Scintillation characteristics of Pr-doped Lu$_3$Al$_5$O$_{12}$ single crystals

H. Ogino$^a$,* A. Yoshikawa$^a$, M. Nikl$^b$, K. Kamada$^a$, T. Fukuda$^a$,*

$^a$Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
$^b$Institute of Physics, AS CR, Cukrovarnická 10, 162 53 Prague, Czech Republic

Available online 5 June 2006

Abstract

Pr-doped Lu$_3$Al$_5$O$_{12}$ (Pr:LuAG) bulk single crystals were grown by Czochralski method. The crystals were seeded-grown in the $\langle 11\bar{1}\rangle$ direction. Dimensions up to 100 mm in length and 1 in in diameter were achieved without cracking. Concentrations of Pr$^{3+}$ in several parts of grown crystals were measured precisely and segregation coefficients of each crystal were determined. Scintillation light yield of each part of the crystals was measured and dependence on light yield on Pr concentration was determined. Optimum concentration of Pr was clarified and compared to the standard Bi$_4$Ge$_3$O$_{12}$ (BGO) sample; Pr optimum concentration was around 0.2–0.3% and light yield of Pr:LuAG was more than two times higher than BGO. Scintillation decay of Pr:LuAG was measured and a dominant decay time of about 20 ns was evaluated.

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PACS: 29.40.Mc; 81.10.Fq; 98.38.Am

Keywords: A1. Characterization; A2. Growth from melt; B1. Oxides; B2. Scintillator materials; B3. Scintillators

1. Introduction

Scintillator materials combined with photo detectors are used to detect high energy photons and particles e.g., in X-ray computed tomography (CT), positron emission tomography (PET) and other medical imaging techniques, high energy and nuclear physics detectors, etc. In the past decades, great effort was made to develop more efficient and fast scintillators to detect ionizing radiation. At present, the best combination of stopping power, decay time, and light yield is achieved by Ce-activated materials, but there is still a continuous demand for new scintillator materials with even better properties.

In the wide band-gap materials having medium or high crystal field strength, the Pr$^{3+}$ ion also shows fast 5d-4f emission [1]. Shorter decay times can be achieved by 5d-4f emission of Pr$^{3+}$, since this emission is characterized by a shorter wavelength compared to 5d-4f emission of Ce$^{3+}$ [2]. Scintillator materials with short decay time would be of interest for a number of applications that require high counting rates and high timing resolution, for example, the time-of-flight PET. However, scintillation materials based on 5d-4f luminescence of Pr$^{3+}$ ions are comparatively less studied than the Ce$^{3+}$-based ones.

Materials based on garnet structure 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. The Ce-doped Lu$_3$Al$_5$O$_{12}$ (Ce:LuAG) single crystal was shown to be a prospective scintillator material with a relatively high density of 6.7 g/cm$^3$, a fast scintillation response of about 60–80 ns (due to the 5d-4f radiative transition of Ce$^{3+}$ providing the emission around 500–550 nm), and prospective light yield of about 12–14,000 phot/MeV [3,4]. In the case of the Y$_3$Al$_5$O$_{12}$ (YAG) matrix, Pr$^{3+}$ doping gives rise to a structured emission band around 320 nm and a photoluminescence decay time of about 11 ns at room temperature (RT) [5]. However, at RT, the emission has already become partially quenched, which lowers the merit of Pr:YAG if a scintillator application is considered [6]. Pr-doped LuAG offers an interesting combination of a higher density host, and a very fast 5d-4f (but not yet quenched at RT) emission.
decay time of about 20–21 ns in the near UV spectral region with emission extending from 290–350 nm with the peak around 308 nm [7,8].

In this paper, we report a detailed study of crystal growth and the scintillation properties of Pr-doped LuAG bulk single crystals.

2. Experimental procedure

A stoichiometric mixture of 4N Pr₆O₁₁, Lu₂O₃ and Al₂O₃ powders (High Purity Chemicals Co.) was used as starting material. Nominally, Lu³⁺ was substituted by Pr³⁺ according to the formula of (Prₓ, Lu₁₋ₓ)₃Al₅O₁₂ for x = 0.01 and 0.03.

Single crystals of Pr:LuAG were grown by Czochralski (Cz) method with an RF heating system. The rotation rate was 15 rpm and the pulling rate was 1.2 mm/h. An automatic diameter control system by crystal weighing was applied to control the crystal diameter. Crystals were grown from an Ir crucible 50 mm in diameter and 50 mm in height. N₂ atmosphere was used to prevent oxidization of the crucible. Seed crystals were /111/ S oriented undoped LuAG crystals.

Chemical composition analyses were performed by inductively coupled plasma (ICP) method by SII SPS3000 (Seiko Instruments Inc.) and electron microprobe analysis (EPMA) using the JEOL JXA-8621MX.

Several plates of 2.5 × 1 × 15 mm were cut along the growth axis and polished for the luminescence spectra measurement and light yield measurement. Other samples with a longitudinally polished “window” of about 1.5 mm width was also cut and used for the scintillation decay measurement.

