Mg co-doping effects on Ce doped $Y_3(Ga,Al)_5O_{12}$ scintillator

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Abstract. Nonstoichiometric $Lu_3Al_{5+x}O_{12}$ (x= 0.05, 0.15, 0.35, 0, -0.05, -0.15, -0.35) crystals were grown by the μ-PD method. Luminescence and scintillation properties such as absorption, excitation and emission spectra, light yield and decay time were evaluated. Expected anti-site defect related host emission have been observed in 250-420nm. Emission intensity was increased by increasing the nonstochiometry. The x=-0.35 sample showed the highest light yield of around 12000 photons/MeV and slowest scintillation decay time of 1.96μs.

Introduction

Scintillators coupled with photodetectors were widely used in radiation imaging applications such medical imaging, security, high energy physics, astrophysics, oil well logging, etc. Cerium doped garnet single crystals are promising candidates for scintillator applications. For example, Ce-doped $Lu_3Al_5O_{12}$ (Ce:LuAG) , Ce:$Gd_3Al_2Ga_3O_{12}$ (GAGG) and Ce: $Y_3Al_5O_{12}$ (YAG) single crystal was reported as a prospective scintillator material[1-4]. Ce:YAG was reported with scintillation properties of a scintillation response of about 91.6 ns, and light yield of about 16,200 phot/MeV[3]. Ce:YAG is also used as a phosphor in white LEDs[5,6]. The function of the Ce:YAG phosphor is to absorb the blue light emitted from the blue LED and converts it to yellow light. In multicomponent garnet of Ce:$(Gd,Y)_3(Ga,Al)_5O_{12}$ (GAGG), noticeable light yield over 40,000 phot/MeV at around 500nm with ~80ns decay time was reported. Improvement of scintillation performance was reported due to co-doping with alkali earth AE^{2+} ions in Ce activated scintillators such as, Ce:LSO [7,8], Ce:GAGG[9], Ce:LuAG[10] and Ce:YAG[11]. In the case of Ce:YAG, light yield was improved up to 2,1000 phot/MeV and decay time was accelerated to 31 ns in heavily Mg co-doped samples.

In this report, Mg co-doping effect on scintillation properties in multicomponent garnet of $Y_3(Ga,Al)_5O_{12}$ (YGAG) were investigated. Optical, luminescence and scintillation properties such light yield and decay time were evaluated.

Experimental

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1.1. Crystal growth procedure

A stoichiometric mixture of 4N $MgCO_3$, CeO_2, Y_2O_3, β-Ga_2O_3 and α-Al_2O_3 powders was used as starting material. Nonstoichiometric $(Mg_{0.0002}Ce_{0.05}Y_{0.095})_3(Ga_xAl_{5-x})O_{12}$ (x=1, 2, 3, 4) and Mg non co-doped YGAG single crystals were grown by the micro-pulling-down (μ-PD) method with an RF heating system. The Mg or non co-doped x=1, 2, 3, 4 crystals are named as Mg or non co-doped G1A4, G2A3, G3A2 and G4A1, respectively. A schematic of the μ-PD growth apparatus is given in Refs. [12]. Typical pulling rates were 0.05–0.12 mm/min and the diameter was around 4 mm. Crystals were grown from an Ir crucible under N_2 atmosphere. The seed crystals were <100> oriented YAG crystals. Plates of 4mmϕ x 1mm were cut and polished for the absorption and luminescence spectra measurement.

1.2. Measurements of scintillation properties

Radio-luminescence spectrum at room temperature was measured with the above spectrometer (EI FLS920) excited by 5.5MeV alpha rays from an ^{241}Am source. To determine the light output, we obtained the pulse height spectrum of this crystal under excitation with 662 keV gamma rays from a ^{137}Cs source. The scintillation photons were detected using by a photomultiplier (PMT; Hamamatsu R7600U), and then the signals from the PMT were amplified (ORTEC 113), shaped (ORTEC 572A), and read out with a multi-channel analyzer (AMPTEK 8000A). Additionally, its scintillation decay time excited by the gamma rays (^{137}Cs) was measured with the PMT and an oscilloscope (Tektronix TDS 3052B). The scintillation decay time was calculated from exponential approximation.

Results

1.3. Crystal growth procedure

Mg co-doped and non co-doped Ce:YGAG crystals were grown by the μ-PD method. Example photographs were shown in figure 1. The inner part of grown crystals were transparent with yellow color with 3-4 mm in diameter and 10-40 mm in length. The surface roughness was coming from thermal etching during crystal growth.

