Growth of Sc doped $\text{RE}_3\text{Al}_5\text{O}_{12}$ (RE=Y, Lu) Single Crystals by micro-pulling-down method and their Scintillation Properties

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Abstract

Sc doped $\text{Y}_y\text{Lu}_{3-y}\text{Al}_5\text{O}_{12}$ ($y=0 - 1$) single crystals were grown by the μ -PD method. EPMA techniques were employed to check their chemical composition. Luminescence characteristics were measured. Antisite defect-related host emission was observed within 280-360nm wavelength. The light yield was increasing with Y concentration and with an optimum for Sc 2% concentration. The Sc2% doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ showed the highest light yield value around 30,000photon/MeV and 670ns scintillation decay time using a photomultiplier detector (R7600U). Substitution effects of the Lu site and their influence on luminescence and scintillation properties were studied.

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 Gd_2SiO_5 (GSO), Lu_2SiO_5 (LSO), $(\text{Lu}_{1-x}\text{Y}_x)_2\text{SiO}_5$ (LYSO), pyrosilicates based on $\text{RE}_2\text{Si}_2\text{O}_7$ (RE=Lu, Y, Gd) and most recently LaX_3 (X=Cl, Br) single crystal hosts[1–11]. Oxide materials based on the garnet structure single crystals are promising candidates for scintillator applications because of well mastered technology developed for laser hosts and other applications, optical transparency and easy doping by rare-earth elements. For example, $\text{Pr}:\text{Lu}_3\text{Al}_5\text{O}_{12}$ (Pr:LuAG) has attracted attention because of its favorable combination of fast Pr^{3+} 5d-4f emission peaking at 311 nm, non-hygroscopic nature, high density (6.7 g/cm^3), high light output (around 20000 photon/MeV), very short decay time (20 ns), and good energy resolution (4.8% at 662 keV for a $10 \times 10 \times 10 \text{ mm}$ LuAG:Pr sample and a Hamamatsu R1791 photomultiplier (PMT)) [12–14]. Isostructural cubic garnet structures of YAG and LuAG form a solid solution and any intermediate mixed composition (i.e. $\text{Y}_x\text{Lu}_{3-x}\text{Al}_5\text{O}_{12}$, for $0 < x < 3$) can be grown. The solidification points of mixed compositions range between 2010°C (for LuAG) and 1930°C (for YAG) [15]. The garnet structure exhibits very flexible cation substitution and such substitution was used to prepare materials with tailored lattice constants [16] and can, in principle, be used for the preparation of highly substituted crystals with a homogeneous composition. However, at the same time, this readiness of solid solution formation in the garnet structure hints at the relative ease of intrinsic anti-site defect formation. Indeed, theoretical studies have shown that the anti-site defect, Y_{Al} , was found as the lowest energy intrinsic defect in both YAG [17–19] and all other REAGs, (RE ranging from Lu to Gd) [20]. Anti-site defect related host emission is observed around 280–360nm with the decay time value of few hundreds nanoseconds. The Sc doping of YAG and LuAG hosts provides new emission band with the maximum

around 280 nm ascribed to Sc-trapped exciton [21,22]. LuAG:Sc shows high light yield of 22500 photon/MeV with decay time of 610ns [21].

In this report, the Sc doped $(\text{Lu,Y})_3\text{Al}_5\text{O}_{12}$ (LYAG) single crystals were grown by the micro-pulling down (μ -PD) method. Luminescence and scintillation properties were evaluated.

2. Experimental

2.1 Crystal Growth

A stoichiometric mixture of 4N Sc_2O_3 , Y_2O_3 , Lu_2O_3 and $\alpha\text{-Al}_2\text{O}_3$ powders (High Purity Chemicals Co.) was used as starting material. More specifically, Al^{3+} sites were substituted by Sc^{3+} according to the formula of $\text{Lu}_y\text{Y}_{3-y}\text{Sc}_x\text{Al}_{5-x}\text{O}_{12}$. Single crystals of Ce:LYGAG were grown by the μ -PD method with an RF heating system. A schematic layout of the μ -PD growth apparatus is given in Refs. [23,24]. Typical growth 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. The seed crystals were $\langle 100 \rangle$ oriented undoped LuAG crystals. Plates of $\varnothing 3\text{mm} \times 1\text{mm}$ were cut and polished for the luminescence spectra and gamma-ray response measurements.

