Crystal Growth and Optical Properties of Ce:(La,Gd)₂Ge₂O₇ Grown by Floating Zone Method

Shunsuke Kurosawa^{1,2,*}, Toetsu Shishido¹, Takamasa Sugawara¹, Kunio Yubuta¹, Pejchal Jan^{1,3}, Akira Suzuki¹, Yuui Yokota², Yasuhiro Shoji¹, Kei Kamada^{2,4} and Akira Yoshikawa^{1,2,4}

¹*Institute for Materials Research (IMR), Tohoku University*

2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

²*New Industry Creation Hatchery Center (NICHe)*

6-6-10 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8579, Japan

³*Institute of Physics AS CR, 10 Cukrovarnicka, Prague 6, 16200, Czech Republic*

⁴*C&A Corporation, 6-6-40 Aoba, Aramaki, Aoba-ku, Sendai, Miyagi 980-8577, Japan.*

Abstract

Some pyrosilicate scintillators such as Ce:Gd₂Si₂O₇ and Ce:Lu₂Si₂O₇ have a good light output, and especially Ce:(Gd,La)₂Si₂O₇ had an excellent light output of over 35,000 ph/MeV. In order to obtain a material of effective atomic number higher than that of (Ce_{0.01},Gd_{0.90},La_{0.09})₂Si₂O₇, we have developed novel scintillation material (Ce_{0.01},Gd_{0.90},La_{0.09})₂Ge₂O₇ using the floating zone method. Although the light output was decreased due to quenching, 5d-4f transition of Ce³⁺ was observed around 480 nm in photo and radio luminescence spectra. This emission wavelength was longer than that of (Ce_{0.01},Gd_{0.90},La_{0.09})₂Si₂O₇ with an emission wavelength of 390 nm.

Keywords: Scintillator; Pyrochlore; Pyrogermanate; Pyrosilicate; Optical property

* 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

Recently, pyrosilicate-based scintillators, such as Ce:Gd₂Si₂O₇ (Ce:GPS) and Ce:Lu₂Si₂O₇ (Ce:LPS) have been investigated, and these crystals were found to have good light outputs of over 20,000 photon/MeV [1-4]. Although Ce:LPS has higher stopping power than Ce:GPS, Ce:LPS has an intrinsic background due to ¹⁷⁶Lu isotope. Thus, it is difficult for Ce:LPS to be applied to low-dose environment radiation monitoring. Ce:GPS has a light output of more than 30,000 ph/MeV and good energy resolution [1-3], while the composition Gd₂O₃-2SiO₂ is not congruent [5]. In order to stabilize the pyrosilicate phase, GPS crystals with heavy Ce-doping (over 2 mol %) were grown [1]. However, for such high Ce-concentration, the light output can be lowered because of the self-absorption or concentration quenching, and an optimal Ce concentration is usually 1 atom% with respect to the substituted site.

Since La³⁺ ion has a similar ionic radius to the Ce³⁺ ion [6], some teams investigated (Ce,Gd,La)₂Si₂O₇ (Ce:La-GPS) crystals [7-8]. We reported scintillation properties of (Ce_{0.01},Gd_{0.90},La_{0.09})₂Si₂O₇ crystal grown by the Floating Zone Method which had a high light output of 35,000 ph/MeV and energy resolution (FWHM) of ~5% at 662 keV when coupled to a photo multiplier tube (PMT) [7].

Gamma-ray stopping power (cross section for gamma-ray photo-absorption) is proportional to the effective atomic number (Z_{eff})^a, where *a* is 4-5. Ce:La-GPS has an effective atomic number (Z_{eff}) of approximately 53, while Ce:GPS, Ce:Gd₂SiO₅ and Tl:Nal have 54, 59 and 49, respectively. Ce:La-GPS has the larger gamma-ray stopping power when compared to some halide scintillators with good energy resolutions of less than 8%(FWHM) at 662 keV. On the other hand, other oxide scintillators have stopping powers larger than that of Ce:La-GPS, while these scintillators have worse resolutions than the Ce:La-GPS.

Pyrogermanate group of materials with formula A₂Ge₂O₇ (A is elements such as Gd, Y) is a member of the pyrochlore groups, and the pyrogermanate crystals are supposed to have good light output like the above pyrosilicate scintillators. However, the studies on optical and scintillation properties for pyrogermanate crystals are quite scarce. In order to obtain a novel scintillator, as a first step, we have grown a Ce:(La,Gd)₂Ge₂O₇ crystal and report the optical and scintillation properties of this crystal in this paper.

