Growth of Nd doped (Lu, Gd)₃(Ga, Al)₅O₁₂ single crystal by the micro pulling down method and their scintillation properties

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ABSTRACT

Nd 1 mol% doped (Lu, Gd)₃(Ga, Al)₅O₁₂ (LGGAG) single crystals were grown by the micro-pulling down (μ -PD) method. Luminescence and scintillation properties such as absorption, excitation and emission spectra, light yield and decay time were evaluated. Nd1%:Lu₃Al₅O₁₂ showed the highest light output of around 8200 photons/MeV among the grown crystals. Scintillation decay time of Nd:Y₃Al₅O₁₂ was 1.32 μ s (36%) 2.02 μ s (64%). Nd:Lu₃Ga₃Al₂O₁₂ was relatively high dense scintillator of 7.38 g/cm³ with good light yield of 6800 photons/MeV and scintillation decay time of 0.20 μ s (5%) 2.60 μ s (95%).

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1. Introduction

Scintillator materials combined with photodetectors are used to detect high energy photons and accelerated particles in medical imaging techniques, high energy and nuclear physics detectors, high-tech industrial applications and most recently also in the advanced homeland security related techniques [1]. In the last two decades, great R&D effort brought several new material systems, namely the Ce-doped orthosilicates as Gd₂SiO₅ (GSO), Lu₂SiO₅ (LSO), (Lu_{1-x}Y_x)₂SiO₅ (LYSO), pyrosilicates based on RE₂Si₂O₇ (RE = Lu, Y, Gd) and most recently LaX₃ (X = Cl, Br) single crystal hosts [1–11]. These guidelines, Materials based on garnet structure are promising candidates for scintillator applications, because of wellmastered technology developed for laser hosts and other applications, optical transparency, and easy doping by rare-earth elements. The Ce-doped Lu₃Al₅O₁₂ (Ce:LuAG) single crystal was shown to be a prospective scintillator material with a relatively high density of 6.7 g/cm³, a fast scintillation response of about 60–80 ns (due to the 5d–4f radiative transition of Ce³⁺ providing the emission around 500–550 nm), and light yield of about 12–14,000 photons/MeV [12–16]. After a decade of R&D of the LuAG-based single crystal scintillators, new material concept was defined, based on multicomponent (Gd, RE)₃(Ga, Al)₅O₁₂ host, RE = Lu, Y. Doped by Ce³⁺, the Gd- and Ga rich host compositions

showed amazingly high light yield up to almost 50,000 photons/MeV [17–19] which is the value exceeding by 30–40% the best LYSO:Ce materials ever seen.

Analogically, other rare-earth doped LuAG is also expected to show good scintillation properties. In the present work, we select Nd as an emission center, as it is a well known and effective luminescence center in laser materials. There have been some reports to investigate scintillation properties of Nd-doped oxides, such as LuPO₄, YPO₄, Y₃Al₅O₁₂ (YAG) and LuAG [20–22]. Nd-doped LuPO₄ and YPO₄ showed the Nd³⁺ 5d–4f emission in the VUV region under X-ray (8 keV) excitation [20]. Reasonable pulse-shape discrimination for γ -ray and α particles was achieved in Nd-doped YAG by investigating shapes of scintillation signals and the decay time constant was 4 μ s [21]. Nd:LuAG showed Nd³⁺ 4f–4f emission in 400–700 nm range and the light yield of 7600 photons/MeV [22]. In addition, Combination between emission wavelength of scintillator and wavelength sensitively of photodetector is important for radiation detectors. Recently development of Si based semiconductor photodetectors such Si-photomultiplier (Si-PM), avalanche photodiodes (APD) and photodiode (PD) have being progressed. In general, Si based semiconductors show high sensitivity in 400–700 nm range and Nd³⁺ 4f–4f emission suit to their sensitive wavelength.

The aim of this work is to investigate and compare the substituting effects of Gd and Ga on luminescence and scintillation properties of (Lu, Gd)₃(Ga, Al)₅O₁₂ (LGGAG) scintillator. In this report, Nd co-doped LGGAG single crystal were grown by the

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micro-pulling down (μ -PD) method and characterized as for the chemical composition. Luminescence and scintillation characteristics were also measured.

