

Suppression of defect related host luminescence in LuAG single crystals

Hiraku Ogino^{1*}, Akira Yoshikawa², Martin Nikl³, Romana Kucerkova³, Jun-ichi Shimoyama¹
and Kohji Kishio¹

¹*School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo,
113-8656, Japan*

²*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
Katahira2-1-1, Sendai, 980-0812, Japan*

³*Institute of Physics AS CR, Cukrovarnicka 10, Prague 16253, Czech Republic*

e-mail address: tuogino@mail.ecc.u-tokyo.ac.jp

Abstract

To study suppression of the unwanted host luminescence in aluminum garnet crystals, effect of Ga substitution in both undoped and Eu doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ single crystal was examined at the crystals grown by the micro-pulling down (μ -PD) method. Optical properties such as excitation spectra, radioluminescence spectra and photoluminescence decay are presented. In the GA-admixed crystal strong suppression of host luminescence due to an exciton localized around the Lu-Al antisite defect was observed even at the Ga concentration of 10mol%. Ga substitution also modify the charge transfer excitation band in the Eu doped LuGAG and change the decay time in the Eu^{3+} red emission lines.

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1. Introduction

Single crystal scintillator materials are widely used for detection of high-energy photons and particles. There are continuous demands for new scintillator materials with higher performance because of increasing number of medical, industrial and other applications. Aluminum garnets are promising hosts for scintillator application, because of their optical transparency, chemical stability and well-developed technology of bulk crystal growth. Ce³⁺-doped Y₃Al₅O₁₂ (YAG) single crystal was investigated as a fast scintillator already in the seventies [1]. Its heavier analogue Ce-doped Lu₃Al₅O₁₂ (LuAG) is advantageous for hard X- and γ -ray detection because of a higher density (6.67 g/cm³) and studied intensively [2,3]. Recently Pr doped LuAG was also investigated. Its high light yield, fast decay time [4,5] as well as good energy resolution (5.2% at 662keV[6]) makes LuAG:Pr as one of the best scintillators available today.

On the other hand, in the luminescence spectrum of Ce or Pr activated YAG and LuAG crystals, broad ultraviolet bands are also observed besides the 5d-4f luminescence of Ce³⁺ or Pr³⁺. These bands are also present in undoped single crystals of YAG [7] and LuAG [8]. In [9,10] this band was ascribed to trapped excitons localized around so-called antisite defects (Y³⁺ or Lu³⁺ ion at Al³⁺ site, abbreviated as Y³⁺_{Al} and Lu³⁺_{Al}). The concentration of such kind of defects in YAG is reported as up to 0.5 at.%[11] and in LuAG is expected to be even higher. Theoretical calculation also indicates relative ease of creation and stability of this type of defects in these hosts[12]. A thermoluminescence (TSL) measurement in LuAG:Ce has identified shallow

electron traps which were ascribed to the $\text{Lu}^{3+}_{\text{Al}}$ defects and are responsible for glow curve peaks within 120-200 K [13]. Such shallow trapping states in LuAG host slow down scintillation decay kinetics and considerable amount of slower decay components was found [14]. To optimize 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 UV emission band caused by this trap was diminished by Ga substitution at the Al site, while it also slightly decreased light yield [15,16]. Furthermore, in LuAG:Ce enhancement of light yield as well as suppression of UV band and slow components in scintillation decay was achieved by Ga substitution [17]. Suppression of UV host emission indicates the way to improve scintillation performance more effectively. To study the effect of Ga substitution in detail, this time we investigated undoped and Eu doped $\text{Lu}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ (LuGAG) single crystals. Contrary to 5d-4f emission of Ce^{3+} and Pr^{3+} , 4f-4f luminescence of Eu^{3+} is not quenched by Ga substitution in LuAG host so that Eu^{3+} is suitable activator to study the effect by Ga substitution in all the concentration range.

To make LuGAG crystals the micro-pulling-down (μ -PD) method was adopted. By using this method single crystalline materials can be produced quickly and relatively inexpensively. The grown samples are of sufficient dimensions for necessary optical characterization [18]. To overcome evaporation of Ga_2O_3 during the growth at high temperature and grow single crystals with high crystallinity, quick sample preparation is necessary. Therefore, the μ -PD method was chosen as efficient tool for the systematic study. In this work, undoped and Eu doped LuGAG crystals were grown by the μ -PD method and the effect of Ga substitution at the Al site in LuAG single crystal was examined.

