Scintillation Properties of 2-Inch-Diameter $Pr : Lu_3Al_5O_{12}$ (LuAG) Single Crystal

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***Abstract*—Pr:LuAG crystals possess interesting properties, such as high density, high light yield, and very fast 5d-4f emission decay time. Recently, we developed a Pr:LuAG single crystal with a diameter of 2 inches for scintillator applications, such as medical imaging. In this study, Pr-doped $Lu_3Al_5O_{12}$ (Pr:LuAG) single crystals with a diameter of 2 inches were grown by means of the Czochralski method; a body length of up to 90 mm was achieved. The Pr:LuAG crystals produced a homogeneous light yield with approximately 2.5 times less intensity compared to that produced by a conventional Ce:LSO crystal. A sample with dimensions of 5 mm × 5 mm × 1 mm exhibited energy resolutions of 4.8% at 662 keV, as measured by using a photomultiplier (PMT: Hamamatsu H6531), and 5.8% at 662 keV, as measured by using an Avalanche photodiode (APD: Hamamatsu S8664-55). The Pr:LuAG crystals exhibited a very fast rise time of approximately 0.4 ns, excited by a pulsed X-ray at room temperature. The decay time was approximately 18 ns, along with a noticeable presence of slower decay components (with a decay time of 55.0 ns). Furthermore, the Pr:LuAG crystals showed good linearity between the energy and pulse height within approximately 4% of the standard deviation in the range from 122 keV (^{152}Eu) to 1.4 MeV (^{241}Am).**

***Index Terms*—Crystal growth, gamma-ray detectors, garnets, Pr3+, 5d-4f luminescence.**

I. Introduction

PRASEODYMIUM ion exhibits fast 5d-4f emission in several host materials. These systems can be applied to obtain crystal scintillators with high figures of merit [1], [2]. Recently, our group intensively examined the scintillation properties of several Pr-doped compounds [3]–[8]. Among those materials, $Pr : Lu_3Al_5O_{12}(Pr : LuAG)$ was found to have interesting properties, such as high density (6.7 g/cm^3), high light output (approximately 20000 photon/MeV by using PMT), good energy resolution, and a very fast 5d-4f emission decay time (20 ns) [5]–[7]. Table I shows a comparison among the Pr:LuAG and popular Cerium-activated scintillators, such as $Ce : Lu_2SiO_5$ (Ce:LSO) [9]–[11], $(Lu, Y)AlO_3$ (LuAP) [12]–[15], and $Ce : LaBr_3$ [15]–[18]. Owing to such excellent scintillation properties, a Pr:LuAG scintillator can be used for applications in medical imaging. In order to apply Pr:LuAG scintillators to these applications, it is necessary to establish mass production of Pr:LuAG single crystals with uniform scintillation performance in the entire crystal.

TABLE I
COMPARISON BETWEEN Pr:LuAG AND POPULAR CERIUM-ACTIVATED SCINTILLATORS

	Pr:LuAG	Ce:LSO	Ce:LuYAP	Ce:$LaBr_3$
Light output (ph/MeV)	20000	38000	<20000	70000
Energy resolution @662 keV	~5%	8%	6.8%	3%
Density (g/cm^3)	6.73	7.4	6.1 –8	5.1
Effective Z	62.9	66	40–63	47
Emission wavelength (nm)	310	420	360	380
Decay time (ns)	~20	40	20	20

In this study, we achieved the growth of Pr:LuAG single crystals with a diameter of 2 inches by means of the Czochralski (CZ) method. We report on the scintillation characteristics of the crystals, such as light yield, energy resolution, γ-ray response, and decay time.

II. Materials and Methods

1) Crystal Growth: The starting materials used in this study were Pr_6O_{11}, Lu_2O_3, and $\alpha-Al_2O_3$ with a purity of 99.99%. Pr_6O_{11} was added to the starting material for luminescent centers as Pr^{3+}. Lu^{3+} was nominally substituted by Pr^{3+} according to the formula of $(Pr_{0.025}Lu_{0.975})_3Al_5O_{12}$.

