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Luminescence Properties of Pr-doped La-GPS Grown by the Floating Zone Method

Rikito Murakami[1], Shunsuke Kurosawa[1,2], Toetsu Shishido[1,2], Akira Suzuki[1], Yasuhiro Shoji[1,4], Yuji Ohashi[1], Jan Pejchal[2,3] Kei Kamada[2,4], Yuui Yokota[2] 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
Phone: +81-22-215-2214 E-mail: r_murakami@imr.tohoku.ac.jp
[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

Scintillation properties of Pr-doped gadolinium lanthanum pyrosilicate (Pr:La-GPS) grown by the Floating Zone method were investigated, because the Pr^{3+} 4f-5d transition is expected to show short decay time. In the alpha-ray radio-luminescence spectrum, an emission peak related to the Pr^{3+} 4f-5d transition was observed around 350 nm. The photoluminescence decay time was found to be as fast as 23 ns.

1. Introduction

In recent years, pyrosilicate-based scintillators such as $Ce:Gd_2Si_2O_7$ (Ce:GPS) and $Ce:Lu_2Si_2O_7$ (Ce:LPS) have been developed. The Ce:GPS showed high light output and good energy resolution [1-5]. Although Ce:GPS melts incongruently, Ce:GPS phase can be stabilized by heavy Ce-doping (approximately, 10 mol%) [4]. However, for such a high Ce-concentration, the light output is lowered because of self-absorption or concentration quenching.

Since ionic radius of La^{3+} ion is similar to that of the Ce^{3+} ion, the substitution of La instead of Ce can be also applied to stabilize the pyrosilicate phase. The grown $(La,Gd)_2Si_2O_7$ (Ce:La-GPS) single crystal doped with only 1 mol% Ce showed higher light output and better energy resolution than Ce:GPS[4, 6].

The decay time of the 4f-5d transition is known to be proportional to λ^3, where λ is an emission wavelength [7]. Since Pr^{3+}-luminescence center has generally shorter emission wavelength than the Ce^{3+}one in the same matrix[8], the decay time of the 4f-5d transition of Pr^{3+} is shorter than that of the Ce^{3+}. Therefore, the scintillation response of the Pr-doped scintillators is expected to be faster.

Actually, Pr(10%):GPS has a scintillation decay time of 26 ns under gamma rays excitation [2], while both Ce(10%):GPS and our Ce:La-GPS showed the scintillation decay times of 46 ns under gamma-ray excitation [4, 6]. Thus, Pr-doped La-GPS is expected to have fast decay time and good light output. In this paper we report the scintillation properties of this crystal.

2. Materials and experimental methods

A $(Pr_{0.01},La_{0.09},Gd_{0.90})\ _2Si_2O_7$ (Pr:La-GPS) crystal was grown by the Floating Zone (FZ) method under dry air atmosphere with flow rate of 500 ml/min. The starting materials were highly pure 99.99% Pr_6O_{11}, La_2O_3, Gd_2O_3, and 99.995% SiO_2 powders which were used for the preparation of a sintered feeding rod. Then, this rod was set in the FZ apparatus (FZASGAL, SS35WV) and melted by high-intensity radiation from infrared lamps focused with a pair of ellipsoidal mirrors. The Pr:La-GPS crystal was grown at a pulling-down rate of 1.0 mm/h and rotation rate of 3-5 rpm. The as-grown crystal was cut into samples with diameters of roughly 2 mm.

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

After polishing the sample, transmittance was measured first (JASCO, V-530). Subsequently, photoluminescence (PL) excitation and emission spectra were measured with a spectrofluorometer (Edinburgh Instruments, EI FLS920) and Xe lamp (EI, Xe-900). PL-decay was also obtained with the above spectrofluorometer and a nanosecond-flash lamp (EI, nF-900).

The radio-luminescence spectrum at room temperature was measured with the above spectrometer (EI, FLS920) under excitation by 5.5-MeV alpha rays from an ^{241}Am source.

3. Results and discussions

A Pr:La-GPS crystal grown by the FZ method is shown in Fig. 1 (a) and (b). Figure 2 shows the result of XRD. This XRD pattern corresponded to a Ce doped La-GPS single crystal grown by the Czochralski process with a triclinic structure, which implies that the Pr:La-GPS also has a triclinic structure.

The onset of the 4f-5d absorption of Pr^{3+} was observed around 250 nm in the transmittance spectrum (Fig. 3). Other peaks located from approximately 270 to 480 nm were ascribed to the 4f-4f transitions of Gd^{3+} and Pr^{3+}. The PL decay time with excitation and emission wavelengths of 311 and 350 nm, respectively, was determined to be roughly 23 ns. This fast decay time would originate from 5d-4f transition of Pr^{3+}.

