

Luminescence properties of $Gd_2Si_2O_7:Ce$ and $Gd_2Si_2O_7:La,Ce$ under vacuum ultraviolet irradiation

M. Koshimizu^{1,*}, T. Yanagida², Y. Fujimoto¹, K. Asai¹

(1. Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan; 2. Graduate School of Materials Science, Nara Institute of Science and Technology, 8916-5 Takayama-Cho, Ikoma, Nara 630-0192, Japan)

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Abstract: The luminescence properties of Ce- or Ce and La-doped gadolinium pyrosilicate ($Gd_2Si_2O_7$, GPS) were characterized using vacuum ultraviolet (VUV) excitation light. A prominent emission band was observed in the luminescence spectra with excitation at 60 nm and ascribed to 5d-4f transition of Ce^{3+} . Because the excitation wavelength of 60 nm corresponded to the excitation in the host matrix, this result indicated that the excitation energy transfer occurred from the host matrix to Ce^{3+} ions. On the basis of the rise in the luminescence time profiles with excitation at 60 nm, the energy transfer occurred within 2 ns, which was much shorter than that of Ce-doped Gd_2SiO_5 . For Ce-doped GPS, the decay rate was slower for the host excitation than that for direct excitation of Ce^{3+} . In contrast, for Ce and La-doped GPS, no significant difference was observed for the host excitation and direct excitation of Ce^{3+} . This result indicated that the energy transfer from the host to Ce^{3+} ions led to a different radiative decay process, and that La doping had an effect on the energy transfer and decay process.

Keywords: energy transfer; scintillation; vacuum ultraviolet; rare earths

Gadolinium pyrosilicate ($Gd_2Si_2O_7$, abbreviated as GPS hereafter) doped with Ce has been attracting considerable attention owing to its excellent scintillation properties. At early stage, excellent scintillation properties were reported by Kawamura et al.^[1-3]. They reported structural, optical, and scintillation properties in detail. According to their papers, Ce-doped GPS crystals exhibit efficient scintillation owing to 5d-4f transition of Ce^{3+} , and the scintillation light yield is significantly larger than that of Ce-doped Gd_2SiO_5 (GSO). In addition, the scintillation decay is slightly faster than that of Ce-doped GSO. Subsequently, several groups reported the scintillation properties of Ce-doped GPS fabricated by various synthesis techniques and their applications for gamma-ray, α -ray, or thermal neutron detection^[4-7]. Recently, Kurosawa et al. reported the stabilization of the pyrosilicate phase by La doping and the excellent scintillation properties of Ce and La-doped GPS^[8,9].

The aim of this study is the analysis of the scintillation processes in Ce-doped and Ce and La-doped GPS. The scintillation processes can be divided into three stages^[10]: Stage 1: generation of excited states in the host matrix by energy deposition of ionizing radiation, Stage 2: excitation energy transfer from the host matrix to luminescence centers (dopants such as Ce^{3+}), and Stage 3: photon emission by radiative deexcitation of the luminescence centers. Among them, the energy transfer process is important; however, it has not been thoroughly analyzed.

As for the energy transfer process in Ce and La-doped GPS, a detailed analysis has been reported in a previous paper^[11]. They proposed an energy level diagram and discussed the photoluminescence properties based on the diagram.

In this study, we analyzed the energy transfer process using vacuum ultraviolet (VUV) spectroscopy. In order to analyze the energy transfer process, it is necessary to generate excited state in the host matrix. In a previous study^[11], the band-gap energy of La-admixed GPS is estimated to be 6.6–6.8 eV. VUV photons having an energy larger than the band-gap energy, as well as ionizing radiation, generate excited states in the host matrix. Thus far, Feng et al. have reported the excitation spectra of Ce-doped GPS in VUV region and discussed the contribution of higher 5d levels within the band-gap^[12]. In this study, we used VUV excitation photons with energies higher than the band-gap energy, and analyzed the energy transfer process. In addition to the measurements of luminescence spectra with VUV excitations, luminescence decay behavior was characterized using a single-photon counting method.

1 Experimental

The samples were GPS crystals doped with Ce at 1 mol.% or 10 mol.%, and GPS crystals doped with Ce at 1 mol.% and La at 10 mol.%. These crystals were grown

