Growth and scintillation properties of praseodymium doped (Lu,Gd)₃(Ga,Al)₅O₁₂ single crystals

Kei Kamada^{1,2}, Martin Nikl³, Shunsuke Kurosawa^{1,4}, Yasuhiro Shoji^{2,4}, Jan
Pejchal^{1,3}, Yuji Ohashi⁴, Yuui Yokota¹, and Akira Yoshikawa^{1,2,4}

¹ Tohoku University

New Industry Creation Hatchery Center, 6-6-10 Aoba, Aramaki, Aoba-ku,
Sendai, Miyagi, 980-8579, Japan

² C&A corporation

T-Biz, 6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

³ Institute of Physics AS CR, Cukrovarnicka 10, 16253 Prague,
Czech Republic

⁴Tohoku University

Institute for Material Research, 2-1-1 Katahira Aoba-ku, Sendai,
Miyagi, 980-8577, Japan

Abstract

Pr doped $(\text{Lu,Gd})_3(\text{Ga,Al})_5\text{O}_{12}$ single crystals were grown by the micro-pulling down (μ -PD) method. The crystals were greenish and transparent with 3.0 mm in diameter, 10-30 mm in length. Neither visible inclusions nor cracks were observed. Luminescence and scintillation properties were measured. The substitution at the Al^{3+} sites by Ga^{3+} in garnet structure has been studied. The Pr^{3+} 5d-4f emission is observed within 300-380 nm wavelength superposed with 312 nm emission line of Gd^{3+} . $\text{Pr}0.2\%:\text{Lu}_{2.5}\text{Gd}_1\text{Ga}_3\text{Al}_2\text{O}_{12}$ shows highest emission intensity. The light yield of $\text{Pr}0.2\%:\text{Lu}_{2.5}\text{Gd}_{0.5}\text{Ga}_2\text{Al}_3\text{O}_{12}$ sample with diameter 3 mm x 1 mm size was around 8,000 ph/MeV. Two-exponential approximation of scintillation decay showed 39.6 ns (30.6%) and 151 ns (69.4%) decay times.

1. Introduction

Single crystal scintillator materials are widely used for detection of high-energy photons and particles, in medical imaging techniques, high energy and nuclear physics detectors, high-tech industrial applications. Recently developed Ce-activated materials show the best Fig.-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 ph/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[7], a new material concept was proposed, based on single crystal multicomponent $(\text{Gd,RE})_3(\text{Ga,Al})_5\text{O}_{12}$ 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 exceeding 50,000 ph/MeV both in single crystal and ceramic materials [7-10].

On the other hand, Pr^{3+} ion also shows the 5d-4f emission with the fast decay time in several host materials and such systems can be another candidate for high Fig.-of-merit scintillator. Among Pr-doped materials the $\text{Pr}:\text{Lu}_3\text{Al}_5\text{O}_{12}$ ($\text{Pr}:\text{LuAG}$) single crystal was found very promising due to the high density (6.7 g/cm^3), high light output (around 20,000 ph/MeV), very good energy resolution (below 5 % @662 keV) and very fast Pr^{3+} 5d-4f emission decay time (20 ns) [7,11-14]. Although the optimized compositions of multicomponent garnets mentioned above provided the values of light yield above 50,000 phMeV in the case of Ce^{3+} doping, the analogous Pr-doped ones show light yield values only up to 4,000 – 4,500 phMeV [15]. Such deterioration of scintillation efficiency and light yield was explained by the unwanted energy transfer from $5d_1$ excited state of Pr^{3+} towards Gd^{3+} and concentration quenching in the Gd-sublattice [16,17]. Composition engineering can, in principle, be a way to set the above mentioned transitions of Pr^{3+} and Gd^{3+} off resonance. As a result, an unwanted depletion of $5d_1$ Pr^{3+} excited state would reduce and the light yield of the material would improve.

In this report, the $\text{Pr}:(\text{Lu,Gd})_3(\text{Ga,Al})_5\text{O}_{12}$ (Pr:LGGAG) single crystals with different host compositions were grown by the micro-pulling down (μ -PD) method. Luminescence and scintillation properties were measured. The substitution phenomenon in the Al^{3+} sites with Ga^{3+} in garnet structure has been studied.

