Comparative study of optical and scintillation properties of Ce:YAGG, Ce:GAGG and Ce:LuAGG transparent ceramics

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We investigated photoluminescence (PL) and scintillation properties of 0.8 mol % Ce-doped (Y, Gd, Lu)3Al2Ga3O12 (Ce:YAGG, Ce:GAGG and Ce:LuAGG) transparent ceramics, which were fabricated by the vacuum sintering method. The obtained samples showed a strong and broad PL emission in the wavelength range from 470 to 600 nm owing to 5d→4f transitions of Ce3+. The PL and scintillation decay curves consisted of two or three exponential components, and the primary components ranged around 35–43 ns. Besides, the scintillation spectra excited by X-rays showed similar features with those in PL. In the X-ray induced afterglow measurements, the Ce:LuAGG sample exhibited the weakest afterglow intensity. The pulse height spectra of these samples showed clear photoabsorption peaks. Among those samples, Ce:LuAGG sample showed the highest scintillation light yield of 18,700 ph/MeV.

Key-words : Scintillator, Ce, YAGG, GAGG, LuAGG

1. Introduction

Inorganic scintillators have been widely used in ionizing radiation detectors. Those detectors are used in various applications such as medical,1) security,2) astrophysics,3) geophysical and resource explorations.4) Scintillators, upon interaction with ionizing radiations, absorb the radiation energy and then convert the absorbed energy into a large number of low energy photons (visible or UV) immediately. Because a cross-section of material against ionizing radiation strongly depends on the type of radiation and material compositions, there are many different scintillators designed for each kind of radiation and applications. Till now, most of the practical scintillators are bulk single crystals due to their outstanding optical properties such as high transparency, intense emission light yield, and strong energy stopping power. However, transparent ceramics, which possess several advantages compared with the corresponding single crystals (e.g. higher mechanical strength, feasibility for more complicated geometric shape, lower production cost), become promising candidates for scintillation applications. Especially thanks to the fast development of advanced ceramic preparation technology,5) transparent ceramics with high optical transparency become more available in the recent decade.

Rare-earth doped (Y, Gd, Lu)3Al2Ga3O12 [(Y, G, Lu)AG] scintillators have attracted much attention due to their high light yield and relatively fast response.6) In these garnet scintillators, Ce-doped Y3Al2Ga3O12 (Ce:YAGG)7)8)9)10) and Lu3Al2Ga3O12 (Ce:LuAGG)11) were widely studied. In addition to those YAG and LuAG crystals, Ce12+) doped Gd3(Al, Ga)5O12 (GAGG) crystal which was developed by us on a cooperation with Furukawa Co., Ltd.12)13) exhibited the best scintillation performance in Ce-doped complex garnet materials, and it showed an extremely high scintillation light yield (46,000 ph/MeV in the crystal form and 70,000 ph/MeV in the ceramic form).12)13)14)15) It is also worth noting that the ceramic sample showed a higher light yield even though it was not fully transparent but translucent.12) Furthermore, transparent ceramic of Ce-doped GAGG was successfully sintered and it also showed high scintillation light yield.12)

In this work, to extend our research, we improved the transparency of garnet transparent ceramics including Ce-doped Y3Al2Ga3O12 (Ce:YAGG), Gd3Al2Ga3O12 (Ce:GAGG), Lu3Al2Ga3O12 (Ce:LuAGG), and studied them for potential scintillator applications. We characterized the optical properties such as the in-line transmittance, photoluminescence (PL) spectrum and PL lifetime of these samples. Furthermore, we also studied the radioluminescence spectra and scintillation lifetime, radiation-induced afterglow and pulse height spectra of these samples. The Ce:YAGG transparent ceramic has been studied for long persistent luminescence applications, and it shows an extremely long and bright persistent luminescence when co-doped with Cr16).17)18) However, only few reports are focusing on scintillation behaviors of Ce-doped YAGG, GAGG and LuAGG transparent ceramics.

