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Single crystal and optical ceramic multicomponent garnet scintillators: A comparative study

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ABSTRACT

Multicomponent garnet materials can be made in optical ceramic as well as single crystal form due to their cubic crystal structure. In this work, high-quality $Gd_3Ga_3Al_2O_{12}$:0.2 at% Ce (GGAG:Ce) single crystal and $(Gd,Lu)_3Ga_3Al_2O_{12}$:1 at% Ce (GLuGAG:Ce) optical ceramics were fabricated by the Czochralski method and a combination of hot isostatic pressing (HIPing) and annealing treatment, respectively. Under optical and X-ray excitation, the GLuGAG:Ce optical ceramic exhibits a broad Ce^{3+} transition emission centered at 550 nm, while the emission peak of the GGAG:Ce single crystal is centered at 540 nm. A self-absorption effect in GLuGAG:Ce optical ceramic results in this red-shift of the Ce^{3+} emission peak compared to that in the GGAG:Ce single crystal. The light yield under 662 keV γ-ray excitation was 45,000 ± 2500 photons/MeV and 48,200 ± 2410 photons/MeV for the GGAG:Ce single crystal and GLuGAG:Ce optical ceramic, respectively. An energy resolution of 7.1% for 662 keV γ-rays was achieved in the GLuGAG:Ce optical ceramic with a Hamamatsu R6231 PMT, which is superior to the value of 7.6% for a GGAG:Ce single crystal. Scintillation decay time measurements under ^{137}Cs irradiation show two exponential decay components of 58 ns (47%) and 504 ns (53%) for the GGAG:Ce single crystal, and 84 ns (76%) and 148 ns (24%) for the GLuGAG:Ce optical ceramic. The afterglow level after X-ray cutoff in the GLuGAG:Ce optical ceramic is at least one order of magnitude lower than in the GGAG:Ce single crystal.

1. Introduction

Inorganic scintillators are widely used in medical imaging techniques such as X-ray computed tomography (CT) and positron emission tomography (PET) [1]. The commercial X-ray CT scans are equipped with $(Y,Gd)_2O_3$:Eu,Pr [2], Gd_2O_2S:Pr,Ce,F [3], or Gemstone^{TM} ceramic scintillators as a key component in the detectors. $Bi_4Ge_3O_{12}$ (BGO) [4], Gd_2SiO_5:Ce (GSO:Ce) [5], and Lu_2SiO_5:Ce (LSO:Ce) [6] single crystals successively appeared and were developed over the last 20 years for use in PET applications. The aluminum garnets and perovskites doped with Ce^{3+} or Pr^{3+} have been considered as well, because of their optical transparency, ease of doping, and well-established synthesis technology due to their use as laser hosts, like the $Y_3Al_5O_{12}$ (YAG) and $Lu_3Al_5O_{12}$ (LuAG) [7], and $YAlO_3$ (YAP) and $LuAlO_3$ (LuAP) hosts [8,9]. However, the highest reported light yield (LY) for Ce^{3+}- or Pr^{3+}-doped garnets and perovskites are far below their theoretical values. This deviation is due in part to the complexity of the crystal structure, in which many types of defects can be formed, mainly the Y_{Al} (or Lu_{Al}) antisite defects [10–12]. Based on the understanding of defect chemistry, effective composition engineering was successfully applied on LuAG and YAG systems. The negative contribution of shallow traps, e.g. antisite defects, can be diminished by lowering the conduction band through partial substitution of Al^{3+} with Ga^{3+} ions, so-called "band-gap engineering" [13], and at the same time increasing the Ce^{3+} fraction [14]. In fact, increasing cerium concentration was proved to possess the better light yield in aluminate garnets, e.g. LuAG:Ce single crystals [15]. The following "energy-level positioning" strategy was to increase the ionization energy by using a Gd^{3+} admixture. In this way, the $5d_1$ level moves downward and can compensate for the upward shift caused by the Ga^{3+} admixture [16]. The resultant Gd and Ga balanced composition $(Gd,Y)_3(Ga,Al)_5O_{12}$:Ce (GYGAG:Ce) and $Gd_3Ga_3Al_2O_{12}$:Ce (GGAG:Ce) optical ceramic (OC) and single crystal (SC) scintillators showed the highest LY performance in oxide scintillators [17–19].