Pr:LuAG single crystals were grown by means of the CZ method using an RF heating system. The rotation rate was 4–12 r/min and the growth rate was 1.0 mm/h. An automatic diameter control system using crystal weighing was applied to control the growth parameters. The crystals were grown from an Ir crucible with a diameter of 100 mm and a height of 120 mm. Ar atmospheres were used to prevent the oxidization of the crucible. The seed crystal was a [100] oriented Pr:LuAG crystal. After the completion of the crystal growth, the crystal was removed from the melt and was gradually cooled down to room

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temperature. The solidification fraction (g) of the grown crystal was 0.45; g is described as follows:

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

2) Light Output and γ-Ray Response Measurements: Light output measurements were performed by using a photomultiplier (PMT) and Avalanche photodiode (APD). Sample pieces with dimensions of $5 \times 5 \times 1$ mm^3 were cut from the grown single crystal, and every surface was mechanically polished. In the case of measurements performed by using the PMT, the 5×5 mm^2 face of the pieces was coupled with the PMT by using optical 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 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 0.5 μs. The bias for the PMT was supplied by an ORTEC 556.

In the case of measurements performed by using the APD, the same sample used in the PMT measurements was used. The 5×5 mm^2 face of the sample was coupled with the APD (Hamamatsu, S8664-55) by using silicone grease (OKEN, 6262A). The sample was covered by using Teflon tape. The signal was fed into a preamplifier (CP580K), shaping amplifier (CP 4417), pocket MCA (Amptec 8000A), and finally to a personal computer (PC). The bias for the APD was supplied by a CP 6641. Sincee the APD was highly sensitive to the ambient temperature, we controlled the temperature at 20 °C by using a heat bath, within $\pm$0.5 K.

3) Rise and Decay Spectra Measurements: The starting rise and decay spectra were measured by using the conventional single photoelectron technique by using a pulsed X-ray source for the excitation. The X-ray pulses were produced in a light-excited X-ray tube N5084 (Hamamatsu Photonics) by using a tungsten anode at a high voltage of 20 kV between the photocathode and anode. The excitation light pulse was produced in a laser diode by using an InGaN: picosecond injection laser (PiLAS, Advanced Laser-diode Systems GmBH, Berlin, Germany). The wavelength was 409.5 nm, and the pulsewidth was $\sim$40 ps in full width at half maximum (FWHM) at a repetition rate of 100 Hz. The generated X-rays were collimated on to the 5×5 mm^2 face of the sample with dimensions of $5 \times 5 \times 1$ mm^3 mm. The scintillation light was detected by using a PMT R4998 (Hamamatsu, bialkali photocathode, borosilicate glass window). The light intensity at the PMT was significantly decreased below the level of one photoelectron per pulse in order to avoid the distortion of the decay spectrum. The timing of the PMT output signal was registered in a computer-automated measurement and control standard (CAMAC) time-to-digital converter (TDC) with respect to the initial clock pulse that triggered the laser diode (see [19]).

III. Results

1) Crystal Growth of 2-inch-Diameter Pr:LuAG: Growth conditions, such as the corn angle, rotation rate, and heat insulation design in the furnace were optimized for obtaining crack-free Pr:LuAG crystals with a diameter of 2 inches and with a uniform light yield in the entire crystal. We referred to some reports for the optimization of the growth conditions [20]–[23].

Fig. 1. Pr2.5%:LuAG single crystal with a diameter of 2 inches grown by the CZ method.