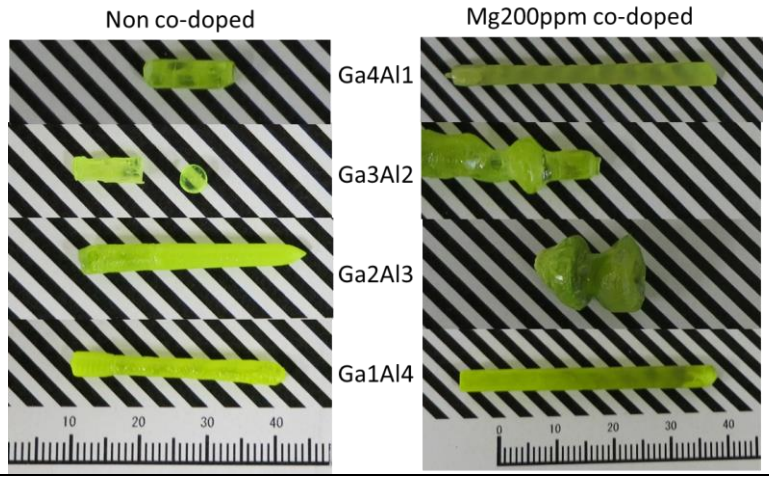

Figure 1. Example photographs of the grown Mg co-doped and non co-doped Ce:YGAG crystals

1.4. Luminescence and gamma-ray response

The absorption spectra of the sample set are presented in Fig. 2(left). In addition of the 4f-5d1,2 absorption bands of Ce^{3+} center at 420 and 350 nm, respectively, the smooth Ce^{4+} CT absorption below 350nm is clearly enhanced by Mg co-doping, similarly to the previous repot in garnet scintilltors [10, 11]. Radioluminescence (RL) spectra of the Mg co-doped and non co-doped G2A3

samples were showed in figure 2(right). There is no energy shift of emission band at 500nm by Mg co-doping.

The typical energy spectra of the Mg co-doped and non co-doped G1A4 samples excited by ^{137}Cs at room temperature are shown in figure 3(left). The Mg co-doped sample showed 180% higher light yield value compared to that of the non co-doped one. The light yield of the sample was calibrated from the ^{55}Fe direct irradiation peak to the APD. Such direct irradiation generates 5.9 keV/3.6 eV = 1640 electron-hole pairs. Based on this value, light yield of Mg co-doped sample was calculated to be approximately 36,000 phot/MeV after correcting the QE, which was 80% at 500 nm. Scintillation decay curves of the Mg co-doped and non co-doped G2A3 samples were shown in figure 3(right). The scintillation decay curves were fitted by second exponential. The decay time was accelerated by Mg co-doping. The Mg co-doped and non co-doped G2A3 samples shows decay time of 19.3ns(80%) and 61.0(20%) respectively. Table 1 shows the scintillation properties. Mg co-doping in G2A3 was most effective for improvement of light yield. According to the previous report, band gap increased and the position of $Ce^{3+}4f5d_1$ level shift to higher energy as decreasing Ga concentration. It is thought that position between conduction band, electron trap coming from anti-site defects, $Ce^{3+}4f5d_1$, and Ce^{4+} levels was optimized at G2A3 composition. The Ce^{4+} center effectively competes with electron traps and contributes to the enhancement of light output and acceleration of decay time.

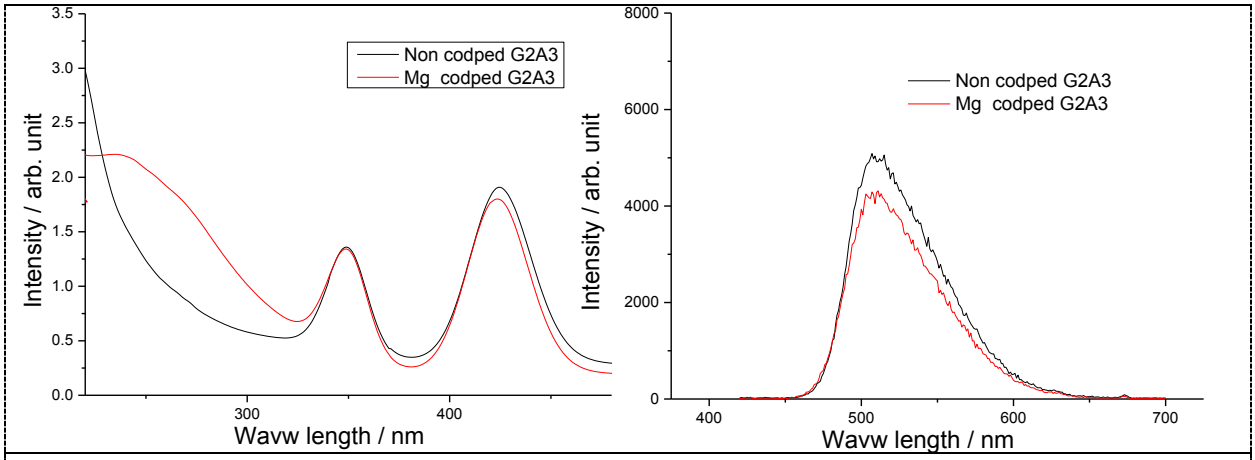

Figure 2. Absorption (left) and radioluminescence spectra (right) of the grown Mg co-doped and non-codoped G2A3 crystals.