2. Experimental

2.1. Crystal growth

A stoichiometric mixture of Nd_2O_3 , Lu_2O_3 , Gd_2O_3 , Ga_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ powders with 99.99% purity (Kanto Chemicals Co.) was used as starting material. Nominally, starting powders were prepared according to the formula of $(\text{Nd}_z, \text{Lu}_y, \text{Gd}_{1-y})_3(\text{Al}_{5-y}\text{Ga}_y)\text{O}_{12}(\text{CO}_3)_x$. Single crystals of Nd doped LGGAG were grown by the μ -PD method with an RF heating system. The z was 0.03 and additionally 1 mol% of $\beta\text{-Ga}_2\text{O}_3$ was added to compensate ignition loss. A schematic of the μ -PD growth apparatus is given in Ref. [23]. Typical pulling rates were 0.05–0.10 mm/min and the diameter was around 3 mm. Crystals were grown from an Ir crucible under the N_2 atmosphere. The seed crystals were $\langle 111 \rangle$ oriented Ce:LuAG crystals. Plates of $\phi 3 \text{ mm} \times 1 \text{ mm}$ were cut and polished for the absorption and luminescence spectra measurements, while the rest of the rods were used for the chemical composition analyses. Pieces of the crystals grown were crushed and ground into powders in a mortar. Powder X-ray diffraction analysis was carried out in the 2θ range $15\text{--}75^\circ$ using RINT Ultima (RIGAKU) diffractometer. The Cu $K\alpha$ X-ray source was used, the accelerating voltage and current were of 40 kV and 40 mA, respectively. Quantitative chemical analyses of the crystals for the Al, Ga, Nd, Gd and Lu content along the growth direction were performed by the electron probe micro-analysis (EPMA; JXA-8621MX, JEOL). So called ZAF correction is used, where Z , A and F are the atomic number, absorption correction factor and fluorescence correction factor, respectively.

2.2. Optical, luminescence and gamma-ray response measurement procedure

Radio-luminescence spectrum at room temperature was measured with the spectrometer (EI FLS920) under an X-ray (Cu $K\alpha$ 40 kV, 30 mA). Light output measurements were performed by using photomultiplier tube (PMT Hamamatsu R7600U). Sample pieces with dimensions of $\phi 3 \times 1 \text{ mm}$ were cut from the grown single crystal, $\phi 3 \text{ mm}$ surfaces were mechanically polished. The samples were coupled by the PMT using silicone grease (OKEN, 6262A). The pieces were covered by using Teflon-tape. To determine the light yield, the energy spectra were collected under 662 keV γ -ray excitation (^{137}Cs source) by using a PMT (Hamamatsu H7600, bialkali photocathode, quartz window). The signal was fed into a shaping amplifier (ORTEC 572A), a multichannel analyzer (MCA) (ORTEC 926), and finally to a personal computer. The shaping time was set as 2 μs . The bias for the PMT was supplied by an ORTEC 556. For the decay time measurement the same setup with the PMT and digital oscilloscope TD5032B were used.

3. Result and discussion

3.1. Crystal growth

Nd1%: $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$, $\text{Lu}_2\text{Gd}_1\text{Al}_5\text{O}_{12}$, $\text{Lu}_2\text{Gd}_1\text{Ga}_3\text{Al}_2\text{O}_{12}$ and $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ crystals were grown by the μ -PD method. Example photographs are shown in Fig. 1. The grown crystals were transparent with purple color and 3–4 mm in diameter, 15–20 mm in length. Some of them look slightly cloudy because of the rough surface coming from the gallium oxide evaporation and thermal etching. However, the inner part of all the crystals is perfectly transparent. Powder XRD patterns indicates that all of the grown Nd:LGGAG contained a cubic single-phase with a space group of

Fig. 1. Example photos of the grown Nd doped LGGAG single crystals.

Ia-3d without any secondary phase. Chemical composition distribution along growth direction of Nd: measured by EPMA is shown in Fig. 2. The effective segregation coefficients of Nd, Lu and Ga ions showed $k_{\text{eff}} = 0.48, 1.030$ and 0.98 values, respectively.

3.2. Luminescence properties

Fig. 3 shows radioluminescence spectra of the Nd: LGGAG samples. The peaks in the wavelengths longer than 400 nm are attributed to $\text{Nd}^{3+} 4f\text{--}4f$ transitions. From the previous data, the initial state is indexed as $^2F(2)_{5/2}$. The $\text{Nd}^{3+} 4f\text{--}4f$ emission intensity decreased with the Gd and Ga concentration increase. $\text{Nd}^{3+} 4f\text{--}4f$ emission was slightly shifted to short wavelength with increasing Ga and Gd concentration. The emission intensity at around 310 nm attributed to $\text{Gd}^{3+} 4f\text{--}4f$ transitions decreased with the Gd concentration increase.

Fig. 2. The Nd, Lu and Ga distribution along growth direction of the Nd1% doped : $\text{Lu}_2\text{Gd}_1\text{Ga}_3\text{Al}_2\text{O}_{12}$ crystal, where C_s is the measured concentration of the cations in the samples, C_0 is the initial concentration in the melt.

Fig. 3. Radioluminescence spectra of the Nd:LGAG crystals. Excitation by X-rays, Cu K α , 40 kV, 30 mA.

