Growth and scintillation properties of 3 inch diameter Ce doped $\text{Gd}_3\text{Ga}_3\text{Al}_2\text{O}_{12}$ scintillation single crystal

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Abstract

The 3 inch size Ce1%:Gd₃Al₂Ga₃O₁₂ single crystals were prepared by the Czochralski (Cz) method. Optical constants were measured. Chemical composition analysis and uniformity of scintillation decay and light yield along growth direction were evaluated. The timing resolution measurement for a pair of 3x3x3mm³ size Ce:GAGG scintillator crystals was performed using Si-PMs.

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 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 $\text{R}_2\text{Si}_2\text{O}_7$ ($\text{R}=\text{Lu}, \text{Y}, \text{Gd}$) and most recently LaX_3 ($\text{X}=\text{Cl}, \text{Br}$) single crystal hosts[1–11]. Oxide materials based on 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. After a decade of R&D of the $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (LuAG)-based single crystal scintillators (see review in [12]), new material concept was defined, based on multicomponent $(\text{Gd}, \text{R})_3(\text{Ga}, \text{Al})_5\text{O}_{12}$ host, $\text{R}=\text{Lu}, \text{Y}$. Doped by Ce^{3+} , the Gd- and Ga rich host compositions showed amazingly high light yield up to almost 50,000 phot/MeV [13–16] which is the value exceeding by 30–40% the best Ce:LYSO materials ever seen. Recently, our group reported about Ce: $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ (GAGG) single crystal and scintillation response of about ~90 ns at emission around 520 nm, excellent light yield of about 56000 photon/MeV, and density of 6.63 g/cm³[15,16]. In order to apply Ce:GAGG to gamma-ray detection applications, we are making efforts to establish mass production of Ce:GAGG single crystals. As a result of our effort, 2 inch diameter Ce:GAGG have been commercially available now [15]. For further developments of Ce:GAGG on scintillator markets, it is necessary to increase the size of Ce:GAGG single crystal for greater production and reduced cost.

In this report, we established single crystal growth of 3 inch diameter Ce:GAGG by the Czochralski (Cz) method. We report their scintillation characteristics such as light yield, energy resolution and decay time. Furthermore timing resolution measurement for a pair of 3x3x3mm³ size Ce:GAGG scintillator crystals was performed using Si-PMs.

2. Experimental

2.1 Crystal Growth

A stoichiometric mixture of 4N CeO_2 , $\alpha\text{-Al}_2\text{O}_3$, $\beta\text{-Ga}_2\text{O}_3$ and Gd_2O_3 , powders (Iwatani Corporation) was used as starting material. Nominally, starting powders were prepared according to the formula of $(\text{Ce}_{0.01}, \text{Gd}_{0.99})_3\text{Ga}_3\text{Al}_2\text{O}_{12}$. Single crystals of Ce:GAGG were grown by the Cz method with an RF heating system. A schematic of the Cz growth apparatus is given in Ref. [15,16]. Typical growth rates were 0.9 mm/h and the diameter was around 76 mm. Crystals were grown from a 150 mm diameter Ir

crucible under the N₂ with 30% CO₂ atmosphere. The seed crystals were <100> and <111> oriented Ce:GAGG crystals. Sample pieces of 5 mm x 5 mm x 5 mm were cut and chemically polished for the absorption and luminescence spectra measurements, while the rest of the rods were used for the chemical composition analyses. Quantitative chemical analyses of the crystals for the Ce, Al, Ga and Gd content along the radius and 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 Refractive index and extinction coefficient measurement procedure

The refractive index, n , and extinction coefficient, k , were measured using a ellipsometer M-2000U (J.A.Woollam). Ellipsometry measures the two values (Δ, Ψ) . Ψ represent the rate of amplitude Fresnel coefficients r_p and r_s for the light waves polarized in the plane p (parallel with plane of incidence) and s (perpendicular on plane of incidence); Δ is the phase difference between the mentioned plane p and s . In spectroscopic ellipsometry, (Δ, Ψ) are measured by changing the wavelength of light. Ellipsometric parameters Ψ and Δ were acquired at three angle of incidence (50°, 60°, 70°) over the spectral range 245–1000 nm. Optical constants are determined by minimizing fitting errors MSE.

2.3 Gamma-ray response measurement procedure

Sample pieces with dimensions of 5 mm × 5 mm × 5 mm were cut from the grown single crystal, and every surface was chemically polished. To determine the light yield, the energy spectra were collected under 662 keV γ -ray excitation (¹³⁷Cs source) by using an Avalanche photodiode (APD, Hamamatsu, S8664-55). The sample was coupled with the APD by using silicone grease (OKEN, 6262A). The sample was covered by using Teflon-tape. The signal was fed into a pre-amplifier (CP580K), shaping amplifier (CP 4417), pocket MCA (Amptek 8000A), and finally to a personal computer. The bias for the APD was supplied by a CP 6641. Because an APD was highly sensitive to the ambient temperature, we controlled the temperature at 23°C by using a heat bath, within ± 0.5 K. Decay time was measured by using a photomultiplier (PMT, Hamamatsu, H6541) with digital oscilloscope TDS3052 of Tektronix, Inc.

