Luminescence study on Eu or Tb doped lanthanum–gadolinium pyrosilicate crystal

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ABSTRACT

(Eu_{0.01}, Gd_{0.90}, La_{0.09})₂Si₂O₇ (Eu:La–GPS) and (Tb_{0.01}, Gd_{0.90}, La_{0.09})₂Si₂O₇ (Tb:La–GPS) crystals were grown by the floating zone method, and their optical and scintillation properties were investigated. Gd³⁺–to–Tb³⁺ or –Eu³⁺ energy transfer processes were found, and photo-luminescence and radio-luminescence emission spectra showed ⁵D_{0–7}F_i (*i* = 1–4) Eu³⁺ transitions in Eu:La–GPS, and ⁵D_{3–7}F_i (*i* = 3–6) and ⁵D_{4–7}F_i (*i* = 3–6) transitions in Tb:La–GPS. Using these scintillators, alpha-ray imaging was possible with a CMOS camera. These materials can be used for X-ray detection as well.

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1. Introduction

Scintillators are applied as radiation detectors in various fields such as medical imaging or high energy physics [1,2]. Recently, new scintillators with a crystal structure of pyrosilicate group have been studied due to good light output [3]. Among them, Ce-doped Gd₂Si₂O₇ (Ce:GPS) was found to have good light output compared with other oxide scintillators such as Ce:Gd₂SiO₅ [4–9], while the composition Gd₂O₃·2SiO₂ is not congruent in the Gd₂O₃–SiO₂ system [10]. Kawamura et al. reported that the GPS phase can be stabilized by heavy Ce-doping (approximately, 10 mol%) [5]. However, in such a high Ce-concentration the light output becomes lowered because of the concentration quenching. Reasonable Ce concentration is usually 1-mol% with respect to the substitution site.

The crystal growth of Ce:GPS was enabled by increasing the average ionic radius for the Gd site resulting from Ce-doping. Since La³⁺ ion is not luminescent and has a similar ionic radius as the Ce³⁺ ion [11], the substitution of La for Ce can be applied to stabilize the pyrosilicate phase. The concentration quenching can be also avoided by the reduction of Ce concentration.

We have reported the scintillation properties of a (Ce_{0.01}, Gd_{0.90}, La_{0.09})₂Si₂O₇ (Ce:La–GPS: Cerium-doped lanthanum–gadolinium pyrosilicate) as a novel scintillator which has a high light output of roughly 35,000–42,000 photons/MeV and energy resolution (FWHM) of ~5% at 662 keV, even if this sample was grown by floating zone (FZ) method [12,13]. Moreover, Tsubota et al. also reported the scintillation properties of a (Ce_{0.025}, Gd_{0.875}, La_{0.1})₂Si₂O₇ crystal grown by the top-seeded solution growth method, whose light yield was 1.2 times larger than that of NaI:Tl [14]. Here, NaI:Tl has a light output of roughly 43,000–45,000 photons/MeV [15–17]. Furthermore, the light output of the Ce:La–GPS was found constant in the temperature range from 0 °C to 150 °C [18].

In addition, optical and scintillation properties of Pr-doped pyrosilicate-group crystals such as Pr:GPS, Pr:La–GPS have been studied [19,20], because Pr-doped scintillators are expected to have shorter scintillation decay time originating from 5d–4f transition of Pr³⁺. Although the pyrosilicate-group crystals with other rare-earth dopants employing 4f–4f luminescence are not expected to have fast decay time, these materials can be used as X-ray detection scintillators. Especially, scintillation emission wavelength of Eu or Tb doped crystals very well matches the sensitivity region of a charge coupled device (CCD) or a complementary metal-oxide semiconductor (CMOS) camera with high quantum efficiency, which is roughly within 500–700 nm [21,22]. In this paper, we show the optical and scintillation

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properties of $(\text{Eu}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Eu:La-GPS) and $(\text{Tb}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Tb:La-GPS).

