

Growth and scintillation properties of Ce doped $\text{Gd}_2\text{Si}_2\text{O}_7/\text{SiO}_2$ eutectics

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Abstract. Ce: $\text{Gd}_2\text{Si}_2\text{O}_7/\text{SiO}_2$ eutectic was grown by the μ -PD method. The square-shape sample with a side of 5 mm and a length of 15 mm was obtained. Two phases of orthorhombic $\text{Gd}_2\text{Si}_2\text{O}_7$ and SiO_2 was observed. Rod-phase was SiO_2 and matrix phase was $\text{Gd}_2\text{Si}_2\text{O}_7$. Ce^{3+} 4f5d emission have been observed at 400nm. The sample showed light yield of around 16,000 photons/MeV. Scintillation decay time was 46.3ns(21%) 249ns(79%).

1. Introduction

A number of halide and oxide scintillator materials have been developed and they are applied to various fields such as astronomy, medical imaging, and homeland security. Although halide scintillators, such as Tl:NaI, Tl:CsI and Ce:LaBr₃ [1], have high light outputs of more than 30,000 photons/MeV, they have hygroscopic nature. In the X-ray imaging, indirect flat panel detector (FPD) composed of a scintillator layer such as CsI:Tl and photo-sensor array requires improvements in their spatial resolution. But, CsI:Tl columnar films reduce the spatial resolution, because the thicker it becomes the more light scattering occurs [2]. Recently submicron-diameter phase-separated scintillator fibers (PSSFs) were reported and they possessed both the properties of an optical fiber and a radiation-to-light conversion. The PSSFs were fabricated using a directionally solidified eutectic (DSE) system. The DSE systems have been discovered in various materials for many applications [3-6]. In PSSFs, the light emitted from the scintillator fibers is confined and transported along the fiber direction by a total reflection mode as shown in Fig.1, so that high-resolution radiation imaging can be achieved. CsI/NaCl [6] and GAP/Al₂O₃[5] have been already reported as PSSFs.

Ce: $\text{Gd}_2\text{Si}_2\text{O}_7$ (Ce:GPS) had a good light output of 30,000 photons/MeV and FWHM energy resolution of 6.0% at 662 keV at room temperature. However, according to the previous report [7-10], Ce:GPS crystals need to be grown with heavy Ce-doping (approximately, 10 mol%) in order to stabilize the crystal growth process. Such high Ce-concentration would lead to lower light output because of self-absorption or concentration quenching. The main reason is the fact that $\text{Gd}_2\text{Si}_2\text{O}_7$ is not congruently melt. When the chemicals with stoichiometric composition is melted, initial melt has apatite phase.

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Scintillator materials combined with photodetectors are used to detect high energy photons and accelerated particles in medical imaging techniques, high energy and nuclear physics detectors, high-tech industrial applications and most recently also in the advanced homeland security related techniques. Recently, Ce:Gd₂Si₂O₇ (Ce:GPS) belonging to the pyrosilicate group has been investigated, and this crystal was found to have much higher light output and shorter decay time than Ce:GSO. [6–8] Toropov et al. found that the composition Gd₂O₃-2SiO₂ is not congruent in the Gd₂O₃-SiO₂ system,[9] and Kawamura et al. reported that the GPS phase can be grown by heavy Ce-doping (approximately 10 mol %).[9] Furthermore, substituting Ce³⁺ site with La³⁺ whose ionic radius is similar to Ce³⁺ is also able to stabilize the congruent phase, and Ce:(La, Gd)₂Si₂O₇ (Ce:La-GPS) scintillator with a good energy resolution was developed [10-13].

In this study, Ce 1mol% doped Gd₂Si₂O₇/SiO₂ eutectics were grown by the micro pulling down (μ-PD) method and their DSE system has been investigated. Investigation of obtained eutectic structure, luminescence and scintillation performances were performed.

2. Experimental

2.1. Crystal growth procedure

A stoichiometric mixture of 4N CeO₃, Gd₂O₃ and glass-SiO₂ powders (High Purity Chemicals Co.) was used as starting material. Ce:Gd₂Si₂O₇/SiO₂ eutectics were grown by the micro-pulling-down (μ-PD) method with an RF heating system at the eutectic composition (25.6mol%Gd_{1.98}Ce_{0.02}O₃-74.4mol%SiO₂). Here, the volume ratio is about Gd_{1.98}Ce_{0.02}Si₂O₇:SiO₂=0.809:0.191, theoretically. Typical pulling rates were 0.3-0.8mm/min. Crystals were grown from an Ir crucible under N₂ atmosphere. A Ir rod was used as a seed. Plates of 5mm x 5mm x 0.5mm were cut and polished for the measurements. The eutectic phase structure was investigated by back scattered electron image (BEI). The phases in the eutectic crystal determined by powder XRD patterns.