In the current year, a comparative study has been reported between a GGAG:Ce single crystal grown at the Furukawa

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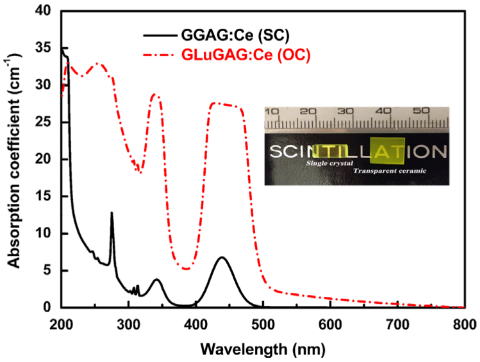

Fig. 1. Optical absorption spectra of GGAG:Ce SC and GLuGAG:Ce OC from 200 to 800 nm. Inset is a photo of the GGAG:Ce SC and GLuGAG:Ce OC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

company and an optical ceramic counterpart that was fabricated by high-pressure vacuum-sintering at the Konoshima Chemical company [20]. Light yield of 70,000 photons/MeV was measured in the GGAG:Ce optical ceramic by using a Hamamatsu UV-enhanced avalanche photodiode (APD). This notable enhancement of light yield over that of the single crystal was ascribed to a difference in actual cerium concentration, the existence of a perovskite phase in the matrix, the scattering effect and the sample thickness compared to single crystal counterpart [20]. For scintillation materials, the performance is strongly dependent on the fabrication techniques. In this work, we will present a systematic comparative study between a GGAG:Ce SC grown via the Czochralski method at the Scintillation Materials Research Center, University of Tennessee and an GLuGAG:Ce optical ceramic (OC) fabricated via the hot isostatic pressing (HIPing) technique at Ningbo Institute of Materials Technology & Engineering (NIMTE), including optical and scintillation properties.

2. Experimental

The GGAG:0.2 at% Ce single crystal was grown by the Czochralski method; details of the growth process are given in Ref. [21]. The GLuGAG:1 at% Ce optical ceramic precursor powders were synthesized by the chemical precipitation method. The powders were then shaped and sintered in an oxygen-rich atmosphere, followed by HIPing and annealing treatment. The details of this fabrication process are described elsewhere [22,23]. The polished samples used in this study are shown in Fig. 1 inset; both are a yellow–green colour. The sizes of the SC and OC samples are $9.7 \times 4.7 \times 4.6\ \text{mm}^3$ and $10 \times 10 \times 1\ \text{mm}^3$, respectively.

Optical absorption spectra were measured with a Varian Cary 5000 UV–VIS–NIR spectrophotometer in the 200–800 nm range. Photoluminescence emission and excitation spectra were acquired with a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer. The excitation light was passed through an excitation monochromator with a 1 nm bandpass to ensure monochromaticity. Similarly, the emission monochromator was set at 1 nm bandpass to select emission light of a specific wavelength. A 450 W continuous xenon lamp was used as the excitation source for the emission and excitation spectra.

Photoluminescence (PL) decay was measured on the same spectrofluorometer using a time-correlated single-photon counting module. HORIBA Jobin Yvon NanoLEDs (pulsed light-emitting diodes) were used as the excitation source. The duration of the light pulse was shorter than 2 ns and therefore was not deconvolved from the much longer decay profiles. The repetition rate for excitation was 1 MHz. For radioluminescence (RL) measurements, an X-ray tube operated at 35 kV and 0.1 mA was used as the excitation source.