2. Materials and experimental methods

$(\text{Eu}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Eu:La-GPS) and $(\text{Tb}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Tb:La-GPS) crystals were grown by the floating zone method (FZ) under argon atmosphere. The starting materials were highly pure 99.99% Eu_2O_3 , Tb_2O_3 , La_2O_3 , Gd_2O_3 and SiO_2 powders, which were used to prepare two sintered bars. Then, the sintered bars were set in the FZ apparatus and melted by the focused heating with a pair of high intensity infra-red lamps and ellipsoidal mirrors. Both Eu:La-GPS and Tb:La-GPS crystals were grown under the pulling down rate 1–5 mm/h and rotation rate 20 rpm. The as-grown crystals were cut into a 1-mm thickness and then polished to a mirror gloss.

After polishing, transmittance was measured with spectrophotometer (V-530, JASCO). Emission and absorption wavelengths of the samples were measured with the following setup as shown in Fig. 1(a); each sample, RE:La-GPS (RE = Eu, Tb), was excited by monochromatic UV photons using a Xenon lamp (150 W) and a Monochromator (Sp2150i, Princeton Instruments) controlled by a computer. Using an optical fiber, the sample was excited with the UV light in an integrating sphere. The emitted photons were detected using a spectrophotometer (PMA-12, Hamamatsu Photonics KK), consisting of Si-semiconductors. Moreover, temperature dependences of quantum yield within 30–175 °C range were evaluated using a heater as shown in Fig. 1(b).

The radio-luminescence spectrum for each sample was obtained under X-ray irradiation. Here, the X-rays were generated by a Cu target under 40 kV and 40 mA, and the emission spectrum was measured using a CCD camera (DU-420-OE, Andor). Moreover, scintillation imaging was tested for these crystals with 5.5 MeV alpha ray irradiation from an ^{241}Am (~4 MBq) source using a CMOS camera (ORCA-Flash4.0 V2, Hamamatsu Photonics K.K.). The detail of the CMOS imaging camera is described in Ref. [21,22].

3. Results and discussion

Fig. 2 shows $(\text{Eu}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Eu:La-GPS) and $(\text{Tb}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Tb:La-GPS) single crystals grown by the FZ

Fig. 2. Photographs of $(\text{Eu}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Eu:La-GPS) (a), $(\text{Tb}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Tb:La-GPS) (b) crystals grown by the floating zone method, and polished Eu:La-GPS (c) and Tb:La-GPS (d) samples for measurement of optical properties.

method. Transmittance spectra of the samples at 200–900 nm are shown in Fig. 3. The broad absorption band for the Tb-doped sample in 210–240 nm range can be ascribed to the $4f$ – $5d$ transition of Tb^{3+} , while the transmittance drop below 250 nm for the Eu-doped one can be ascribed to the charge transfer band (CTB) of Eu^{3+} – O^{2-} [23,24]. Additionally, spectra for both samples had sharp lines related to the $4f$ – $4f$ transitions of Gd^{3+} : $^8\text{S}_{7/2}$ – $^6\text{I}_i$ and $^8\text{S}_{7/2}$ – $^6\text{P}_j$, where $i = 13/2, 11/2, \dots, 7/2$, $j = 7/2, 5/2$, around 280 and 310 nm, respectively. Photo-luminescence emission wavelength as a function of excitation wavelength for the each sample is shown in Fig. 4. Excitation peaks for both samples located at around 280 and 310 nm corresponded to the absorption peaks of Gd^{3+} , which is a proof of the energy transfer from Gd^{3+} to Tb^{3+} or Eu^{3+} . Also the energy transfer from Gd^{3+} to Eu^{3+} or Tb^{3+} were reported for other materials such as Eu^{3+} : Gd_2SiO_5 [25], gadolinium–terbium-doped silicate glasses [26].

