Optical Materials 66 (2017) 410–414

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Scintillation properties of Ce-doped $(Gd_{0.32}Y_{0.68})_3Al_5O_{12}$ transparent ceramics

Shotaro Hirano [a,*], Go Okada [a], Noriaki Kawaguchi [a], Hideki Yagi [b], Takagimi Yanagitani [b], Takayuki Yanagida [a]

[a] *Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama, Ikoma, Nara 630-0192, Japan*
[b] *Konoshima Chemical Co., Ltd., 80 Kouda, Takuma, Mitoyo, Kagawa 769-1103, Japan*

ARTICLE INFO

Article history:
Received 4 January 2017
Received in revised form
3 February 2017
Accepted 23 February 2017

Keywords:
Scintillation
Ce^{3+}
GYAG
Garnet
Transparent ceramics

ABSTRACT

In this work, we have investigated optical and scintillation properties of 0.35–0.65% Ce:$(Gd_{0.32}Y_{0.68})_3Al_5O_{12}$ (Ce:GYAG) transparent ceramics prepared by the vacuum sintering method. Obtained samples showed high transmittance in the spectral region longer than 500 nm, and two strong absorption bands were clearly observed below 380 nm and between 400 and 500 nm due to the 4f-5d transitions of Ce^{3+}. Under UV and X-rays, we have also observed emission due to the 5d-4f transitions of Ce^{3+} which appeared around 500–700 nm. The emission decay profile of PL consisted of a single exponential decay component with the decay time of 62.7–64.1 ns while the scintillation decay profile was approximated by a second-order exponential decay function with the decay times of 87.3–100 ns and 1.14–1.32 μs. In addition, it has been revealed that 0.65% Ce:GYAG transparent ceramic showed a notable light yield of 18,000 ph/MeV and low afterglow (13 ppm).

1. Introduction

Scintillator is a class of phosphor materials which shows a function to efficiently convert an ionizing radiation into a large number of visible photons instantly through a generation of electrons and holes and energy migration to emission center such as Ce^{3+} [1]. Therefore, we are able to indirectly detect ionizing radiation by using scintillator together with a conventional photodetector, and there are a wide range of applications in the fields of medicine [2], security [3], well-logging [4], environmental monitoring [5], high energy physics [6,7] etc. Today, scintillator has been further required to increase the performance (e.g. larger light yield and shorter decay time) due to the fast progress of medical technology or increased demands in security fields since these fields are of fundamental importance to our daily life. Most scintillators available today are in a form of single crystal due to its superior optical properties. In general, scintillators are used in a bulk form (cm^3 ~ m^3) since the detection efficiency to ionizing radiations strongly depends on the volume as well as the cross-section of composing chemical elements.

Among the scintillator materials available today, Ce-doped garnet ($(Y, Gd, Lu)_3Al_5O_{12}$ or Ce:(Y, Gd, Lu)AG), is one of the most well-known phosphor materials as it shows superior optical and luminescent properties. For example, Ce:YAG has been applied for white LED as the yellow emitter combined with GaN-based blue LED [8]. Ce:(Y, Gd, Lu)AG has also attracted much attention as a scintillator due to their high optical transparency, high scintillation light yield and fast response. Typically, they show green-yellow luminescence under irradiation, and the emission spectrum is in a good agreement with a Si-based photodetectors. This is an important characteristic of garnet scintillators over conventional UV-blue emitting scintillators. Historically, Ce:YAG transparent ceramic was the first garnet material tested for scintillation performance and now recognized as a pioneering work [9]. Further, Gd-based garnet material was the first garnet specie examined for an integrated scintillation detector system [10]. Today, scintillation detector consisting of garnet scintillator and Si-photodiode are widely available in practice.

