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Luminescence properties and Crystal structures of Pr-doped GPS

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Crystal structures and scintillation properties of praseodymium-doped gadolinium pyrosilicate ($Gd_2Si_2O_7:Pr$, GPS:Pr) were investigated as a part of systematic studies of a $Gd_2Si_2O_7$ system as scintillation materials. Transparent yellowish-green polycrystalline GPS:Pr was grown using the floating zone growth method. The crystal structure, which is strongly related with the mean ionic radius of rare-earth elements, was orthorhombic with $Pna2_1$ space group for 5 and 10 mol% Pr concentration. It was triclinic with $P1$ space group for 15 mol% and 20 mol% Pr concentration. A fluorescence spectrum was composed of a peak located at 300 nm and a broad peak around 360 nm. Light yield of ca. 80% of a GSO:Ce scintillator was confirmed with GPS:Pr (Pr=10 mol%) for 662 keV gamma rays; the decay time was 26 ns. Unexpectedly, GPS:Pr with a triclinic structure, i.e. Pr=15 and 20 mol%, showed no scintillation for gamma rays.

KEY WORDS: $Gd_2Si_2O_7$, scintillators, crystal structure, decay time, light output

I. Introduction

In the past several decades, inorganic scintillators with high light yield, high detection efficiency, and fast decay time have been sought in the fields of nuclear medical diagnostics systems, high-energy physics, and others^{1),2)}. To obtain higher detection efficiency, a scintillation material with a large product of density and the fourth power of an effective atomic number, ρZ_{eff}^4 , is necessary. Consequently, extensive studies have specifically examined rare-earth oxide materials. Moreover, aiming at large light yield and fast decay time, investigations of effective activators have also been conducted. Consequently, high-performance rare-earth oxide scintillators using Ce^{3+} activator, i.e., GSO:Ce, LSO:Ce etc. have been developed^{3),4),5)}. A recently developed $LaBr_3$ scintillator with 1.5 times greater light yield than that of a conventional NaI:Tl scintillator⁶⁾ also uses Ce^{3+} as an activator.

As a promising newly developed scintillator, a cerium doped gadolinium pyrosilicate exists: $Gd_2Si_2O_7:Ce$ (GPS:Ce). First, GPS:Ce was investigated as a neutron scintillator for neutron scattering experiments because of its extremely large neutron capture cross section of Gd⁷⁾. This scintillator had a five-times-greater light yield than conventional BGO scintillator and a decay time of 46 ns. Furthermore, a GPS:Ce scintillator had a value of ρZ_{eff}^4 higher than that of NaI:Tl and $LaBr_3:Ce$. Moreover, the GPS:Ce showed no deliquescence and no self-activity. Therefore, development of a large single crystal of GPS:Ce is underway, aimed at applications for gamma rays measurement^{8),9)}.

Rare-earth pyrosilicates have polymorphism according to a mean ionic radius containing rare-earth elements^{10),11)}. Consequently, crystal structures and luminescence properties were changed on amounts of rare-earth activators, i.e. cerium.

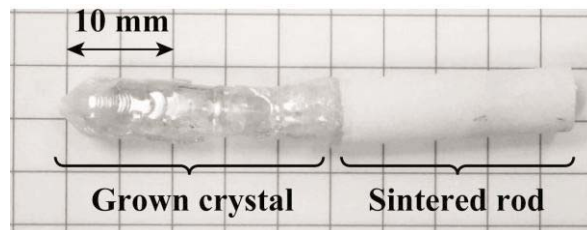


Fig. 1 Pr-doped GPS polycrystals grown using the floating zone method. Yellowish-green transparent crystals were obtained. Polycrystals were usually composed of single crystals of several millimeters.

For cerium-doped GPS, orthorhombic, triclinic, and other structures appeared depending on the cerium concentration; two peaks of the light yield occurred at cerium concentrations of 2.5 mol% and 15 mol%¹²⁾.

For lutetium pyrosilicates (LPS), Pidol et al. investigated scintillation properties using Ce^{3+} , Pr^{3+} , and Nd^{3+} activators. The Pr-doped LPS had a fast decay time of 15 ns¹³⁾. Transitions of Pr^{3+} and $4f^n-4f^{n-1}5d^1$ have an energy band gap that is 1.5 eV wider than that of Ce^{3+} in the same host¹⁴⁾. In general, a rough correlation exists between the emission wavelength and transition rate¹⁵⁾; Pr^{3+} -doped compounds have been investigated as fast scintillators¹⁶⁾.

Crystal structures and scintillation properties of Pr-doped GPS crystals were investigated for systematic studies of the $Gd_2Si_2O_7$ system as a scintillation material. The praseodymium concentration was 5–20 mol% in this study.