3 Result and discussion

3.1 Crystal growth

In order to optimize growth direction, 3 inch diameter Ce:GAGG single crystals were growth using <100> and <111> Ce:GAGG seed crystals at the same growth set up and condition. Grown crystals were

shown in Fig.1. The grown crystal along <111> direction showed much stronger twisting tendency. According to this result, As shown, <100> direction was suitable and selected for large size growth of Ce:GAGG. At the beginning of optimization of growth condition, even the grown crystal along <100> direction had cracks and twisting formation. Possible causes for twisting formation are asymmetric temperature distribution come from unstable melt convection in the melt. The force of the natural convection is one of important factors for the twisting formation [17]. So we examined the degree of natural convection by changing the positions of an RF coil and constructions of ceramic insulators supporting a crucible.

As a result of optimization of growth conditions such as cone angle, rotation rate, positions of an RF coil and ceramic insulation design in the furnace, crack-free 3 inch diameter Ce:GAGG single crystal with a length of 130 mm was successfully grown (Fig. 2). The solidification fraction (g) was about 0.23. Here, g is described as the equation blow.

$$g = (\text{mass of grown crystal}) / (\text{mass of starting materials in crucible})$$

The composition distributions in grown crystals were monitored by the EPMA. The composition distribution along the growth direction of the Ce1% doped GAGG crystal is shown in Fig. 3. The effective segregation coefficient of Ce, Ga and Al ions showed $k_{\text{eff}}=0.028, 0.94$ and 1.06 value.

3.2 Refractive index and extinction coefficient

Refractive index and extinction coefficient were important factors to design optical contact between scintillator and photodetectors. The refractive index, n , and extinction coefficient, k , were shown in Fig. 4. The refractive index, n , and extinction coefficient, k , were determined as 1.87 and 0.14, respectively, at 520 nm (emission peak of Ce:GAGG).

3.3 Gamma-ray response

The typical energy spectra of Ce1%:GAGG at $g=0.06$ excited by ^{137}Cs at room temperature and measured using the APD are shown in Fig. 5. 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 [28]. Based on this value, light yield of Ce:GGAG was $\sim 55,500$ photon/MeV with correcting the QE, which is at 80% at 520 nm. Energy resolution of the Ce1%:GGAG sample was 5.2 % @662keV. The dependence of the light yield on the solidification fraction is shown in Fig. 6. The light yield was decreased with increasing the solidification fraction. Scintillation decay curve was obtained by using

PMT R7600U Hamamatsu and digital oscilloscope TD5062A irradiated by ^{137}Cs . The Ce:GAGG crystal shows decay time of 88.2 ns (81%) with a slower components of 353 ns (19 %) decay time at $g=0.06$ (Fig. 7). The decay time was accelerated with increasing the solidification fraction. It is thought that these decay time acceleration and light yield decrease were caused by increase of Ce concentration with increasing the solidification fraction.

The timing resolution for a pair of 3 mm x 3 mm x 3 mm size samples with chemical polishing were conducted using Si-PMs (Hamamatsu MPPC S12573, 3mm x 3mm input area) readout with high speed amplifiers (mini circuit, TB4083) and a digital oscilloscope (Agilent Technology DSO-8104A: 1GHz, 20 Gs/s). Schematic drawing is shown in Fig. 7. The details of this digital oscilloscope based timing resolution evaluation method are reported in [18]. Timing resolutions were measured 5 times (Table 1) and the average timing resolution was 363 ps. At the same set-up LYSO standard (Saint Go-Bain) showed 180 ps of timing resolution.

4 Conclusion

After optimization of growth conditions, 3inch size Ce:GAGG single crystal was successfully grown using a $\langle 100 \rangle$ seed by the Cz method. The refractive index, n , and extinction coefficient, k , were determined in 245-1000nm range and 1.87 and 0.14, respectively, at 520 nm. The light yield of Ce:GAGG was ~55,500 photon/MeV. Energy resolution of the Ce1%:GGAG sample was 5.2 % @662keV. The Ce:GAGG crystal shows decay time of 88.2 ns (81%) with a slower components of 353 ns (19%) decay time at $g=0.06$. The light yield was decreased and decay time was accelerated with increasing the solidification fraction. The average timing resolution of Ce:GAGG was 363 ps