* Corresponding author: M. Koshimizu (E-mail: koshi@qpc.che.tohoku.ac.jp; Tel.: +81227157219)

with floating zone method. Raw material powders were Lu_2O_3 (99.999%), SiO_2 (99.999%), La_2O_3 (99.99%) and CeO_2 (99.99%) and they were mixed as the above molar ratios. After the mixing, powders were shaped to the cylinder by the hydrostatic pressure. The cylinders were sintered at 1600 °C for 6 h under an air atmosphere to obtain GPS ceramic. In the crystal growth, the rotation rate was 20 r/min and we pulled down the sintering rod to obtain a crystal with a rate of 3–8 mm/h. Hereafter the samples are referred to with their dopant concentrations in the melt. The X-ray-irradiated radioluminescence spectra were obtained using an X-ray generator. The applied voltage and the tube current was 80 kV and 2.5 mA, respectively. The spectra were recorded with a CCD detector (Andor, DU-420-OE) equipped with a grating monochromator (Oriel Instruments)^[13]. The characterization of the luminescence properties was performed at BL-7B of UVSOR, Institute for Molecular Science, Japan. The samples were placed in a vacuum chamber and excited with VUV or UV photons. The luminescence spectra were recorded with a CCD detector (Roper Scientific) equipped with a monochromator (Acton, 300i). The luminescence decay behavior was observed using time-correlated single photon counting technique. Single bunch operation of the UVSOR was used, and the time period between the successive excitation pulses was 176 ns. Emitted photons were monochromatized with the monochromator and detected with a multichannel-plate-mounted photomultiplier tube (Hamamatsu, R3809U-50). The time difference of the luminescence photon detection signal and the excitation pulse were accumulated into a histogram as luminescence time profile.

2 Results and discussion

Fig. 1 shows the X-ray-irradiated radioluminescence spectra of the Ce-doped and Ce and La-doped GPS crystals. Fig. 2 shows the luminescence spectra of the Ce-doped and Ce and La-doped GPS crystals. The excitation wavelength was 60 nm. Judged from the host excitation band peaking at 126 nm in a previous paper^[12], the excitation wavelength of 60 nm corresponds to a

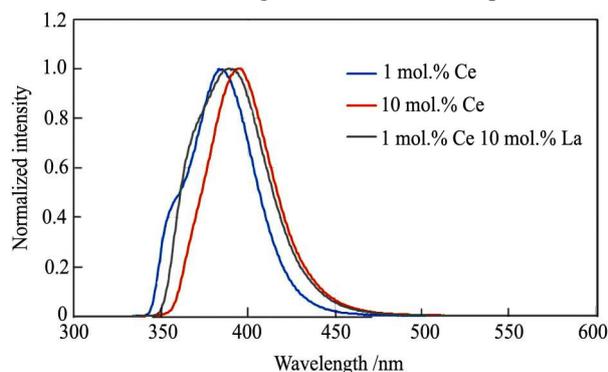


Fig. 1 X-ray-irradiated radioluminescence spectra of the Ce-doped and Ce and La-doped GPS

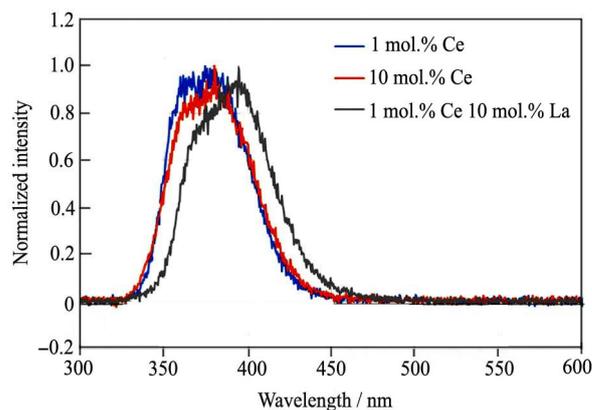


Fig. 2 Luminescence spectra of the Ce-doped and Ce and La-doped GPS (The excitation wavelength was 60 nm)

photon energy much higher than the band-gap energy, and excited states are generated in the host matrix. In both spectra, a prominent band is observed at approximately 390 nm and ascribed to 5d-4f transition of Ce^{3+} . Thus, Ce^{3+} emission is observed in the case of photoexcitation of the host matrix, as well as in the case of scintillation. The result in Fig. 2 indicates that the emission occurs after the energy transfer from the host matrix to Ce^{3+} ions.

Figs. 3–5 show the luminescence time profiles of Ce-doped GPS at 1 mol.%, Ce-doped GPS at 10 mol.%, and Ce and La-doped GPS crystals, respectively. The excitation wavelengths were 60 and 300 nm, which correspond to excitation in the host matrix and of Ce^{3+} ions, respectively. The excitation wavelength of 60 nm corresponds to the photon energy of about three times the