2.2. Measurements of scintillation properties

Radio-luminescence spectrum at room temperature was measured with the above spectrometer (EI FLS920) excited by 5.5MeV alpha rays from an 241Am source. To determine the light output, we obtained the pulse height spectrum of this crystal under excitation with 662 keV gamma rays from a ¹³⁷Cs source. The scintillation photons were detected using by a photomultiplier (PMT; Hamamatsu R7600U-200), and then the signals from the PMT were amplified (ORTEC 113), shaped (ORTEC 572A), and read out with a multi-channel analyzer (AMPTTEK 8000A). The pulse height of Bi₄Ge₃O₁₂ (BGO) crystal, which has a light output of 8,500 photons/MeV 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 (Tektronix TDS 3052B). The scintillation decay time was calculated from exponential approximation.

3. Results

3.1. Crystal growth procedure

Ce:Gd₂Si₂O₇/SiO₂ eutectic was grown by the μ-PD method. The square-shape sample with a side of 5 mm and a length of 15 mm was obtained (Fig.1). The BEI image of transverse cross-section of the eutectic is shown in Fig. 2. The phases were determined as orthorhombic Gd₂Si₂O₇ and SiO₂ glass by the EDX measurement and powder XRD pattern of the grown eutectic. Rod-phase was SiO₂ and matrix phase was Gd₂Si₂O₇ according to the EDX measurement result. The diameter of SiO₂ scintillation fiber was approximately 700 nm (Fig.2) and dispersed well on the transverse cross-section.

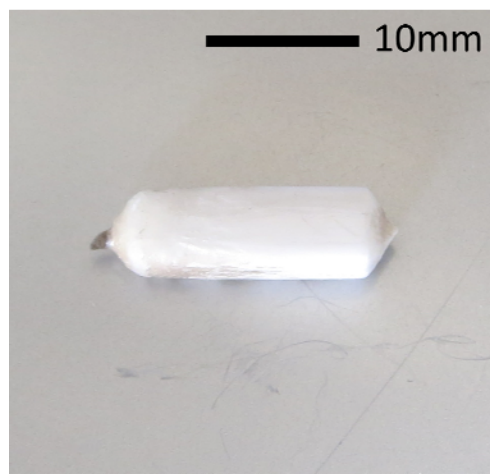


Figure 1. Photograph of the grown Ce:Gd₂Si₂O₇/SiO₂ eutectic

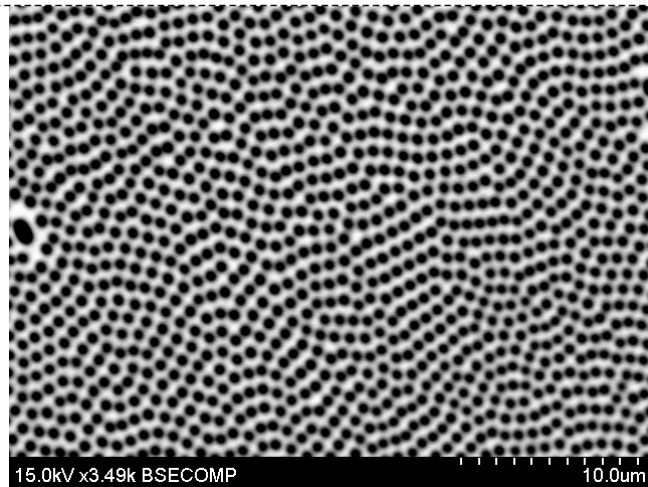


Figure 2. BEI of transverse cross-section of the grown Ce:Gd₂Si₂O₇/SiO₂ eutectic. White phase was Ce:Gd₂Si₂O₇ and black phase was SiO₂.

3.2. Luminescence and gamma-ray response measurement procedure

Figure 3 shows radioluminescence spectra of the Ce:Gd₂Si₂O₇/SiO₂ eutectic samples. Expected Ce³⁺ 4f5d emission have been observed in 350-440nm peaking at 400nm. Figure 4 exemplifies energy spectra of the Ce:Gd₂Si₂O₇/SiO₂ eutectic samples. The samples irradiated by ¹³⁷Cs, where 662 keV. The sample showed light yield of around 14,000-16,000 photons/MeV considering with the emission wavelength of the samples and quantum efficiency of the PMT (45%@390nm, 32%@480nm). Scintillation decay curves were obtained by using the PMT and digital oscilloscope and the sample was irradiated by ¹³⁷Cs (Figure 5). Scintillation decay time was 46.3ns(21%) 249ns(79%).