2. Experiment

2.1 Sample preparation

0.8 mol % Ce-doped Y3Al2Ga3O12, Gd3Al2Ga3O12 and Lu3Al2Ga3O12 (Ce:YAGG, Ce:GAGG and Ce:LuAGG, respectively) transparent ceramics were fabricated by vacuum sintering method. The chemicals of Y2O3, Gd2O3, Lu2O3, Al2O3, Ga2O3, CeO2 (4N purity) were used as raw materials. The starting powder was...
mixed by ball milling method with ZrO₂ ceramic balls and anhydrous alcohol for several hours. 0.8–1.2 wt% tetaethyl orthosilicate (TEOS) and 0.8–1.5 wt% dispersant (Kyoeisha Chemical Co., Ltd., Flowlen G-700) were added as sintering aid and surfactant during ball milling process, respectively. The mixed powder was dried at 80°C for 36 h and compacted to form a ceramic green body (φ20 mm × 2–3 mm thick) under uniaxial pressing of 50 MPa without further cold isostatic pressing (CIP), then pre-heated at 800°C for 60 h in air to remove the organic substances, and finally sintered at 1600–1650°C for 10–20 h under vacuum atmosphere. The as-sintered specimens were double-mirror polished using a copper plate and diamond slurry.

2.2 Optical characterizations

The transmittance spectra were measured by using JASCO V670 spectrometer in the wavelength range of 190–2700 nm with 0.5 nm intervals. The PL emission map and PL quantum yield (QY) were measured using Quantaurus-QY (C11347, Hamamatsu). The spectral ranges measured for the excitation and emission were 250 to 500 nm and 200 to 950 nm, respectively. The excitation interval was 10 nm. The absolute QY was calculated as $QY = N_{\text{emit}}/N_{\text{absorb}}$ where $N_{\text{emit}}$ and $N_{\text{absorb}}$ are the numbers of emission and absorption photons, respectively. The PL decay lifetime was measured using Quantaurus-t (C11367, Hamamatsu) which had a timing resolution of 60 ps. The excitation wavelength was fixed at 470 nm for all the samples, and the monitored emission wavelengths were 515 nm for Ce:YAGG and Ce:LuAGG and 550 nm for Ce:GAGG.

2.3 Scintillation properties

The radioluminescence spectra were measured using a setup described elsewhere but briefly: a CCD-based spectrometer (DU920-BU2NC, ANDOR) was used to measure the emission spectrum, which was excited by X-rays generated by a conventional X-ray tube. Here, the supplied bias voltage and tube current were 80 kV and 2 mA, respectively. The scintillation decay time and X-ray induced afterglow profiles were measured by our original setup equipped with a pulsed X-ray tube. The X-ray pulse width is ~80 ps and the repetition rate is 100 kHz. For the afterglow measurements, the emission photons were counted over 50 ms after 2 ms of X-ray exposure was interrupted, and this measurement cycle was repeated at the frequency of 10 Hz to accumulate the signal until the S/N became sufficient.

In order to characterize the absolute scintillation light yield induced by γ-rays, pulse height spectroscopy measurements were performed. In these measurements, a ceramic sample wrapped by a Teflon tape was placed on a photomultiplier tube (PMT; R877-100, Hamamatsu) with optical grease (OKEN6262A). The bias voltage of -1500V was applied to the PMT by a DC power supply (ORTEC556), and the electrical signal output from the anode of the PMT was amplified by a pre-amplifier (ORTEC 113). Further, the amplified signal was processed by a shaping amplifier (ORTEC 572) with 5 μs shaping time to obtain the light output upon a single event, which was then accumulated by a multichannel analyzer (Pocket MCA 8000A, Amptek) to obtain the pulse height spectrum. The radiation source used in this measurement was a sealed radioactive ¹³⁷Cs γ-ray source. A previously characterized Ce:YAG transparent ceramic was used as a reference to calibrate the scintillation light yield because its emission wavelength range is nearly the same with that of our current samples and a measurement uncertainty arose by the spectral response of PMT becomes negligible. The absolute scintillation light yield of Ce:YAG transparent ceramic is approximately 20,000 ph/MeV, which was measured by using Si-APD and ⁵⁳Fe X-ray source.