Absolute light yield measurements were conducted by using a pulse processing chain consisting of a Hamamatsu R2059 photomultiplier tube (PMT) operated at $-1500\ V_{\text{bias}}$, a Canberra model 2005 pre-amplifier, an Ortec 672 shaping amplifier, and a Tukan 8k multi-channel analyser. Each sample was directly coupled to the PMT with mineral oil, and a Spectralon dome-shaped reflector with a 50 mm radius was used to maximize the collection of light. The photoelectron yield of the samples was calculated by using the single photoelectron peak method [24]. Measurements were made with a shaping time of 2 μs. Each sample was measured under irradiation with a 15 μCi ^{137}Cs source.

For energy resolution and non-proportionality measurements, a 2 in. Hamamatsu R6231-100 high quantum efficiency PMT was used. This PMT was operated at $-1000\ V_{\text{bias}}$. We used ^{133}Ba, ^{241}Am, ^{109}Cd, ^{57}Co, ^{137}Cs, and ^{22}Na γ-rays sources to excite the crystals at energies between 14.4 and 1274 keV.

X-ray excited luminescence spectra were measured using X-ray tube operated at 35 kV and 0.1 mA as the excitation source. Scintillation decay times were measured under ^{137}Cs source excitation by using a time-correlated single photon counting technique [25].

For the afterglow measurements, the crystals were coupled to a Hamamatsu R2059 photomultiplier tube with Dow Corning Q2-3067 optical couplant and covered withTetratex TX3104 PTFE membrane. The crystals were irradiated with X-rays using an X-ray tube (35 kV, 0.1 mA) at room temperature for 15 min, after which a Uniblitz XRS6S2P1-040 shutter was used to cut off the X-ray beam within 3 ms and the luminescence emitted from crystal was recorded as a function of time.

3. Results and discussion

The optical absorption spectra of GGAG:Ce SC and GLuGAG:Ce OC are displayed in Fig. 1. Typical 4f–5d$_{1,2}$ absorption bands of Ce^{3+} peaking at 439 and 343 nm and the 4f–4f absorption lines of Gd^{3+} peaking at 246, 254, 275, 302, 308 and 313 nm can be observed in both GGAG:Ce SC and GLuGAG:Ce OC [26]. An absorption band in the region from 200 to 330 nm, corresponding to the charge (electron) transfer state from O^{2-} ligands (energy levels at top of valence band) towards Ce^{4+} [27,28], can be clearly identified in GLuGAG:Ce OC. This could be associated with its fabrication technique, since the GGAG:Ce OC was fabricated in an oxygen-rich environment in comparison to the oxygen-poor environment used for single crystal growth. More importantly, it is found that the absorption coefficient of the Ce^{3+} 4f–5d$_2$ transition in GLuGAG:Ce OC is about seven times higher than that of the SC (4f–5d$_1$ cannot be compared because of its absorption saturation in GLuGAG:Ce OC). The absorption coefficient can be expressed by using Smakula's equation [29]:

$$nf = 10^{17}\frac{n_0}{(n_0^2+2)^2}\alpha W \tag{1}$$

where n is concentration of absorption centres, f is the oscillator strength of the optical transition, n_0 is the refractive index of the crystal, α is the absorption coefficient of the centres, and W is the half-width of the band in eV. W_{OC} and W_{SC} of the 4f–5d$_2$ absorption are 0.39 and 0.31 eV, respectively. Due to the nearly identical matrix composition with isotropic cubic phase in SC and OC and the allowed transition of Ce^{3+} 4f–5d, n_0 and f could be regarded as almost the same in SC and OC. Thus, the $n_{\text{OC}}/n_{\text{SC}}$ of Ce^{3+} is about 8.8. The cerium concentration in the initial starting melt for the single crystal was 0.2 at% with respect to the rare earth; assuming a segregation coefficient of 0.322 the Ce concentration in the finished crystal should be lower than 0.065 at% [19]. This is more than 10 times lower than the 1 at% Ce concentration in the OC. Considering that the