Figure 4 shows the alpha-ray excited radio-luminescence spectrum of Pr:La-GPS, which is dominated by sharp emission band at around 310 nm ascribed to a 4f-4f emission of Gd^{3+} . The broad 5d-4f emission of Pr^{3+} is situated around 350 nm. .

Although the light output of this material was also measured, it was estimated to be less than 1,000 photons/(5.5-MeV alpha ray). The reason for the degradation of the light output may be the change in band structure or/and the formation of a shallow electron trap between the conduction band and the 5d energy level of Pr^{3+}. Optimization of the band gap structure (e.g. adjusting La/Gd ratio) may help to increase the light output. In this presentation, the above results will be shown and the energy transfer from Gd^{3+} to Pr^{3+} will be discussed.

3. Conclusions

A $(Pr_{0.01},La_{0.09},Gd_{0.90})_2Si_2O_7$ (Pr:La-GPS) crystal was grown by the floating zone method, and the dominating emission peak was at 310 nm in the radio-luminescence spectrum. Moreover, the broad emission was observed around 350 nm, and its fast decay time of ~23 ns was measured from the photoluminescence decay curve. It was ascribed to the 5d-4f transition of Pr^{3+}.

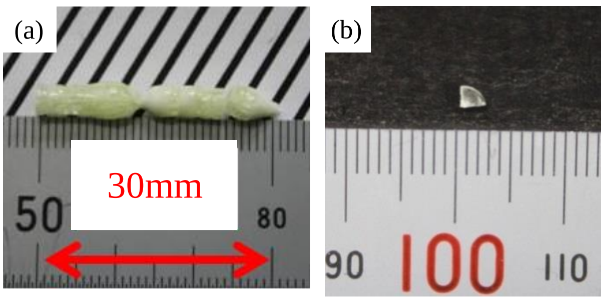

Fig. 1 (a) Photograph of a $(Pr_{0.01},La_{0.09},Gd_{0.90})_2Si_2O_7$ crystal grown by the floating zone method. (b) A part of the single crystal cut from (a).

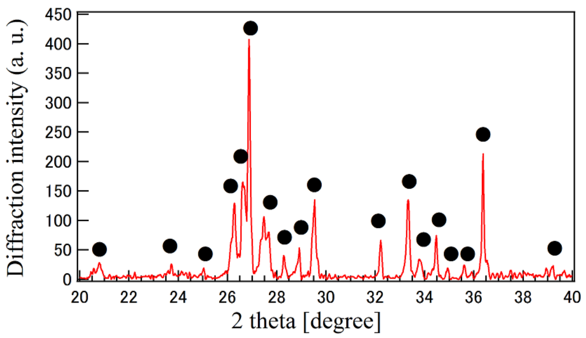

Fig. 2 X-ray diffraction pattern of $(Pr_{0.01},La_{0.09},Gd_{0.90})_2Si_2O_7$. Closed circles denote the peaks of a Ce doped La-GPS single crystal, with triclinic structure, grown by the Czochralski process.

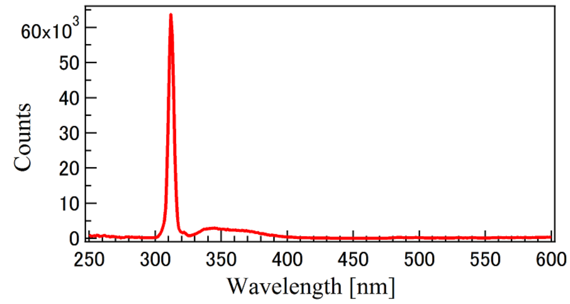

Fig. 3 Transmittance of $(Pr_{0.01},La_{0.09},Gd_{0.90})_2Si_2O_7$.

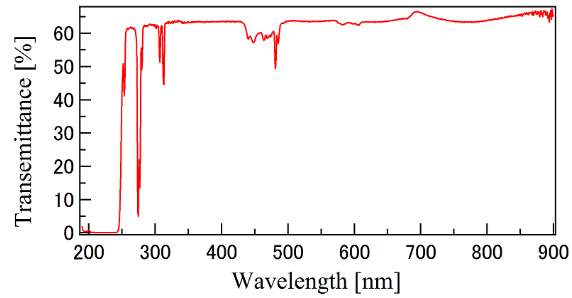

Fig. 4 Radio-luminescence spectrum of $(Pr_{0.01},La_{0.09},Gd_{0.90})_2Si_2O_7$ irradiated by alpha-rays from an ^{241}Am source.

Acknowledgements

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