Growth of 2 inch size Ce:doped $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ single crystal by the Czochralski method and their scintillation properties

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Abstract

Ce1% doped $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ (LGAGG) single crystals with a diameter of 50mm and length of 150 mm were grown by the Czochralski (Cz) method using an RF heating system. The EPMA techniques is employed to check homogeneity of chemical composition. Luminescence and scintillation properties were also evaluated. The grown LGAGG showed light yield of around 25,000photon/MeV and energy resolution was 9.8%@662keV. The scintillation decay time was 53.6ns at room temperature

Keywords: A2. Single crystal growth, B1.Oxides, B2. Scintillator materials, B3. Scintillators

1. Introduction

Scintillator materials combined with photodetectors are used to detect high energy photons and particles in X-ray computed tomography (CT), positron emission tomography (PET) and other medical imaging techniques, high energy and nuclear physics detectors, etc. In the last two decades, great effort was made to develop more efficient and faster scintillators in order to detect ionizing radiation. Recently developed Ce-activated materials show the best figure-of-merit given by a combination of stopping power, speed, and light yield [1-3]. The latest generation of Ce^{3+} -doped scintillators based on aluminum garnets (LuAG:Ce) show high intrinsic scintillation efficiency and light yield up to 26 000 phot/MeV [4,5]. However, their performance is always negatively influenced by shallow electron traps which delay an energy transfer to Ce^{3+} emission centers and scintillation decay time contains a considerable amount of slow components [6]. After systematic study of $\text{Lu}_3\text{Al}_5\text{O}_{12}$ -based single crystal scintillators, for the review see [7], a new material concept was proposed, based on single crystal multicomponent $(\text{Gd},\text{RE})_3(\text{Ga},\text{Al})_5\text{O}_{12}$ host, RE = Lu, Y. Doped by Ce^{3+} , such a host lattice, with balanced combination of the admixed Gd and Ga (called as multicomponent garnets) demonstrated very high light yield both in single crystal and ceramic materials [7-11]. In these reports, Ce:($\text{Lu}_y\text{Gd}_{1-y}$)₃($\text{Ga}_x\text{Al}_{1-x}$)₅O₁₂ scintillator grown by μ -PD method were investigated and $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ showed light yield of about 21000photon/MeV decay time of 46ns and density of 7.13 g/cm³[10]. In this report, Ce: $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ (Ce:LGAGG) single crystals were grown by the Czochralski (Cz)

method. Segregation coefficients of Ce in grown crystals were investigated. Luminescence and scintillation properties such as light yield, non-proportionality, temperature dependence of light yield and decay time were also investigated.

2. Experimental

2.1 Crystal growth procedure

A stoichiometric mixture of 4N CeO_2 , Lu_2O_3 , Gd_2O_3 , $\beta\text{-Ga}_2\text{O}_3$ and $\alpha\text{-Al}_2\text{O}_3$ powders (High Purity Chemicals Co.) was used as starting material. The Gd^{3+} site was partially substituted by Ce^{3+} according to the formula of $\text{Ce}_{0.03}\text{Lu}_2\text{Gd}_{0.97}\text{Al}_2\text{Ga}_{3.15}\text{O}_{12}$. Ce:LGAGG single crystals were grown by means of the Cz method using an RF heating system. Here, 3 mol% of $\beta\text{-Ga}_2\text{O}_3$ was added in excess to compensate ignition loss. The rotation rate was 4–12 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. Crystals were grown from a 100mm diameter Ir crucible under Ar with adding 2% of O_2 atmosphere to prevent evaporation of gallium oxide. The seed crystal was a [100] oriented LuAG crystal. After the completion of the crystal growth, the crystal was removed from the melt and was gradually cooled down to room temperature. Plates of 5mm x 5mm x 1mm were cut and polished for the purposes of the luminescence and gamma-ray response measurements, while the remaining rods were used for the structure and chemical composition analysis.

