

Energy Transfer Mechanism in  $\text{Gd}_2(\text{SiO}_4)\text{O}:\text{Ce}$  Scintillators

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**Abstract**

The scintillation decay of cerium-doped gadolinium oxyorthosilicate  $\text{Gd}_2(\text{SiO}_4)\text{O}:\text{Ce}$  is lengthened by the energy transfer from Gd to Ce. To investigate the role of the Gd in the scintillation processes, the Gd was partially replaced by optically inactive rare earth elements, Y and Lu, and the effective transfer rates from Gd to Ce were measured as a function of Gd and Ce concentrations using UV- and gamma-ray excitations. The data clearly indicate the dilution of the Gd by the Y and the Lu further lengthens the migration time through the Gd in the energy transfer process from Gd to Ce.

**I. INTRODUCTION**

Gadolinium oxyorthosilicate  $\text{Gd}_2(\text{SiO}_4)\text{O}$  [1] has a high density ( $6.7 \text{ g/cm}^3$ ) and a high effective atomic number (59) for the efficient detection of x- and  $\gamma$ -radiation. Therefore, if  $\text{Gd}_2(\text{SiO}_4)\text{O}$ , which has an energy gap of  $\sim 6 \text{ eV}$ , is used as a scintillator, it is expected to be optically transparent and be an ideal environment to an efficient and fast light emitting activator, the  $\text{Ce}^{3+}$  ion. However, the relatively slow scintillation decay ( $\sim 56$  and  $600 \text{ ns}$ ), and the strong dependence of light output [2] and decay time constants [3] on Ce concentration cannot be explained in terms of the exponential decay of  $\text{Ce}^{3+}$  ( $22\text{--}25 \text{ ns}$ ) [4] following prompt recombination of electrons and holes.

When GSO absorbs the energy of the incident radiation, many electrons, holes and excitons are created. Some electrons, holes and excitons migrate through the GSO crystal to excite the  $\text{Ce}^{3+}$  and recombine. We can thus separate the scintillation mechanism into two parts [5]: primary and secondary processes. The primary processes are the transfer of energy from the ionizing radiation to the luminescent centers ( $\text{Ce}^{3+}$ ); the secondary processes are the processes by which excited  $\text{Ce}^{3+}$  ions lose their energy.

In our previous work [6] we studied the secondary processes independently by direct excitation of the  $\text{Ce}^{3+}$  using UV

excitation. We proposed that GSO has two different activation centers (Ce1 and Ce2) because the host rare earth, Gd, occupies two different crystallographic sites in GSO [7], which is based on our observation of two types of excitation and emission spectra and two decay constants. We also investigated the temperature-dependence of the two Ce centers. At room temperature most of the Ce2 emission is thermally quenched and the Ce1 emission dominates (fig. 1 [6]). At temperatures  $< 300 \text{ K}$  the gamma-ray excited emission can be reconstructed by an appropriate combination of Ce1 and Ce2 emissions.

We have also previously studied [4], [8] the primary processes. The gamma-ray excited decay curve of GSO at room temperature has a build-up and a slow decay component (of the order of hundreds of nanoseconds). Since  $\text{Ce}^{3+}$  itself, which dominates the emission at room temperature, has a single exponential decay ( $22\text{--}25 \text{ ns}$ ), the observed slow decay with gamma-ray excitation is attributed to the slow energy transfer from the ionizing radiation to the  $\text{Ce}^{3+}$ , i.e., due to slow primary processes. A possible explanation for these slow primary processes is the resonant energy transfer from

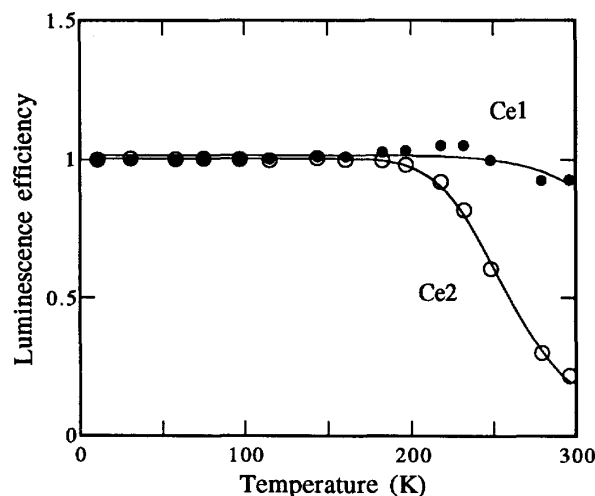


Fig. 1 Luminescence efficiency of Ce1 and Ce2 centers between 11 K and 300 K. The luminescence intensity at each temperature is normalized to the intensity at 11 K.