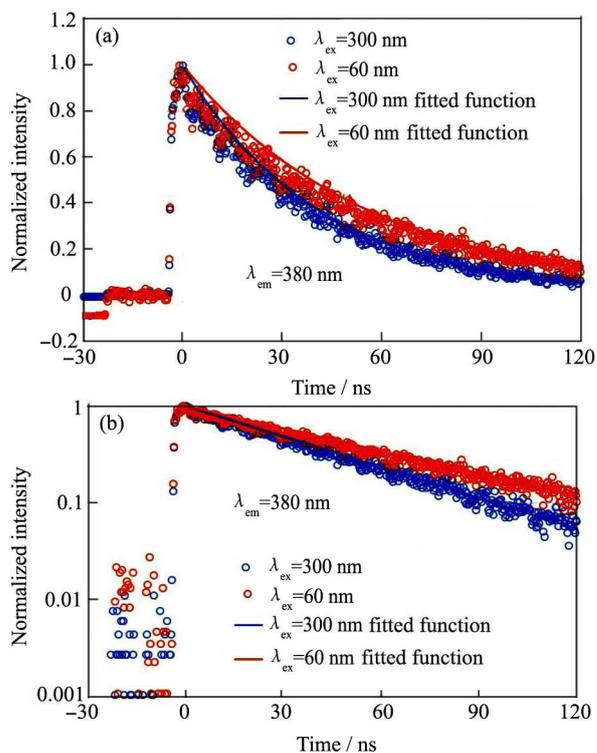


Fig. 3 Luminescence time profiles of GPS doped with Ce at 1 mol.% (a) In linear scale; (b) In semi-log scale

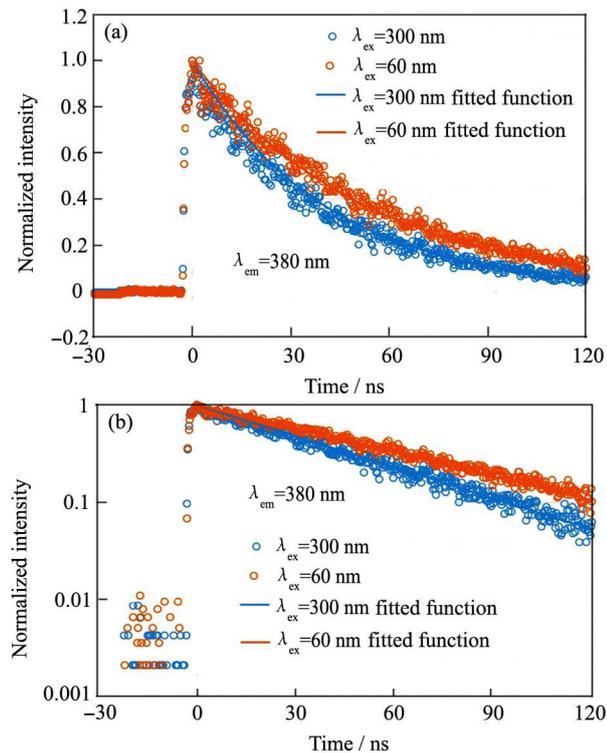


Fig. 4 Luminescence time profiles of GPS doped with Ce at 10 mol.%

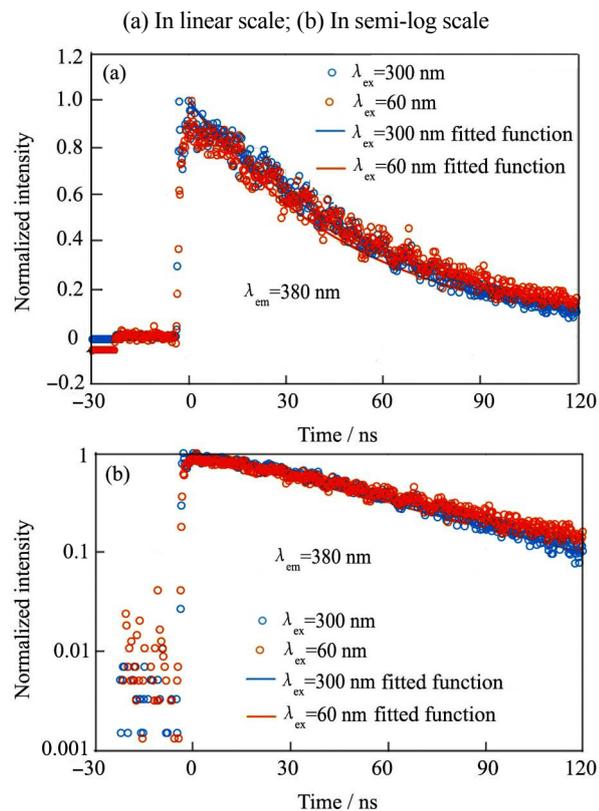


Fig. 5 Luminescence time profiles of GPS doped with Ce at 1 mol.% and La at 10 mol.%

(a) In linear scale; (b) In semi-log scale

band-gap energy. For such photon energy, thermalization and diffusion of electron-hole pairs in the host matrix play an important role in the luminescence process. Such process has been analyzed in a previous paper in detail^[14].