Quantitative chemical analysis of the crystals for the Al, Sc, Y and Lu 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.

2.2 Luminescence and gamma-ray response measurement procedure

Radioluminescence spectra at room temperature (RT) were measured at Horiba Jobin Yvon, custom made 5000M model using an X-ray tube (operated at 35 kV and 16 mA, Mo cathode) for the excitation, respectively. Single grating excitation and emission monochromators and photon counting detection were employed.

Light output measurements were performed by using PMT Hamamatsu R7600U. Sample pieces with dimensions of $\varnothing 3 \times 1\text{ mm}$ were cut from the grown single crystal, $\varnothing$

3mm surfaces were mechanically polished. The samples were optically coupled to the PMT photocathode using silicone grease (OKEN, 6262A) and wrapped by 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 H6531 (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

Sc1, 2 and 5% doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$, $\text{Lu}_2\text{Y}_1\text{Al}_5\text{O}_{12}$, $\text{Lu}_1\text{Y}_2\text{Al}_5\text{O}_{12}$, $\text{Y}_3\text{Al}_5\text{O}_{12}$ crystals were grown by the μ -PD method. Example photos are shown in Figure 1. The grown crystals were colorless, transparent with approx. 3 mm in diameter and 10-30 mm in length. Some of them looked slightly cloudy because of the rough surface caused by thermal etching. However, the inner part of all the crystals was perfectly transparent.

The composition distribution in grown crystals was monitored by the EPMA. The composition distribution along the growth direction of Ce1% $\text{Lu}_2\text{Y}_1\text{Ga}_2\text{Al}_3\text{O}_{12}$ is shown in figure 2. The effective segregation coefficients of Y and Sc ions showed $k_{\text{eff}} = 0.99$ and 0.91 values, respectively.

3.2. Luminescence properties

Radioluminescence spectra in Figure 3 show characteristics of selected Sc1%: $\text{Lu}_y\text{Y}_{3-y}\text{Al}_5\text{O}_{12}$ and undoped YAG samples. The anti-site defect related host emission [22,25] has been observed in 280-360nm with the shoulder at high energy side due to the excitons localized around Sc dopant [21,22]. Emission intensity was increased with increasing Y concentration for the constant value of Sc doping. It is worth noting that aluminum garnet nonstoichiometry has been recently recognized as a parameter which is strongly influencing the antisite defect-related emission intensity in case of YAG powder samples [26]. In our case the composition of the raw materials has been defined under the assumption that all the Sc dopant is embedded at the Al octahedral site while

recent NMR study points to its distribution in both the dodecahedral and octahedral sites [27]. Such Sc distribution, in fact, will shift the composition out of stoichiometry towards the Lu-rich one which can lead to intensity increase of the antisite-related UV emission [26] and is indeed observed in Figure 3. Sharp line around 314 nm is due to accidental contamination by Gd^{3+} ions. Such a sample nonstoichiometry can also explain the observed dominating emission related to the antisite defects instead of Sc-trapped exciton observed in LuAG:Sc crystals [21]

3.3 *Gamma-ray response*

The typical energy spectra of Sc2%: $Lu_yY_{3-y}Al_5O_{12}$ excited by ^{137}Cs at RT are shown in Figure 4. Light yield was increasing with Y concentration for a constant Sc concentration. The highest light yield value was achieved in Sc2%:YAG and the light yield was 1.5 times higher than that of a Pr:LuAG standard Cz-grown sample (LY:20000photon/MeV, emission wavelength:310nm). We used Pr:LuAG as a standard to estimate light yield because emission wavelength of Pr:LuAG is comparable to that observed in the present Sc:LYAG sample set. The light yield of Sc2%:YAG can be thus estimated to 30000 photon/MeV and is by 30% higher compared to the values provided for Sc-doped LuAG single crystal earlier [21].