2. Experimental

2.1 Crystal Growth

A stoichiometric mixture of 4N Pr_6O_{11} , 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 Pr^{3+} according to the formula of $(\text{Pr}_z\text{Lu}_y\text{Gd}_{1-y-z})_3(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}$. Single crystals of Pr:LGGAG were grown by the μ -PD method with an RF heating system. Parameter y was 0.01 and 3 mol% of $\beta\text{-Ga}_2\text{O}_3$ was added in excess to compensate ignition loss. A schematic layout of the μ -PD growth apparatus is given in Refs. [18,19]. Typical pulling rates were 0.05–0.07 mm/min and the diameter was around 3 mm. Crystals were grown from an Ir crucible under N_2 atmosphere with 1 % of O_2 added to prevent evaporation of gallium oxide. The seed crystals were $\langle 111 \rangle$ oriented undoped LuAG crystals. Plates of 3ϕ mm x 1 mm 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 Structure determination

Pieces of the grown crystals were crushed and ground into powder in a mortar. Powder X-ray diffraction analysis was carried out in the 2θ range of $15^\circ - 75^\circ$ using RINT Ultima (RIGAKU) diffractometer. The $\text{CuK}\alpha$ X-ray source was used, the accelerating voltage and current were of 40 kV and 40 mA, respectively.

Quantitative chemical analysis of the grown crystals for the Al, Ga, Pr 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 Optical, 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 [17] 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 a PMT (Hamamatsu H7600, super bialkali photocathode, quartz window). The 3ϕ mm² face of the pieces was coupled with the PMT by using optical grease (OKEN, 6262A). The pieces were covered by using Teflon-tape. 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 0.5 μ s. The bias for the PMT was supplied by an ORTEC 556.

3 Result and discussion

3.1 Composition and structure properties of as-grown crystals

Pr doped $\text{Lu}_2\text{Gd}_1(\text{Ga}_y\text{Al}_{1-y})_5\text{O}_{12}$ ($y= 0, 1, 2, 3, 4$ and 5) , $\text{Lu}_1\text{Gd}_2(\text{Ga}_y\text{Al}_{1-y})_5\text{O}_{12}$ ($y= 0, 1, 2, 3, 4$ and 5) and $\text{Lu}_{2.5}\text{Gd}_{0.5}(\text{Ga}_y\text{Al}_{1-y})_5\text{O}_{12}$ crystals were grown by the μ -PD method. Example photos of as-grown crystals are shown in Fig. 1. The grown crystals were transparent with greenish color, 2-3 mm in diameter and 10-30 mm in length. Some of them looked slightly cloudy because of the rough surface caused by gallium oxide evaporation or thermal etching. However, the inner part of all the crystals was perfectly transparent.

Powder X-ray diffraction was performed to identify crystal phase of grown crystals. Selected results of the powder X-ray diffraction of Pr1% $\text{Lu}_1\text{Gd}_2(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}$ ($x= 1, 2, 3, 4$ and 5) as a function of the Ga^{3+} concentration are shown in Fig. 2. All of the grown crystals showed the cubic garnet phase. As the Ga^{3+} concentration increases, the peaks are shifted to the left. The composition distribution in grown crystals was monitored by the EPMA.

The composition distribution for Ga of the grown Pr1%:LGGAG crystals is shown in Fig. 3-a and for Pr in Fig. 3-b. The cation Gd^{3+} was distributed almost uniformly along the growth axis. The composition distributions of Pr: $\text{Lu}_2\text{Gd}_1\text{Ga}_2\text{Al}_3\text{O}_{12}$ in radial direction are shown in Fig. 4. According to the previous report [9], segregation coefficients of Lu ,Ga and Pr ions were $k_{\text{eff}} > 1$, $k_{\text{eff}} < 1$ and $k_{\text{eff}} < 1$, respectively, considering the diagnostic distribution curves.

3.2. Optical and luminescence properties

Fig. 4 shows absorption spectra of the Pr:LGGAG samples. Pr-doped samples show expected 4f-5d_{1,2} transitions marked in the Fig. and also the transitions related to Gd^{3+} are marked. There is strange peak at about 230 nm in Pr: $\text{Gd}_3\text{Ga}_2\text{Al}_3\text{O}_{12}$ the origin of which is not clear (not related neither to Gd^{3+} nor to Pr^{3+}). Absorption peaks of Pr^{3+} 4f-5d_{1,2} shifted to shorter wavelength with increasing Lu concentration. It is good agreement with our previous report [9].

