

# Single Crystal Growth and Co-doping Effects of Lanthanum Substituted Gadolinium Pyrosilicate Scintillator

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**Abstract.** Ca 100, 200, 500, 1000 and 3000 at. ppm co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  single crystals were grown by the  $\mu$ -PD method. Luminescence and scintillation properties such as radioluminescence spectra, light yield and decay time were evaluated. Expected  $\text{Ce}^{3+}$  4f5d emission have been observed in 350-430nm peaking at 360nm. Emission intensity took maximum at the Ca 100at.ppm co-doped sample and decreased by increasing the Ca concentration. The Ca 100at.ppm co-doped sample showed the highest light yield of around 20,000 photons/MeV. Scintillation decay time was accelerated with increasing Ca concentration. Scintillation decay time of the Ca 0, 100, 200, 1000 and 3000 at. ppm co-doped samples were 66.5ns(21%) 468ns(79%) and 44.0ns(22%) 430ns(78%), respectively.

## 1. Introduction

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. [1] In the last two decades, great R&D effort brought several new material systems, namely the Ce-doped orthosilicates as  $\text{Gd}_2\text{SiO}_5$  (GSO),  $\text{Lu}_2\text{SiO}_5$  (LSO),  $(\text{Lu}_{1-x}\text{Y}_x)_2\text{SiO}_5$  (LYSO), pyrosilicates based on  $\text{RE}_2\text{Si}_2\text{O}_7$  (RE=Lu, Y, Gd) and most recently  $\text{LaX}_3$  (X=Cl, Br) single crystal hosts [1–5]. Recently,  $\text{Ce:Gd}_2\text{Si}_2\text{O}_7$  (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  $\text{Gd}_2\text{O}_3$ -2 $\text{SiO}_2$  is not congruent in the  $\text{Gd}_2\text{O}_3$ - $\text{SiO}_2$  system, [9] and Kawamura et al. reported that the GPS phase can be grown by heavy Ce-doping (approximately 10 mol %). [9] Furthermore, substituting  $\text{Ce}^{3+}$  site with  $\text{La}^{3+}$  whose ionic radius is similar to  $\text{Ce}^{3+}$  is also able to stabilize the congruent phase, and  $\text{Ce:}(\text{La}, \text{Gd})_2\text{Si}_2\text{O}_7$  (Ce:La-GPS) scintillator with a good energy resolution was developed [10].

More recently, the improvement of scintillation properties with co-doping divalent (e.g.  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) for Ce:(Lu, Y) $_2\text{Si}_2\text{O}_5$  (Ce:LYSO) have reported [11]. The reason of improving light yield in  $\text{Ca}^{2+}$  co-doped Ce:LYSO systems was explained by decreasing the rate of electron capturing involved by  $\text{O}^{2-}$  defects [11]. Co-doped divalent introduce negative charge by substituting  $\text{Lu}^{3+}$  or  $\text{Y}^{3+}$  site, and it interact with the positive charge of  $\text{O}^{2-}$  defect [11]. Accordingly, this mechanism would prevent electron trapping [11].

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The aim of this work is to investigate Ca co-doping effects on luminescence and scintillation properties of Ce doped La-GPS. Ca co-doped  $\text{Ce}:(\text{La}_{0.3}\text{Gd}_{0.7})_2\text{Si}_2\text{O}_7$  single crystal were grown by the micro-pulling down ( $\mu$ -PD) method. Luminescence and scintillation properties were evaluated.

## 2. Experimental

### 2.1. Crystal growth procedure

A stoichiometric mixture of 4N  $\text{La}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Gd}_2\text{O}_3$  and glass- $\text{SiO}_2$  powders (High Purity Chemicals Co.) was used as starting material.  $\text{Ca}^{2+}$  was co-doped in the rare-earth site of  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$ . Ca co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  single crystals were grown by the micro-pulling-down ( $\mu$ -PD) method with an RF heating system. A schematic of the  $\mu$ -PD growth apparatus is given in Refs. [11,12]. Typical pulling rates were 0.05–0.08 mm/min and the diameter was around 3 mm. Crystals were grown from an Ir crucible under  $\text{N}_2$  atmosphere. The seed crystals were  $(\text{La}_{0.3}\text{Gd}_{0.7})_2\text{Si}_2\text{O}_7$  crystals. Plates of 3mm $\phi$  x 1mm were cut and polished for the measurements.

