Crystal growth and characterization of Ce:Gd₃(Ga,Al)₅O₁₂ single crystal using floating zone method in different O₂ partial pressure

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Multicomponent garnet Ce:Gd₃(Ga,Al)₅O₁₂ (Ce:GAGG) single crystals show very high light yield with reasonably fast scintillation response. Therefore, they can be promising scintillators for gamma-ray detection. However, in the decay curve a very slow component does exist. Therefore, it is necessary to optimize further the crystal growth technology of Ce:GAGG. In this study, Ce:GAGG single crystals were grown by the floating zone (FZ) method under atmospheres of various compositions such as Ar 100%, Ar 80% + O₂ 20%, Ar 60% + O₂ 40% and O₂ 100%. Radioluminescence spectra are dominated by the band at about 540 nm due to Ce³⁺ 5d→4f transition. The Ce:GAGG single crystal grown under Ar atmosphere shows an intense slower decay component. It can be related to the processes of the delayed radiative recombination and thermally induced ionization of 5d level of Ce³⁺ center possibly further affected by oxygen vacancies. This slower decay process is significantly suppressed in the samples grown under the O₂ containing atmosphere.

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1. Introduction

Scintillators are important radiation sensors in many applications such as medical diagnostics, medical radiography, and industrial defectoscopy. High light yield, fast decay with minimized afterglow and high Z_eff are the most important parameters for hard X-ray and γ-ray scintillation material.

Although the Ce-doped Lu₃Al₅O₁₂ (LuAG:Ce) single crystal is the high-density analog of the well-known YAG:Ce scintillator, LuAG:Ce was evaluated as a non-prospective scintillation material in the comparison with the high density aluminum perovskite (LuAP:Ce) in 1995 [1] and has not been further studied in the 1990s of last century.

In 2004–2005 we started the study of Pr-doped LuAG single crystal and its comparison with the other Pr-doped materials using both micro-pulling down and Czochralski methods [2–7]. LuAG:Pr has shown an exceptional figure-of-merit among Pr-doped garnets and silicates mainly due to negligible thermal quenching of Pr³⁺ center up to 500 K, fast luminescence and scintillation response dominated by the 20 ns component and excellent energy resolution as well [8,9]. However, slow decay components due to retrapping of charge carriers at shallow traps during the transport stage to the emission center were observed in the scintillation decay measurements [10]. In the attempt to minimize the undesirable effect of these shallow electron traps, the Ga-admixed LuAG:Pr appeared as a very promising material system [10].

Though the Ga-admixture in Pr:LuAG was not effective for light yield increase due to an early onset of thermally induced ionization of the 5d1 excited state of Ce³⁺, it did make a positive impact in Ce³⁺-LuAG in this respect [11]. In the combinatorial scintillator-oriented search in the multicomponent (Gd,Lu,Y)₃(Ga,Al)₅O₁₂:Ce material system the simultaneous presence of balanced Gd and Ga concentrations enabled to keep sufficiently high ionization barrier of 5d₁ level of Ce³⁺ and to diminish undesirable trapping effects in the transport stage of scintillator mechanism [12,13]. Consequently, new class of ultra-efficient scintillators was discovered where the light yield of 46,000 phot/MeV was achieved for Gd₃Ga₂Al₃O₁₂:Ce (GAGG:Ce) Czochralski-grown single crystal [14].

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The delayed recombination processes are generally responsible for the slow-down of scintillation response and any electron traps incl. oxygen vacancies may intensify them. Therefore, it is desirable to employ another crystal growth technology, namely the optical floating zone (FZ) method, to grow these crystals under atmospheres with different O\textsubscript{2} partial pressure to influence the oxygen vacancy concentration.

Based on the above idea, this study is focused on the growth of GAGG:Ce single crystal using FZ method under different O\textsubscript{2} partial pressure and their luminescence and scintillation characterization.

2. Experimental procedure

2.1. GAGG:Ce single crystal elaboration

The basic concept of FZ method is that ellipsoidal mirrors are used to focus the light from xenon lamps onto a vertically positioned rod-shaped ceramic sample to produce a molten zone, which is then moved along the sample in order to grow a single crystal. The use of light heating makes the technique suitable for both conducting and non-conducting materials.

The advantage of FZ method is that it is crucible-less method. Therefore, various atmospheres can be applied.

Powders of Gd\textsubscript{2}O\textsubscript{3} (99.99%), \(\alpha\)-Al\textsubscript{2}O\textsubscript{3} (99.99%), \(\beta\)-Ga\textsubscript{2}O\textsubscript{3} (99.99%) and CeO\textsubscript{2} (99.99%) were used as starting materials. They were mixed in an alumina mortar. After mixing, the powder was rubber-pressed under a hydrostatic pressure of 50 MPa to become a rod, and then sintered at 1300°C for 10 h in air. The sintered rod was almost single phase and had the garnet structure. The typical dimensions of these feeding sintered rods for the floating-zone growth were 4–5 mm in diameter and 30 mm in length.