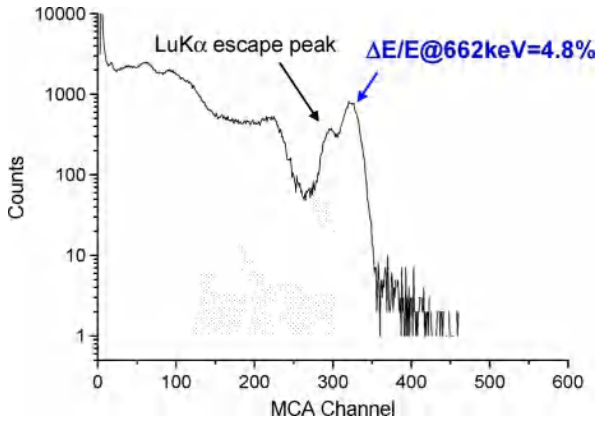

Fig. 2. Typical energy spectrum of Pr2.5%:LuAG excited by ^{137}Cs and measured by using the PMT.

The Pr2.5%:LuAG single crystal with a diameter of 2 in and length of 90 mm was grown with a nominal composition of $(Pr_{0.075}Lu_{2.925})Al_5O_{12}$ (Fig. 1). The solidification fraction (g) of the grown crystal was 0.45.

2) Light Output Measurements: The typical energy spectra of Pr2.5%:LuAG excited by ^{137}Cs at room temperature and measured by using the PMT (Hamamatsu H6531) are shown in Fig. 2. A photoabsorption peak and $\mathrm{LuK}\alpha$ escape peak are clearly observed. The photoabsorption peak was fit by using a single Gaussian function to estimate energy resolution. The light yield of Pr:LuAG was approximately 2.5 times less intense than that of a conventional Ce:LSO sample with dimensions of same dimentions. The energy resolution of Pr:LuAG was 4.8%. The energy resolution of Ce:LSO was obtained as 7.8% for the same measurement setup.

In the case of measurements using the APD (Hamamatsu, S8664-55), the avalanche gain required to achieve the optimum energy resolution was $\sim$20; we supplied a high voltage of 310 V (avalanche gain = 19.4) at 20 °C. The shaping time of the shaping amplifier was set as 2 μs throughout this study. The typical energy spectra of Pr2.5%:LuAG excited by ^{137}Cs at room

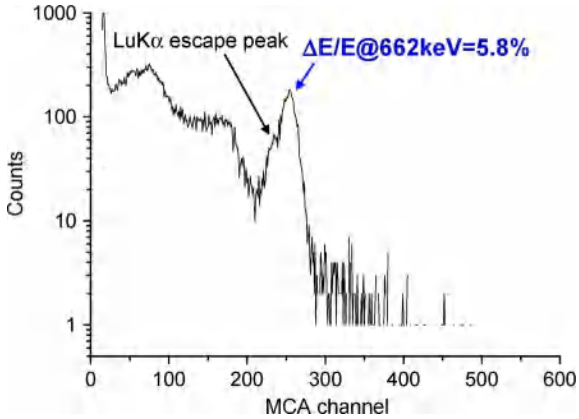

Fig. 3 Typical energy spectrum of the Pr2.5%:LuAG excited by ^{137}Cs and measured by using the APD.

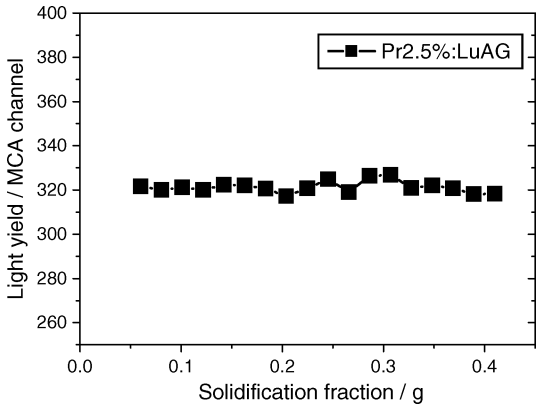

Fig. 4. Dependence of the light yield on the solidification fraction for Pr2.5%:LuAG.

temperature and measured by using the APD are shown in Fig. 3. The energy resolution of Pr:LuAG is 5.8%.