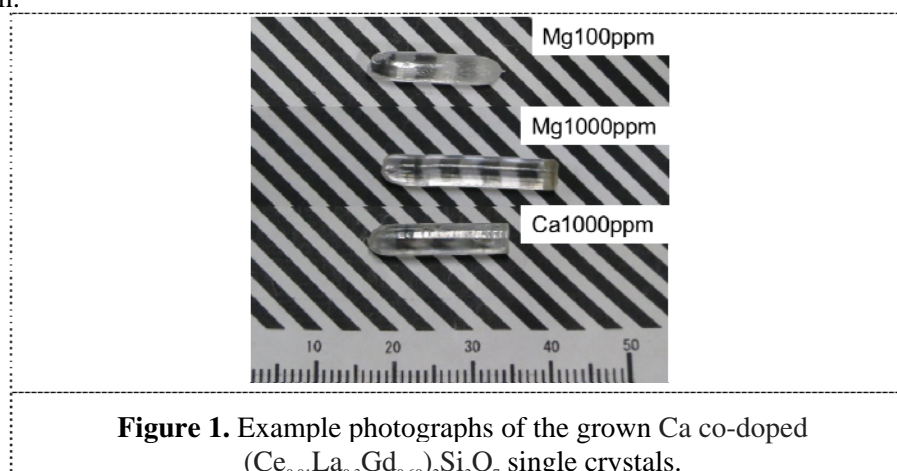
### 2.2. Measurements of scintillation properties

Radio-luminescence spectrum at room temperature was measured with the above spectrometer (EI FLS920) excited by 5.5MeV alpha rays from an  $^{241}\text{Am}$  source. To determine the light output, we obtained the pulse height spectrum of this crystal under excitation with 662 keV gamma rays from a  $^{137}\text{Cs}$  source. The scintillation photons were detected using by a photomultiplier (PMT; Hamamatsu R7600U), 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  $\text{Bi}_4\text{Ge}_3\text{O}_{12}$  (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 ( $^{137}\text{Cs}$ ) 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

Ca 100, 200, 500, 1000 and 3000 at. ppm co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  single crystals were grown by the  $\mu$ -PD method. Although  $\text{Gd}_2\text{Si}_2\text{O}_7$  can not be grown from melt because of its incongruent melt composition,  $(\text{La}_{0.3}\text{Gd}_{0.7})_2\text{Si}_2\text{O}_7$  became congruent melt by substituting La in GPS. Example photos are shown in Figure 1. The grown crystals were colorless transparent with 3 mm in diameter and 15-20 mm in length.



**Figure 1.** Example photographs of the grown Ca co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  single crystals.

### 3.2. Luminescence and gamma-ray response measurement procedure

Figure 2 shows radioluminescence spectra of the Ca co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  samples. Expected  $\text{Ce}^{3+}$  4f5d emission have been observed in 350–430nm peaking at 360nm. Emission intensity took maximum at the Ca 100at.ppm co-doped sample and decreased by increasing the Ca concentration.