The growth apparatus used was an image furnace (ASGAL, Japan), which has double ellipsoidal mirrors, in which halogen lamps of 1.5 kW were set as heating source (see Fig. 1). The growth conditions were as follows: growth rate 1–5 mm/h, rotation rate 10–20 rpm and growth atmosphere (Ar 100%, Ar 80% + O\textsubscript{2} 20%, Ar 60% + O\textsubscript{2} 40%, and O\textsubscript{2} 100%) flowing at 500 ml/min.

The growth crystals were cut perpendicularly to the growth direction, and then polished to a high optical quality grade.

To identify the generated phase and to investigate lattice constants of each phase, powder X-ray diffraction analysis was carried out in the 2θ range from 20° to 80° at room temperature (RT) using the Rigaku diffractometer (RINT2000). Measurements were performed in air and the X-ray source was Cu K\(\alpha\), accelerating voltage 40 kV, tube current 40 mA. Distribution of the cations in Ce:GAGG single crystals were measured by electron probe micro-analysis (EPMA) using SEM (Hitachi S-3400N) equipped with EPMA (Oxford Instruments INCA WAVE500).

2.2. Optical and scintillation properties of GAGG:Ce single crystal

Optical transmission spectra were measured using JASCO V550 spectrophotometer. Luminescence measurements were carried out using the Spectrofluorometer FLS920 (Edinburgh Instruments) equipped with the hydrogen steady-state and nano-second pulsed flashlamp (IBH Scotland). Spectral range of both equipments is equipped with the hydrogen steady-state and nano-second pulsed flashlamp (IBH Scotland). Spectral range of both equipments is 175–800 nm.

For the scintillation yield and decay measurements, the crystals were covered with several layers of Teflon tape and optically coupled to the light entrance window of photo-multiplier tube (PMT) R7600 (Hamatsu) with an optical grease. The high voltage was supplied by ORTEC 556, and signals were red out from the anode of PMT. Then, the signals passed a shaping amplifier ORTEC 570 with 0.5 µs shaping time, converted to digital signals by a multi-channel analyzer Pocket MCA 8000A provided by Amptek Co. and recorded in a computer. Decay time is also evaluated using a memory oscilloscope, Tektronix TDS304B.

3. Results and discussion

3.1. GAGG:Ce crystal growth and characterization

As shown in Fig. 2a, \((\text{Gd}_{0.998},\text{Ce}_{0.002})_2\text{Ga}_2\text{Al}_3\text{O}_{12}\) (Ce 2%:GAGG) single crystal with 4 mm in diameter 20 mm in length were grown by the FZ method. Yellow color is typical for the Ce doped garnet. Growth atmospheres were Ar flow, Ar 80% + O\textsubscript{2} 20% flow, Ar 60% + O\textsubscript{2} 40% flow and O\textsubscript{2} flow.

It should be noted that when crystal is grown under Ar flow atmosphere, remarkable amount of \(\beta\)-Ga\textsubscript{2}O\textsubscript{3} were evaporated and deposited at the lower temperature area in the furnace. This is similar phenomenon, which is observed at the growth of \(\beta\)-Ga\textsubscript{2}O\textsubscript{3} single crystal [15]. It is found that the admixture of O\textsubscript{2} gas effectively suppresses its evaporation.

Using powder XRD, it is confirmed that all the obtained crystals were of single phase with the garnet structure. From the result of EPMA, homogeneous Ce distribution was observed along the growth direction in all the samples. However, the ratio between Al and Ga are changing along the growth direction. Higher concentration of Ga is observed under higher O\textsubscript{2} growth atmosphere. This confirms suppression of Ga evaporation when using higher O\textsubscript{2} content atmosphere during the crystal growth process (see Fig. 2b).

3.2. Optical properties

The absorption spectra of Ce:GAGG are shown in Fig. 3. Ce\textsuperscript{3+} 4f–5d\textsubscript{1} absorption is observed around 440 nm and is slightly shifted to shorter wavelength in the sample grown under 100% O\textsubscript{2} atmosphere. It is due to lower Ga evaporation in oxygen-rich growth atmosphere, because increasing Ga concentration in GAGG host shifts 4f–5d\textsubscript{1} transition towards shorter wavelength [12,13,16]. Furthermore, in this sample somewhat increased absorbance below approx. 350 nm may indicate the presence of Ce\textsuperscript{3+} which shows broad band in this spectra region due to charge transfer absorption transition of Ce\textsuperscript{4+} [17]. Fig. 4 shows an example of the excitation and emission spectra of Ce:GAGG. Ce\textsuperscript{3+} emission band due to 5d\textsubscript{1}–4f transition shows maximum around 530 nm. The shape of this emission band is identical in all the samples studied, it is just 3–4 nm shifted towards shorter wavelength in the sample grown under 100% O\textsubscript{2} atmosphere, consistently with the absorption characteristics in Fig. 3. Two peaks based of the Ce\textsuperscript{3+} 4f–5d\textsubscript{2,3}
transitions were observed in excitation spectra around 340 and 440 nm, respectively. Comparing the excitation spectra between the $x = 20\%$ and $x = 100\%$ samples, a slight high energy shift of the 440 nm peak is noted in the latter, which is consistent with the absorption spectra in Fig. 3. Furthermore, comparatively less intense signal below some 350 nm in the latter sample is due to the above mentioned competing parasitic absorption of Ce$^{4+}$ in this spectral region.

