Crystal Growth and Scintillation Properties of 2-Inch-Diameter \( \text{Pr:Lu}_3\text{Al}_5\text{O}_{12} \) (Pr:LuAG) Single Crystal

Kei Kamada, Kousuke Tsutsumi, Yoshiyuki Usuki, Hiraku Ogino, Takayuki Yanagida, and Akira Yoshikawa

Abstract—In this work we tried to grow 2-inch-diameter and high quality Pr:LuAG single crystals by the Czochralski (Cz) method. To grow the large diameter Pr:LuAG single crystal, we have optimized growth conditions and the furnace design. As a result, we have succeeded in the growth of 2-inch-diameter Pr:LuAG single crystal with a length of 110 mm. To determine light yield and energy resolution the energy spectra were collected under 662 keV \( \gamma \)-ray excitation (\(^{137}\)Cs source) and detection by a photomultiplier (Hamamatsu H7826). The light yield was around three times higher than that of BGO and almost homogeneous with increasing solidification fraction up to 0.32. The energy resolution was around 8%. Furthermore, scintillation decay time was around 23 ns and almost homogeneous all over the crystal.

Index Terms—5d-4f luminescence, crystal growth, gamma-ray detectors, garnets, Pr\(^{3+}\).

I. INTRODUCTION

SINGLE crystal scintillator materials are widely used for applications of high-energy physics and medical imaging, which require high light output, a high density and a fast scintillation decay time. Recently our group intensively examined scintillation properties of several Pr-doped compounds \([1],[2]\), and found out that Pr:LuAG has interesting properties of high density (6.7 g/cm\(^3\)), high light yield (three times higher than \(\text{Bi}_4\text{Ge}_3\text{O}_{12}\)) and a very fast 5d-4f emission decay time (\(\sim 22\) ns) \([3]–[5]\). Therefore, national project supported by Japan Science and Technology Agency (JST) for the attempts to fabricate Positron Emission Mammograph (PEM) using Pr:LuAG, has started. In order to apply Pr:LuAG scintillator to commercial PET and PEM equipment, voluminous production of this material is a very important issue.

In this report, we tried to grow 2-inch-diameter and high quality Pr:LuAG single crystals by the Czochralski (Cz) method. We report their scintillation characteristics such as light yield and decay time.

II. EXPERIMENTAL PROCEDURE

A. Crystal Growth

Starting materials used in this study were \(\text{Pr}_6\text{O}_{11},\text{Lu}_2\text{O}_3\) and \(\alpha-\text{Al}_2\text{O}_3\) with a purity of 99.99%. \(\text{Pr}_6\text{O}_{11}\) was added to the starting material for luminescent centers as \(\text{Pr}^{3+}\). Namely, \(\text{Lu}^{3+}\) was substituted for \(\text{Pr}^{3+}\) according to the formula of \((\text{Pr}_{0.95}\text{Lu}_{0.05})_3\text{Al}_2\text{O}_{12}\).

Pr:LuAG single crystals were grown by Cz method with an RF heating system. The rotation rate was 8–12 rpm and the growth rate was 1.0 mm/h. An automatic diameter control system by crystal weighing was applied to control the crystal diameter. Crystals were grown from an Ir crucible 100 mm in diameter and 100 mm in height. Ar atmosphere was used to prevent oxidation of the crucible. The seed crystals were [111] oriented Pr:LuAG crystals. After the completion of growth, the grown crystal was cut off from the melt and was gradually cooled down to room temperature.

B. Chemical and Optical Measurements

Chemical composition analysis was performed by electron microprobe analysis (EMPA) using JEOL JXA-8621MX.

Fig. 1 shows the experimental setup for measurements of scintillation properties such as light output and decay time. Several pieces with 2.45 \(\times\) 5.1 \(\times\) 15 mm\(^3\) size were cut along the growth axis. Every surface was mechanically polished. The pieces were wrapped with teflon tape as a reflector and coupled with the PMT using optical grease. To determine light yield, the
energy spectra were collected under 662 keV $\gamma$-ray excitation ($^{137}\text{Cs}$ source), using an amplifier with a shaping time of 1 $\mu$s, a photomultiplier (Hamamatsu H7826) and a multichannel analyzer in the pulse height mode. The decay time was also measured using digital oscilloscope TDS3052 of Tektronix, Inc.