3. Results and discussion

3.1 Samples

Figure 1 shows the photograph of Ce:YAGG, GAGG and LuAGG transparent ceramics fabricated by the vacuum sintering method. The sizes of these samples were approximately 15 mm diameter and 1.5 mm thickness. With an UV excitation (365 nm), the PL emission was visually confirmed to be very strong as illustrated in Fig. 1. The luminescence color of Ce:YAGG and Ce:LuAGG looked yellowish green and Ce:GAGG showed a yellow color. As shown in Fig. 1 (right), YAGG and LuAGG samples show considerably strong long persistent luminescence even 10 s after cutting off the excitation.

3.2 Optical properties

The transmittance spectra of Ce:YAGG, Ce:GAGG and Ce:LuAGG samples are shown in Fig. 2. For all the samples the transmittance was 75–80% at the wavelengths longer than 480 nm without any additional absorption features. However, in the shorter wavelength region, absorption bands were observed around 230, 340 and 460 nm, and these are typical absorptions by the 4f-5d transitions of Ce³⁺. No additional absorptions due to unexpected contamination or defects were observed.

Figure 3 shows PL emission maps of Ce: YAGG, Ce:GAGG and Ce:LuAGG ceramic samples. They exhibited a broad emission from 470 to 600 nm due to the 5d-4f transitions of Ce³⁺ as typically seen in many Ce³⁺-doped garnet materials. PL excitation bands for this emission were around 340 and 450 nm which are consistent with the observed absorption bands in the transmittance. For Ce:YAGG, Ce:GAGG and Ce:LuAGG, $QY = 56.8$, 22.2 and 72.7%, respectively, by 450 nm excitation. We also measured $QY$ for 0.8 mol% Ce-doped YAG transparent ceramic prepared by Konoshiba Chemical as a reference, and the value was 90.9%. The lower value for $QY$ observed in the current samples can be explained by thermal ionization, which is an electron transfer process from the excited energy level to the ground state.
bottom of conduction band. The thermal ionization process in Ce:YAGG was already proved by photocurrent excitation spectrum and its temperature dependence by some of our group.\(^{23}\) Since the bandgap of these Ga-substituted samples is smaller compared with YAG, this energy loss by thermal ionization is more pronounced.\(^{24}\) This interpretation is supported by the fact that \(QY\) becomes smaller with the bandgap energy of material, which is the largest for LuAGG followed by YAGG and GAGG, respectively. Furthermore, in fact, \(QY\) of Ce-doped GAGG was previously reported to be 89.1\(^{\%}\),\(^{13}\) which is much larger than our measurement value. This is probably because an additional energy transfer from the Ce\(^{3+}\):5d\(^1\) excited state to the intrinsic defects exists in our samples. We have observed afterglow after the excitation was interrupted. In general, a presence of phosphorescence is an evidence of shallow traps. The traps can be attributed to intrinsic defects, such as oxygen vacancies, because the samples were sintered under vacuum at high temperature.

The PL decay time profiles of all the ceramic samples are shown in Fig. 4. All decay curves are not perfect single exponential. This is not due to the excitation light scattering because our separate measurement result (not shown) with Ce\(^{3+}\):Y\(_2\)Al\(_5\)O\(_12\) gives a single decay curve with the same measurement conditions. It is known that if there are some energy transfers by multi-polar interaction\(^{25}\) or charge transfer,\(^{26}\) the decay curves do not follow the single exponential. Our Ga-substituted garnets doped with Ce\(^{3+}\) has the thermal ionization process (i.e. charge transfer) as mentioned above, so that the PL decay curves are not single exponential. In order to compare the PL decay lifetime in the non-single exponential decays, the average lifetime were estimated using by two exponential decay fitting.\(^{27}\) The average lifetime decreases in the order of Ce:LuAGG (\(\tau_{\text{ave}} = 39\) ns), Ce:YAGG (\(\tau_{\text{ave}} = 36\) ns) and Ce:GAGG (\(\tau_{\text{ave}} = 28\) ns). This is because the non-radiative rate by thermal ionization increases due to the small energy gap between the 5d\(^1\) and CB.\(^{28}\)