II. Experimental

1. Crystal Growth

For this study, GPS:Pr crystals were grown using a floating zone (FZ) growth method. Starting materials were powders

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of Gd_2O_3 , SiO_2 with 99.999% purity and Pr_6O_{11} with 99.99% purity. These materials were weighed and mixed at compositions of $(\text{Gd}_{1-x}\text{Pr}_x)_2\text{Si}_2\text{O}_7$ ($x=0.05, 0.10, 0.15, 0.20$). Then the mixed powders were pressed isostatically (60 MPa) into 5 mm diameter rods and sintered at 1650°C for 8 hr in air.

These sintered rods were fixed on upper and lower shafts of a four mirror image furnace (FZ-T-10000-H-III-P-TK; Crystal Systems Inc., Yamanashi, Japan) for which four halogen lamps with maximum power of 750 W were used as a heating source. Crystal growth procedures were taken in a reduction atmosphere in N_2 , with a growth rate of 2 mm/h and a counter-rotation rate of 15 rpm. **Figure.1** presents an example of Pr-doped GPS polycrystals grown in this study; crystals were yellowish-green and transparent. The color deepened with increased praseodymium concentration.

Parts of the Pr-doped GPS polycrystalline crystals were cut into 2 mm thickness using a diamond cutter; then both sides of these samples were mechanically polished. A typical size of evaluated GPS:Pr samples was $3 \times 3 \times 2$ mm. Although size differences were found, the evaluated samples consisted of one or a few pieces of single crystals. Because of the lack of color uniformity, the distribution of Pr^{3+} was not observed in any samples. These samples were used for photoluminescence and scintillation property measurements.

2. Crystal structure analysis by XRD

Crystal structures of grown crystals were identified using X-ray powder diffraction (XRD). Crystals were ground into powder using an agate mortar and pestle. The powder sam-

ples were measured using a powder X-ray diffractometer (JDX-3500; JEOL, Tokyo, Japan) with a Cu X-ray target with bias voltage of 30 kV and beam current of 20 mA. The obtained X-ray patterns were compared to data of the Joint Committee on Powder Diffraction Standards (JCPDS) to determine crystal structures.

3. Photoluminescence and scintillation property measurements

Excitation and emission spectra of photoluminescence were measured at room temperature using a spectrometer (FP6500; Jasco Inc., Tokyo, Japan). Wavelengths of excitation were 220–330 nm. The measurement range of wavelengths for emission spectroscopy was 300–700 nm.

For scintillation property measurements, gamma rays of 662 keV from a ^{137}Cs source were used. A GPS:Pr sample was set on a photomultiplier tube (H7195; Hamamatsu Photonics K.K., Shizuoka, Japan) using optical grease. As a reflector, a polytetrafluoroethylene tape was used. Output signals from the photomultiplier tube were connected to a delay line amplifier (460; Ortec, Oak Ridge, U.S.A.) for spectroscopy; the integral time of 0.1 μs was chosen. A linear gate and stretcher (542; Ortec, Oak Ridge, U.S.A.) and a multi-channel analyzer (WE7562; Yokogawa, Tokyo) were used. In addition, output signals were measured using a digital oscilloscope with analog bandwidth of 1 GHz (LT584; Le-croy Corp., New York, U.S.A.).

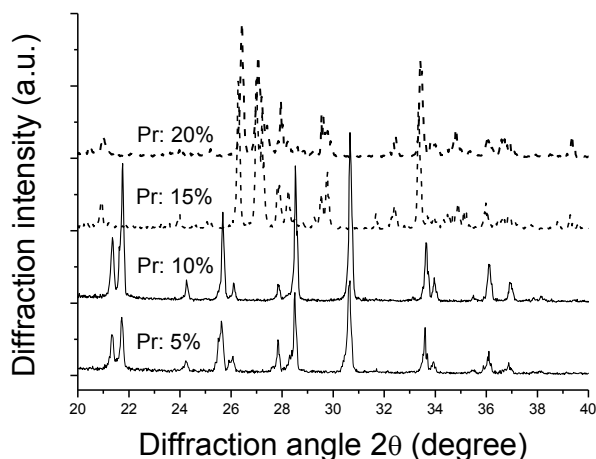


Fig. 2 X-ray diffraction patterns obtained with Pr-doped GPS crystals; concentrations of praseodymium were, respectively, 5, 10, 15, 20 mol%. For Pr concentrations of 5 and 10 mol%, a crystal structure was orthorhombic with the $\text{Pna}2_1$ space group. For Pr concentrations of 15 and 20 mol%, it was triclinic with the $\text{P}1$ space group