2.2 Characterization of obtained phase

Pieces of the grown crystals were crushed and ground into powder in a mortar. Powder X-ray diffraction analysis was carried out in the 2 θ range of

15° - 75° using RINT Ultima (RIGAKU) diffractometer. The CuK α X-ray source was used, the accelerating voltage and current were of 40kV and 40mA, respectively.

Quantitative chemical analysis of the grown crystals for the Al, Ga, Ce, Lu and Gd content along the growth direction was performed by electron probe microanalysis (EPMA; JXA-8621MX, JEOL). So called ZAF correction was used, where Z stands for atomic number, A for absorption correction factor and F for fluorescence correction factor, respectively.

2.3 Luminescence and gamma-ray response measurement procedure

Absorption spectra were measured by the Shimadzu 3101PC spectrometer in the 190-800 nm range. Radioluminescence (RL) spectra and photoluminescence decays at room temperature (RT) were measured at custom made 5000M model of Horiba Jobin Yvon spectrofluorometer using an X-ray tube (operated at 35 kV and 16 mA, Mo cathode) and the pulsed nanosecond hydrogen-filled flashlamp for the excitation, respectively, see [9-11] for further experimental details.

To determine the light yield, the energy spectra were collected under 662 keV γ -ray excitation (^{137}Cs source) by using an avalanche photodiode (APD, Hamamatsu, S8664-55). The $5 \times 5 \text{ mm}^2$ face of the sample was coupled with the APD using silicone grease (OKEN, 6262A). The sample was covered by Teflon-tape. The signal was fed into a pre-amplifier (CP580K), shaping amplifier (CP 4417), pocket multichannel analyzer (MCA, Amptec 8000A), and finally to a personal computer. The bias for the APD was supplied by a power supplier (CP 6641). Because the APD was thermally sensitive, its temperature was controlled to be $20 \pm 0.5^\circ\text{C}$ using a heat bath. Decay time was measured with a photomultiplier (PMT, Hamamatsu, H7600) with digital oscilloscope TDS3052 of Tektronix, Inc.

3. Result and discussion

3.1 The growth of Ce:LGAGG single crystal

2-inch size $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ crystal with a diameter of 50 mm and length of 160 mm were grown. The grown crystals are shown in fig.1. The grown crystals are looked slightly cloudy because of the rough surface caused by gallium oxide evaporation or thermal etching. Metallic stripes on the crystal surfaces were identified as Ir deposit comes from oxidation of the crucible. Grown crystal was yellow transparent without incursion at the beginning part of the crystal, however incursions were observed remarkably at the center position and tail part of the grown crystal. Powder X-ray diffraction was performed to identify crystal phase of the end part of the grown crystal.

Results of the powder X-ray diffraction is shown in Figure 2. Obtained spectrum showed the single cubic garnet phase. A Q-mass analysis with vacuum chamber was performed to investigation of contents of the inclusions. Ar and O_2 gasses were detected by the Q-mass analysis and the incursions are guessed as gas bobbles from supersaturated melt. It is considered that bubble nucleation occurred at the center of concave melt/solid interface by constitutional undercooling.

The composition distributions of Lu, Ga and Ce ions along the growth direction and radius direction are shown in Fig. 3 and 4. The solidification fractions (g) of the grown crystals were 0.37. Here g is described as follows:

$$g = (\text{mass of solidified part}) / (\text{total mass of starting raw material in the crucible})$$

Segregation coefficients of Lu, Ga and Ce were $k_{\text{eff}} = 1.12, 0.92$ and 0.21 , respectively. The composition distributions in the radius direction were almost homogeneous. The k_{eff} of Ce in $\text{Lu}_2\text{Gd}_1\text{Al}_2\text{Ga}_3\text{O}_{12}$ is much lower than that of $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ ($k_{\text{eff}} = 0.36$, [11]). These are good agreement with difference between the ionic radii of Ce and host cations in dodecahedral site ($\text{Ce} > \text{Gd} > \text{Lu}$).