Fig. 5. Scintillation decay curves of the Nd:LGAG crystals. Excitation by ^{137}Cs radioisotope (662 keV).

3.3. Gamma-ray response

The typical energy spectra of Mg co-doped Ce:GAGG excited by ^{137}Cs at room temperature and measured using the PMT are shown in Fig. 4. The pulse height of $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ (BGO) crystal, which has a light output of 8500 photons/MeV [13] was also measured as a reference. Light yield was corrected by a quantum efficiency (QE) of the PMT at the emission wavelength of BGO (QE = 25%@480 nm) and Nd:LGAG (QE = 40%@400 nm). Light output was decreased with increasing Ga and Gd concentration. Nd1%:Lu $_3$ Al $_5$ O $_{12}$ showed the highest light output of around 8200 photons/MeV among the grown crystals and Nd1%:Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$ showed light output of around 6800 photons/MeV. Scintillation decay curves were obtained by using the PMT and digital oscilloscope and the sample was irradiated by ^{137}Cs (Fig. 5). Scintillation decay is approximated by the sum of two exponentials according to Eq. (1) for the first component.

$$I(t) = \sum A_i \exp[-t/\tau_i], \quad i = 1, 2. \quad (1)$$

Ratio (%) is calculated using Eq. (2)

$$A_1 \tau_1 / (A_1 \tau_1 + A_2 \tau_2) \times 100\% \quad (2)$$

Scintillation decay time of Nd:Lu $_3$ Al $_5$ O $_{12}$ and Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$ were 1.32 μs (36%) 2.02 μs (64%) and 0.20 μs (5%) 2.60 μs (95%), respectively. Calculated density, light yield and scintillation decay time values of the Nd:LGAG crystals were shown in Table 1.

Fig. 4. Energy spectra of the Nd:LGAG crystals. Excitation by ^{137}Cs radioisotope (662 keV).

Table 1

Calculated density, light yield and scintillation decay time values of the Nd:LGAG crystals. Scintillation decay is approximated by the sum of two exponentials $I(t) = \sum A_i \exp[-t/\tau_i]$, $i = 1, 2$. Ratio (%) is calculated as $A_1 \tau_1 / (A_1 \tau_1 + A_2 \tau_2) \times 100\%$ for the first component.

Chemical composition	Density (g/cm 3)	Light output (photon/MeV)	1st decay time (μs)/ratio(%)	2nd decay time (μs)/ratio(%)
Nd1%:Lu $_3$ Al $_5$ O $_{12}$	6.73	8200	1.32/36	2.02/64
Nd1%:Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$	7.38	6800	0.20/5	2.60/95
Nd1%:Lu $_2$ Gd $_1$ Al $_5$ O $_{12}$	6.47	N.D.	–	–
Nd1%:Lu $_2$ Gd $_1$ Ga $_3$ Al $_2$ O $_{12}$	7.13	1500	0.44/56	0.96/44
Nd1%:Gd $_3$ Ga $_3$ Al $_2$ O $_{12}$	6.63	N.D.	–	–

N.D.: not detected.

Nd:Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$ is relatively dense scintillator with good light yield of 6800 photons/MeV and scintillation decay time of 0.20 μs (5%) 2.60 μs (95%).

4. Conclusion

Nd1%:Lu $_3$ Al $_5$ O $_{12}$, Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$, Lu $_2$ Gd $_1$ Al $_5$ O $_{12}$, Lu $_2$ Gd $_1$ Ga $_3$ Al $_2$ O $_{12}$ and Gd $_3$ Ga $_3$ Al $_2$ O $_{12}$ crystals were grown by the μ -PD method. The peaks in the wavelengths longer than 400 nm were observed and attributed to Nd $^{3+}$ 4f–4f transitions. The Nd $^{3+}$ 4f–4f emission intensity decreased with the Gd and Ga concentration increase. The initial state is indexed as $^2\text{F}(2)_{5/2}$. Nd $^{3+}$ 4f–4f emission was slightly shifted to short wavelength with increasing Ga and Gd concentration. Nd1%:Lu $_3$ Al $_5$ O $_{12}$ showed the highest light output of around 8200 photons/MeV among the grown crystals. Scintillation decay time of Nd:Y $_3$ Al $_5$ O $_{12}$ was 1.32 μs (36%) 2.02 μs (64%). Nd:Lu $_3$ Ga $_3$ Al $_2$ O $_{12}$ was relatively high dense scintillator of 7.38 g/cm 3 with good light yield of 6800 photons/MeV and scintillation decay time of 0.20 μs (5%) 2.60 μs (95%). Scintillation response improvement is expected due to much higher quality of Czochralski-grown crystal samples.

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