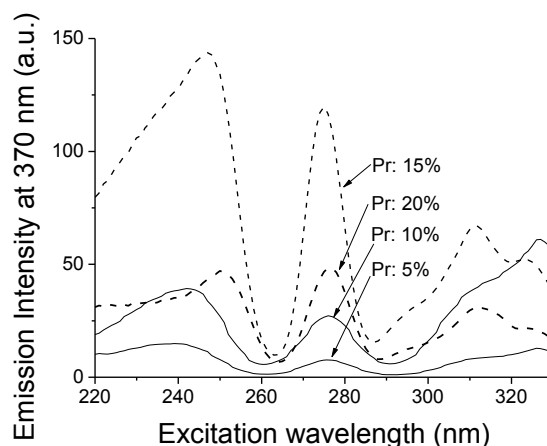


Fig. 3 Photoluminescence excitation spectra obtained with the Pr-doped GPS crystals. The wavelength of emission light for monitoring was set at 370 nm. The peaks located at 275 nm correspond to transitions from $4f^2$ ground state to the $4f^1 5d^1$ state of Pr^{3+} in the host lattice.

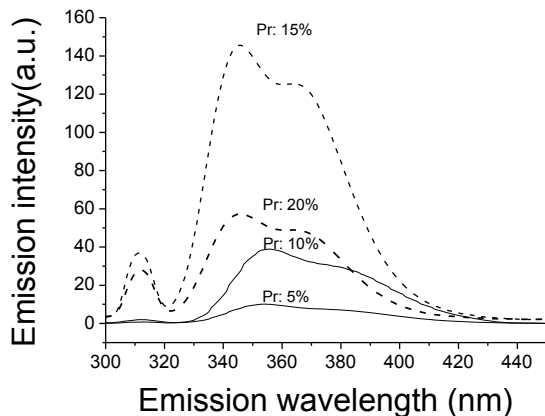


Fig. 4 Photoluminescence emission spectra obtained with the Pr-doped GPS crystals. The excitation wavelength was set at 275 nm. Emission spectra were classified as one of two types according to their crystal structure: triclinic or orthorhombic structures

III. Experimental results and Discussion

1. Change of crystal structures of GPS according to the praseodymium concentration

As described in the *Introduction*, a crystal structure of rare-earth pyrosilicates is governed by a mean ionic radius containing rare-earth elements. **Figure.2** portrays X-ray diffraction patterns obtained with Pr-doped GPS crystals; the Pr concentrations were 5, 10, 15, and 20 mol%, respectively. For Pr concentrations of 5 and 10 mol%, a crystal structure was orthorhombic with Pna2₁ space group. For Pr concentrations of 15 and 20 mol%, it was triclinic with P/1 space group. The crystal structures obtained in this study were almost consistent with those described in an earlier report ¹⁰.

2. Photoluminescence and scintillation properties

Excitation and emission spectra were measured and classified as two types according to their crystal structures, orthorhombic for Pr concentration of 5 and 10 mol%, and triclinic for Pr concentration of 15 and 20 mol%. Scattering occurred in the size of the evaluated GPS samples. It is therefore difficult to compare the excitation and emission intensity quantitatively from these results.

The relation between excitation and emission spectra of photoluminescence was measured first. According to this result, the most intense emission wavelength, i.e. 370 nm, was chosen for excitation spectrum measurements.

Figure.3 shows the dependence of emission yield on the excitation wavelength obtained using Pr-doped GPS crystals. The excitation spectra include peaks located at 275 nm and broad peaks around 240 and 310 nm. The peaks around 240 nm and at 275 nm probably correspond to transitions from the 4f² ground state to the 4f¹5d¹ state of Pr³⁺ in the host lat-

tice ¹⁶. However, the ratio between light yield of peaks at 250 nm and 275 nm increased concomitantly with increased concentration of praseodymium. In addition, assuming that the peaks around 240 nm consisted of two peaks, the peaks were, respectively, 230 nm and 250 nm. In the case of the triclinic GPS, the intensity of the peak around 240 nm was higher than that obtained with the orthorhombic GPS; it was probably caused by a change in the crystal structure.

