Czochralski growth of $\text{Gd}_3(\text{Al}_{5-x}\text{Ga}_x)\text{O}_{12}$ (GAGG) single crystals and their scintillation properties

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Abstract

Ce: $\text{Gd}_3(\text{Al}_x\text{Ga}_{1-x})_5\text{O}_{12}$ ($x=2.5/5$ and $3/5$, Ce:GAGG-2.5 and Ce:GAGG-3) crystals were grown by the Czochralski process in order to reduce cost of the starting materials as compared with conventional Ce: $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (Ce:GAGG-2) crystal which have high light output. Although perovskite phase was detected in Ce:GAGG-3, Ce:GAGG-2.5 had single-phase garnet structure. Solidification fraction for the Ce:GAGG-2.5 growth was 0.52. Optical properties including transmittance, emission, and excitation spectra of 30 samples cut from the Ce:GAGG-2.5 bulk ingot did not depend on their original position along the growth axis. These samples had light outputs of approximately $58,000 \pm 3,000$ photons/MeV. However, scintillation decay times varied from 140 to 200 ns and depended on the position clearly.

Keywords: Scintillator; GAGG

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1. Introduction

Many oxide scintillators such as Ce:(Lu,Y)₂SiO₅ (Ce:LYSO) and Bi₄Ge₃O₁₂ (BGO) are not hygroscopic and demonstrate gamma-ray stopping power greater than that of halide scintillators as Ce:LaBr₃ and Tl:Nal [1-7]. On the other hand, corresponding oxide crystals have low light output and energy resolution when compared with the halides. However, Ce-doped Gd₃Al₂Ga₃O₁₂ scintillator has good light output of 46,000 photon/MeV [8]. It is non-hygroscopic, and it has high stopping power exceeding that observed in the halide group. Thus, the Ce:Gd₃Al₂Ga₃O₁₂ crystals are expected to be used in various highly demanded applications including radiation monitoring and medical imaging. Following these circumstances, development of the Czochralski (Cz) process for the growth of this type crystals is required to establish their mass production.

Ce:Gd₃(Al_xGa_{1-x})₅O₁₂ (0<x<1) crystals belong to the garnet structural family. Their optical and scintillation properties had been examined for only Ce:Gd₃Al₂Ga₃O₁₂, (x=2/5) crystal that was grown by the Cz process. Other crystals having different x ratios and grown by the Cz process have not been yet reported. Ga₂O₃ is more expensive than Al₂O₃. Therefore, purpose of the current project was to estimate maximum substitution of Ga with Al achievable in the Ce:Gd₃(Al_xGa_{1-x})₅O₁₂ crystals to reduce cost of the starting materials and the crystals. Moreover, the effective atomic number of Ce:Gd₃(Al_xGa_{1-x})₅O₁₂ (2/5<x<4/5) is similar to that of Ce:Gd₃Al₂Ga₃O₁₂, and gamma-ray stopping power is also similar. In this report, growth of these crystals with x=2.5/5 and 3/5 using the Cz process is demonstrated together with evaluation of their optical and scintillation properties such as light outputs and scintillation decay times.

2. Materials and Experimental Methods

The (Ce_{0.01},Gd_{0.99})₃(Al_xGa_{1-x})₅O₁₂ crystals (x = 2.5/5 and 3/5) were grown by the Cz process from the melt produced from 99.99% pure starting oxides of α-Al₂O₃, β-Ga₂O₃, Gd₂O₃, and CeO₂. The growth was performed from Ir-crucible on the seed made of Gd₃Al₂Ga₃O₁₂ single crystal. The pulling and rotation rates were 0.8 mm/h and 12 rpm, respectively. The growth atmosphere was Ar (98%)+O₂(2%) mixture.

The chemical composition of the as grown crystals and distribution of their constituents along and perpendicular to the growth axis were examined using the electron probe microanalyzer (EPMA) (JXA-8621MX, JEOL). The measurements were made under accelerating voltage of 20 kV and current of 1.2×10⁻⁸ A.

The transmittance and reflectance spectra were recorded with spectrophotometers: V-530 (JASCO) and UV-2550 (SHIMADZU), respectively. Photo-luminescence (PL) spectra at room temperature were examined with a spectrofluorometer (FLS920, Edinburgh Instrument) using a Xenon lamp as an excitation source. Moreover, quantum yields were evaluated with a device including integrating sphere (C9920-02G, Hamamatsu).