RL spectra of the as-grown Pr:LGGAG crystals are given in Fig. 5. The expected 312 nm emission of Gd^{3+} 4f-4f, 290-420 nm emission of Pr^{3+} 4f-5d and 480-800 nm emission of Pr^{3+} 4f-4f transition were observed. In fig.5(a), the highest RL intensity of 5d-4f emission of Pr^{3+} within 300-400 nm (excluded 312 nm line of Gd^{3+}) is obtained for $\text{Lu}_2\text{Gd}_1\text{Ga}_2\text{Al}_3\text{O}_{12}$ composition. Maximum of 5d-4f emission of Pr^{3+} is substantially shifted to longer wavelength beyond 350 nm which may indicate selective depletion of

radiative transitions from 5d₁ level ending at 3H₄ and 3H₅ ones which are in resonance with Gd³⁺ transitions [16,17] For Pr:Lu_{2.5}Gd_{0.5}Ga₂Al₃O₁₂: the emission maximum shifts to shorter wavelength of about 300 nm with respect to pure Pr:LuAG (at 308 nm) and gets partially out-of-resonance with Gd³⁺ transitions within 305-310 nm. RL intensity of Pr: Lu_{2.5}Gd_{0.5}Ga₂Al₃O₁₂ shows of about 500 % BGO (fig.5(b))

3.3 Gamma-ray response

Fig. 6 shows the energy spectra of the grown Pr: LGGAG samples and a Pr:LuAG standard produced by Furukawa Co. Ltd.[20] irradiated by ¹³⁷Cs (662 keV photons). As shown in Fig. 6, Pr0.2%:Lu_{2.5}Gd_{0.5}Ga₃Al₂O₁₂ sample shows the highest light output which is consistent with its high RL intensity in Fig. 5b. The light output of Pr0.2%:Lu_{2.5}Gd_{0.5}Ga₃Al₂O₁₂ sample was around 40 % of Czochralski (Cz)grown Pr:LuAG standard, of about 8,000 ph/MeV.

Scintillation decay curves were observed by using the PMT and digital oscilloscope TD5032B irradiated by ¹³⁷Cs. Fig. 7 shows decay curve of the Pr0.2%:Lu_{2.5}Gd_{0.5}Ga₂Al₃O₁₂ sample. Two-exponential approximation provided decay time values (component intensities) of 39.6 ns (30.6 %) and 151 ns (69.4 %)

4 Conclusion

Pr doped LGGAG single crystals were grown by the μ -PD method with RF heating system. The highest RL intensity of 5d-4f emission of Pr³⁺ within 300-400 nm (excluded 312 nm line of Gd³⁺) is obtained for Lu_{2.5}Gd_{0.5}Ga₂Al₃O₁₂ composition. Maximum of 5d-4f emission of Pr³⁺ is substantially shifted to longer wavelength beyond 350 nm which may indicate the selective depletion of radiative transitions from 5d₁ level ending at 3H₄ and 3H₅ ground state ones which are in resonance with the Gd³⁺ absorption transitions. The light output of Pr0.2%:Lu_{2.5}Gd_{0.5}Ga₃Al₂O₁₂ sample was around 40 % of the Cz grown Pr:LuAG standard and its value was calculated around 8,000 ph/MeV. Scintillation decay times (component intensities) were evaluated as 39.6 ns (30.6 %) and 151 ns (69.4 %).

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Fig. captions

Fig.1. Example photographs of grown Pr:LGGAG crystals.

Fig.2. Powder X-ray diffraction results of the grown Pr1% $\text{Lu}_1\text{Gd}_2(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}$ ($x= 1, 2, 3, 4$ and 5) crystals.

Fig.3. The composition distribution of a) Ga in the as-grown Pr1% $\text{Lu}_1\text{Gd}_2(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}$ ($x= 1, 2, 3$ and 4) crystals and b) Pr in the Pr1%: $\text{Lu}_2\text{Gd}_1\text{Ga}_3\text{Al}_2\text{O}_{12}$ crystal, where C_s is the measured concentration of the cations in the samples and C_0 is the initial concentration in the melt.

Fig.4. Absorption spectra of the as-grown Pr:LGGAG crystals , undoped LGAGG and Pr:LuAG standard.

Fig.5. RL spectra of the as-grown Pr:LGGAG crystals.

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

Fig. 7. Scintillation decay curve of the Pr1%: $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ crystal. 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.

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a)

b)

a)

b)