Scintillation decay curves were measured under excitation by ^{137}Cs 662 keV photons. Scintillation decay curves of Sc1% $Lu_yY_{3-y}Al_5O_{12}$ ($y=0, 1$ and 2) crystals are shown in Figure 5. The decays were accelerated with increasing Lu concentration. The scintillation decay times were 550ns, 604ns and 733ns in Sc1% $Lu_yY_{3-y}Al_5O_{12}$ ($y=0, 1$ and 2) samples, respectively. Scintillation decay curves of Sc 0, 2 and 5% YAG crystals are shown in Figure 6. The scintillation decay times became longer with increasing Sc concentration showing the values of 513ns, 670ns and 954ns, respectively. These values are comparable with those of LuAG:Sc crystals reported earlier [21] Table 1 shows light yield and scintillation decay time values of all the Sc:(Lu,Y) $_3Al_5O_{12}$ samples studied.

4 Conclusion

The Sc1, 2 and 5% doped $Lu_3Al_5O_{12}$, $Lu_2Y_1Al_5O_{12}$, $Lu_1Y_2Al_5O_{12}$, $Y_3Al_5O_{12}$ crystals were grown by the μ -PD. The expected anti-site defect related host emission

has been observed in 280-360nm spectral region with a shoulder at high energy side ascribed to the Sc-trapped exciton. Emission intensity was increasing with Y concentration. The light yield was increased with decreasing Lu content and showed a maximum value for the Sc2% doped samples.. The scintillation decay times became longer with increasing Y and Sc concentrations. The Sc2% doped $\text{Y}_3\text{Al}_5\text{O}_{12}$ sample showed the highest light yield value around 30,000photon/MeV and 670ns scintillation decay time. Departure of crystal stoichiometry towards the Y- or Lu-rich composition is recognized as the reason for increase of scintillation efficiency and light yield as well and can be used for further aluminum garnet-based single crystal scintillator optimization.

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Figure captions

Figure1. Example photos of grown Sc:LYAG crystals.

Figure2. The composition distribution along growth direction of Sc2% $\text{Lu}_2\text{Y}_1\text{Ga}_2\text{Al}_3\text{O}_{12}$ crystal

Figure3. Radioluminescence spectra of the Sc:LYAG samples

Figure4. Energy spectra of Sc2% LYAG samples and Pr:LuAG standard excited by a 662 keV gamma-ray

Figure 5. Scintillation decay curve of Sc1% $\text{Lu}_y\text{Y}_{1-y}\text{Al}_5\text{O}_{12}$ crystals using the PMT and digital irradiated by ^{137}Cs

Figure6. Scintillation decay curve of Sc 0, 2 and 5% YAG crystals using the PMT and digital irradiated by ^{137}Cs

Table 1. Light yield and scintillation decay time of Sc doped $(\text{Lu},\text{Y})_3\text{Al}_5\text{O}_{12}$

Kamada, et al, Figure 2

Kamada, et al, Figure 4

Kamada, et al, Figure 5

Kamada, et al, Figure 6

Kamada, et al, Table 1

	Sc concentration (%)	L.Y. (photon/ MeV)	decay time (ns)
Y ₃ Al ₅ O ₁₂	0	9871	513
Y ₃ Al ₅ O ₁₂	1	22387	733
Y ₃ Al ₅ O ₁₂	2	30452	670
Y ₃ Al ₅ O ₁₂	5	15290	954
Lu ₁ Y ₂ Al ₅ O ₁₂	0	10194	489
Lu ₁ Y ₂ Al ₅ O ₁₂	1	17355	689
Lu ₁ Y ₂ Al ₅ O ₁₂	2	21806	785
Lu ₁ Y ₂ Al ₅ O ₁₂	5	14645	850
Lu ₂ Y ₁ Al ₅ O ₁₂	0	6645	*N.D
Lu ₂ Y ₁ Al ₅ O ₁₂	1	16065	558
Lu ₂ Y ₁ Al ₅ O ₁₂	2	18065	688
Lu ₂ Y ₁ Al ₅ O ₁₂	5	12968	843
Lu ₃ Al ₅ O ₁₂	0	5161	*N.D
Lu ₃ Al ₅ O ₁₂	1	16516	484
Lu ₃ Al ₅ O ₁₂	5	11226	749

N.D. (Not detected).