Owing to the recent advancement of ceramic processing technologies, ceramic materials can now be synthesized in an optically transparent form [11]. As soon as the discovery, the transparent ceramic was of great interest for laser applications [12] and for long persistent luminescent materials [13–15]. In addition, it made a breakthrough in the field of scintillator development as the

---

[*] Corresponding author.
E-mail address: hirano.shotaro.hh2@ms.naist.jp (S. Hirano).

http://dx.doi.org/10.1016/j.optmat.2017.02.047
0925-3467/

detection efficiency is generally restricted by the opacity of the scintillator body. For example, the most common ceramic scintillators is Gd_2O_2S (GOS), and they are used only in a thin plate form due to its high opacity [16]. In addition, ceramic material has a wide range of advantages over single crystals such as a high mechanical strength, homogeneous doping of emission centers, near-net shaping and low fabrication cost. In addition, some chemical compositions which cannot be grown by the conventional melt growth due to extremely high melting temperature can be obtained in a bulk transparent form since the ceramic synthesis temperature is lower than the melting point. Moreover, our group have succeeded in developing the transparent ceramic materials which have higher scintillation performance than single crystal materials for scintillation detectors (e.g. Ce:YAG [17], Ce:LuAG [18], Pr:LuAG [19], Ce:GAGG [20] and Yb:Lu_2O_3 [21]).

In this study, we investigated the scintillation properties of 0.35–0.65% Ce:$(Gd_{0.32}Y_{0.68})_3Al_5O_{12}$ (hereafter Ce:GYAG) transparent ceramics. The ratio of the concentration of Gd ion to that of Y is 1/2, therefore one-third of the rare earth sites are substitute by Gy. Previous studies showed scintillation properties of Ce:$(Gd_XY_{1\text{-}X})$AG single crystal ($X = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) [22] and Ce:$(Gd_XY_{1\text{-}X})$AG transparent ceramics ($X = 0.5$) [10], and photoluminescence (PL) properties of Ce:$(Gd_XY_{1\text{-}X})$AG ceramics ($X = 0.25, 0.50, 0.75, 1.0$) [23] and nanoparticles ($X = 0.1, 0.3, 0.6, 0.99$) [24]. However, we hardly found a report on scintillation properties of Ce:GYAG transparent ceramics with the composition of Gd:Y = 1:2. The purpose of this study is to characterize GYAG transparent ceramics doped with different concentrations of Ce for radiation measurement applications.

2. Experimental

Ce-doped $(Gd_{0.32}Y_{0.68})_3Al_5O_{12}$ transparent ceramics were synthesized by Konoshima Chemical Co. by the vacuum sintering method. The concentration of Ce varied as 0.35, 0.50 and 0.65%.

The in-line transmittance spectrum was measured by using JASCO V670 spectrometer in the range of 190–2500 nm with 1 nm interval. The PL excitation and emission spectra as well as PL quantum yield (QY) was evaluated by using Quantaurus-QY (C11347, Hamamatsu). The spectral ranges measured for the excitation and emission were 250–600 nm and 200–900 nm, respectively. The PL decay time profiles monitoring at 560 nm under the excitation at 470 nm were evaluated by using Quantaurus-τ (C11367, Hamamatsu).

Pulse height spectrum was measured to characterize the scintillation light yield. A sample piece was firmly placed on a photomultiplier tube (PMT; R877-100, Hamamatsu) using silicone grease and covered by layers of Teflon reflector sheet to guide the scintillation photons to the PMT. The PMT converted the scintillation photons into electrical signals. These signals were fed into a sequence of preamplifier (113, ORTEC), shaping amplifier (572, ORTEC) with 0.5 μs shaping time, multichannel analyzer (MCA8000A, AMPTEK) and finally computer.

