

Single crystal growth of Mg, Ce co-doped $\text{Lu}_2\text{Gd}_1(\text{Ga},\text{Al})_5\text{O}_{12}$ by micro-pulling down method and their luminescence properties

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Abstract

Effects of Mg co-doping on scintillation properties of $\text{Ce:Lu}_2\text{Gd}_1(\text{Ga},\text{Al})_5\text{O}_{12}$ (LGGAG) single crystals with different Ga/Al ratios were investigated. The growth of Mg 200 ppm (in the melt) co-doped Ce:LGGAG single crystals was performed by micro pulling down (μ -PD) method and then, cut, polished and annealed for the each measurement. Absorption spectra, radioluminescence (RL) spectra, pulse height spectra, and the scintillation decay were measured to reveal the effect of Mg codoping. Ce^{4+} charge transfer (CT) absorption band peaking at ~ 260 nm was observed in Mg-codoped samples, which is in good agreement with previous reports for the Ce^{4+} CT absorption band in other garnet-based crystals. The scintillation decay time showed the tendency to be accelerated and the light yield showed the tendency to be decreased by Mg codoping for higher Ga concentration.

1. Introduction

Scintillator materials combined with photodetectors are often applied in wide range of medical imaging applications such as X-ray imaging plate, X-ray computed tomography, positron emission tomography (PET) and others. In particular, concerning the application like PET, the properties generally required for scintillators are the high light yield, the high density, and the fast decay time (for the timing resolution). Among many kinds of scintillator materials, oxide scintillation materials based on Ce-doped $\text{Lu}_3\text{Al}_5\text{O}_{12}$ (Ce:LuAG) garnets are promising candidates for scintillator applications because of high density, high scintillation performances and the well mastered large-size growth techniques. In addition, Gd and Ga admixture in the Ce:LuAG showed enhancement of light yield due to suppression of shallow traps [1]. Among of the admixed garnets, $\text{Ce:Gd}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ (GAGG) with density of 6.7 g/cm^3 , light yield of 56,000 photon/MeV and fast decay time of 92ns is now commercially produced. Furthermore, heavy $\text{Ce:Lu}_2\text{Gd}_1\text{Ga}_3\text{Al}_2\text{O}_{12}$ (LGGAG) garnet with density of 7.13 g/cm^3 , light yield of 25,000 photon/MeV and fast decay time of 53.6ns was recently reported in the ref. [2]. In the garnet scintillators, the slow decay components originating from re-trapping of electrons at shallow electron traps related to anti-site (Lu_{Al}) defects are often the problematic issue concerning for the scintillator applications requiring high timing resolution such as PET.

In the recent investigation, the alkali-earth codoping effects also in the multi-component garnet-based scintillators like $\text{Ce:Lu}_3(\text{Ga},\text{Al})_5\text{O}_{12}$ (LGAG) [3] and Ce:GAGG [4] were investigated and both enhancement of light yield and acceleration of the decay time were found in Mg,Ce:LGAG [4], while only the decay time was improved in Gd-containing garnet, Mg,Ce:GAGG [4]. The Ce^{4+} ions stabilized by divalent ions play an important role in these positive effect, which is mainly due to the suppression of such slow delayed recombination processes, even though the traps in silicates are related to different defects when compared to garnets. Their luminescence mechanism and the related improvement of scintillation performance has been explained in ref. [4] in detail. In this report, the host composition of LGGAG crystals were selected from the point of view of the advantages of the high density and the large size growth of the promising Mg-codoped compositions in the future and the Mg-codoping effects on their luminescence and scintillation properties were investigated.

2. Results

Mg 200 ppm (in the melt) co-doped $\text{Ce0.5\%:LGGAG}$ crystals were grown by the μ -PD method. The selected sets of their photographs (Mg/non co-doped $\text{Ce:Lu}_2\text{Gd}_1\text{Ga}_x\text{Al}_{5-x}\text{O}_{12}$, $x = 0, 1, 2, 3$ and 4) are shown in figure 1. The left side of the pictures corresponds to the seed side of the crystal and the tail side is on the right. The grown crystals are transparent with yellow-to-green color and 2-3 mm in diameter, 15-50 mm in length. Some of the as-grown crystals show the rough surface due to thermal etching. However, the inner parts of the crystals were transparent.

The absorption spectra of the selected samples (Mg/Non co-doped Ce:LGGAG) are presented in figure 2. In addition to the $4f-5d_1$ absorption bands of Ce^{3+} centered between 450 - 418 nm and $4f-5d_2$ around 342 - 355 nm, the enhancement of absorption peak around 240 nm were observed in figure 4 for the Mg-codoped sample. The peak around 240 nm were ascribed to the Ce^{3+} -related absorption bands, namely $4f-5d_{3,4,5}$ states formed by the crystal field splitting of the 5d-state according to the ref. [3].

The pulse height spectra of Mg/Non co-doped Ce:LGGAG and Ce:GAGG reference sample by the 662 keV gamma-rays excitation of ^{137}Cs source were collected at room temperature using the PMT. The LY were estimated by the comparisons

of the each photo-peak channel with Ce:GAGG standard reference sample considering the QE of the PMT at emission wavelength of the GAGG standard and each LGGAG samples. The dependence of the LY on the material composition is shown in figure 3. The Mg-codoping decreases the light yield significantly for the samples with high Ga concentration sample ($x = 3$), while the light yield for the Ga index of around 1 increases with Mg codoping. These effects are most probably caused by changes in the stability of the tetravalent Ce and separation of its 5d-state from the conduction band.

