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ARTICLE

Dependence of Crystal Structures and Scintillation Properties on Cerium Concentration in $Gd_2Si_2O_7$:Ce Powder Synthesized by Solid State Reaction

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Dependence of the crystal structure and scintillation property of $Gd_2Si_2O_7$:Ce (GPS:Ce) were investigated using polycrystalline samples synthesized using a solid-state reaction method. Crystal structures of three types were observed according to the cerium concentration. The largest light yield for UV light and alpha particle excitations was observed for an orthorhombic structure whose cerium concentration was approximately 2.5 mol%.

KEYWORDS: Scintillator, $Gd_2Si_2O_7$:Ce, solid state reaction, scintillation properties

I. Introduction

Inorganic scintillators with high light yield and energy resolution are necessary for use in the fields of nuclear medical diagnostics, non-destructive inspection, nuclear engineering, and others.

Recently, a promising scintillation material was invented: cerium-doped gadolinium pyrosilicate, GPS:Ce[1,2]. The material, which comprises $Gd_2Si_2O_7$ and a Ce activator, was first developed for neutron detection[3]. Kawamura et al. reported that a GPS scintillator grown by a floating zone method had light yield several times higher than that of a conventional BGO scintillator. In addition, the GPS had high energy resolution of 5.0% for 662 keV gamma-rays from ^{137}Cs[4].

Yagi et al., after synthesizing GPS with several compositions using sol-gel method, reported the phase transformation of the crystal structure of pyrosilicate, type E, F and G, when the ratio of cerium against gadolinium was increased[4]. According to J. Felsche[6], crystal structures of rare-earth pyrosilicate ($RE_2Si_2O_7$) depend on the mean ionic radius of RE^{3+}. GPS:Ce contains Gd^{3+} and Ce^{3+} as RE^{3+}, which presents the possibility that Ce^{3+} changed both the crystal structure and the luminescence property.

To optimize the performance of GPS:Ce scintillator, it is necessary to investigate the dependence of cerium concentration, light yield, and crystal structures. In this study, crystal structures, photoluminescence and scintillation properties of GPS:Ce powders synthesized using a solid state reaction were evaluated.

II. Experimental

1. Synthesize of GPS samples with several cerium concentrations

We used a box type furnace and two-mirror-image floating zone furnace for synthesis of crystals. The GPS power becomes infrared-transparent at a low cerium concentration. It is extremely difficult to grow crystals using the floating zone method. Consequently, in this study, solid-state reaction was adopted. Near single-phase GPS with cerium concentration of 0–100 mol%, $(Gd_{1-x}Ce_x)_2Si_2O_7$ (x = 0–1), was prepared.

The starting materials were powders of Gd_2O_3, SiO_2 with 5N purity and CeO_2 with 4N purity. The powders were weighed at a composition of $(Gd_{1-x}Ce_x)_2Si_2O_7$ (x = 0–1), and mixed using an agate mortar.

The mixture was stuffed into a rubber bag and pressed under hydrostatic pressure of 60 MPa to form a rod with subsequent solid-state reaction between 1500 and 1600 °C in air for 10 hr. The sintered sample was ground in an agate mortar and crystalline phase was identified using X-ray powder diffraction (XRD). The process, i.e. grounding, firing, and XRD, was repeated until single-phase $(Gd_{1-x}Ce_x)_2Si_2O_7$ was obtained.

2. Measurement procedure

To obtain the luminescence properties, photoluminescence measurement was conducted for each sample. The emission spectra (250–450 nm) and excitation spectra (225–350 nm) were measured using a fluorophotometer (FP-6500; Jasco Corp.).

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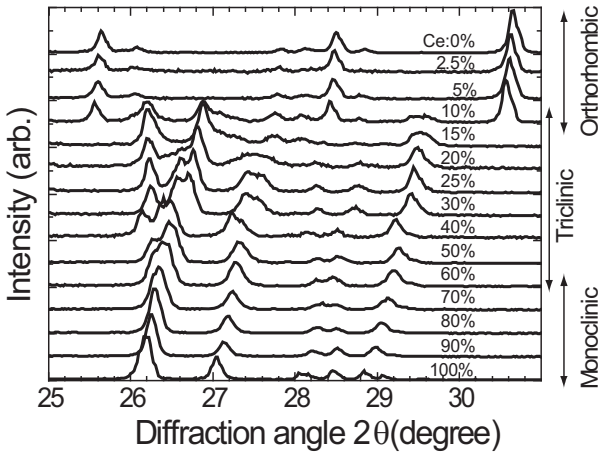

Fig. 1 XRD spectra of GPS powders with cerium of several concentrations. Crystal structures of three types were apparent: orthorhombic, 0–10%; triclinic, 10 – 60%; monoclinic, 60–100%.