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$\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ . This may occur because the excited states of  $\text{Gd}^{3+}$  ion overlap the absorption bands of  $\text{Ce}^{3+}$  (fig. 2 [4]). We measured the decay rates of the  ${}^6\text{I}_7$  multiplets of  $\text{Gd}^{3+}$  as a function of  $\text{Ce}^{3+}$  concentration and showed that the decay rates linearly depend on  $\text{Ce}^{3+}$  concentration, which agrees well with theoretical predictions for resonant transfer. We also showed that the gamma-ray excited decay curves are composed of prompt  $\text{Ce}^{3+}$  emission and delayed  $\text{Ce}^{3+}$  emission (transfer of energy through  $\text{Gd}^{3+}$ ).

In the current study, to examine further the role of the  $\text{Gd}^{3+}$  in the scintillation process, we diluted  $\text{Gd}^{3+}$  with optically inactive rare earth elements, Y and Lu, and analyzed the decay kinetics of  $\text{Ce}^{3+}$  emission using UV- and gamma-ray excitations. We attempted to measure the  $\text{Gd}^{3+}$  emission decay. However, because of its weak intensity, we could not measure it; this limits our understanding of the stages of the  $\text{Gd}^{3+}$  decay, the nature of donor-donor and donor-acceptor interactions, and the migration mechanism among  $\text{Gd}^{3+}$  ions. The dilution of the  $\text{Gd}^{3+}$  is expected to increase the average  $\text{Gd}^{3+}$ - $\text{Gd}^{3+}$  distance and cause the migration of energy between  $\text{Gd}^{3+}$  ions to be slowed. Hence, the transfer from  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  also will be slowed.

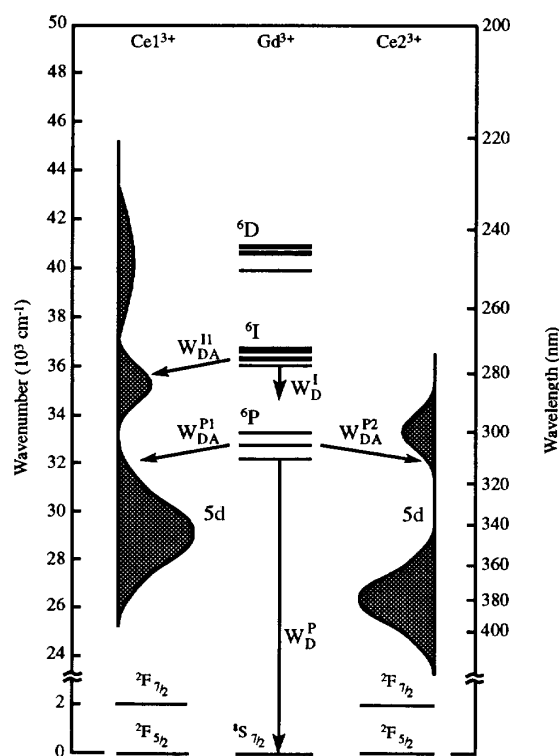


Fig. 2 Energy levels of  $\text{Gd}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{Ce}^{2+}$ .  $W_{\text{DA}}^{\text{I}}$  indicates the effective transfer rate from the  ${}^6\text{I}_7$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ ,  $W_{\text{DA}}^{\text{P}}$  represents the rate from the  ${}^6\text{P}_7$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ , and  $W_{\text{DA}}^{\text{P2}}$  indicates the rate from the  ${}^6\text{P}_7$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{2+}$ .

In analyzing the energy transfer mechanism, we follow the theory of the energy transfer developed by Burshtein [9] and Henderson et al. [10] and apply their theory to GSO. We assume that the energy transfer from  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  in GSO is dominantly non-radiative (resonant) and that the back transfer from  $\text{Ce}^{3+}$  to  $\text{Gd}^{3+}$  can be neglected [4].

When donor-donor ( $\text{Gd}^{3+}$ - $\text{Gd}^{3+}$ ) energy transfer exists in addition to donor-acceptor ( $\text{Gd}^{3+}$ - $\text{Ce}^{3+}$ ) transfer, the donor decay becomes complex. After short-pulse excitation of the donor system ( $\text{Gd}^{3+}$ ), the decay processes of the excited donor can be divided into three stages [11]:

- (1) Static ordered decay; (2) Static disordered decay; (3) Migration-limited decay.

