Scintillation properties of a La,Lu-Admix Gadolinium Pyrosilicate Crystal

Shunsuke Kurosawa^{a,b}, Toetsu Shishido^a, Akira Suzuki^a, Takamasa Sugawara^a, Akiko Nomura^a, Kunio Yubuta^a, Yasuhiro Shoji^{a,c}, Yuui Yokota^b, Jan Pejchal^{b,d}, Yuji Ohashi^a, Kei Kamada^{b,c}, Akira Yoshikawa^{a, b, c}

^a*Institute for Materials Research (IMR), Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan*

^b*New Industry Creation Hatchery Center (NICHe)
6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan*

^c*C&A Corporation, 6-6-40 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8577, Japan.*

^d*Institute of Physics, AS CR, Cukrovarnická 10, 162 53 Prague, Czech Republic.*

Abstract

In order to obtain new scintillator with higher effective atomic number, a pyrosilicate crystal with a composition $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{La}_{0.20})_2\text{Si}_2\text{O}_7$ (Ce:LaLu-GPS) was grown by the floating zone method. Emission wavelengths of this material were at 370 and 390 nm. Gamma-ray-excited pulse height and scintillation decay measurement showed that Ce:LaLu-GPS had a light output of $34,000 \pm 2,000$ photons/MeV, an FWHM energy resolution of $6.9 \pm 0.2\%$, and the decay time components of 59 ± 1 ns (13%) and 570 ± 20 ns (87%).

Keywords: Scintillator; Pyrosilicate Crystal; Ce-Doped $(\text{La}, \text{Lu}, \text{Gd})_2\text{Si}_2\text{O}_7$

* Corresponding author. Present address: Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, JAPAN

Tel.: +81 22 217 2214; fax: +81 22 217 2217.

E-mail address: kurosawa@imr.tohoku.ac.jp (Shunsuke Kurosawa)

1. Introduction

A number of halide and oxide scintillator materials have been developed to find their applications in various fields such as astronomy, medical imaging, and homeland security. Although halide scintillators, such as Tl:NaI, Tl:Csl and Ce:LaBr₃, have high light outputs of more than 30,000 photons/MeV, they are hygroscopic [1-4]. Recently, Ce:Gd₂Si₂O₇ (Ce:GPS) belonging to the pyrosilicate group has been investigated. This crystal was found to have much higher light output and shorter decay time when compared to Ce:GSO [5-7]. Since the Gd₂O₃·2SiO₂ composition is not congruent in the Gd₂O₃ – SiO₂ system [8], it is difficult to grow GPS from the melt using a Bridgman or Czochralski method. However, Kawamura et al. show that GPS phase can be stabilized by heavy Ce-doping (approximately, 10 mol%) [5]. However, for such high Ce-concentration the light output is lowered because of the self-absorption or concentration quenching. Here, an optimal Ce concentration is usually 1-atomic % with respect to the substituted cation.

Since La³⁺ ion has a similar ionic radius to the Ce³⁺ ion [9], the substitution of La instead of Ce can be also applied to stabilize the pyrosilicate phase. Thus scintillation properties of (Ce_{0.01}, Gd_{0.90}, La_{0.09})₂Si₂O₇ (Ce:La-GPS) have been reported. The Ce:La-GPS crystal had a light output of approximately 35,000 photons/MeV, and FWHM energy resolution of 5.0% at 662 keV [10, 11].

The Ce:La-GPS is estimated to have an effective atomic number(*Z_{eff}*) of ~54 using the following equation:

$$Z_{eff} = \{\sum f_i Z_i^m\}^{1/m}, \quad (1)$$

where $\sum f_i = 1$ and $m=2.94$ [12, 13]. On the other hand, other conventional oxide-scintillators such as Ce:GSO, Ce:(Lu,Y)₂SiO₅ have larger numbers of roughly 59 – 75. Therefore, La, Lu-admixed GPS, Ce:(Gd, La, Lu)₂Si₂O₇, is expected to have a larger effective atomic number than Ce:La-GPS, and its gamma-ray stopping power can be improved. Therefore, a (Ce_{0.01}, Gd_{0.54}, La_{0.25}, Lu_{0.20})₂Si₂O₇ crystal was grown by the floating zone method as the first step, and the scintillation properties of Ce:(Gd, La, Lu)₂Si₂O₇ are reported in this paper. Here, atomic ratio of Lu was chosen from ionic radii of Lu, La and Gd.