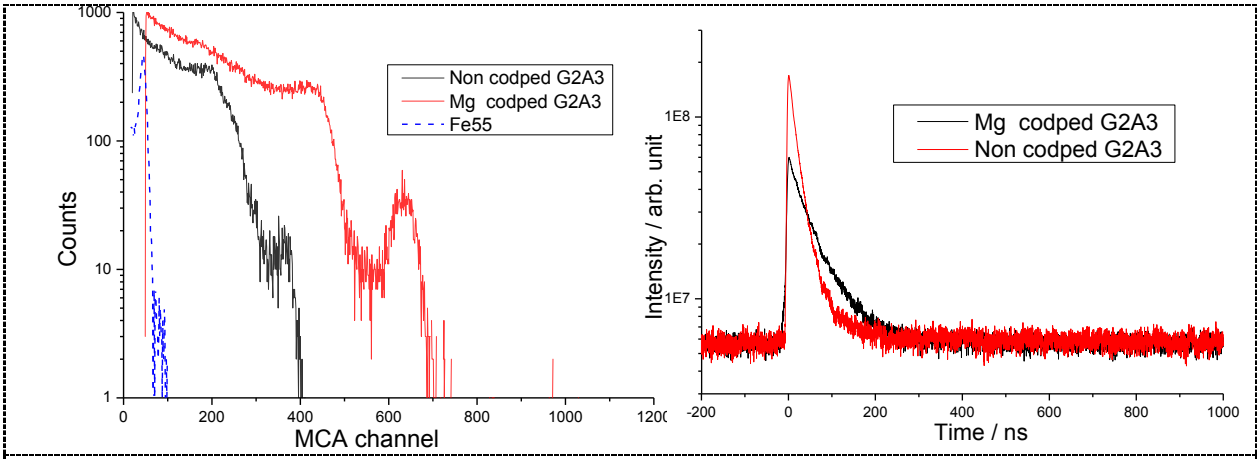

Figure 3. Energy spectra of the grown Mg co-doped and non-codoped G2A3 crystals (left) and decay curves of the grown G2A3crystals (right) excited by a 662 keV gamma ray.

Table 1. Scintillation properties of the grown Mg co-doped and non co-doped YGAG crystals

	Mg concentration (mol.ppm)	Emission wavelength (nm)	Light yield (phot/MeV)	1st decay time (ns)/ratio(%)	2nd decay time (ns)/ratio(%)
G0A5	0	480	16,200	91.6/77	464/23
G1A4	0	489	12,900	7.9/57	15.3/43
G2A3	0	501	13,600	12.7/3	57.3/97
G3A2	0	509	33,400	25.5/10	53.9/90
G4A1	0	517	22,500	38.1/26	79.2/74
G0A5	200	480	19,500	89.3/90	544/10
G1A4	200	492	16,400	19.8/11	51.2/89
G2A3	200	503	36,000	19.3/80	61/20
G3A2	200	510	38,800	11.3/4	54.4/96
G4A1	200	520	29,600	-	68.5/100

Conclusion

The Mg co-doped and non co-doped Ce:YGAG single crystals were grown by the μ-PD method and their optical, luminescence and scintillation characteristics were measured. The absorption of the Ce^{4+} CT band below 250 nm was observed at the Mg co-doped samples. The scintillation decays were accelerated by Mg co-doping and dominant decay time decreased down to 19.3 ns. Maximum light yield value of 38,800 phot/MeV was observed at G3A2 sample. The most significant increase of light yield value due to Mg-codoping was obtained for G2A3 sample, the light yield value of which was 36,000 phot/MeV. These results indicate that Mg co-doped G3A2 and G2A3 can be promising scintillator for application which require high light yield and fast timing resolution without self-radiation such as gamma camera and high energy physics applications. In the near future we will report about the bulk crystal growth of Mg co-doped Ce: YGAG by the Cz method. Improvement on scintillation response is expected due to much higher quality of Czochralski-grown crystal samples.

References

[1]. M. Moszynski, et al, IEEE Trans. Nucl. Sci. 44, (1997) 1052.
[2]. K. Kamada, et al, Crystal Growth & Design, 11 (2011) 4484.
[3]. J.A. Mares, et al.Opt.Mater. 24 (2003) 281.
[4]. M. Nikl, et al, Adv. Opt. Mater. 3, (2015) 463
[5]. K. Bando, et al. J. Light Vis. Environ., 22 (2008) 1.
[6]. J. Meyer, et al, Adv. Opt. Mater. 3, (2015) 424
[7]. C. L. Melcher, et al. IEEE Trans. Nucl. Sci., 39 (1992) 502.
[8]. M. A. Spurrier, et. al, J. Cryst. Growth 310 (2008) 2110.
[9]. K. Kamada, et al, Opt. Mater. 41(2015)63-66
[10]. K Kamada, et al.Nucl. Instrum. Methods Phys. Res. A, 11 (2015)9
[11]. A. Nagura, et al. Japan.J. App. Phy.54 (2015) 04DH1
[12]. Yoshikawa, et al. J. Crystal Growth 205 (1999)305-