Scintillation decay curves were measured using a digital oscilloscope TDS3052B under the excitation by ^{137}Cs radioisotope (662 keV). Figure 4 shows the scintillation decay curves of Mg/Non co-doped Ce:Lu₂Gd₁Ga₂Al₃O₁₂ crystals. The decay time showed the tendency to be accelerated by Mg codoping, which can be interpreted by the same positive role of Ce⁴⁺ center in the scintillation mechanism as described for the garnet crystals (Ce:LGAG [3], Ce:GAGG [4]) codoped with alkali-earth ions.

3. Conclusions

The optical, luminescence and scintillation characteristics were measured for the Mg co-doped Ce:LGGAG single crystals prepared by the micro pulling down method. The peak around 260 nm in absorption difference spectra was observed and has been ascribed to the CT transition from the O²⁻ levels at the top of valence band (VB) to the Ce⁴⁺ ground state.

With Mg co-doping, the decreasing trend of the light yield in the samples with high Ga concentration ($x = 3$) were observed, while the light yield around the Ga index of 1 showed the increase with Mg codoping.

The acceleration of the scintillation decay time and the improvement of the intensities of the 1st component were obtained by Mg co-doping, which means that Mg co-doping could thus improve the timing characteristics of Ce:LGGAG. The obtained results in these Gd-containing garnet crystals lead to the deeper understanding of the co-doping effects on Ce-doped garnet scintillator crystals and also indicate that Mg co-doped Ce:Lu₂Gd₁Ga₃Al₂O₁₂ ($x = 3$) can be the most promising scintillator of LGGAG crystals for applications which require both the high density and the fast timing resolution such as PET.

References

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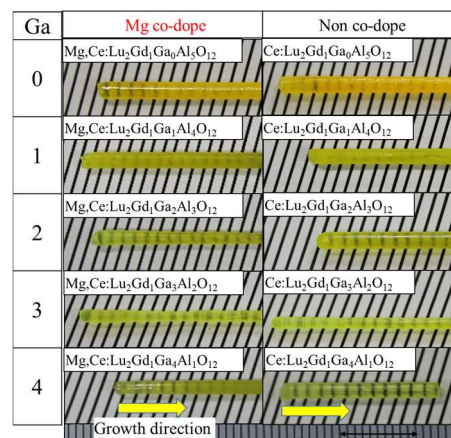


Figure 1. Photographs of the grown Mg co-doped and non co-doped Ce:Lu₂Gd₁Ga_xAl_{5-x}O₁₂ (Ga index, $x = 0-4$) crystals.

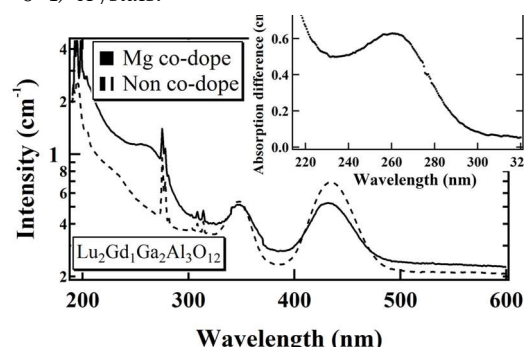


Figure 2. The absorption spectra of Mg co-doped and non co-doped Ce:Lu₂Gd₁Ga₂Al₃O₁₂ and their absorption difference between Mg-codoped and Non-codoped sample (the inset).

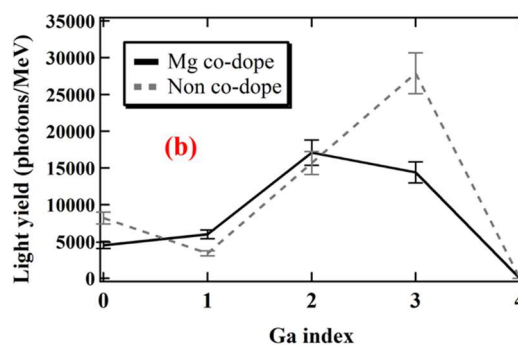


Figure 3. The dependence of the light yield on the material composition of Mg/Non co-doped Ce:Lu₂Gd₁Ga_xAl_{5-x}O₁₂ ($x = 0-4$). Excitation by ^{137}Cs radioisotope (662 keV).

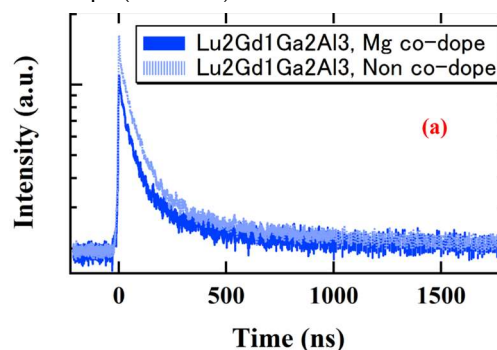


Figure 4. The scintillation decay curves of Mg co-doped and non co-doped Ce:Lu₂Gd₁Ga₂Al₃O₁₂,