2. Materials and Experimental Methods

(Ce_{0.01},Gd_{0.90},La_{0.09})₂Ge₂O₇ (La-GPG) single crystal was grown by the floating zone (FZ) method under argon atmosphere. The starting materials were highly pure 99.99% CeO₂, La₂O₃, Gd₂O₃, and GeO₂ powders which were used for preparation of two sintered bars. Then, these bars were set in the FZ apparatus (FZASGAL) and melted by the focused heating with a pair of high-intensity IR lamps and ellipsoidal mirrors. The Ce: La-GPG crystal was grown under the pulling-down rate of 1-5mm/h and rotation rate of 20 rpm. The as-grown crystal was cut into a 2mm diameter circle and mirror-polished.

A part of the grown crystal was crushed into powder, and powder X-ray diffraction (XRD) analysis was carried out in the 2 θ range of 20-80° using a diffractometer (RINT 2000, RIGAKU). The X-ray source was Cu-K α (accelerating voltage: 40 kV, beam current: 40 mA).

After polishing, photoluminescence (PL) excitation and emission spectra were measured with a spectrofluorometer (Edinburgh Instruments; EI FLS920) and a Xe lamp (EI Xe-900), and its PL-decay was also obtained with the above spectrofluorometer and a nanosecond-flash lamp (EI nF-900). The PL-decay time was calculated from exponential approximation. The Radio-luminescence spectrum at room temperature was measured with the above spectrometer (EI FLS920) excited by 5.5-MeV alpha rays from an ²⁴¹Am source.

3. Results and discussion

Ce:La-GPG crystal grown by the FZ method is shown in Fig. 1. It was not possible to prepare a large single crystal sample. The XRD pattern is shown in Fig. 2, and many peaks corresponded with the known XRD data for Gd₂Ge₂O₇, whose space group is *P*4₁2₁2 and the cell parameters as follows: *a* = 0.6885 nm, *b* = 0.6885 nm, *c* = 1.2525 nm, $\alpha = \beta = \gamma = 90^\circ$ [9-13]. However, some peaks did not correspond to the previous data and the possible candidate for the related impurity phase would be Gd₂GeO₅ [14]. The effective atomic number of this material is calculated to be 52.

Figure 3 shows emission spectrum excited by 375-nm photons and excitation spectrum for the emission wavelength of 485 nm for Ce:La-GPG. Emission spectrum peak was as wide as approximately 100 nm, and this result suggested that it can be ascribed to the 5d-4f transition of Ce³⁺. Ce:La-GPS has an emission wavelength of approximately 390 nm [7], and we found that the emission peak shifted to longer wavelength. Moreover, excitation peak was located at approximately 375 and 345 nm for Ce:La-GPG and Ce:La-GPS, respectively, and the energy of 5d-4f transition of Ce³⁺ in the Ce:La-GPG was smaller than for the Ce:La-GPS. This wavelength and transition shift would be due to change of lattice constant and crystal fields between the pyrosillicate and pyrogermanate.

Photo-luminescence (PL) decay time of this sample is shown in Fig. 4, where excitation wavelength was 375 nm and 485-nm emission photons were monitored. Moreover, the instrument response was measured. Using these data, the decay time was evaluated by fitting with double exponential function. As a result, the decay curve had two decay time components with decay time of 1.2 and 3.4 ns. This result was too short

when compared to the other Ce^{3+} doped scintillators or phosphors which emit photons originating from 5d-4f transition of Ce^{3+} . These results suggested that the 5d-4f emission of Ce^{3+} was quenched, and small light output is expected.

Figure 5 shows comparison of the radioluminescence spectrum of the Ce:La-GPG crystal irradiated with alpha rays from an ^{241}Am source with that of Ce:La-GPS as a reference. The emission peak of the Ce:La-GPG was around 480 nm, so the radioluminescence spectrum was also shifted to longer wavelength with respect to that of Ce:La-GPS. Since the light output of the Ce:La-GPS sample was small, evaluation of light output using photon-counting method was difficult. Considering the reason of the quenching, it is thought that the lowest 5d excited state of Ce^{3+} is very closed enough to the host conduction band to enable thermal ionization of the lowest 5d excited state. Also, the lowest 5d excited state might be already included in the host conduction band.

These results indicated that replacement from Si to Ge in the Ce-doped phosphor make emission wavelength longer. We expect to optimize the host composition to obtain optimized band gap structure for the $(\text{Ce}, \text{Gd}, \text{La})_2(\text{Si}_x, \text{Ge}_{1-x})_2\text{O}_7$, where $0 \leq x \leq 1$, to prevent the emission quenching. As results, this material can have a better light output and can be applied in scintillator field or as a phosphor in other applications.

4. Conclusions

$(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$ (La-GPG) single crystal, which is belonging to pyrogermanate group, was grown by the floating zone method, and we succeeded in evaluation of its optical and scintillation properties. Although the luminescence was quenched, 5d-4f transition of Ce^{3+} was observed around 480 nm in photo and radio luminescence spectra. These results suggest that (i) emission wavelength modification from 390 to 480 nm is possible and (ii) light output might be increased after optimization of the composition and band-gap width of the $(\text{Ce}, \text{Gd}, \text{La})_2(\text{Si}_x, \text{Ge}_{1-x})_2\text{O}_7$, ($0 \leq x \leq 1$), crystals.