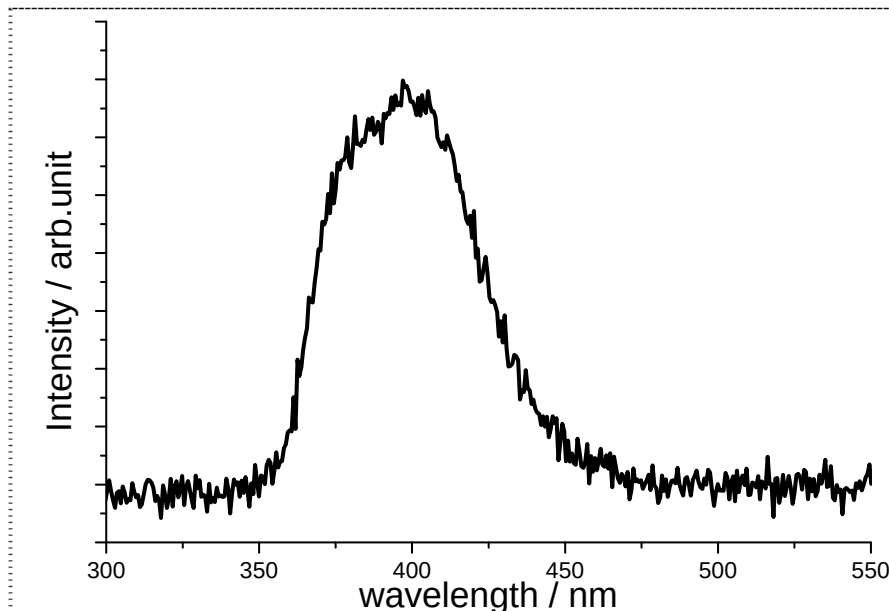


Figure 3. Radioluminescence spectra of the Ce:Gd₂Si₂O₇/SiO₂ eutectic sample.

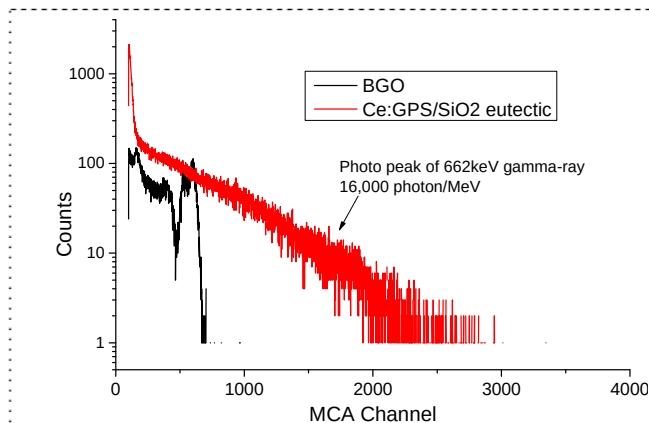


Figure 4. Energy spectra of the $\text{Ce:Gd}_2\text{Si}_2\text{O}_7/\text{SiO}_2$ eutectic sample and BGO standard excited by a 662 keV gamma ray.

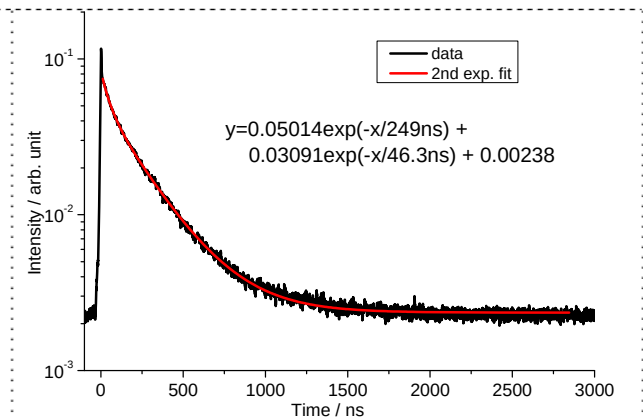


Figure 2. Scintillation decay curve of the $\text{Ce:Gd}_2\text{Si}_2\text{O}_7/\text{SiO}_2$ eutectic sample excited by a 662 keV gamma ray.

4. Conclusion

The sub-micron diameter SiO_2 glass fibers surrounded with Ce:GPS matrix from directionally solidified eutectics were fabricated. In this crystal, the length of longest fiber of SiO_2 along the growth direction was about 200 μm or so. Expected $\text{Ce}^{3+} 4f5d$ emission have been observed in 350-440nm peaking at 400nm. The sample showed light yield of around 16,000 photons/MeV. Scintillation decay time was 46.3ns(21%) 249ns(79%). By using DSE system of $\text{Ce:Gd}_2\text{Si}_2\text{O}_7/\text{SiO}_2$ eutectic, high resolution X-ray imaging can be expected.

5. References

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