2. Experimental procedure

Sample preparation

Mixtures of 4N purity Eu_2O_3 , Lu_2O_3 , $\beta\text{-Ga}_2\text{O}_3$, and 5N $\alpha\text{-Al}_2\text{O}_3$ powders (High Purity Chemicals) were used as starting materials. Nominal composition was calculated by Lu^{3+} substitution for Eu^{3+} and Al^{3+} substitution for Ga^{3+} according to the formula $\text{Lu}_3(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}(\text{LuGAG})$ or $(\text{Eu}_{0.001}\text{Lu}_{0.999})_3(\text{Ga}_x\text{Al}_{1-x})_5\text{O}_{12}(\text{LuGAG:Eu})$. The range of nominal concentrations of Eu was 0.001 and that of Ga was $0 \leq x \leq 1.0$ in the melt. Additionally 5mol% of $\beta\text{-Ga}_2\text{O}_3$ was added to compensate ignition loss. The starting materials were sintered at 1400°C for 24h prior to melting. Rod shaped single crystals of undoped and Eu doped LuGAG were grown by the $\mu\text{-PD}$ method using an RF heating system. The scheme of a typical $\mu\text{-PD}$ method and the growth procedure details are given in Refs.[19,20]. The crystals were grown from an Ir crucible with typical pulling rate of 2~3mm/h. The seed crystals were [111] oriented undoped LuAG crystals grown by the $\mu\text{-PD}$ method as well. Crystals were grown under $\text{N}_2 + 1\% \text{O}_2$ atmosphere to prevent ignition loss of Ga.

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 2θ 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 $\text{Cu-K}\alpha$ (40 kV, 40 mA). Optical measurements are done for the samples cut from each crystals. Measured samples were all 0.96 or 0.95 mm thick and their area was $\sim 3 \text{ mm} \times 6 \text{ mm}$. Radioluminescence spectra, excitation spectra and photoluminescence decays of $\mu\text{-PD}$ grown crystals were measured with a modified Spectrofluorometer 199S,

Edinburgh Instruments, using excitation by an X-ray tube (Mo- K_{α} , 40 kV, 15 mA), hydrogen lamp and pulsed xenon flashlamp, respectively.

3. Results and discussion

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 of ignition loss of Ga_2O_3 . To suppress this effect, 5% excess Ga_2O_3 was added and growth was carried under $\text{N}_2 + 0.5\% \text{O}_2$ atmosphere. Under such conditions transparent and crack-free crystals were obtained. The images of the single crystals are shown in Fig. 1. As-grown crystals were colorless for undoped and slight pale green for Eu doped LuGAG. All crystals only garnet phase was detected by power XRD measurement and lattice constants of each crystal calculated from XRD were almost proportional with Vegard's law of LuAG-LGG solid solution.

Optical properties of the grown Crystals

Radioluminescence spectra of the undoped LuGAG crystals are shown in Fig. 2. Broad UV band around 230-400nm was observed in Ga-free sample, which becomes strongly suppressed by admixture of Ga. As this emission has been ascribed to an exciton localized around the Lu_{Al} antisite defect [21], such a result indicates inefficient localization of exciton around Lu_{Al} antisite defect or the disappearance of the latter. This result also pointed out that Ga substitution substantially suppress UV emission host band independently on the activator.

Radioluminescence spectra of LuGAG:Eu crystals are shown in Fig. 3. Intensities of each spectrum were normalized by $\text{Eu}^{3+} \ ^5\text{D}_0 > \ ^7\text{F}_4$ emission. All crystals showed typical transitions of

5D_0 - 7F_x of Eu^{3+} , while the host emission around 300 nm in the Ga free LuGAG:Eu is rapidly suppressed by increasing Ga concentration and above 20% of Ga substitution. Influence of Ga substitution was similar as found earlier in the investigated Pr-doped and Ce-doped LuAG samples[15-17]. There are also tiny changes in the fine structure of 4f-4f emission lines around 590 to 650 nm due to changing local symmetry and interaction between Eu_{Lu} site and nearest surrounding.

In the excitation spectra shown as Fig. 4, charge transfer (CT) transition of Eu^{3+} were observed. There was change of the shape of CT transition at high energy side depending on Ga concentration. The spectrum was cut around 200 nm in 60% Ga and around 220 nm in 100% Ga concentration. This indicate that the conduction band bottom edge became lower along with Ga substitution and inhibit charge transfer transition of Eu^{3+} .