Fig. 5 shows emission spectra of Eu:La-GPS and Tb:La-GPS excited by 280 and 310-nm photons, respectively. The spectrum for Eu:La-GPS contains $4f$ – $4f$ transitions of Eu^{3+} : $^5\text{D}_0$ – $^7\text{F}_i$ ($i = 1$ – 4), and that for Tb:La-GPS contains the Tb^{3+} transitions including $^5\text{D}_3$ – $^7\text{F}_j$ ($j = 3$ – 6) and $^5\text{D}_4$ – $^7\text{F}_k$ ($k = 3$ – 6). Quantum yields of Eu:La-GPS and Tb:La-GPS at room temperature were determined to be ~43% for $^5\text{D}_0$ – $^7\text{F}_2$ emission of Eu^{3+} (600–635 nm, 273 to 285-nm excitation) and ~57% for $^5\text{D}_4$ – $^7\text{F}_5$ emission of Tb^{3+} (530–570 nm, 298 to 320-nm excitation), respectively. The temperature dependences of these quantum yields are shown in Fig. 6. Quantum yields of Eu:La-GPS and Tb:La-GPS were degraded at higher temperatures. Fig. 7 shows radio-luminescence spectra for both samples excited by X rays. The emission peaks corresponded to

Fig. 1. Schematic view of set up for photo-luminescence measurement (a) and quantum yield measurement at several temperature with a heat device (b).

Fig. 3. Transmittance spectra of Eu:La-GPS and Tb:La-GPS.

Fig. 4. Emission wavelength as a function of excitation wavelength for Eu:La-GPS (a) and Tb:La-GPS (b).

Fig. 5. Emission spectra of Eu:La-GPS (a) and Tb:La-GPS (b).

Fig. 6. Quantum yields as a function of temperature for Eu:La-GPS (open circles) and Tb:La-GPS (open squares). The values are normalized to the values at room temperature (28.5 °C).

Fig. 7. Radio-luminescence spectra of Eu:La-GPS and Tb:La-GPS excited by X rays.

Fig. 8. Photo graph of Eu:La-GPS (a) and Tb:La-GPS (c) crystals on the ^{241}Am source, where white dotted squares denote radiation region, and imaging results of Eu:La-GPS (b) and Tb:La-GPS (d).

the photo-luminescence emission peaks. The results of imaging tests for Eu:La-GPS and Tb:La-GPS are shown in Fig. 8, where exposure times were 10 s. Here, the crystal samples had some cracks which are different from the samples for the above measurements for optical and scintillation properties, and these cracks were found in the alpha-ray images.

4. Conclusions

We succeeded in growing $(\text{Eu}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Eu:La-GPS) and $(\text{Tb}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (Tb:La-GPS) crystals by the floating zone method. The photo-luminescence emission and excitation spectra showed Gd^{3+} -to- Tb^{3+} or - Eu^{3+} energy transfer processes; $^8\text{S}_{7/2}$ - $^6\text{I}_i$ and $^8\text{S}_{7/2}$ - $^6\text{P}_j$, ($i = 13/2, 11/2, \dots, 7/2$, $j = 7/2, 5/2$) lines of Gd^{3+} were found for the excitation spectra for the corresponding Eu^{3+} and Tb^{3+} emission lines, which were $^5\text{D}_0$ - $^7\text{F}_i$ ($i = 1-4$) transitions for Eu^{3+} in Eu:La-GPS, and $^5\text{D}_3$ - $^7\text{F}_i$ ($i = 3-6$) and $^5\text{D}_4$ - $^7\text{F}_i$ ($i = 3-6$) transitions for Tb^{3+} in Tb:La-GPS were found. Scintillation light was also observed for both crystals, and the radioluminescence emission peaks were corresponding to the photo-luminescence emission peaks. Moreover, we succeeded in obtaining some images using a CMOS camera, so we can conclude that these materials can be used as X-ray imaging scintillators.

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