorbed photon number at 438 nm is almost the same among the samples, so that the PA intensity at 438 nm can be compared. The PA intensity at 438 nm in GdYAG and Gd75YAG is much stronger compared with LuAG:Ce, LuYAG:Ce, YAG:Ce. The PA intensity at 438 nm of Gd75YAG:Ce is approximately 1.8 times higher than that of YAG:Ce. This result is corresponding to the the decrease of QE in GdYAG and Gd75YAG.

Figure 5. Integrated intensity of 5d\textsubscript{1} photoacoustic band (black circle), photoacoustic intensity at 438 nm (green diamond), number of absorbed photon at 438 nm (blue triangle) and quantum efficiency by 438 nm excitation (red square) of different samples.

Figure 6. Persistent luminescence excitation (PersLE) spectra at room temperature in LuYAG, YAG, GdYAG and Gd75YAG doped with Ce\textsuperscript{3+} and PersLE spectrum at 100 °C in Gd75 YAG.
luminescence. In the PersLE at room temperature, the strong PersLE band was observed at around 350 nm, which can be attributed to the 4f-5d transition of Ce3+, in all the samples. This result shows that the thermal ionization from the 5d level to the conduction band occurs at room temperature. On the other hand, in the range between 375 nm and 450 nm, only GdY AG and Gd75Y AG shows weak PersLE band at room temperature. On the other hand, in the range between 375 nm and 450 nm, only GdY AG and Gd75Y AG shows weak PersLE band at room temperature. In the PersLE spectrum of Gd75Y AG:Ce at 100°C, a clear excitation band was observed around 470 nm due to the 4f-5d transition. This is strong evidence of thermal ionization from the 5d level. Therefore, in the Ce3+-doped GdY AG and Gd75Y AG, the additional heat generation can be caused by the nonradiative relaxation process from 5d1 to 4f via the thermal ionization process.

Conclusions

Ceramics of Lu3Al5O12 (LuAG), (Lu0.5Y0.5)3Al5O12 (LuYAG), Y3Al5O12 (YAG), (Gd0.5Y0.5)3Al5O12 (GdYAG), (Gd0.75Y0.25)3Al5O12 (Gd75Y AG) doped with Ce3+ (0.1% at the Ln dodecahedral site) were synthesized by solid-state reactions. By the blue excitation on the 5d1 state, the photoacoustic signal was detected in all the samples, which means that the excited energy is converted to the thermal energy. In YAG:Ce3+, the 5d1 peak in the photoacoustic spectrum is 10 nm shorter than that in photoluminescence excitation spectrum. This is because the heat generation was caused by the phonon relaxation within 5d1 state. The PA intensity becomes much stronger with increasing average ionic radius of Ln site. On the other hand, the luminescence quantum efficiency becomes much lower in Ce3+-doped GdY AG and Gd75Y AG compared with LuAG, LuYAG and YAG. In the PersLE spectra of GdY AG and Gd75Y AG, the 5d1 excitation band was observed, which indicated the thermal ionization occurs from the 5d1 level. Therefore, Ce3+-doped GdY AG and Gd75Y AG possess the additional heat generation process that is the nonradiative relaxation process explained by the thermal ionization.

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References