3.3 Scintillation properties

Figure 5 shows the radioluminescence spectra of Ce:YAGG, Ce:GAGG and Ce:LuAGG. As seen in the PL spectra, these ceramics also exhibited a single broad emission in the wavelength range from 470 to 600 nm. Since the spectral position agrees with the ones observed in PL, this emission should also be by the 5d\(^-\)4f transitions of Ce\(^{3+}\). The emission wavelength of Ce:GAGG was longer, and the spectral shape was broader than those of the other two samples and it was similar to Ce-doped transparent ceramic.\(^{15}\) As an integrated scintillation signal, Ce:GAGG showed the strongest signal among our new samples in spite of the lowest value of \(QY\).

Figure 6 shows scintillation decay curves of Ce:YAGG, Ce:YAGG and Ce:LuAGG under a pulsed X-ray irradiation. The decay curve profiles of all the samples can be approximated by two or three exponential functions by the same manner done for the PL decay analyses described above. The fast component around 50 ns was ascribed to the 5d\(^-\)4f transitions of Ce\(^{3+}\). Only Ce:GAGG have 5 ns decay time, and this is possibly attributed the instrumental response. The decay time of 0.8 mol \% Ce-doped YAG was 78 ns, so our new samples are faster than a conventional scintillator. According to the earlier study, the scintillation decay time became faster by substitution of Ga to the Al-site, and
this was explained as that the Ga substitution prevents from a creation of defects and charge trapping centers.\textsuperscript{29} Therefore, we think that Ga substitution made the decay time faster.

Figure 7 demonstrates the X-ray induced afterglow time profiles of Ce:YAGG, Ce:GAGG, Ce:LuAGG and Ce:YAGG transparent ceramics. Afterglow is a form of thermally stimulated luminescence around room temperature and one of the most important properties for integrated-type scintillation detectors such as X-ray CT and security systems often seen at the airports. Among our new samples, the Ce:LuAGG exhibited the smallest afterglow level while the Ce:YAGG showed the largest afterglow signal, suggesting that the larger number of shallow traps are present. The afterglow levels of our new samples are considerably higher than the conventional Ce:YAGG transparent ceramic. Although the decay time becomes faster, the Ga substitution may make shallow traps.

The pulse height spectra of Ce:YAGG, Ce:GAGG and Ce:LuAGG under\textsuperscript{137}Cs exposure are illustrated in Fig. 8. All the samples showed a clear photoabsorption peak and Compton edge. The absolute scintillation light yield of the Ce:LuAGG was around 18,700 \textit{ph}/MeV which was the highest light yield among the samples measured. Ce:GAGG showed around 15,500 \textit{ph}/MeV and Ce:YAGG exhibited 13,700 \textit{ph}/MeV. As a reference, the light yield of the Ce:YAG ceramic is about 20,000 \textit{ph}/MeV.\textsuperscript{19} The energy resolution at 662 MeV which was the highest light yield among the samples measured using Ce:YAGG, Ce:GAGG and Ce:LuAGG transparent ceramics.

### 4. Summary and conclusions

Ce:YAGG, Ce:GAGG and Ce:LuAGG transparent ceramics with high optical transmittance were successfully fabricated by the vacuum sintering method. The PL spectra of these samples exhibited broad emissions from 470 to 600 nm due to the 5d-4f transitions of Ce\textsuperscript{3+}. The PL decay time of slow component monitoring Ce\textsuperscript{3+} emission was 35–43 ns. The radioluminescence spectra showed a similar spectral shape as those observed in PL. The scintillation decay times also monitoring Ce\textsuperscript{3+} emission were similar to those in PL, which were around 50 ns. In the X-ray induced afterglow measurement, the Ce:LuAGG sample exhibited the lowest afterglow level. Our new samples exhibited high scintillation light yields of 13,700 \textit{ph}/MeV (Ce:YAGG), 15,500 \textit{ph}/MeV (Ce:GAGG) and 18,700 \textit{ph}/MeV (Ce:LuAGG). They can be promising candidates for potential scintillation detector applications. For the aforementioned reasons, Ce:LuAGG showed the best performance as a scintillation detector among the new transparent ceramic studies in this work.

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