The X-ray induced scintillation spectrum was measured as follows [20]. An X-ray generator equipped with a tungsten anode target and beryllium window (XRB80P&N200X4550, Spellman) was used as the irradiation source. The applied tube bias voltage and current were 40 kV and 5.2 mA, respectively. During the measurement, the scintillation emission was collected by an optical fiber and guided to the spectrometer (Andor DU920-BU2NC CCD with Shamrock 163 monochrometer). The CCD detector was cooled down to 188 K to reduce the thermal noise. The spectral range of the measurement was 180–700 nm. The X-ray induced scintillation decay time and afterglow profiles were also measured by using our original set-up [25]. The system is equipped with a pulse X-ray tube, and the applied tube voltage was 30 kV so the averaged X-ray energy was around 20 keV. The equipped PMT had a sensitivity in 160–650 nm.

3. Results and discussion

Fig. 1 shows Ce:GYAG transparent ceramic samples doped with varying concentrations of Ce (0.35, 0.50 and 0.65%). The samples were prepared by Konoshima Chemical. The sample size was fixed to 18 mm in diameter and 1.0 mm in thickness. The samples were visually transparent and yellow. Under the UV light (302 nm), strong yellow emission was clearly observed by naked eye, as shown in Fig. 1 (bottom).

Fig. 2 shows the in-line transmittance spectra of Ce:GYAG samples between 190 and 2500 nm. All the samples showed high transparency in a wide spectral range. Below 380 nm and between 400 and 500 nm, strong bands were observed. These absorptions are typical for Ce-doped material and the origins are due to the 4f-5d transitions of Ce^{3+}. No other absorption bands were observed in the longer wavelength range. The 0.5% Ce:GYAG sample showed slightly lower transmittance in the range from 550 to 2500 nm compared with the other samples. This may indicate that a fraction of grain boundary and void is included and acting as scattering center.

The PL excitation/emission contour graph of 0.35% Ce:GYAG sample is shown in Fig. 3 (top). A single broad and intense emission band was observed around 500–700 nm while two separate excitation bands were observed around 350 and 400–550 nm. These excitation bands coincided well with the absorption bands shown in Fig. 2, and the origins were attributed to the $4f \rightarrow 5d_1$ (400–550 nm) and $5d_2$ (350 nm) transitions. The 0.50 and 0.65%

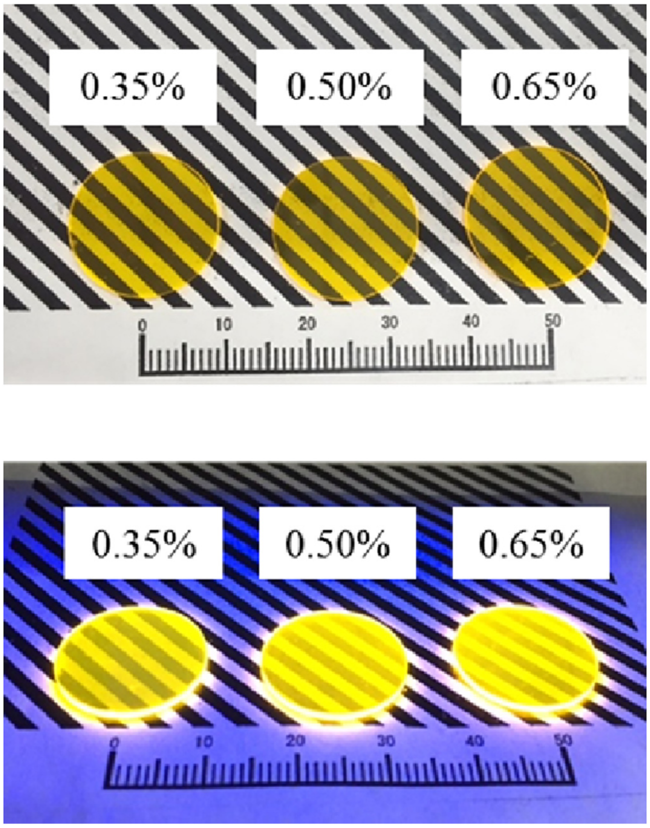

Fig. 1. Ce:GYAG transparent ceramic samples under room light (top) and UV light (bottom). The percentage values in the photographs indicate the concentration of Ce.