Growth and optical properties of Lu₃(Ga,Al)₅O₁₂ single crystals for scintillator application

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Abstract

Effect of Ga substitution in a (Ce,Lu)₃Al₅O₁₂ scintillator was examined at the crystals grown by the micro-pulling down (m-PD) method. Strong suppression of unwanted host luminescence due to an exciton localized around Lu–Al antisite defect was observed even at the Ga concentration of 10 mol%. Less-intense slower components in scintillation decay were obtained upon increasing the amount of Ga. While the radioluminescence intensities of the 5d–4f luminescence of Ce³⁺ were not strongly changed, light yield was increased by Ga substitution. The 20% Ga-substituted sample showed even higher light yield than typical Czochralski-grown Ga-free LuAG:Ce.

1. Introduction

Single-crystal scintillator materials are widely used for the detection of high-energy photons and particles. There are continuous demands for new scintillator materials with higher performance because of the increasing number of applications of scintillators such as medical and industrial purpose.

Materials based on aluminum garnets are promising hosts for scintillator application, because of the well-mastered technology of bulk crystal growth developed for laser host, excellent mechanical properties, chemical stability and so on. Ce³⁺-doped Y₃Al₅O₁₂ (YAG) single crystals were investigated as a fast scintillator already in the seventies [1]. Its heavier analog Lu₃Al₅O₁₂ (LuAG) is advantageous for hard X- and γ-ray detection because of the higher density (6.67 g/cm³) than that of YAG (4.56 g/cm³). Ce-doped LuAG was intensively studied due to its favorable scintillation characteristics [2,3]. Recently, LuAG:Pr was also investigated and its high light yield and fast decay time of about 20 ns [4,5] make it one of the high figure-of-merit scintillators available today.

On the other hand, in the luminescence spectrum of YAG:Ce and LuAG:Ce crystals, besides the 5d–4f luminescence of Ce³⁺, broad ultraviolet bands are also observed, which exist in undoped single crystals of YAG [6] and LuAG [7]. In the literature [8,9], this band was ascribed to trapped excitons localized around so-called antisite defects (Y³⁺ or Lu³⁺ ion at Al³⁺ site, abbreviated as Y₃⁺ and Lu₃⁺). The concentration of such kind of defects in YAG and LuAG is reported to be up to 0.5 at% [10]. Theoretical calculation also indicates that this type of defects is energetically stable and favorable in these hosts [11]. A thermoluminescence (TSL) measurement in LuAG:Ce has identified electron traps that are related to Lu₃⁺ defects, which are responsible for glow curve peaks within 120–200 K [12]. Such shallow trapping states in the LuAG host slow down scintillation decay kinetics, and considerable amount of slower decay components was found [13]. To optimize the performance of LuAG-based scintillator towards their intrinsic limits, understanding and control of such kind of defects through manufacturing technology are of crucial importance.

Recently, it was found that in LuAG:Pr this trap was diminished by Ga substitution at the Al site, while it also slightly decreased light yield [14,15]. In LuAG:Ce, an even higher ratio of slow component than LuAG:Pr is reported [16]. So the suppression of such shallow traps in this host may improve scintillation performance even more effectively. This motivated us to study the Ce³⁺-doped Lu₃(Ga,Al)₅O₁₂ (LuGAG) single crystals.

To prepare LuGAG crystals, the micro-pulling down (m-PD) method was adopted. By using this method, single-crystalline materials can be produced quickly and relatively inexpensively and the grown samples are of sufficient dimensions for necessary characterization [17]. To overcome the evaporation of Ga₂O₃ during the growth at high temperature and to grow single crystals with high crystallinity, quick sample preparation is necessary. Therefore, the m-PD method was chosen as an efficient tool for the...
systematic study. In this work, LuGAG:Ce crystals were grown by the μ-PD method and the effect of Ga substitution of the Al site in a LuAG:Ce scintillator was examined.