In Fig. 5, photoluminescence decay of Ce 0.2% doped GAGG single crystal is shown. The leading decay component with 50 ns decay was observed belonging to the Ce$^{3+}$ 5d–4f transition and is consistent with [12,13]. Presence of a slower, weak decay component indicates an onset of thermally induced ionization of the 5d$_1$ excited state of Ce$^{3+}$ evidenced by the delayed recombination decay in the same host composition [18].

### 3.2.1. Scintillation properties

Radioluminescence spectra are dominated by the 530 nm band, in all the samples, see Fig. 6. The peak is identical with that in photoluminescence spectra in Fig. 4.

Scintillation decay is shown in Fig. 7. Faster component with the decay time value around 100 ns is consistent with the data in [12] for analogous material composition. This value is distinctly longer than found in photoluminescence decay of Ce$^{3+}$ in Fig. 5 so that an additional delay due to the energy transfer process arises even if its exact nature is not yet understood. An onset of the Ce$^{3+}$ 5d$_1$ excited state ionization around room temperature mentioned above probably also contributes. The decay time and respective component intensities (see also caption of Fig. 7) are summarized in Table 1.

Though the evaluation of component intensities in Fig. 7 does not provide a unique trend it should be noted that only the Ce 0.2% doped GAGG single crystal grown under pure Ar atmosphere shows distinctly higher intensity of the slower decay component as...
The decay times and respective component intensities of fits from this article.)

References to color in this figure legend, the reader is referred to the web version of this article.

The black curve in Fig. 6 does not reach the background level even after 2 µs. It can be also due to the processes of the delayed radiative recombination and mentioned ionization of the 5d\(^1\) state of Ce\(^{3+}\). Though the nature of these processes and related shallow electron traps is yet to be understood it is worth noting the above mentioned Ga evaporation may lead to Ga deficiency. Arising material non-stoichiometry will naturally lead to higher material defectiveness. Consequently, the oxygen vacancies and various electron trap configurations may arise. Suppression of Ga evaporation in the samples grown in O\(_2\)-rich atmosphere led to better material stoichiometry. Consequently, better scintillation performance is obtained in the scintillation decay and light yield (see below) measurements.

In order to test further the effect of oxygen vacancies, annealing in reducing atmosphere (Ar + H\(_2\)) was carried out at 1000 °C for 48 h. Comparing with the as grown sample, the decay slow down and the amplitude/background ratio decreased which points to enhanced intensity of very slow decay processes (Fig. 8). As shown in Fig. 7, the crystals grown in higher O\(_2\) partial pressure have lower ratio of slow decay component and vice versa. Thus, the tendency in Fig. 8 is in good agreement with the data shown in Fig. 7.

Pulse height spectra of Ce:GAGG are shown in Fig. 9. Positive effect of O\(_2\) atmosphere is noted as the position of photopeak (i.e. light yield value) is by about 10–15% higher in the case of 100% O\(_2\) atmosphere (see Fig. 9).

4. Conclusions

Ce:GAGG single crystals were grown by the FZ method under various atmospheres with compositions of Ar 100%, Ar 80% + O\(_2\) 20%, Ar 60% + O\(_2\) 40% and O\(_2\) 100%. Both photoluminescence and radioluminescence spectra are dominated by the Ce\(^{3+}\) 4f–5d transition. The Ce\(^{3+}\) 4f–5d\(_{1,2}\) bands were confirmed in the absorption and excitation spectra measurements as well. In the Ce:GAGG single crystal grown under pure Ar (O\(_2\)-free) atmosphere higher relative intensity of slow decay component was obtained. It can be due to retrapping processes at shallow electron traps in the host. This much slower component is notably suppressed in the samples grown under O\(_2\) containing atmosphere, which suggests that the shallow traps might arise also due to Ga-deficiency, as significant Ga evaporation was confirmed when oxygen-free atmosphere was used in the growth process. The highest light yield achieved in the sample grown in 100% O\(_2\) atmosphere also support the above provided explanation.

Table 1

<table>
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<tr>
<th>O(_2) ratio in the atmosphere (%)</th>
<th>(I_j/t_j) (ns)</th>
<th>(I_2/t_2) (ns)</th>
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<td>0.81/121</td>
<td>0.19/482</td>
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<td>0.15/437</td>
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<tr>
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<td>0.20/349</td>
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