2. Materials and Experimental Methods

(Ce_{0.01}, Gd_{0.54}, La_{0.25}, Lu_{0.20})₂Si₂O₇ (Ce:LaLu-GPS) crystal was grown by the floating zone (FZ) method under argon atmosphere. The starting materials were highly pure 99.99% CeO₂, Gd₂O₃, La₂O₃, Lu₂O₃ and SiO₂ powders which were used for preparation of two sintered bars. Then, these bars were set in the FZ apparatus (FZ-ASGAL) and melted by the focused heating with a pair of high-intensity infra-red lamps and ellipsoidal mirrors. The Ce:LaLu-GPS crystal was grown under the pulling-down rate of 1 ~ 5 mm/hour and rotation rate 20 rpm. A 2-mm diameter circle was cut out from the crystal and mirror-polished.

Part of the grown crystal was crushed into powder, and powder X-ray diffraction (XRD) analysis was carried out in the 2θ range of 25-80° using a diffractometer (RINT 2000, RIGAKU). The X-ray was generated from a Cu-Kα target with electrons (accelerating voltage: 40 kV, beam current: 40 mA). In addition, actual chemical composition of the as-grown crystal was investigated by a scanning electron microscope with an electron probe micro-analyzer (SEM/EPMA, JXA-8621MX, Nihon Denshi).

After polishing, transmittance, photoluminescence (PL) and PL-decay were measured. The transmittance was measured with spectrophotometer (V-530, JASCO). The PL excitation and emission spectra were measured with a spectrofluorometer (FLS920, Edingurgh Instrument: EI) and a Xe lamp (EI, Xe-900), and the PL-decay was also obtained with the above spectrofluorometer and a Nanosecond-Flash lamp (EI, nF-900). The PL-decay time was calculated using an exponential approximation.

The scintillation properties of the Ce:La-GPS crystal were investigated as follows: Radio-luminescence spectrum at room temperature was measured with the above spectrometer (FLS920, EI) excited by 5.5-MeV alpha rays from an ²⁴¹Am source. To determine the light output and energy resolution, we obtained the pulse height spectrum for this crystal under excitation with 662-keV gamma rays from a ¹³⁷Cs source. The scintillation photons were detected by a photomultiplier (PMT, R7600U, Hamamatsu), and then the signals from the PMT were amplified (model 113, ORTEC), shaped (572A, ORTEC), and read out with a multi-channel analyzer (8000A, AMPTEK). The pulse height of the Ce:Gd₂SiO₅ (Ce:GSO) crystal, which has a light output of 12,500 photons/MeV [14], was also measured as a reference. Additionally, its scintillation decay time excited by the gamma rays (¹³⁷Cs) was measured with the PMT and an oscilloscope (TDS 3052B, Tektronix). The scintillation decay time was calculated from an exponential approximation. Moreover, the sample was irradiated with gamma rays from several gamma-ray sources (⁵⁷Co, ¹³³Ba, ²²Na, ¹³⁷Cs, ⁵⁴Mn and ⁶⁰Co)

3. Results and discussion

We succeeded in growth of Ce:LaLu-GPS crystal, and Fig. 1 shows the powder X-ray diffraction pattern of this sample. Although some diffraction peaks related to Ce:LaLu-GPS around 21 and 70° are different from those related to Ce:La-GPS, most of the diffraction peaks approximately corresponded to the Ce:La-GPS crystal structure. Kaneko et al. reported the diffraction pattern for heavily Ce-doped GPS which is similar to that of our Ce:LaLu-GPS, though it is shown with a diffraction-angle (2θ) range only from 25-31° [15]. It is also suggested that, Ce:LaLu-GPS can have Triclinic or Monoclinic structure [15].

From the results of the EPMA, the cation composition C_{data} of the Ce:LaLu-GPS (Ce, Gd, La, Lu and Si)

was similar to the nominal (initial) composition C_{nominal} as listed in Table 1.

Table 1: Cation concentration in $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ using an EPMA .

	Gd	Lu	La	Ce	Si
$C_{\text{data}}/C_{\text{nominal}}$	1.02 ± 0.02	0.98 ± 0.05	0.86 ± 0.05	0.8 ± 0.1	1.03 ± 0.01

A 1mm thick circle was cut from the Ce:LaLu-GPS for the evaluation of optical and scintillation properties. Figure 2 shows the transmittance spectrum of the sample. Its transparency was lower than usual. This would be due to some small bubbles in the crystal. PL excitation and emission spectra are shown in Fig.3. The emission peaks were observed at around 370 and 390 nm under 348nm excitation and were ascribed to 5d-4f ($5d$ to $^2F_{5/2}$ and $^2F_{7/2}$ states, respectively) transitions of Ce^{3+} . PL-decay time for Ce:LaLu-GPS was estimated to be 25 ± 2 ns, while Ce:La-GPS has 31 ns[10]. In addition, radio-luminescence spectra for Ce:La-GPS and Ce:LaLu-GPS excited by 5.5-MeV alpha rays mostly corresponded to the photoluminescence emission curve (Fig. 4), and Ce:LaLu-GPS had an emission peak shifted to shorter wavelengths by 10nm when compared with Ce:La-GPS . The band gap structure of Lu-admixed sample or crystal field around Ce^{3+} ion is suggested to be changed with respect to Ce:La-GPS, and therefore the emission wavelengths and PL-decay time were changed.