2. Experimental procedure

2.1. Sample preparation

Mixtures of 4 N purity CeO$_2$, Lu$_2$O$_3$, β-Ga$_2$O$_3$ and 5 N α-Al$_2$O$_3$ powders (Kojundo Chemical Laboratory) were used as starting materials. Nominal composition was calculated by Lu$^{3+}$ substitution for Ce$^{3+}$ and Al$^{3+}$ substitution for Ga$^{3+}$ according to the formula (Ce$_x$Lu$_{1-x}$)$_3$(Ga$_y$Al$_{1-y}$)$_5$O$_{12}$. The range of nominal concentrations of Ce was 0.007 ≤ x ≤ 0.02 and Ga was 0 ≤ y ≤ 0.2 in the melt. Additionally, 5 mol% of β-Ga$_2$O$_3$ was added to compensate ignition loss. The starting materials were sintered at 1400 °C for 24h prior to melting. Rod-shaped single crystals of LuGAG:Ce were grown by the μ-PD method using an RF heating system. The scheme of a typical μ-PD method and the growth procedure details are given in Ref. [18]. The crystals were grown from an Ir crucible with a typical pulling rate of 2–3 mm/h. The seed crystals were [111]-oriented undoped LuAG crystals grown by the μ-PD method as well. Crystals without Ga were grown under N$_2$ or N$_2$+0.5% O$_2$ atmosphere and crystals containing Ga were grown under N$_2$+0.5% O$_2$ atmosphere to prevent ignition loss of Ga.

2.2. Characterization

To identify the obtained phase and determine the lattice constants of each phase, powder X-ray diffraction (XRD) analysis was carried out in the 20 range from 5° to 80° at room temperature (RT) using a RIGAKU RINT Ultima diffractometer. Measurements were performed in air and the X-ray source was Cu-K$_\alpha$ (40 kV, 15 mA). The chemical composition was analyzed by electron microprobe analysis (EPMA) using the JEDL JXA-8621MX. Samples cut from each position of the grown crystals were analyzed. Radioluminescence (RL) spectra and scintillation decays of μ-PD-grown crystals were measured with a modified Spectrofluorometer 1995, Edinburgh Instruments, using excitation by an X-ray tube and $^{22}$Na radioisotope, respectively. Scintillation response of LuGAG:Ce crystals was measured under γ-ray excitation ($^{137}$Cs 662 keV lines) using setup with HPMT. Details of the measurements are given in Ref. [19]. Measured samples were all 0.96 or 0.95 mm thick and their area was ~3 mm × 6 mm. From the energy spectra, number of photoelectron yield ($N_{\text{ph}}$) per 1 MeV was evaluated.

3. Results and discussion

3.1. Crystal growth by the μ-PD method

While Ga-free samples could be grown from stoichiometric melt, the growth of Ga containing samples from stoichiometric...
melt resulted in cracking and opacity. Because the melting point of LuAG is around 150 °C higher than that of Lu$_3$Ga$_5$O$_{12}$, ignition loss of Ga$_2$O$_3$ strongly affects the phase stability of LuGAG with low Ga concentration. With 5% excess Ga$_2$O$_3$ and growth under N$_2$+0.5% O$_2$ atmosphere, transparent and crack-free crystals were obtained. The starting concentration of Ce$^{3+}$ was optimized at 0.7 mol% by preliminary investigation of luminescence intensities of the crystals. The images of the single crystals are shown in Fig. 1. As-grown crystals were yellow colored. Only the garnet phase was detected by powder XRD measurement and the lattice constants of each crystal calculated from XRD were almost proportional with Vegard’s law of LuAG–LGG solid solution as shown in Fig. 2.

3.2. Optical properties of the grown crystals

RL spectra (Mo-K$_\alpha$, 40 kV) of the LuGAG:Ce crystals are shown in Fig. 3. In all the samples, a strong 5d–4f emission band of Ce$^{3+}$ peaking at approximately 450–650 nm was observed, which was consistent with that of a previous study [20]. Besides this band, broad UV band around 230–400 nm was observed in the Ga-free sample. Influence of Ga is similar to that earlier investigated for Pr-doped LuAG samples [14,15]: this UV band is strongly suppressed by an admixture of Ga. As this emission has been ascribed to an exciton localized around the LuAl antisite defect [21], such a result indicates the inefficient localization of exciton around the LuAl antisite defect or the disappearance of the latter defect. Mild decrease of the RL intensity in 20% Ga content was observed, but the effect was rather small as the 20% Ga sample showed more than 95% of RL intensity of the Ga-free sample.

