Luminescent properties of Gd₃(Al,Ga)₅O₁₂ crystal co-doped with Ce and M⁴⁺

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Abstract. Since the light output of Zr⁴⁺ co-doped Ce:Gd₂SiO₅ scintillator improved compared with the Ce:Gd₂SiO₅ one, the light output and other scintillation properties of M⁴+/Ce₃⁺ co-doped Gd₃Al₂Ga₃O₁₂ (GAGG), where M = Zr, Hf, were investigated. (Gd₁₋ₓ, Ce₀.₀₁, Mₓ)₃Ga₃Al₂O₁₂ (M=Zr, Hf, x = 0.001 and 0.0002) crystals were grown by the micro-pulling down (µ-PD) method. We found these samples had longer decay time constants and the light outputs of these co-doped samples were degraded compared with that of the conventional Ce:GAGG.

1. Introduction

Scintillation materials have been investigated and applied in many fields such as homeland security, medical imaging system, oil well logging and astronomy [1, 2]. Some Compton cameras consist of scintillators, and can be applied in medical imaging or astronomy [3-8]. Ce-doped Gd₃Al₂Ga₃O₁₂ (Ce:GAGG) was found to have high light-yield (~ 46,000 photon/MeV) and good energy resolution (~ 4.9 % at 662 keV, FWHM) [9 - 11]. Ce³⁺-dopant is crystallographically substituted for Gd³⁺ in the dodecahedral site coordinated by eight oxygen atoms. The scintillation emission is related to the 5d-4f transition of Ce³⁺ with an emission wavelength of approximately 500 to 550 nm [9].

Shimura et al. reported that Ce:Gd₃SiO₅ (Ce:GSO) doped with around 200 ppm Zr⁴⁺ has shown maximum light output which is about 20% larger than that of conventional GSO:Ce [12]. On the other hand, light output of Ce:(Lu, Y)₂SiO₅ (Ce:LYSO) co-doped with divalent cation (e.g. Mg²⁺, Ca²⁺) was improved compared with the conventional Ce:LYSO scintillator [13]. However, the light output of the Ca²⁺/Ce³⁺ co-doped GAGG was degraded [14]. Up to now, effect of codoping with tetravalent cation has not been sufficiently investigated for Ce: GAGG. In this paper, we investigate the light output and other scintillation properties of M⁴⁺/Ce³⁺ co-doped GAGG, where M = Hf.
2. Materials and Methods

(Gd1-x, Ce0.01, Mx)3Ga3Al2O12 (M= Hf, x = 0.001 and 0.0002) crystals were grown by the micro-pulling down (μ-PD) method, and the powders of (α-Al2O3, Ce2O3, β-Ga2O3, Gd2O3, HfO2) of 99.99% purity were used as the crystal materials. The growth atmosphere was N2 (flow, 1 atm) and an Ir crucible was used. To grow the crystal, Lu11Al5O12 crystal was used as the seed, and the pulling rate was approximately 0.1 mm/min. Moreover, a conventional co-dopant-free Ce:GAGG crystal (x=0) was also grown by the same way as the above.

The crystals were cut and polished to the 1 mm thickness for the evaluation of their optical and scintillation properties. Transmittance spectra from 200 to 700 nm were measured with a spectrophotometer V-530 (JASCO). Photo-luminescence emission spectra were obtained with a spectrofluorometer (FLS920, Edingurgh Instrument) and Xe lamp as an excitation source.

Radio-luminescence spectra excited by 5.5-MeV alpha rays from an 241Am source were measured with the same spectrophotometer used for the photo-luminescence measurement. To determine the light output and energy resolution, we obtained the pulse height spectra of these crystals under excitation with 662-keV gamma rays from a 137Cs source. Here, the scintillation photons were detected by a photomultiplier (R7600U-200, Hamamatsu). Additionally, we used an oscilloscope (TDS 3052B, Tektronix) to measure the PMT output in order to estimate the decay times of these samples irradiated with the gamma rays (137Cs). The decay curves were fitted with the following equation:

\[ I(t) = A_1 \exp[-t/\tau_1] + A_2 \exp[-t/\tau_2] + c, \]  

where \( A_i \) and \( \tau_i \) denote the amplitude and decay time \( i = 1, 2, \tau_1 < \tau_2 \). The term \( c \) indicates the background.

3. Results and discussions

We succeeded in growing the (Gd1-x, Ce0.01, Hfx)3Ga3Al2O12 (x = 0.001 and 0.0002) crystals as shown in Fig 1. The polished samples with thicknesses of 1 mm had good transmittance of over 70%. Emission maximum peaks for all the samples including the conventional Ce:GAGG were located at the similar wavelength positions.

Figure 2 shows 5.5-MeV alpha-ray excited radio-luminescence spectra of (Gd1-x, Ce0.01, Hfx)3Ga3Al2O12, where x = 0.0002, 0.001, and conventional Ce:GAGG. These samples had also the similar radio-luminescence spectra when compared to the conventional Ce:GAGG. These results were the same as the results of the photo-luminescence emission spectra.

From the pulse height spectra of these crystals, all the samples co-doped with Hf4+ had lower light output than the conventional Ce:GAGG by 10-20% as shown in Fig. 3. Moreover, the co-doped samples had similar decay time (primary) components of roughly 100 – 110 ns to the conventional one (~120 ns) as shown in Fig. 4. Meanwhile, co-doped samples had secondary decay time components of 400 – 420 ns, although intensity ratios, defined as \( A_2/(A_1 + A_2) \), were only 5%. Thus, some defects or some traps could be generated by these tetravalent cations, and light outputs of these samples were degraded slightly.

![Fig. 1 Photograph of (Gd1-x, Ce0.01, Hfx)3Ga3Al2O12, where x= 0.0002(a) and 0.001(b).](image-url)
Fig. 2 Radio-luminescence spectra of (Gd$_{1-x}$, Ce$_{0.01}$, M$_x$)$_3$Ga$_3$Al$_2$O$_{12}$, where (M, x) = (Hf, 0.0002, open circles), (Hf, 0.001, closed circles) and (none, 0, solid line) excited by 5.5-MeV alpha rays from an $^{241}$Am source.

Fig. 3 Pulse height spectra of (Gd$_{1-x}$, Ce$_{0.01}$, M$_x$)$_3$Ga$_3$Al$_2$O$_{12}$, where (M, x) = (Hf, 0.0002, open circles), (Hf, 0.001, closed circles) and (none, 0, solid line) irradiated with gamma rays from a $^{137}$Cs source.

Fig. 4 Decay time curves of (Gd$_{1-x}$, Ce$_{0.01}$, M$_x$)$_3$Ga$_3$Al$_2$O$_{12}$, where (M, x) = (Hf, 0.0002, blue open circles), (Hf, 0.001, red closed circles) and (none, 0, black solid line) irradiated
3. Conclusions

\((\text{Gd}_{1-x}, \text{Ce}_{0.01}, \text{Hf}_x)_3\text{Ga}_2\text{Al}_2\text{O}_{12} \ (x = 0.001 \text{ and } 0.0002)\) crystals were grown by the micro-pulling down method, and their emission spectra were almost the same as that of the conventional Ce-doped \(\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}\) (Ce:GAGG). However, these samples had longer decay time constants and their light output of was degraded compared with the conventional Ce:GAGG.

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