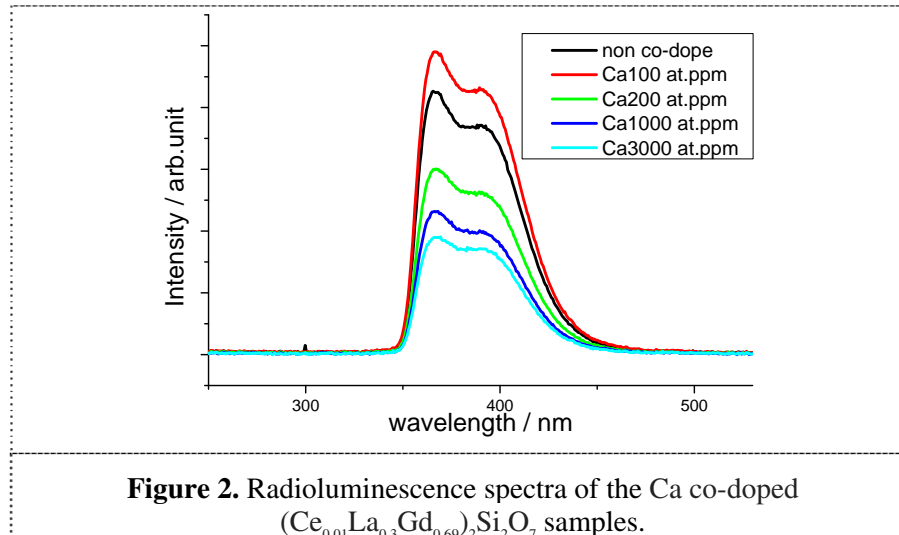
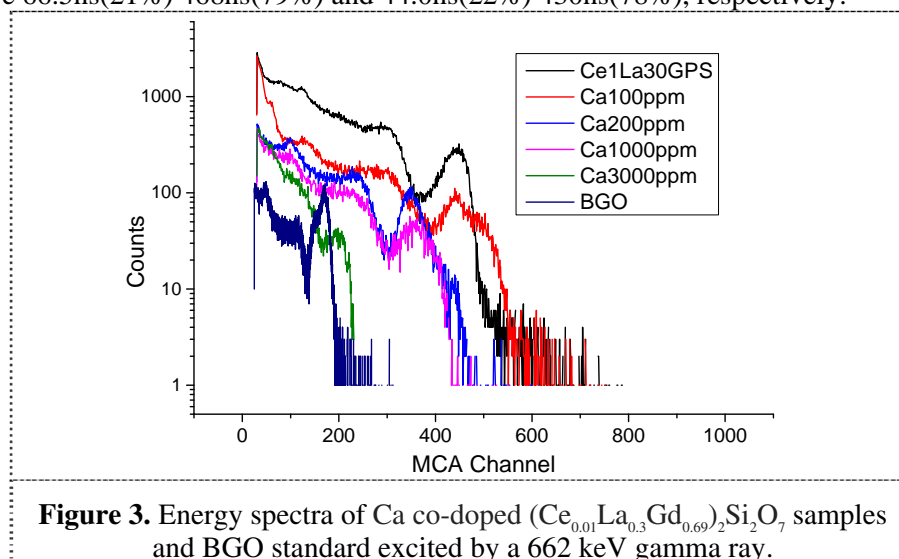
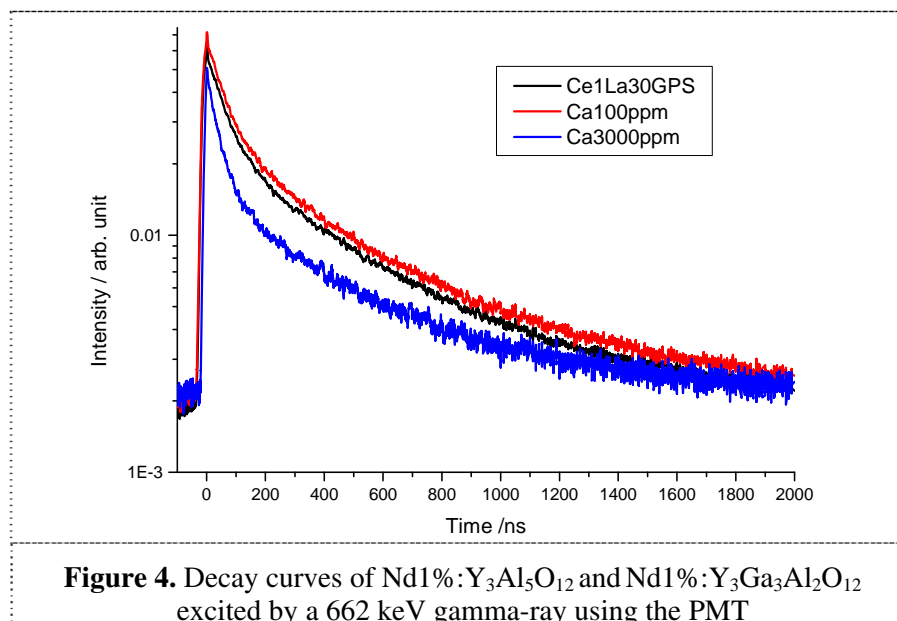