Figure 5 shows the pulse height spectra of Ce:LaLu-GPS and Ce:GSO. Although the Ce:LaLu-GPS sample had small transmittance, it had a good light output of $34,000 \pm 2,000$ photons/MeV. Moreover, FWHM energy resolution was $6.9 \pm 0.2\%$ at 662 keV. The scintillation decay curve under the excitation by gamma rays from a ^{137}Cs source is displayed in the Fig. 6. The scintillation decay time components were determined to be 59 ± 1 ns (13%) and 570 ± 20 ns (87%). The secondary decay time component (~ 570 ns) can originate from 5d-4f transitions of Ce^{3+} excited by energy transfer from Gd^{3+} . We assume that for the Ce:LaLu-GPS crystal, which has lower Gd concentration, the energy migration over the Gd sublattice becomes slower, which results in enhancement of the slow components in the scintillation decay curve. Figure 6 shows the FWHM energy resolutions from 14 to 1,333 keV. The best-fit line for the data points is represented by $\alpha = 7.5 \pm 0.3$, $\beta = 0.37 \pm 0.02$ using the following equation:

$$\text{resolution}(\%) = \alpha \times \left(\frac{E}{662 \text{ keV}} \right)^{-\beta} \quad (2),$$

where E is the incident photon energy. Due to the low transmittance the energy resolution was degraded, even the light output was as high as $34,000 \pm 2,000$ photons/MeV. Thus, the light output and the energy resolution can be improved after crystal quality is improved. Moreover, even now the Ce:LaLu-GPS has the light output higher than Ce:Lu₂Si₂O₅ (26,300 photons/MeV).

4. Conclusions

The (Ce_{0.01}, Gd_{0.54}, La_{0.25}, Lu_{0.20})₂Si₂O₇ (Ce:LaLu-GPS) crystal grown by the floating zone method showed a good light output of $34,000 \pm 2,000$ photons/MeV, while the FWHM energy resolution at 662 keV was $6.9 \pm 0.2\%$ when measured with a photo multiplier. The energy resolutions from 14 to 1,333 keV were degraded because of low transmittance of less than 30%. Thus, the energy resolution is expected to be improved after crystal quality is improved. The scintillation decay time of Ce:LaLu-GPS was shorter than (Ce_{0.01}, Gd_{0.90}, La_{0.09})₂Si₂O₇, due to slightly suppressed energy migration over Gd sublattice in the Ce:LaLu-GPS crystal with lowered Gd concentration. After optimization of the component ratio of Gd, Lu and La, the migration over Gd³⁺ can be tuned to improve the scintillation decay time.

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Table captions

Table 1. Result of the cation component in $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ using an EPMA.

Figure captions

Figure1. Powder X-ray diffraction pattern of $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ (a) and $(\text{Ce}_{0.01}, \text{Gd}_{0.9},$

205 $\text{La}_{0.09}\text{Si}_2\text{O}_7$ as reference (b).

206 Figure2. Transmittance spectrum of the $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$

207 Figure3. Photo-luminescence excitation (dotted line) and emission (solid line) spectra of $(\text{Ce}_{0.01}, \text{Gd}_{0.54},$

208 $\text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$

209 Figure4. Radio-luminescence spectra of the $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ (solid line) and $(\text{Ce}_{0.01},$

210 $\text{Gd}_{0.9}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ (open circles) excited by 5.5-MeV alpha rays from an ^{241}Am source.

211 Figure5. Pulse-height spectra of the $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ and $\text{Ce}:\text{Gd}_2\text{SiO}_5$ irradiated with

212 gamma rays from a ^{137}Cs source.

213 Figure6. Scintillation decay curve of $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ excited with gamma rays from a

214 ^{137}Cs source, and best fit line.

215 Figure7. FWHM energy resolution of $(\text{Ce}_{0.01}, \text{Gd}_{0.54}, \text{La}_{0.25}, \text{Lu}_{0.20})_2\text{Si}_2\text{O}_7$ as a function of energy

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218 Table

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220 Table 1

	Gd	Lu	La	Ce	Si
$C_{\text{data}}/C_{\text{nominal}}$	1.02 ± 0.02	0.98 ± 0.05	0.86 ± 0.05	0.8 ± 0.1	1.03 ± 0.01

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Figure1

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