In Fig. 4 scintillation decays of the crystal set are given approximated by the sum of two exponentials. In Table 1, evaluation of decay fits ($A_i$, $\tau_i$) as well the relative amplitude of slow decay components using the so-called coefficient alpha [22]...
Experimental data are fitted by the function
\[ I(t) = A_0 \times A_2 \exp(-t/\tau_2) + A_0 \times A_1 \exp(-t/\tau_1) \]
Coefficient \( \chi = \frac{t_{\text{slow}}}{t_{\text{fast}} \times 100\%} \) is given as well.

is provided. It is interesting to note the monotonically decreasing value of coefficient alpha with increasing Ga content, indicating the suppression of very slow components (tens–hundreds of microseconds), which is consistent with the observed decrease of intrinsic emission of the host and can be explained by the suppressed ability of the LuAl defects to localize excitons or to trap an electron. The decay time of the second slower submicrosecond component also decreases with Ga concentration, but the component amplitude \( A_2 \) increases, which may point to the decay acceleration even in submicrosecond time scale.

Energy spectra and \( N_{\text{ph}} \) photoelectron yield per 1 MeV of LuGAG:Ce are shown in Fig. 5. \( N_{\text{ph}} \) was evaluated from the scintillation pulsed height spectra of the samples under excitation by 662 keV \( \gamma \)-ray lines of radioisotopes. There are differences in light yield values also due to growth atmosphere: LuAG:Ce crystal grown under a \( N_2+0.5\% \) \( O_2 \) atmosphere shows lower light yield than a crystal grown under \( N_2 \). Except for the crystal grown under \( N_2 \) atmosphere, systematic increase of light yield was observed by increasing the Ga content. Light yield of the 20% Ga sample of 1859 phels/MeV exceeds that of the Ga-free sample grown under \( N_2 \) atmosphere, and even the typical light yield of commercially available Czochralski-grown LuAG:Ce crystals measured with the same setup, which were around 1200–1600 phels/MeV [23]. It is interesting to note that the trends in intensities of RL and the light yields do not coincide. As only the fast component of the scintillation light can contribute to the light yield, enhancement of the light yield by Ga admixture is achieved not by improvement of total efficiency but due to conversion of the slower components into the fast one. This fact suggests that the ability to trap electrons of LuAl antisite defect is strongly suppressed by Ga admixture.

is known that in Ga garnets there is a higher concentration of antisite \( \text{RE}_{\text{Ga}} \) because of the smaller difference in radius of both cations in the crystal lattice [24] and in mixed crystals Ga ions occupy both tetrahedral and octahedral sites [25]. The above facts indicate that the Ga admixture cannot erase the antisite defects directly. Possible explanation for the suppression of host luminescence is that Ga\(^{3+} \) wave functions will lower the edge of the conduction band, which obtains the LuAl defect levels closer to it. This can make the related electron trap shallower in Ga containing samples. This can also allow more easy ionization of the relaxed 5d\(_1 \) level of Ce\(^{3+} \), i.e., facilitate an escape of electron from 5d\(_1 \) to the conduction band at elevated temperatures.

4. Summary

Single crystals of LuGAG:Ce with different Ga concentrations were grown by the \( \mu \)-PD method. Substitution of Ga at the Al site strongly suppresses the UV emission band, which is related to Lu\(^{3+} \) antisite defect. Moreover, less–intense very slow components in scintillation decays and higher light yield in the Ga admixeded samples were obtained. The 20% Ga-substituted sample shows even higher light yield than that of typical commercially available Czochralski-grown LuAG:Ce crystals. Further improvement of the scintillation performance of LuGAG:Ce might be possible through optimization of composition and growth conditions.

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