To determine light yield (LY) and energy resolution the energy spectra were collected under 662 keV γ-ray excitation (137Cs source) and detection by a photomultiplier (Hamamatsu H6521). Scintillation decays were studied using a spectrofluorometer 199S using the 22Na radioisotope (511 keV photons) as an excitation source and time-correlated single photon counting method.

3. Results and discussion

Photographs of single crystals grown by Cz method are shown in Fig. 1. Concentrations of Pr³⁺ in the melt were 1 at% (Pr¹%:LuAG) and 3 at% (Pr³%:LuAG) of the Lu³⁺, respectively. Transparent and crack-free crystals were obtained for both compositions. As-grown crystals were slightly colored yellowish green and the Pr³%:LuAG sample had a stronger color. The end part of Pr³%:LuAG was opaque because of a high concentration of inclusions, whose composition was characterized by EPMA. It was found that the inclusions rarely contained Lu. Ratio of each ion is Lu:Pr:Al:O = 0.1:3.0:35.0:61.9, which is close to PrAl₁₂O₁₉. Origin of this secondary phase was a very small segregation coefficient of Pr in this host material as written below.

The distribution of the Pr³⁺ ion along the crystal growth axis was inspected in six samples taken along this axis for both crystals by ICP method. Samples were cut from each position of the grown crystals and dissolved in a mixture of sulfuric and phosphoric acid. Concentrations of Pr³⁺ as a function of solidification fraction, g, are shown in Fig. 2. In the crystal this concentration was around 0.07–0.15 mol% for Pr¹%:LuAG and around 0.2–0.7 mol% for Pr³%:LuAG. For Pr¹%:LuAG, the measured concentration of the Pr³⁺ along the crystal yielded a distribution coefficient k_eff of 0.06. This value was calculated using the normal freezing equation: 

\[ C_s = C_0 k_{eff} \left( \frac{1}{g} \right) \]

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 \( k_{eff} \) is the effective distribution coefficient of Pr³⁺. The distribution coefficient was small as expected, due to the large ionic radius of the Pr³⁺ compared to that of Lu³⁺. In the case of Pr³%:LuAG, \( k_{eff} \) of around 0.065 was calculated, but the calculated line and observed values deviated towards the end of the crystal as shown in Fig 2(b). Reason for this phenomenon is that as in ICP sample preparation/solution even inclusions which contain much higher Pr³⁺ ion are dissolved. As a consequence, the apparent Pr³⁺ concentration becomes higher towards the end of the crystal compared to the real value. Such small \( k_{eff} \) value is derived from difference of the ionic radii of Lu and Pr.

Typical energy spectra of Pr¹%:LuAG and Pr³%:LuAG samples cut from the center of the crystals are shown in Fig. 3. The relative scintillation light yields were calculated from the position of the photopeak and were around two to three times higher than that of a standard BGO sample. There was a rather large difference of light yield between Pr¹%:LuAG and Pr³%:LuAG. Dependence of light yield...
on the solidification fraction along the crystal growth axis was also characterized as shown in Fig. 4. In Pr1%:LuAG, light yield was increased monotonously with solidification fraction, while in Pr3%:LuAG, light yield was maximized at the middle and decreased towards the end of the crystal. Light yield of Pr3%:LuAG was higher than that of Pr1%:LuAG throughout the whole area except the end of the crystal.

From the result of ICP analysis and light yield measurements, the relation between Pr3+ concentration in the crystal and light yield were established as shown in Fig. 5. There was a clear dependence of light yield on Pr3+ concentration in the crystal. In the concentration region lower than 0.2%, light yield monotonically increased with the Pr3+ concentration. The LY was increased as a function of the Pr3+ concentration passing through the maximum at around 0.2–0.3% and then decreased as shown in Fig. 5.

Measurement of the Pr1%LuAG scintillation decay is given in Fig. 6. The dominant component was about 20 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 (~450 ns decay time) points to retrapping processes and delayed radiative recombination at Pr$^{3+}$ emission centers similar to the observed characteristics of Ce-doped LuAG [10].

4. Conclusions

Pr-doped LuAG single crystals were grown by Cz method. Segregation coefficient of Pr$^{3+}$ in LuAG host was determined and the value was about 0.06. Scintillation light yield of Pr:LuAG was dependent on the Pr concentration in the crystals and maximum light yield was observed when concentration of Pr$^{3+}$ in the crystal was around 0.2–0.3% of the Lu$^{3+}$. Light yield was around two to three times higher than that of BGO and dominant scintillation decay time of about 20 ns was noticeably faster than that of the present oxide scintillators. Such a combination of desirable properties makes Pr-doped LuAG a very attractive candidate for fast and efficient scintillators.

Acknowledgments

This work was partially supported by the Innovation Plaza Miyagi project from the Japan Science and Technology Agency (JST) and the Industrial Technology Research Grant Program in 03A26014a from the New Energy and Industrial Technology Development Organization (NEDO) as well as a Grant in Aid for Young Scientists (A), 15686001, 2003 from the Ministry of Education, Culture, Sports, Science and Technology of the Japanese government (MEXT). Partial support of the Czech MSMT, KONTAKT Grant 1P2004ME716 is also gratefully acknowledged.

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