As shown in Fig. 5, photoluminescence decay of Eu^{3+} from 5D_0 level shows single exponential decay with the decay time between 3-4 ms depending on Ga concentration. There is also clear rising edge in the decay which is approximated by decay times 20-50 microseconds depending also slightly on the Ga concentration. Rising edge can be interpreted as due to the intracenter transition 5D_2 - 5D_0 of Eu^{3+} . Such change of photoluminescence decay is due to small changes of local symmetry and interaction with surroundings.

It is known that in Ga garnets there is higher concentration of antisite RE_{Ga} because of smaller difference in radius of both cations in crystal lattice [22]. The facts indicate that Ga admixture does not diminish antisite defects directly. Possible explanation for the suppression of UV band is that the Lu_{Al} (Lu_{Ga}) defect levels become closer to edge of the conduction band in Ga substituted samples. This can make related electron trap shallower and trapping ability around room temperature diminishes. The cut of the high energy side of CT band in excitation spectra of

LuGAG:Eu pointed out that Ga^{3+} wave functions lower the edge of the conduction band, which is consistent with the above hypothesis, but further studies by thermoluminescence and other techniques are necessary to confirm it.

4. Summary

Single crystals of undoped and Eu doped LuGAG with different Ga concentrations were grown by the μ -PD method. Substitution of Al site by Ga strongly suppress UV host emission band which is enabled due to the existence of the Lu^{3+}Al antisite defects. In Eu doped LuGAG, Eu^{3+} luminescence is clearly manifested in all the Eu-doped LuGAG samples with characteristic line spectrum within 590-710 nm and millisecond decay times while UV emission band is suppressed at more than 20% of the Ga substitution. Minor changes in the excitation, emission spectra and decay times are observed depending on Ga concentration due to small changes of local symmetry and interaction with surroundings. Ga substitution substantially suppressed host luminescence. The change of the excitation band in Eu doped LuGAG indicates that suppression of the host luminescence might be achieved through conduction band lowering and burial of antisite defect-related traps into its bottom edge.

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Figure captions

Fig. 1. LuGAG crystals grown by the μ -PD method.: (a) undoped, $x = 0$, (b) undoped, $x = 0.1$, (c) undoped, $x = 0.2$ (d) Eu doped, $x = 0$, (e) Eu doped, $x = 0.1$, (f) Eu doped, $x = 0.2$, (g) Eu doped, $x = 1.0$. Scale is given in mm. Compositions of Eu^{3+} in the melt were 0.1mol% for all crystals.

Fig. 2. Radioluminescence spectra of undoped LuGAG at room temperature excited by 40kV 15mA

Fig. 3. Radioluminescence spectra of Eu doped LuGAG at room temperature excited by 40kV 15mA Mo- K_{α} .

Fig. 4. Excitation spectra of $^5\text{D}_2$ to $^7\text{F}_0$ transition of Eu^{3+} in LuGAG:Eu at room temperature ($\lambda_{\text{em.}} = 598\text{nm}$).

Fig. 5 (a) Photoluminescence decay time of Eu doped LuGAG($x = 0$) at room temperature. Experimental data are fitted by the function $I(t) = A_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$. ($\lambda_{\text{ex.}} = 242\text{nm}$, $\lambda_{\text{em.}} = 610\text{nm}$) (b) Dependence of photoluminescence decay time and rising time of the decay on Ga concentration.

