Growth and Scintillation Properties of Li and Ce co-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ scintillator

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30 **Abstract**

31 The Li^+ co-doped $\text{Ce:Lu}_3\text{Al}_5\text{O}_{12}$ single crystals were prepared by micro pulling down
32 method. Absorption and luminescence spectra were measured together with several other
33 scintillation characteristics, namely the scintillation decay and light yield to reveal the
34 effect of the co-doping. The smooth Ce^{4+} CT absorption below 350nm is clearly enhanced
35 with increasing concentration of Li. The scintillation decays were accelerated and light
36 yields were increased by Li co-doping.

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40 Scintillators

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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[1]. Oxide materials based on garnet structure single crystals 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 $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (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 light yield of about 12–14,000 phot/MeV [2-5]. In the silicate, perovskite and garnet scintillators the slow tunneling-driven radiative recombination between Ce emission centers and nearby lying electron traps can deteriorate scintillation performance [6,7]. Ce:LSO and Ce:LYSO single crystals co-doped with Ca^{2+} have been recently investigated and improvement in their scintillation characteristics, namely afterglow suppression and scintillation decay acceleration, were claimed[8] which is based on the suppression of such slow delayed recombination processes. Positive role of stable Ce^{4+} centres has been proposed in [9-12] to explain the improved scintillation performance of Mg-codoped Ce:LuAG and Ce: $\text{Y}_3\text{Al}_5\text{O}_{12}$. Its light yield was enormously enhanced and the presence of Ce^{4+} was clearly identified by its characteristic charge transfer (CT) absorption in the near UV range below 350 nm [13].

The aim of this work is to investigate the monovalent alkali metal ion Li^+ co-doping effects on luminescence and scintillation properties of Ce:LuAG single crystal scintillator. In this report, Li co-doped Ce:LuAG single crystals were grown by the micro-pulling down (μ -PD) method and characterized as for the chemical composition. Luminescence and scintillation characteristics were also measured.

2. Experimental

2.1 Micro-pulling down prepared crystals and their structure by X-ray diffractometer

A stoichiometric mixture of 4N Li_2CO_3 , CeO_2 , $\alpha\text{-Al}_2\text{O}_3$ and Lu_2O_3 , powders was used as starting material. Nominally, starting powders were prepared according to the formula of $(\text{Li}_x, \text{Ce}_y, \text{Gd}_{1-y})_3\text{Al}_5\text{O}_{12}(\text{CO}_3)_x$. Single crystals of Li co-doped and 1 atomic% Ce doped LuAG were grown by the μ -PD method with an RF heating system. The parameter values y was 0.01 and x's were 0.0002, 0

001 and 0.005. These samples will furthermore be noted as Li200, Li1000 and Li5000. A schematic of the μ -PD growth apparatus is given in Ref. [14]. Typical pulling rates were 0.05–0.07 mm/min and the diameter was around 4 mm. Crystals were grown from an Ir crucible under the N₂ atmosphere. The seed crystals were <111> oriented Ce:LuAG crystals. Plates of ϕ 4mm x 1mm were cut and polished for the absorption and luminescence spectra measurements. Pieces of the grown crystals were crushed and ground into powders in a mortar. Powder X-ray diffraction analysis was carried out in the 2θ range 15° - 75° using the RINT Ultima (RIGAKU) diffractometer. The CuK α X-ray source was used, the accelerating voltage and current were 40 kV and 40 mA, respectively.

2.2 Optical, luminescence and gamma-ray response measurement procedure

Absorption spectra were measured by the Shimadzu 3101PC spectrometer in the 190-800 nm range. At the SR-163 spectrometer (ANDOR TECHNOLOGY) equipped with the CCD detector DU920P (ANDOR TECHNOLOGY) the radioluminescence (RL) spectra were measured under an X-ray (40 kV, 30 mA) tube. Light output measurements were performed by using photomultiplier tube (PMT Hamamatsu R7600U). Sample pieces with dimensions of ϕ 4 × 1 mm were cut from the grown single crystal, ϕ 4mm surfaces were mechanically polished. To determine the light yield, the energy spectra were collected under 662 keV γ -ray excitation (¹³⁷Cs source) by using an avalanche photodiode (APD, Hamamatsu, S8664-55). The sample was coupled with the APD by using silicone grease (OKEN, 6262A). The sample was covered by using Teflon-tape. The signal was fed into a pre-amplifier (CP580K), shaping amplifier (CP 4417), pocket multichannel analyzer (pocket MCA, Amptek 8000A), and finally to a personal computer. The bias for the APD was supplied by a power supplier (CP 6641). Because the APD was thermally sensitive, we controlled the ambient temperature at 20± 0.5°C by using a heat bath. Decay time was measured by using a photomultiplier (PMT, Hamamatsu, R7600U) with digital oscilloscope TDS3052 of Tektronix, Inc.

3 Result and discussion

3.1 Crystal growth

Non co-doped and Li 200, 1000 and 5000 ppm co-doped 1%Ce:LuAG single crystals were grown by the μ -PD method. Example photographs are shown in Fig. 1. The grown crystals were transparent with yellow color and 4 mm in diameter, 20-40 mm in length. Some of them look slightly cloudy because of the rough surface coming from thermal etching. However, the inner part of all the crystals is perfectly transparent.

Powder X-ray diffraction was performed to identify crystal phase of grown crystals. Example results of the powder X-ray diffraction of the grown non co-doped and Li 200, 1000 and 5000 ppm co-doped 1%Ce:LuAG crystals are shown in Fig. 2. All of the grown crystals show the single cubic garnet phase.