III. CRYSTAL GROWTH AND CAUSES FOR CRACKING

Grown 2-inch-diameter Pr:LuAG(2.5%) single crystals were shown in Figs. 2 and 3. As shown Fig. 2, there are many cracks in shoulder and tail part of the crystals at the beginning of our work. By investigating the shape of tail part of the grown crystal in Fig. 3, it seems melt/crystal interface tends to form concave shape toward the melt in tail part of Pr:LuAG crystal. These results led to conclusion that possible causes for cracking are the stresses induced during the process:

1) Thermal stress in the shoulder part due to large cone angle.
2) Stress in the tail part due to concave shape of melt/crystal interface.

IV. PREVENTING CRACKS

A. Thermal Stress in the Shoulder Part Due to Large Cone Angle

Growth with a larger cone angle forces the crystal shoulder to view more directly upward, toward the coolest portion of the growth enclosure, while also exposing a greater length the vertical surface of the crystal exterior to the hot inner crucible wall. This abrupt change in the thermal environment near the corner of the crystal shoulder results in much larger temperature gradients there [6], [7]. This effect can be responsible for cracking in the crystal shoulder. From this point of view, we change the cone angle from 90° to 45° to reduce thermal stress in the shoulder part.

B. Stress in the Tail Part Due to Concave Shape of Melt/Crystal Interface

Flattening melt/crystal interface is important to obtain high quality single crystal. There have been several numerical works on the interface shape. Several groups performed a numerical study on the Cz system for growth of oxide single crystal and showed that the interface shape can change depending on whether the flow field is dominated by the forced convection or the natural convection. They demonstrated that the interface shape changes from concave to convex toward the melt as the crystal rotation rate decreases and temperature gradient along the growth direction increases [8], [9].

From this point of view, we changed the rotation rate from 10 rpm to 6 rpm in the tail part to reduce the forced convection. In addition, we arranged the insulator design to decrease the temperature gradient along the growth direction. Finally, we changed the temperature gradient from 40°C/cm to 20°C/cm to increase the natural convection. These can result in flattening the melt/crystal interface.

V. CRYSTAL GROWTH OF 2-INCH-DIAMETER PR:LUAG

Growth conditions such as cone angle, rotation rate and insulator design in the furnace were optimized for obtaining crack-free 2-inch-diameter Pr:LuAG crystals with uniform light yield and decay time in the whole crystal.

Two-inch-diameter Pr:LuAG(2.5%) single crystal with a length of 110 mm was grown with a nominal composition of $\text{Pr}^{3+}_{0.075}\text{Lu}_{2}\text{O}_{3}\text{Al}_{5}\text{O}_{12}$ (Fig. 4). The crystal yield of grown crystal was about 40% of raw material in the crucible.

Concentration of $\text{Pr}^{3+}$ as a function of solidification fraction is shown in Fig. 5. In the crystal this concentration was around 0.18–0.25 mol%. The measured concentration of the $\text{Pr}^{3+}$ along the crystal yielded a distribution coefficient $k_{\text{eff}}$ of 0.07. This value was calculated using the normal freezing equation: $C_{s} = C_{0}(1 - g)^{k_{\text{eff}} - 1}$, where $C_{s}$ is the measured concentration in the samples, $C_{0}$ is the initial concentration in the melt, g is the solidification fraction, and $k_{\text{eff}}$ is the effective distribution coefficient of $\text{Pr}^{3+}$. The distribution coefficient was
VI. SCINTILLATION PROPERTIES

A. Uniformity of Light Yield

Typical energy spectra of BGO and Pr:LuAG(2.5%) are shown in Fig. 6. The relative scintillation light yield was calculated from the position of the photoabsorption peak. The light yield of Pr:LuAG was around three times higher than that of a standard BGO sample and energy resolution was around 8%. The dependence of light yield on solidification fraction was shown in Fig. 7. The standard deviation of the light yield was around 9%.

B. Uniformity of Decay Time

Scintillation decay time spectra of Pr:LuAG(2.5%) at room temperature under 662 keV γ-ray excitation (137Cs source) is shown in Fig. 8. The dominant component was about 23 ns, which is much shorter than the scintillation decay time of other oxide scintillators (BGO:300 ns, LSO:40 ns). This together with a noticeable presence of slower decay components (96.8 ns decay time) points to retrapping processes and delayed radiative recombination at Pr3+ emission centers [11]–[14]. The dependence of decay time on solidification fraction is shown in Fig. 9. The decay time was as short as 23 ns and the standard deviation of the decay time was around 8%.

VII. CONCLUSION

We demonstrated 2-inch-diameter Pr:LuAG single crystal with a length of 110 mm grown by the Cz method. Pr:LuAG crystals have homogeneous light yield which is around three
times higher than that of a standard BGO crystal and short decay time (∼23 ns) over entire crystal.

REFERENCES