In stage (1), the excited donors, which have nearby acceptors, decay with a high transfer probability, and the donor decay becomes exponential. This is followed by stage (2) in which the excited donors transfer their energy to the acceptors located farther from them, and the donor decay becomes non-exponential. In both stages (1) and (2), the D-A transfer probabilities are independent of donor density,  $N_{\text{D}}$ . In stage (3), the D-A energy transfer is preceded by the energy migration among  $\text{Gd}^{3+}$  ions. That is, the energy initially localized at a particular  $\text{Gd}^{3+}$  ion migrates through the  $\text{Gd}^{3+}$  sublattice until one of the  $\text{Gd}^{3+}$  ions transfers its energy to an energy sink, a  $\text{Ce}^{3+}$  ion. In this stage the  $\text{Gd}^{3+}$  decay again becomes exponential.

Since the  $\text{Gd}^{3+}$ - $\text{Gd}^{3+}$  nearest neighbor distance is small, the  $\text{Gd}^{3+}$ - $\text{Gd}^{3+}$  transfer rate must be very high; thus, the decay of the excited donors becomes exponential at an early time. Here we assume that stage (3) dominates on our time scale. As the  $\text{Gd}^{3+}$  concentration decreases by partial substitution of the Y or Lu, the separation between the  $\text{Gd}^{3+}$  increases, and the strength of the resonant energy transfer between  $\text{Gd}^{3+}$  ions is reduced. This dilution of the  $\text{Gd}^{3+}$  slows the migration of the excitation and lengthens the time required to reach the  $\text{Ce}^{3+}$ , to which the energy of the excited  $\text{Gd}^{3+}$  is then transferred irreversibly. The net result of the dilution is that the lifetime of the excited  $\text{Gd}^{3+}$  increases monotonically as the  $\text{Gd}^{3+}$  concentration decreases.

For a particular pair of ions let us define the D-D transfer rate as  $W_{\text{dd}}$ , and the D-A transfer rate as  $W_{\text{da}}$ . The notation for the transfer rates are [12]:

$$W_{\text{dd}} = C_{\text{dd}} f(R) \quad \text{and}$$

$$W_{\text{da}} = C_{\text{da}} f(R),$$

where  $R$  is the distance between the interacting ions and  $f(R)$  are the functions whose forms are determined by the nature of the D-D and D-A interactions.  $C_{\text{dd}}$  and  $C_{\text{da}}$  are the microscopic parameters for the D-D and D-A interactions, respectively. In stage (3), the macroscopic transfer rate from  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  can be described by an effective transfer rate ( $W_{\text{eff}}$ ). If the ion densities of the donors and the acceptors are

defined as  $N_D$  and  $N_A$ , the effective transfer rate  $W_{\text{eff}}$  at stage (3) can be a function of four parameters [12]:  $C_{dd}$ ,  $C_{da}$ ,  $N_D$ , and  $N_A$ .  $W_{\text{eff}}$  linearly depends on  $N_A$  regardless of the type of interaction (multipolar or exchange) between the donors, and between the donor and the acceptor. If both D-D and D-A interactions are dipole-dipole in nature,  $W_{\text{eff}}$  also linearly increases with the donor density  $N_D$ , that is,  $W_{\text{eff}}$  depends linearly on the product  $N_A \times N_D$ . The exact form of  $W_{\text{eff}}$ , however, varies depending on whether the migration is hopping-limited or diffusion-limited [13].

We choose the excited  $^6I_1$  multiplets of  $\text{Gd}^{3+}$  in analyzing the energy transfer mechanism from Gd to Ce. The different multiplets of  $^6I_1$  states are treated together since we are not concerned with the detailed optical properties. The transfer rate from  $^6P_1$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  in GSO is low [8] and is difficult to analyze on the relatively short time scale ( $< 170$  ns) of our UV excitation experiments. Transfer from the higher excited states of  $\text{Gd}^{3+}$  (e.g.  $^6D_1$  and  $^6G_1$ ) was not considered in the present analysis.

## II. EXPERIMENT

The crystals used in this experiment were grown by the Czochralski technique using raw materials ( $\text{Gd}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Lu}_2\text{O}_3$ , and  $\text{CeO}_2$ ), which have purities of at least 99.99%. GSO crystals were used as seeds. The starting melt material had chemical compositions  $(\text{Gd}_{1-x-y}\text{Ce}_x\text{Y}_y)_2(\text{SiO}_4)\text{O}$  or  $(\text{Gd}_{1-x-y}\text{Ce}_x\text{Lu}_y)_2(\text{SiO}_4)\text{O}$ . The structure of all the crystals was analyzed with the X-ray diffraction method. The exact chemical composition of all the crystals was analyzed by X-ray Assay Laboratory using inductively-coupled plasma mass spectrometry.