Figure 3 exemplifies energy spectra of the Ca co-doped  $(\text{Ce}_{0.01}\text{La}_{0.3}\text{Gd}_{0.69})_2\text{Si}_2\text{O}_7$  samples. The samples irradiated by  $^{137}\text{Cs}$ , where 662 keV. The Ca 100at.ppm co-doped sample showed the highest light yield of around 20,000 photons/MeV considering with the emission wavelength of the samples and quantum efficiency of the PMT (45% @360nm, 32% @480nm). Light yield was decreased with increasing Ca concentration above 100 at.ppm. This result is good agreement with the result of radioluminescence spectra measurement. The Ca 100at.ppm co-doped sample showed the highest light yield. Light yields of the Ca 0, 200, 1000 and 3000 at. ppm co-doped samples were 18000, 14000, 14400 and 8000 photons/MeV, respectively.

Scintillation decay curves were obtained by using the PMT and digital oscilloscope and the sample was irradiated by  $^{137}\text{Cs}$  (Figure 4). Scintillation decay time was accelerated with increasing Ca concentration. Scintillation decay time of the Ca 0, 100, 200, 1000 and 3000 at. ppm co-doped samples were 66.5ns(21%) 468ns(79%) and 44.0ns(22%) 430ns(78%), respectively.





#### 4. Conclusion

Ca 100, 200, 500, 1000 and 3000 at. ppm co-doped (Ce<sub>0.01</sub>La<sub>0.3</sub>Gd<sub>0.69</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> single crystals were grown by the  $\mu$ -PD method. Although Gd<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> can not be grown from melt because of its incongruent melt composition, (La<sub>0.3</sub>Gd<sub>0.7</sub>)<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> became congruent melt by substituting La in GPS. Ce<sup>3+</sup> 4f5d emission have been observed in 350-430nm Emission intensity took maximum at the Ca 100at.ppm co-doped sample and decreased by increasing the Ca concentration. The Ca 100at.ppm co-doped sample showed the highest light yield of around 20,000 photons/MeV. Light yield was decreased with increasing Ca concentration above 100 at.ppm. Scintillation decay time was accelerated with increasing Ca concentration. Scintillation decay time of the Ca 0, 100, 200, 1000 and 3000 at. ppm co-doped samples were 66.5ns(21%) 468ns(79%) and 44.0ns(22%) 430ns(78%), respectively.

#### 5. References

- [1] M. Nikl, "Scintillation detectors for X-rays", Meas. Sci. Technol. Vol.17, pp.R37-R54, Feb. 2006
- [2] C. L. Melcher, et al., IEEE Trans. Nucl. Sci., vol. 39, no. 4, pp.502–505, Aug. 1992.
- [3] P. Lecoq, et al., IEEE Trans. Nucl. Sci., vol. 49, no. 4, pp. 1651–1654, 2002.
- [4] M. Moszynski, et al., Nucl. Instr. And Meth. A 385, pp. 123–131, Jan. 1997.
- [5] K. S. Shah, et al., IEEE Trans. Nucl. Sci., vol. 50, no. 6, pp. 2410–2413, Dec. 2003.
- [6] Yagi, K. et al., IEEE Nuclear Science Symp. Conf. Rec., 2006, p. 1160.
- [7] S. Kawamura, et al., Nucl. Instrum. Methods Phys. Res., Sect. A 583 (2007) 356.
- [8] J. H. Kaneko, et al., Nucl. Instrum. Methods Phys. Res., Sect. A 529 (2004) 307.
- [9] N. A. Toropov, et al., Russ. Chem. Bull. 10 (1961) 497.
- [10] A. Suzuk, et al., Appl. Phys. Express, **5**, 2012, 102601
- [11] S. Blahuta et al., IEEE Trans. Nucl. Sci. Vol.60, No4, 2013, pp. 3134-3140