Figure.4 portrays emission spectra obtained from the Pr-doped GPS crystals; the excitation wavelength was set at 275 nm. Peaks located at 310 nm were only observed for spectra obtained with the triclinic GPS. In addition, the tric-

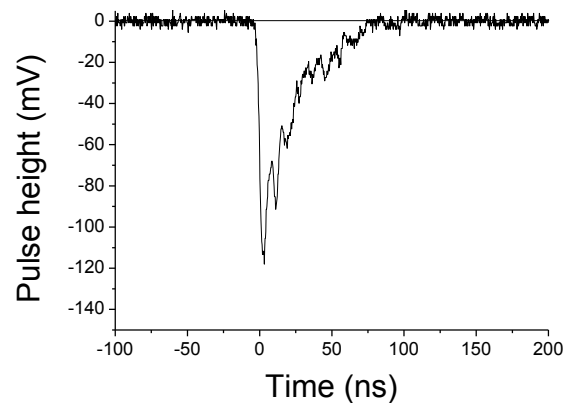


Fig. 5 An example of typical output signals from the orthorhombic GPS with Pr concentration of 10%. This output signal was obtained using a H7195 photomultiplier and gamma rays of 662 keV from a ¹³⁷Cs checking source. The average decay time was ca. 26 ns.

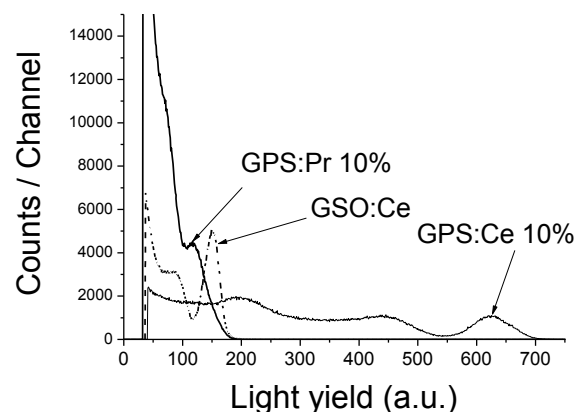


Fig. 6 Comparison of light yields of three scintillators: a commercially available 1.0 mol% Ce-doped GSO, a 10 mol% Ce-doped GPS, and the 10 mol% Pr-doped GPS for 662 keV gamma rays; the 10 mol% Ce-doped GPS was triclinic. Although the Ce-doped GPS has ca. 4.1 times higher light yield than the GSO scintillator, the Pr-doped GPS was ca. 0.8 times light yield compared to GSO.

linic GPS showed strong emission at 320–420 nm; peaks were located, respectively, at 340 and 365 nm. However, considering the scattering of the sample sizes, the triclinic GPS had light yield larger than that of the orthorhombic GPS. The orthorhombic GPS showed emissions of 330–420 nm; peaks were located at 350 and 380 nm. These peaks were shifted to a longer wavelength than those with the triclinic GPS.

An example of typical output signals from the orthorhombic GPS with Pr concentration of 10% is presented in **Fig. 5**. This output signal was obtained with the photomultiplier and gamma rays of 662 keV from a ^{137}Cs checking source. An average decay time of the orthorhombic GPS with Pr concentration of 10% was 26 ns. Although the triclinic GPS showed strong emission light yield in the photoluminescence measurement, they had no response to gamma rays. A possibility is that emission light from the Pr-doped triclinic GPS has very slow decay time. However, no signal was observed by oscilloscope with longer time division up to 0.1 s. Another possibility is that some inefficient energy transfer from the host lattice to Pr^{3+} activators occurred. Further investigation of the response of the triclinic GPS to gamma rays is necessary.

Figure.6 presents a comparison of light yields of three scintillators: a commercially available 1.0 mol% Ce-doped GSO, a 10 mol% Ce-doped GPS, and the 10 mol% Pr-doped GPS for 662 keV gamma rays; the 10 mol% Ce-doped GPS was triclinic. Although the Ce-doped GPS has ca. 4.1 times higher light yield than the GSO scintillator, the Pr-doped GPS had ca. 0.8 times the light yield that GSO had.

In this comparison, Pr-doped GPS crystal have some cracks and strongly colored. Consequently, the full absorption peak has broad peaks for the Pr-doped GPS scintillator. From the perspective of light yield and energy resolution, further investigation using crack-free single crystals is necessary.

IV. Conclusion

Luminescence properties and crystal structures of Pr-doped GPS scintillator were investigated. For 10 mol% Pr-doped GPS, fast decay time of 26 ns was achieved. Although the triclinic GPS had a higher light yield than the orthorhombic GPS in photoluminescence spectroscopy, it showed no response to gamma rays.

To develop a higher performance scintillator, a scintillation mechanism of GPS scintillator must be clarified. Consequently, a systematic study and further understanding on a GPS system including Pr-doped GPS is necessary. In addi-

tion, from the perspective of application, the Pr-doped GPS had 0.8 times the light yield of a GSO scintillator. It had fast decay time of 26 ns with neither self-radioactivity nor deliquescence. Therefore, a Pr-doped GPS can be a practically useful scintillator. Further investigations of Pr-doped GPS scintillators using large single crystals of 10 mm are indispensable to their development.

Acknowledgment

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