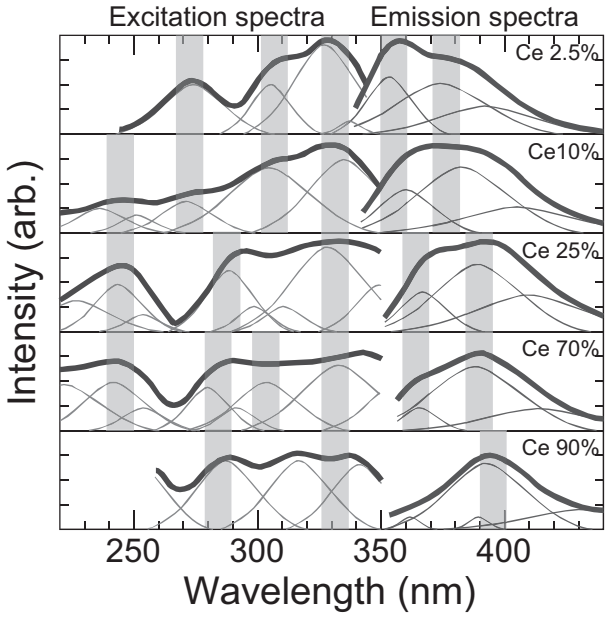

Fig. 2 Photoluminescence spectra of GPS powder with several cerium concentrations.

For scintillation properties measurement, alpha particles from an ^{241}Am source were used. A photomultiplier tube (H7195; Hamamatsu Photonics K.K.), a delay line amplifier (460; Ortec), a linear gate stretcher (542; Ortec), and a multi-channel analyzer (2100; Labo.) were used. In addition, output signals from the photomultiplier tube were measured using a digital oscilloscope (LT584; LeCroy Corp.).

III. Experimental results

1. Crystal structures

Figure 1 shows XRD spectra obtained using GPS powder with cerium of several concentrations. Crystal structures of three types appeared according to cerium concentrations: orthorhombic, 0–10%; triclinic, 10–60%; and monoclinic, 60–100%. Doping of cerium changed lattice

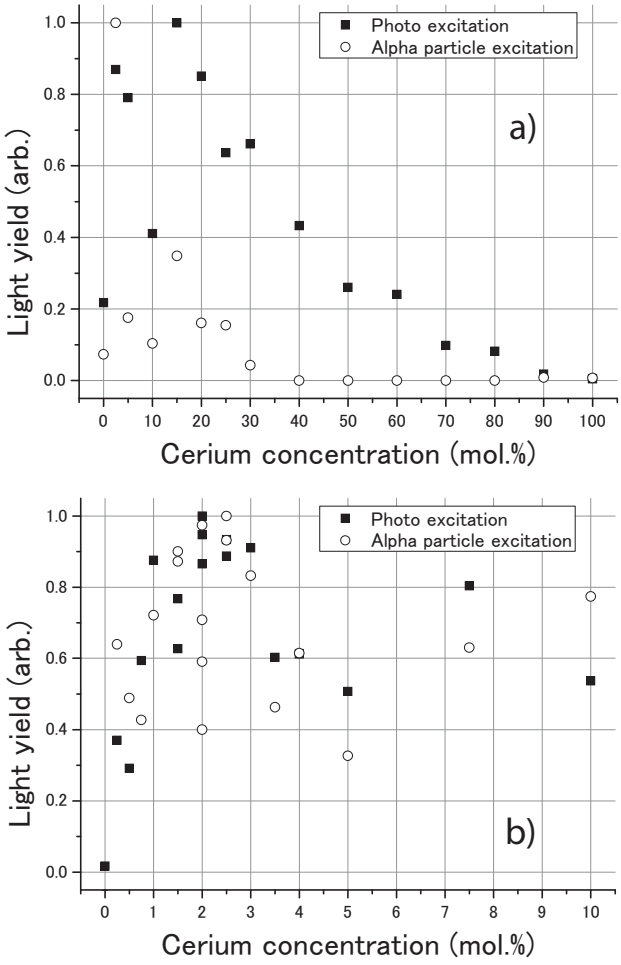

Fig. 3 Light yield of GPS powder with several cerium concentrations. a) Ce:0–100%, b) Ce: 0–10%.

parameter of $Gd_2Si_2O_7$ because the ionic radius of Ce^{3+} is larger than that of Gd^{3+}. The GPS with 10% of cerium consisted of two phases: orthorhombic and triclinic. This cerium concentration is thought to correspond only to the phase change.