3) Light Output Uniformity: The light output uniformity of the grown Pr:LuAG single crystal was evaluated by using a PMT (Hamamatsu H6531). The grown crystal was cut at the end of the shoulder and body parts. The solidification fractions at the end of the shoulder and body parts were approximately 0.06 and 0.41, respectively. A cylindrical crystal boule with a diameter of 50 mm and length of 92 mm was obtained. A plate with dimensions of $5 \times 1 \times 92$ mm^3 was cut along the growth axis. Subsequently, 18 pieces with dimensions of $5 \times 5 \times 1$ mm^3 mm were cut from this plate, and every surface was mechanically polished. The dependence of the light output on the solidification fraction is shown in Fig. 4. The standard deviation of the light yield is approximately 1.4%.

4) γ-Ray Response: The γ-ray response measurement was performed by using a PMT (Hamamatsu H6531). A sample with dimensions of $5 \times 5 \times 1$ mm^3 was used for this measurement. The sample was excited by using ^{152}Eu, ^{22}Na, ^{133}Ba, ^{137}Cs and ^{241}Am. Then, each photoabsorption peak was fit with a single Gaussian function, and the energy resolution and peak channel for each energy level were estimated. The lines of 122 keV (^{152}Eu), 511 keV (^{22}Na), 1274 keV (^{22}Na), 356 keV (^{133}Ba), 662 keV (^{137}Cs), and 1408 keV (^{241}Am) were utilized to evaluate the variation in pulse height with energy linearity. Fig. 5

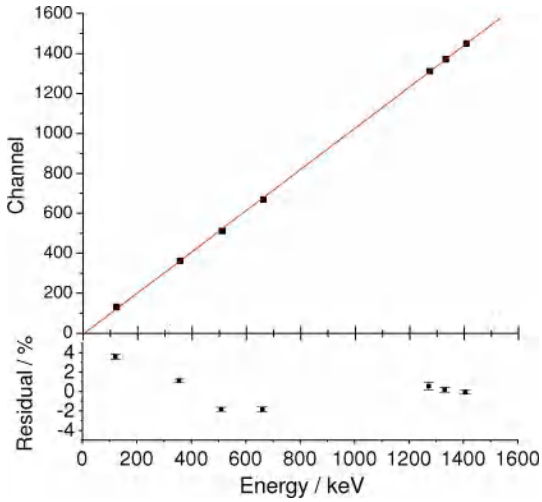

Fig. 5. γ-ray response in the range from 122 keV (^{152}Eu) to 1.4 MeV (^{241}Am) measured by using a PMT (Hamamatsu H6531). The line is a least-squares best fit to the data points.

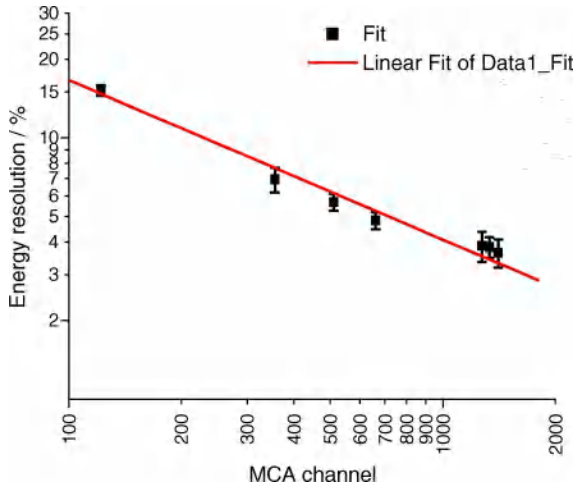

Fig. 6. Energy resolution in the range from 122 keV (^{152}Eu) to 1.4 MeV (^{241}Am) measured by using a PMT (Hamamatsu H6531). The energy resolution was 15.3% at 122 keV, 7.2% at 356 keV, 5.6% at 511 keV, 4.8% at 662 keV, 4.0% at 1274 keV , 3.9% at 1332 keV , and 3.9% at 1408 keV. The line is a least-squares best fit to the data points.

shows the relationship between the energy and pulse height, which exhibits good linearity within ~4% between 122 keV and 1408 keV. The Pr:LuAG crystal exhibits good linearity between the energy and energy resolution (Fig. 6). The energy resolution fit to the line is calculated by using the equation: $\delta \propto 1/E^{1/2}$, where δ denotes the energy resolution and E denotes the energy of the gamma ray.