Figure 1

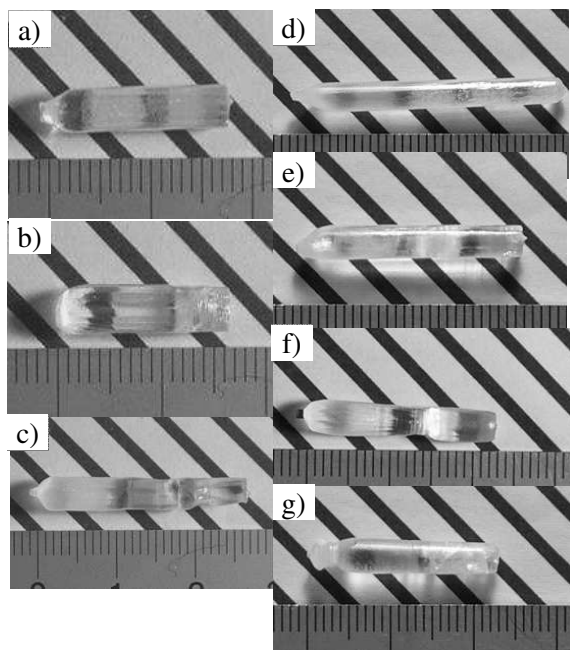


Figure 2

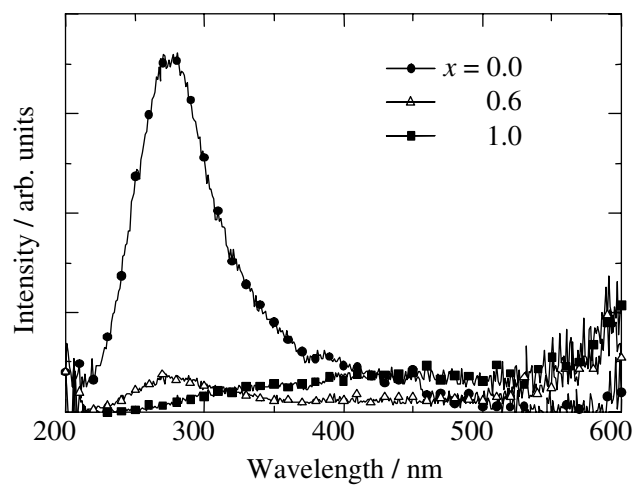


Figure 3

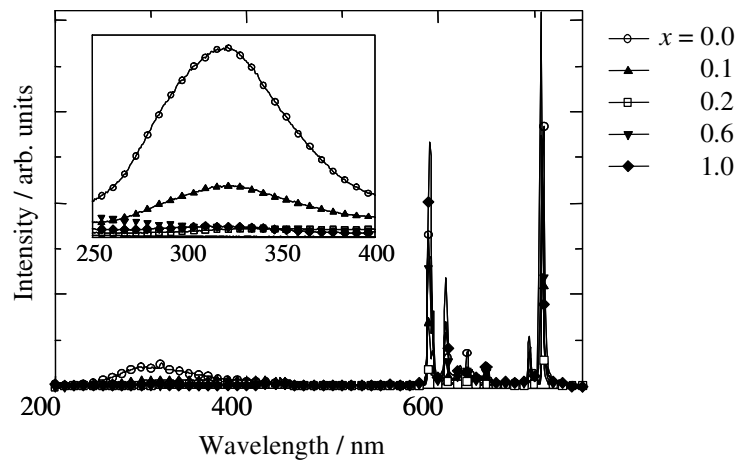


Figure 4

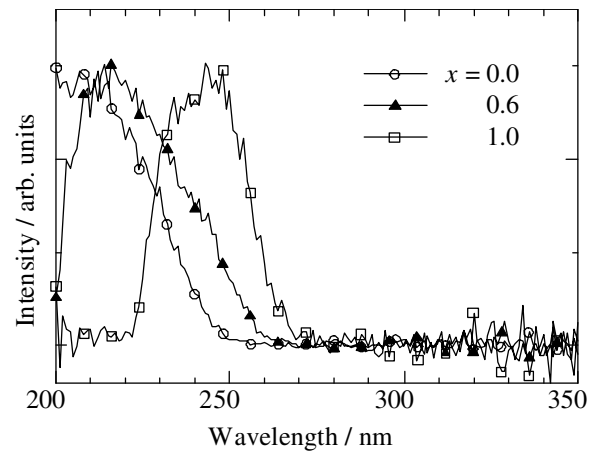
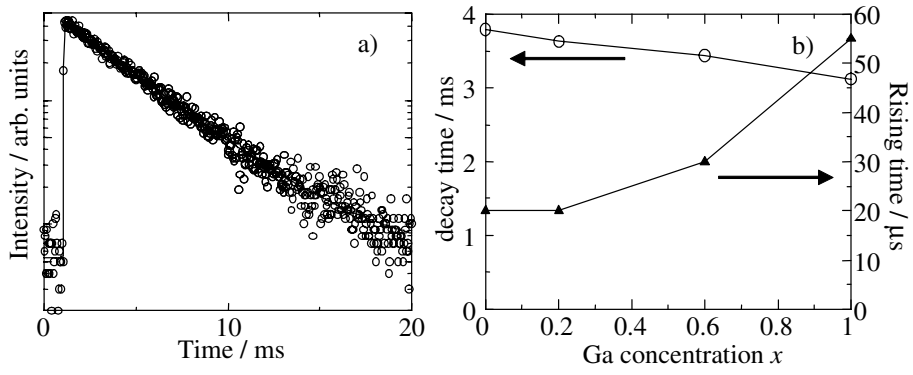


Figure 5



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