The radio-luminescence spectra at room temperature were recorded with the same spectrofluorometer

used for the PL measurements using 5.5-MeV alpha particles (^{241}Am) as the excitation source. To determine light yields, the pulse height spectra of the crystals irradiated by 662-keV gamma rays from a ^{137}Cs source were also recorded. First, the scintillation photons were detected by a photomultiplier (PMT, R7600U, Hamamatsu). Thereafter, the signals from the PMT were amplified (model 113, ORTEC) and shaped (572A, ORTEC) with a shaping time of 2 μs . The readout was produced by a multichannel analyzer (8000A, Amptek). In addition, the pulse height of a $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystal was measured to produce reference signal (light output of 8,200 photons/MeV) [2]. 662-keV photoabsorption peak channels of BGO and the samples were compared after correction for the PMT quantum efficiency, and finally the light output of the samples was determined. In addition, an oscilloscope (TDS 3052B, Tektronix) was used to measure the PMT output to obtain the decay times of the samples irradiated with gamma rays (^{137}Cs).

3. Results and discussion

Figure 1 shows $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3(\text{Al}_x\text{Ga}_{1-x})_5\text{O}_{12}$ ($x = 2.5/5$ and $3/5$) crystals of 1 inch in diameter grown by the Cz process. The $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ ($x=2.5/5$) single crystal was perfectly single phase material, and the solidification fraction of this process was 0.52. However, the $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_3\text{Ga}_2\text{O}_{12}$ crystal ($x=3/5$) had poly-crystalline zone at its end (tail) part that was mostly result of formation of secondary perovskite phase. Therefore, this material was not considered as promising one regarding its mass-production. Based on this conclusion, $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ (Ce:GAGG-2.5) crystal was the only one inspected for its optical and scintillation properties.

Ce:GAGG-2.5 crystal was cut to the specimens suitable for complete characterization of the crystal according to Fig.2. The samples were identified as “A”, “B”, “C”, and “Dn” series (from “D1” to “D31”) as it is also illustrated in Fig. 2. Some explanations are given below.

Sample “A” was cut parallel to the growth axis (Fig.2, a and b) for estimation of the crystal evolution with the progress of the growth process. Each position (z) at the sample “A” corresponded to certain stage of the growth and distance from the seed from $z = 0$ mm (initiation of the growth) to $z = 62$ mm (termination of the growth).

Samples “B” and “C” were cut perpendicular to the growth axis (Fig.2, a and c) to compare properties of the crystal produced at the beginning of the growth at $z = 0$ mm and those just before the growth was terminated ($z = 62$ mm).

Samples “Dn” (from “D1” to “D31”) were also cut perpendicular to the growth axis (Fig.2, a and d) with dimensions of 5 mm x 5 mm x 1 mm and step of 2 mm. Thus, these samples corresponded to distances of $z=2n$ mm ($n=1, 2, \dots, 31$).

Variations of the chemical composition along the growth axis of the $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ crystal were then examined by EPMA using elongated sample A. The results demonstrated that the host cations of Gd^{3+} were distributed almost uniformly along this direction (Fig. 3). This was not surprising because the

Gd^{3+} cations were the only candidates in the system suitable for occupation of the dodecahedral sites of the garnet structure except negligible amount of the doping Ce^{3+} cations. On the other hand, the composition ratio between Al and Ga was not constant (Fig. 3, a-1). Continuous decrease of Al content and increase of Ga content with solidification fraction was clearly observed. On the other hand, chemical uniformity of the crystal along radial direction was comparatively high; the host cations of Gd^{3+} , Ga^{3+} , and Al^{3+} were distributed almost uniformly along radial axes of the samples B and C (Fig. 3 b,c).

Transmittance and reflectance spectra of the sample “D1” at wavelength range of 200–900 nm are shown in Fig. 4, and all “D” samples had transmittances of over 70%. Additionally, significant differences between these spectra were not observed for all the samples of “Dn” series. Figure 5 and 6 show the photo- and radio luminescence spectra of the sample “D1”, and also there were no significant difference between these spectra recorded for all other “D”-type samples.

Figure 7 illustrates the light outputs measured for the some of the “D”-type samples irradiated with gamma rays obtained from a ^{137}Cs source and quantum yields of all “D”-type samples. The light outputs among “D” samples were approximately $58,000 \pm 3,000$ photons/MeV. Compared with a conventional GAGG crystal, $(Ce_{0.01}, Gd_{0.99})_3Al_3Ga_2O_{12}$, the light output of Ce:GAGG-2.5 increased. Although the light outputs tended to be corresponding to quantum yields, the light output uniformity among the “D”-type samples was within 15% of the light output. This uniformity or variability of the light output or quantum yields most probably originate from the Ce-concentration variability illustrated in Fig. 3. Generally speaking, the observed light-output variability is lower than gain uniformity of the photo-detectors such as photo-multiplier tube.