The emission wavelength was 380 nm. For comparison, the luminescence time profile of GSO doped with Ce at 1 mol.% is shown in Fig. 6. The emission wavelength was 440 nm. As mentioned in the above paragraph, the excitation wavelength of 60 nm corresponds to the excitation in the host matrix. Hence, the time profiles reflect the energy transfer process in addition to the radiative transition of Ce^{3+} ions. In contrast, the excitation wavelength of 300 nm corresponds to the direct excitation of Ce^{3+} ions, and thus the time profiles reflect only the radiative transition of Ce^{3+} ions.

At first, a clear difference is seen at the rise of the time profiles of GPS and GSO. The rise of the time profile of GSO with excitation at 60 nm is much slower than that with excitation at 300 nm. This result is in line with that of a previous paper^[15]. The slow rise indicates the slow energy transfer process, i.e., the typical time of the energy transfer corresponds to the rise time of ~ 20 ns. On the other hand, in the time profiles of the GPS crystals, no significant difference in the rise was observed. This result indicates that the energy transfer in GPS crystals is much faster than that in GSO, although the chemical compositions of the crystals are similar. On the basis of the rise in the time profiles, the energy transfer in GPS crystals occurs in less than 2 ns with excitation at 60 nm.

In addition, the decay behavior was different for GPS crystals with and without La. Table 1 shows the decay time constants for GPS samples. For Ce-doped GPS, the decay is slower with excitation at 60 nm than that with excitation at 300 nm. In contrast, in the case of Ce and La-doped GPS, the decay behavior was similar for both cases. As clearly shown in Figs. 3–5 with a vertical axis in logarithmic scale, the difference in the decay behavior cannot be explained with appearance or disappearance of another component. The decay rate was different at least for 100 ns with different excitation wavelengths for Ce-doped GPS. If a slow energy transfer from the host matrix to Ce^{3+} ions contributes to the time profile, a slow rise would be observed similarly to the case of Ce-doped GSO. The difference lies in the decay part, hence, the radiative decay process is different. The results in Figs. 3 and 4 indicate that the energy transfer from the host ma-

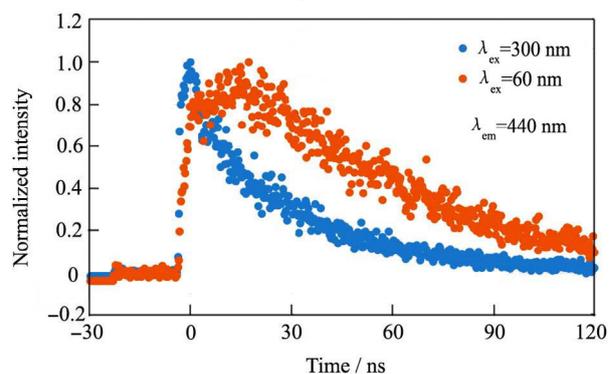


Fig. 6 Luminescence time profiles of GSO doped with Ce at 1 mol.%

Table 1 Decay time constants obtained by fitting the decay part of the luminescence time profiles of the GPS samples

Samples	Excitation at	
	300 nm/ns	60 nm/ns
GPS doped with Ce at 1 mol.%	41	56
GPS doped with Ce at 10 mol.%	41	53
GPS doped with Ce at 1 mol.% and La at 10 mol.%	52	60

trix to Ce^{3+} ions leads to a decay process significantly different from that in the case of direct excitation of Ce^{3+} . In addition, the results of Figs. 3–5 indicate that the La doping influences the energy transfer and decay process. The 5d levels of La is considered to form the bottom of the conduction band in GPS^[11]. According to a previous paper on scintillation properties of Ce and La-doped GPS^[11], the La doping increased scintillation efficiency, which was attributed to the local fluctuation in the band-gap energy leading to suppressed diffusion of charge carriers and enhanced radiative recombination probability. Taking this discussion into consideration, the effect of La doping in this study may be ascribed to the change in the energy transfer process owing to the change in the conduction band structure.

3 Conclusions

The luminescence properties of Ce- and Ce and La-doped GPS crystals were characterized using VUV excitation light. With excitation at 60 nm, which corresponded to the excitation in the host matrix, a prominent emission band owing to 5d-4f transition of Ce^{3+} was observed. The rise in the luminescence time profiles indicated that the energy transfer from the host matrix to Ce^{3+} ions in the GPS crystals occurred in less than 2 ns, which was much faster than that of Ce-doped GSO. In addition, the decay was slower for the host excitation than that for direct excitation of Ce^{3+} in Ce-doped GPS. This difference indicated the different radiative decay processes for Ce^{3+} direct excitation or via energy transfer from the host matrix. For the La-doped crystal, this difference was not observed. These results indicated that the La doping had an effect on the energy transfer and radiative decay process in the photoluminescence process, similarly to the case of scintillation.

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