5) Rise and Decay Time: The rise-time spectra of the Pr2.5%:LuAG sample excited by a pulsed X-ray at room temperature are shown in Fig. 7. Pr2.5%:LuAG shows a very fast rise time of approximately 0.4 ns. The decay time spectra of Pr2.5%:LuAG are shown in Fig. 8. The dominant component is approximately 18 ns, which is significantly less than the scintillation decay time of other oxide scintillators (BGO:300 ns, LSO:40 ns). This short decay time along with a noticeable presence of slower decay components (55.0 ns) indicate retrapping processes and a delayed radiative recombination at Pr^{3+} emission centers [2], [24].

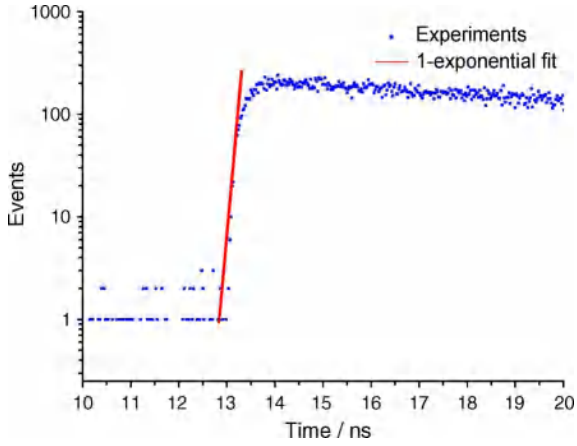

Fig. 7 Rise-time spectra of the Pr2.5%:LuAG sample excited by a pulsed X-ray at room temperature.

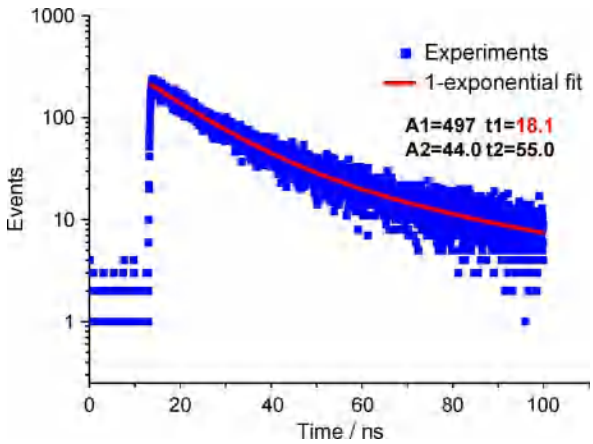

Fig. 8 Decay time spectra of the Pr2.5%:LuAG sample excited by a pulsed X-ray at room temperature.

IV. Conclusion

We demonstrated the growth of a Pr:LuAG single crystal with a diameter of 2 inches and a length of 160 mm by means of the CZ method. The solidification fraction was approximately 0.45. The grown Pr:LuAG crystals produced a homogeneous light yield that is approximately 2.5 times less intense than that of a conventional Ce:LSO. The sample, with dimensions of $5\times5\times1\,mm^3$, exhibited energy resolutions of 4.8% at 662 keV, as measured by using the PMT (Hamamatsu H6531), and 5.8% at 662 keV, as measured by using the APD (Hamamatsu S8664-55). The Pr2.5%:LuAG crystal exhibits a very fast rise time of approximately 0.4 ns, excited by the pulsed X-ray at room temperature. The decay time was approximately 18 ns, along with a noticeable presence of slower decay components (with a decay time of 55.0 ns). Furthermore, Pr:LuAG shows good linearity between the energy and pulse height within around 4% of the standard deviation in the range from 122 keV (^{152}Eu) to 1.4 MeV (^{241}Am).

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