3.2. Optical and luminescence properties

The absorption spectra of the sample set are presented in Fig. 3. In addition of the 4f-5d_{1,2} absorption bands of Ce³⁺ center at 450 and 340 nm, respectively, the smooth Ce⁴⁺ CT absorption below 350nm is clearly enhanced by Li co-doping similarly to what was observed in [10,11]. Radioluminescence (RL) spectra in Fig. 4 show an enhancement of the Ce³⁺ emission band at 520nm by Li co-doping. Intensity of Ce³⁺ emission was maximized at Li 200 ppm co-doping. Anti-side defects (Lu_(Al) or Al_(Lu)) related emission band at 310nm were also observed. 310nm emission was decreased by Li co-doping. Scintillation performance of Ce-doped garnet is strongly degraded by shallow electron traps which delay energy delivery to the Ce³⁺ emission centers and give rise to intense slow components in the scintillation response [15,16].

3.3 Scintillation properties

The Pulse height spectra of Li co-doped Ce:LuAG excited by 662 keV gamma-ray of ¹³⁷Cs at room temperature and measured using the APD are shown in Fig. 5. Light yield was increased by Li co-doping. The light yield of the sample was calibrated from the ⁵⁵Fe direct irradiation peak to APD. Such direct irradiation generates 5.9 keV/3.6 eV = 1640 electron-hole pairs. Based on this value, light yield of Li 200 ppm co-doped sample was calculated to be approximately 24,000photon/MeV with correcting the QE, which was 80 % at 520 nm, which is around 220 % of light yield of the non co-doped sample and around 140 % of light yield of a reference Ce:LuAG scintillator produced by Czochralski (Cz) method. The light yield was calculated by an equation below,

$$LY = (\text{Peak channel of a sample}) / (\text{Peak channel of } ^{55}\text{Fe direct irradiation}) \times 1640 / 0.8 / 0.662.$$

Scintillation decay curves were observed by using digital oscilloscope TD5032B under the excitation by ¹³⁷Cs radioisotope (662 keV). Scintillation decay curves of Li co-doped Ce:LuAG crystals were shown in Fig. 6. The scintillation decay curves were accelerated by Li co-doping and decay time value decreased down to 43.0 ns at the Li 5000ppm sample. Table 1 shows the survey of light yield and scintillation decay time values. Li 200 ppm co-doped samples showed the highest light yield among all the grown Li co-doped samples and Mg co-doped sample in previous report.

Stabilization of the Ce^{4+} center could be occurred by monovalent Li^+ as same as Mg^{2+} and Ca^{2+} co-doping in Ce:LuAG [10,11]. According to the obtained results, monovalent and divalent ions co-doping can be effective to improve scintillation properties on Ce:LuAG.

4 Conclusion

The Li 200, 1000 and 5000 ppm co-doped Ce:LuAG single crystals were grown by the μ -PD method and their optical, luminescence and scintillation characteristics were measured. The intensity enhancement of the Ce^{3+} emission band at 520 nm in radioluminescence spectra was observed at Li co-doped. The scintillation decays were accelerated by Li co-doping and dominant decay time decreased down to 43.0 ns at the Li 5000 ppm sample from 49.7 ns at the non co-doped sample. Li 200 ppm co-doped samples showed the highest light yield of 24,000 photon/MeV among all the grown Li co-doped samples. These results indicate that Li co-doped Ce:LuAG can be promising scintillator for application which require fast timing resolution such as positron emission tomography. In the near future we will report about the bulk crystal growth of Li co-doped Ce:LuAG by the Cz method. Improvement on scintillation response is expected due to much higher quality of Czochralski-grown crystal samples.

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200 Figure captions

201

202 Figure1. Appearance of crystals prepared by the μ -PD method.

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204 Figure2. Results of the powder X-ray diffraction of the Li co-doped
205 1%Ce:LuAG crystals.

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207 Figure3. Absorption spectra of the AE co-doped Ce:LuAG crystals

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209 Figure4. Radioluminescence spectra of the Li co-doped Ce:LuAG crystals .
210 Excitation by X-rays, 40 kV, 30 mA, $\text{CuK}\alpha$.

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212 Figure5. Pulse height spectra of the Li co-doped Ce:LuAG crystals. (excitation
213 662 keV of ^{137}Cs radioisotope).

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215 Figure 6. Scintillation decay curves of the Li co-doped Ce:LuAG crystals .
216 (excitation 662 keV of ^{137}Cs radioisotope).

217

218 Table 1. Light yield and scintillation decay time values of the AE co-doped
219 Ce:LuAG crystals . Scintillation decay is approximated by the sum of two
220 exponentials $I(t) = \sum A_i \exp[-t/\tau_i]$, $i=1,2$. Ratio (%) is calculated as $A_i \tau_i / (A_1 \tau_1 +$
221 $A_2 \tau_2) \times 100\%$ for $i=1,2$.

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Kamada,et al, Figure 1

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Kamada, et al, Figure 5

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Kamada, et al, Figure 6

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Kamada, et al, Table 1

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Samples	Light yield [photon/MeV]	1st component decay time(ns)/ intensity(%)	2nd component decay time(ns)/ intensity(%)
non co-doped	10500	49.7/48	298/52
Mg200 ^[11]	21300	44.4/56	337/44
Li200	24000	47.2/49	341/51
Li1000	23000	45.0/46	363/54
Li5000	15000	43.0/40	315/60
Ce:LuAG-Cz ^[11]	17200	58/42	958/58