GSO has a monoclinic structure of space group  $P2_1/c$  [7]. Gd has two different sites (Gd1 and Gd2) in GSO. We designate the two Gd sites by Felsche's definition. Gd1 has the first three nearest neighbor Gd ions at Gd1 sites with an average distance of 3.57 Å [4]. Gd2 has, on the other hand, the first three nearest neighbor Gd ions at the Gd2 site with an average distance of 3.56 Å. In considering the energy transfer from Gd to Ce, we make no distinction between Gd1 and Gd2.

The structure of the crystals changes from  $P2_1/c$  to  $C2/c$  by partially substituting the smaller rare earths,  $\text{Y}^{3+}$  (0.910 Å) and  $\text{Lu}^{3+}$  (0.848 Å), into the  $\text{Gd}^{3+}$  (0.938 Å) site. The change of the lattice structure produces an entirely different crystal field and space group, and changes the energy splitting of the 4f-5d transitions of  $\text{Ce}^{3+}$ . In this study we, therefore, focused only on 10 diluted GSO samples, which have the monoclinic structure  $P2_1/c$  with relatively low Y (or Lu) concentration ( $y \leq 0.28$ ) (table I). The ratio of the Gd, Y, and Lu in the crystals were approximately (within 12%) the same as that in the melt. The distribution coefficient of Ce varied from  $\sim 0.55$  to  $\sim 0.81$ . The data obtained from undiluted GSO samples,  $(\text{Gd}_{1-x}\text{Ce}_x)_2(\text{SiO}_4)\text{O}$  [4], were also used in this study.

Table I

Chemical compositions of the rare earths in diluted GSO, and decay rates of the excited  $\text{Gd}^{3+}$  states ( $^6I_1$  and  $^6P_1$ ) calculated from the decay curves by fitting the eqs. (4) and (5). The fifth column indicates the decay rate ( $W_D^I + W_{DA}^I$ ) of the excited  $^6I_1$  multiplets obtained from the UV-excited decay curve. The sixth and seventh columns show the decay rates of the excited  $^6I_1$  and  $^6P_1$  multiplets calculated from the gamma-ray excited decay curves. All the decay rates are given by their reciprocals (in ns).

no.	Chemical composition $[\text{Gd}_{1-x-y}\text{Ce}_x(\text{Y or Lu})_y]_2\text{SiO}_5$			$^6I_1$ (ns)	$^6I_1$ (ns)	$^6P_1$ (ns)
	1-x-y	x	y	(UV)	( $\gamma$ )	( $\gamma$ )
1	0.96	0.0015	0.044(Y)	51	57	440
2	0.94	0.0038	0.056(Y)	33	34	395
3	0.94	0.0061	0.055(Y)	21	23	300
4	0.78	0.0016	0.22(Y)	60	74	538
5	0.72	0.0032	0.28(Y)	45	53	527
6	0.72	0.0054	0.28(Y)	30	37	370
7	0.95	0.0014	0.049(Lu)	60	61	485
8	0.84	0.0017	0.16(Lu)	59	67	567
9	0.76	0.0015	0.24(Lu)	73	85	634
10	0.75	0.0034	0.25(Lu)	48	61	491

The measurements of emission and excitation spectra were made with a SPEX Fluorolog-2 spectrofluorometer. The sample was cooled to 11 K using a CTI-CRYOGENICS refrigeration system (Model 21). The optical configuration of the spectrofluorometer with the refrigeration system has been described previously [6]. The UV excited decay curves of the diluted GSO crystals were measured using the U9B beam line of National Synchrotron Light Source at Brookhaven National Laboratory. The duration of the excitation pulse was  $\sim 1.0$  ns. The details of the experimental set up are described elsewhere [4]. The gamma-ray excited decay curves were measured with a  $^{137}\text{Cs}$  source. Both UV- and gamma-ray excited decay curves were obtained with the time-correlated single photon technique [14], and the data were analyzed with a least squares fitting routine. When diluted GSO crystals are excited by gamma rays, both Ce1 and Ce2 emit photons at room temperature. To measure selectively the decay curve of Ce1, which has an emission peak at 425 nm, a bandpass filter (CORION S40-400) was placed between the crystal and the stop photomultiplier. This filter is transparent at  $\sim 400$  nm and eliminates Ce2 emission, which has an emission peak at 480 nm.