3.2 Luminescent characteristics

RL spectra of the grown Ce:LGAGG crystals are given in Figure 5. The 310 nm emission of Gd^{3+} 4f-4f, and 510 nm emission of Ce^{3+} 4f-5d transition were observed.

3.3 Gamma-ray response

The typical energy spectra of Ce1%:GAGG excited by ^{137}Cs at room temperature and measured using the APD are shown in Fig. 6. The light yield of the sample was calibrated from the ^{55}Fe direct irradiation peak to APD. Such direct irradiation generates $5.9 \text{ keV} / 3.6 \text{ eV} = 1640$ electron-hole pairs [11]. Based on this value, LY of Ce:LGAGG was calculated to be approximately 25,000photon/MeV with correcting quantum efficiency (QE) of the APD which was 80% at 510 nm. Energy resolution of the Ce1%:GAGG sample was 9.8% @ 662keV. The dependence of the light yield on the solidification fraction is shown in Fig. 7. Light yield was decreased with increasing solidification fraction and, at the same time, increasing Ga concentration (See Fig.3). This tendency is good agreement with our previous reports [9,10]. Light yield of center position in radius direction is lower than that of edge position. It is guess that existence of light scattering center by the gas bobbles at center position affects degradation of light yield.

In fig. 8 and 9, temperature dependences of the light output and dominant decay time of grown Ce:LGAGG and Ce1%Gd₃Al₂Ga₃O₁₂ (GAGG) sample produced by Furukawa were measured using the PMT (Hamamatsu R1288) and digital oscilloscope TD5032B excited by ¹³⁷Cs gamma-ray. Temperature dependence of prompt ns decay times also indicates that scintillation efficiency of Ce:LGAGG should not decrease until 70°C. Ce:LGAGG showed the higher temperature stability of light output. These results are in good agreement with our previous report on Ce:(Gd,Lu)₃(Al,Ga)₅O₁₂ [10]. The Gd-rich sample has lower position of 5d₁ level of Ce³⁺, which secures sufficient separation of 5d₁ level from the bottom of conduction band of the host. The onset of thermal quenching/ionization of Ce³⁺ center is certainly higher than in Gd-less samples and ensures effective scintillator functioning in room temperature applications. Increase of scintillation efficiency can be enabled also by the decrease of host band gap value, i.e. the decrease of energy for creation of one electron hole pair.

4. Conclusion

Ce1%:Lu₂Gd₁Al₂Ga₃O₁₂ single crystal with a diameter of 50 mm and length of 160 mm was grown by the CZ method. Segregation coefficients of Lu, Ga and Ce were $k_{eff} = 1.12, 0.92$ and 0.21 , respectively. Temperature dependence of light yield and scintillation decay time were investigated in the grown crystals. The grown LGAGG showed light yield of around 25,000 photon/MeV and energy resolution was 9.8% @ 662 keV. The scintillation decay time was 53.6 ns at 20°C.

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Fig. 1 Photographs of grown Ce:LGAGG crystals

Fig. 2 Powder X-ray diffraction results of the end part of the grown crystal

Fig. 3. The composition distribution of Lu, Ga and Ce ions along the growth direction.

Fig. 4. The composition distribution of Lu, Ga and Ce ions in the radius direction.

Fig.5. RL spectra of grown Ce:LGAGG crystals

Fig. 6. Energy spectra of Pr:LGAGG crystal excited by a 662 keV gamma-ray source using the PMT at room temperature.

Fig. 7. Light yield variation in the grown crystal

Fig. 8 Temperature dependence of relative light output measured by using the PMT excited by ^{137}Cs gamma-ray.

Fig. 9 Temperature dependence of decay time measured by using the PMT and digital oscilloscope excited by ^{137}Cs gamma-ray