Decay times of the “D” samples were also measured, and it was found that this was the only property that was very dependant of the position of the crystal from where the specimen was taken. The decay time varied from approximately 140 to 200 ns (Fig. 8) and increased monotonically with increasing solidification fraction of the growth process. Although origin of this dependence is not clear, it may be associated with variations of chemical composition of the specimens, and/or different concentration of the defects or oxygen vacancies. It is assumed that annealing of these samples could be one of the ways that will improve decay-time uniformity among “D” samples and a whole crystal body.

4. Conclusions

Single-phase and crack-free $(Ce_{0.01}, Gd_{0.99})_3Al_{2.5}Ga_{2.5}O_{12}$ garnet single crystal was grown by the Czochralski process, while $(Ce_{0.01}, Gd_{0.99})_3Al_{3.0}Ga_{2.0}O_{12}$ ingot produced by similar process contained secondary phase of perovskite. The $(Ce_{0.01}, Gd_{0.99})_3Al_{2.5}Ga_{2.5}O_{12}$ crystal had good transmittance and light output uniformity ($58,000 \pm 3,000$ photons/MeV). The scintillation decay time was the only parameter that varied along the growth axis from approximately 140 (at the beginning of the growth) to

200 ns (at the end of the growth). Since this variation is probably originated from the defects or oxygen vacancies formed in the crystal, the annealing is considered as one of the ways that will improve decay-time uniformity. If high decay-time uniformity in the $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ crystals is achievable, then application of these crystals in various fields such as medical imaging and radiation monitoring could be proposed. Advantage of $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ is associated with its lower cost compared to $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.0}\text{Ga}_{3.0}\text{O}_{12}$ due to partial substitution of relatively expensive Ga_2O_3 with cheaper Al_2O_3 .

Acknowledgments

This work is partially supported by (i) Japan Society for the Promotion of Science (JSPS) Research Fellowships for Young Scientists (S. Kurosawa), (ii) the funding program for next generation world-leading researchers, JSPS, (iii) Development of Systems and Technology for Advanced Measurement and Analysis, Japan Science and Technology Agency (JST) (iv) Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP), JST, (v) the Association for the Progress of New Chemical Technology, (vi) The Murata Science Foundation and (vii) Nippon Sheet Glass Foundation for Materials Science and Engineering. In addition, we would like to thank following persons for their support: r. Yoshihiro Nakamura of the Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University and Yoshihiro Murakami, Mr. Hiroshi Uemura, Ms. Keiko Toguchi and Ms. Megumi Sasaki of IMR, Tohoku University.

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Figure captions

Figure1. View of 1-inch $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3(\text{Al}_x\text{Ga}_{1-x})_5\text{O}_{12}$ crystals, where $x = 2.5/5$ (a) and $3/5$ (b).

Figure2. Schematic diagrams and view of the actual samples cut from the $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ bulk crystal. (a) is whole crystal view, (b) and (c) are the samples produced for measurement of the chemical composition along (sample “A”) and perpendicular (sample “B” and “C”) to the growth axis, respectively, and (d) illustrates the samples produced for the light output evaluation.

Figure3. Results of the chemical composition analysis of the $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Al}_{2.5}\text{Ga}_{2.5}\text{O}_{12}$ crystal performed by EPMA. (a-1) is the distributions of the crystal constituents along growth axis measured using sample “A” (a-2) vs. position z representing distance from the beginning of the growth. (b-1) is the distributions of the constituents in radial direction for the sample “B” (b-2), and (c-1) is those for the sample “C” (c-2).

Figure4. Transmittance (a) and reflectance (b) spectra of the sample “D1” (Fig.2d).

Figure5. Excitation (a) and emission (b) spectra of the sample “D1” (Fig.2d).

Figure6. Radio luminescence spectrum of the sample “D1” excited by 5.5-MeV alpha rays (Fig.2d).

Figure7. Light outputs (a) and quantum yields (b) of the samples of the “Dn” ($n=1,2,\dots,31$) series (Fig.2d).

Figure8. Scintillation decay times as a function of the sample position in the crystal (Fig.2d).

Fig.1

Fig.2

Fig.3-1

Fig.3-2

Fig.3-3

(c-1)

(c-2)

Fig. 4

Fig. 5

Fig.6

Fig.7

Fig.8