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References

- [1] M. Nikl, Meas. Sci. Technol. Vol.17, pp.R37-R54, 2006
- [2] C. L. Melcher and J. S. Schweitzer, IEEE Trans. Nucl. Sci., vol. 39, no. 4, pp.502–505, 1992.
- [3] M. Kapusta, P. Szupryczynski, C. L. Melcher, M. Moszynski, M. Balcerzyk, and A. A. Carey et al., IEEE Trans. Nucl. Sci., vol. 52, no. 4, pp. 1098–1104, 2005.
- [4] M. A. Spurrier, P. Szupryczynski, A. A. Carey, and C. L. Melcher, IEEE Trans. Nucl. Sci., NS-55, no. 3, pp. 1178–1182, 2008.
- [5] P. Lecoq and M. Korzhik, IEEE Trans. Nucl. Sci., vol. 49, no. 4, pp. 1651–1654, 2002.
- [6] M. Moszynski, D. Wolski, T. Ludziejewski, M. Kapusta, A. Lempicki, and C. Brecher et al., Nucl. Instr. And Meth. A vol. 385, pp. 123–131, 1997.
- [7] S. Weber, D. Christ, M. Kurzeja, R. Engels, G. Kemmerling, and H. Halling, IEEE Trans. Nucl. Sci., vol. 50, no. 5, pp. 1370–1372, 2003
- [8] M. Conti, Physica Medica vol. 25, pp.1-11, 2009
- [9] K. S. Shah, J. Glodo, M. Klugerman, W. W. Moses, S. E. Derenzo, M. J. Weber, IEEE Trans. Nucl. Sci., vol. 50, no. 6, pp. 2410–2413, 2003
- [10] K. W. Kramer, P. Dorenbos, H. U. Gudel, C. W. E. van Eijk, J. Mater. Chem., vol. 16, pp.2773–278, 2006
- [11] M.S. Alekhin, J.T.M. de Haas, I.V. Khodyuk, K.W. Kramer, P.R. Menge, V. Ouspenski, P. Dorenbos, Appl. Phys. Letters. vol. 104, 211908, 2014
- [12] M.Nikl, A. Yoshikawa, K. Kamada, K. Nejezchleb, C.R. Stanek, J.A. Mares, K. Blazek, Progr. Cryst. Growth Charact. Materials vol. 59, pp.47-72, 2013
- [13] N. J. Cherepy, J. D. Kuntz, Z. M. Seeley, S. E. Fisher, O. B. Drury, B. W. Sturm, et al, Proc. SPIE vol. 7805, pp. 780501-780505, 2010
- [14] K. Kamada, T. Endo, K. Tsutumi, T. Yanagida, Y. Fujimoto, A. Fukabori, et al., Crystal Growth & Design, vol. 11, pp. 4484-4490, 2011.
- [15] K. Kamada, T. Yanagida, T. Endo, K. Tsutumi, Y. Usuki, M. Nikl, et al., J. Cryst. Growth vol.352, pp. 88-90, 2012

- [16] K. Kamada, P. Pursa, M. Nikl, V. V. Kochurikhin, T. Endo, K. Tsutumi, H. Sato, S. Kurosawa, Y. Yokota, K. Sugiyama, A. Yoshikawa, *Opt. Mater.* Vol. 36 pp.1942-1945, 2014
- [17] Q. Xiao, J. J. Derby, *J. Crystal Growth*, 128 (1993) 188.
- [18] J. Y. Yeom, S. Yamamoto, S.E. Derenzo, V.Ch. Spanoudaki, K. Kamada, T. Endo, and C. S. Levin, *IEEE Trans. Nucl. Sci.* vol. 60(2), pp. 988-992, 2013

Figure captions

Figure 1. 3 inch diameter Ce:GAGG crystal grown by the Cz method using a) $\langle 100 \rangle$ and b) $\langle 111 \rangle$ seeds at the beginning of our study.

Figure 2. 3 inch diameter Ce:GAGG crystal grown by the Cz method after optimization of growth conditions.

Figure3. The Ce, Ga and Al distribution in the grown Ce:GAGG single crystal along the growth direction.

Figure 4. Measured refractive index and extinction coefficient.

Figure 5. Energy spectra of the Ce:GAGG at $g=0.06$ sample. Excitation by ^{137}Cs radioisotope (662 keV).

Figure 6. Dependence of the light yield on the solidification fraction for the grown Ce:GAGG.

Figure 7. Scintillation decay curves of the Ce:GAGG at $g=0.06$ sample.. Excitation by ^{137}Cs radioisotope (662 keV).

Figure 8. Dependence of the faster decay component on the solidification fraction for the grown Ce:GAGG.

Figure 9. Schematic drawing of measurement set-up for timing resolution

Table 1. Results of the timing resolution measurement.

a)

b)

Kamada, et al, Figure 2

Kamada, et al, Figure 3

Kamada, et al, Figure 4

Kamada, et al, Figure 5

Kamada, et al, Figure 6

Kamada, et al, Figure 9

Kamada, et al, Table 1

	trigger [mV]		timing resolution [ps FWHM]
	ch.1	ch.3	
①	400	380	402.0
②	405	385	362.6
③	415	393	353.9
④	430	395	351.3
⑤	435	407	347.2