Acknowledgments

This work is partially supported by (i) Japan Society for the Promotion of Science (JSPS) Research Fellowships for Young Scientists (S. Kurosawa), (ii) the funding program for next generation world-leading researchers, JSPS, (iii) Development of Systems and Technology for Advanced Measurement and Analysis, Japan Science and Technology Agency (JST) (iv) Adaptable & Seamless Technology Transfer Program through Target-driven R&D (A-STEP), JST, (v) the Association for the Progress of New Chemical Technology, (vi) The Murata Science Foundation and (vii) Nippon Sheet Glass Foundation for Materials Science and Engineering. In addition, we would like to thank following persons for their support: Mr. Hiroshi Uemura, Ms. Keiko Toguchi, Ms. Megumi Sasaki and Ms. Yuka Takeda in IMR/Tohoku University.

References

- [1] S. Kawamura, J. H. Kaneko, M. Higuchi, T. Yamaguchi, J. Haruna, Y. Yagi, K. Susa, F. Fujita, A. Homma, S. Nishiyama, H. Ishibashi, K. Kurashige, and M. Furusaka: IEEE Nuclear Science Symp. Conf. Rec., 2006, p. 1160.
- [2] S. Kawamura, J. H. Kaneko, M. Higuchi, F. Fujita, A. Homma, J. Haruna, S. Saeki, K. Kurashige, H. Ishibashi, and M. Furusaka: Nucl. Instrum. Methods Phys. Res., Sect. A 583 (2007) 356.
- [3] J. H. Kaneko, N. Susa, S. Tsuchida, M. Watanabe, S. Miura, T. Mizuno, Y. Yamauchi, M. Hashiba, T. Oku, A. Homma, F. Fujita, T. Ino, M. Furusaka, T. Sawamura, H. M. Shimizu, and Y. Kiyanagi, Nucl. Instrum. Methods Phys. Res., Sect. A 529 (2004) 307.
- [4] L. Pidol, A. Kahn-Harari, B. Viana, E. Virey, B. Ferrand, P. Dorenbos, J. T. M. de Haas, and C. W. E. van Eijk, IEEE Trans. Nucl. Sci. 51 (2004) 1084.
- [5] N. A. Toropov, F. Ya. Glakhov, and S. F. Konovalova: Russ. Chem. Bull. 10 (1961) 497.
- [6] R. D. Shannon: Acta Crystallogr., Sect. A 32 (1976) 751.
- [7] A. Suzuki, S. Kurosawa, T. Shishido, J. Pejchal, Y. Yokota, Y. Futami, and A. Yoshikawa, Applied Physics Express 5 (2012) 102601
- [8] Y. V. Gerasymov, V. N. Baumer, S. V. Neicheva, N. Starzhinskiy, V. A. Tarasov, O. V. Zelenskaya, O. T. Sidletskiy, Functional Materials 20 (2013) 15.
- [9] National Institute for Materials Science, AtomWork, <http://crystdb.nims.go.jp/> (downloaded on 2013,07,01)
- [10] Y. Xu, M. Yamazaki, and P. Villars, Jpn. J. Appl. Phys. 50 (2011) 11RH02.
- [11] R. Saez- Puche, M. Bijkerk, F. Fernandez, E.J. Baran, I.L. Botto, J. Alloys Compd., 184 (1992) 25.
- [12] U.W. Becker, J. J. Felsche, Less-Common Met. 128 (1987) 269.
- [13] G. Bocquillon, J. Maugrion, J.C. R. Lories, Seances Acad. Sci., Ser. C, 287(1978)5.
- [14] L. Brixner, J. Calabrese, H.Y. Chen, Journal of the Less Common Metals 110 (1985)397.

Figure captions

Figure1. Photograph of a $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$ crystal grown by the floating zone (FZ) method.

Figure2. Powder X-ray diffraction patterns of the $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$ crystal (a) and its enlarged view of squared region in (a) (b).

Figure3. Excitation (a) and emission (b) spectra of the $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$.

Figure4. Photo- luminescence decay curve of the $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$.

Figure5. Radio luminescence spectra of the $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Ge}_2\text{O}_7$ and $(\text{Ce}_{0.01}, \text{Gd}_{0.90}, \text{La}_{0.09})_2\text{Si}_2\text{O}_7$ crystals irradiated with alpha rays from an ^{241}Am source.

Figure 1

55 mm

(a)

(b)

excitation spectrum

 $\lambda_{\text{em}} = 485 \text{ nm}$

Figure 4