These results generally correspond to those presented in Felsche's report[5]. All crystal structures obtained in this study are high-temperature polymorphs because of the firing temperature above 1500 °C. Lack of phase transition into the low forms was observed for all compositions even though polycrystalline samples were used.

2. Photo excitation and emission spectrum

Figure 2 shows photoexcitation and emission spectra obtained using GPS powder synthesized using cerium of several concentrations. Both emission and excitation spectra exhibited different shapes depending on the crystal structures. The excitation spectrum of the orthorhombic phase had three peaks at 275, 310, and 335 nm. The emission spectrum showed peaks at 360 and 380 nm. The triclinic phase had three peaks at 240, 295, and 330 nm in the excitation spectrum. Two peaks at 370 and 390 nm were observed in the emission spectrum. GPS with 10% of cerium

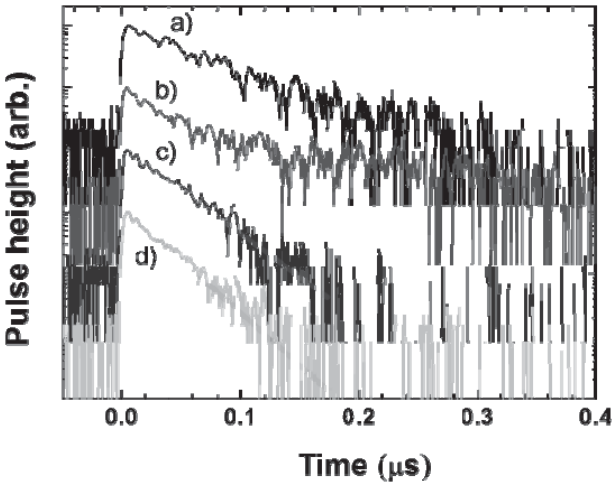

Fig. 4 Decay curves of output signals from a photomultiplier connected with GPS powders. Cerium concentrations: a) 2.5%, b) 0.25%, c) 10%, d) 15%.

concentration showed a broad peak in both excitation and emission spectra, which results from the coexistence of two phases: orthorhombic and triclinic. The luminescence intensity of the monoclinic phase was much lower than that of other phases.

All luminescence observed in this study can be attributed to the 5d–4f transition of Ce^{3+} because the energy level of 5d orbital is susceptible to the crystal field.

3. Dependence of emission light yield and decay time on cerium concentrations

Figure 3 shows dependence of light yield of GPS powder on cerium concentration. Both results for photoexcitation and alpha particle excitation are depicted in the same graph. Sometimes a large difference observed in light yield by the mode of excitation. For praseodymium-doped GPS, high emission light yield was obtained by photoexcitation only[7]. In contrast, the same tendency was observed for both excitations in the cerium-doped GPS.

Some scattering of light yield was observed. This scattering might have occurred by oxidation of cerium ions to Ce^{4+} by synthesis atmosphere or existence of traces of secondary phase, i.e. apatite. The light yield showed a maximum peak at around cerium concentration of 2.5 mol%, orthorhombic structure. The second peak was located at cerium concentration of 8–10 mol%, mixture of orthorhombic and triclinic structure. At the region of cerium concentration higher than the second peak, the light yield gradually decreased concomitantly with the increase of cerium concentration.

Figure 4 presents decay curves of output signals from a photomultiplier related to GPS powders. The triclinic GPS showed the fastest decay time, ca. 80 ns, in these three types. Orthorhombic GPS was slow, at ca. 150 ns.

IV. Conclusion

GPS with 0–100 mol% of cerium was synthesized using a repeated solid-state reaction. Dependence of crystal structure and scintillation property on the cerium concentration of GPS:Ce was investigated. Crystal structures of three types were observed according to the cerium concentration. The highest light yield was observed for the orthorhombic structure with 2.5 mol% of cerium. The second largest peak was observed for triclinic GPS with 10–15 mol% of cerium concentration. The triclinic GPS exhibited the fastest decay time of 80 ns, whereas orthorhombic GPS was slow, ca. 150 ns.

If large size single crystal growth succeeds, the orthorhombic GPS will be an ideal scintillator for SPECT. On the other hand, the triclinic GPS will be contribute neutron radiograph and some neutron scattering experiment by its fast response and high neutron detection efficiency. Further development for large size single crystal growth and scintillator plates are required.

Acknowledgment

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