## III. RESULTS

First, the emission and excitation spectra of 10 diluted GSO crystals were investigated using UV-excitation at room temperature. Although the emission and excitation bands of Ce2 were not well resolved because of thermal quenching, the bands of Ce1 were observed at almost the same wavelengths as observed for undiluted GSO (containing neither Y nor Lu).

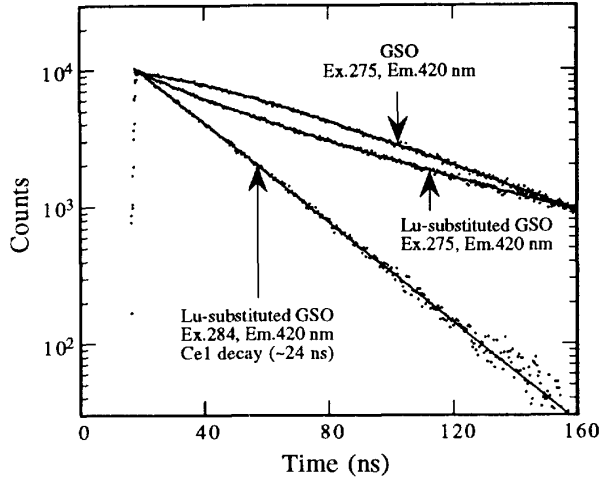


Fig. 3 UV-excited decay curves of  $(\text{Gd}_{0.99}\text{Ce}_{0.0018})_2(\text{SiO}_4)_2\text{O}$  and  $(\text{Gd}_{0.76}\text{Ce}_{0.0015}\text{Lu}_{0.24})_2(\text{SiO}_4)_2\text{O}$  (Lu-substituted GSO, crystal no. 9). The data are fit with a single exponential ( $\sim 24$  ns) or eq. (4) (solid line).

That is, the excitation bands of Ce1 were at 250, 284, and 345 nm (fig. 2). The emission band of Ce1 was at 425 nm [6].

The decay curves of the 10 diluted GSO samples were measured with excitation wavelengths of 275 nm (into  ${}^6\text{I}_J$  multiplets) and 284 nm (directly into  $\text{Ce1}^{3+}$  band), and an emission wavelength of 420 nm. All the decay curves excited at 284 nm could be fit with a single exponential ( $\sim 24$  ns) (fig. 3). That is,  $W_A^{-1} = 24$  ns. On the other hand, the decay curves

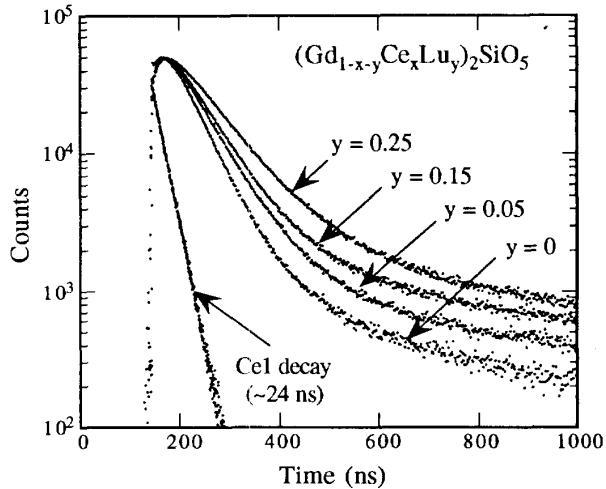


Fig. 4 Gamma-ray excited decay curves of crystals (no. 7 ~ 9) and undiluted GSO, which has a chemical composition of  $(\text{Gd}_{0.99}\text{Ce}_{0.0018})_2(\text{SiO}_4)_2\text{O}$ . The Ce1 decay from crystal (no. 9) is also shown.

excited at 275 nm show different amounts of build-up. Fig. 3 also shows the decay curves of two GSO samples (excited at 275 nm) which have approximately the same Ce concentration but have different Gd concentrations. As we expected, Lu-substituted GSO has a slower build-up, which suggests slower migration through the  $\text{Gd}^{3+}$  sublattice.

The gamma-ray excited decay curves were also measured for the 10 diluted GSO samples. The Ce2 emission, which is weak but has a fast decay constant ( $\sim 5$  ns) [8], is eliminated with the bandpass filter. Fig. 4 shows the decay curves of three Lu-substituted GSO samples and of an undiluted GSO sample. The UV-excited decay curve of the Ce1 emission ( $\sim 24$  ns) is also displayed. These four samples have approximately the same Ce concentration, i.e.,  $x$  slightly varies from 0.0014 to 0.0018. As Gd concentration decreases with the partial substitution of Lu, the decay of  $\text{Ce1}^{3+}$  (both the build-ups and the long decay components) becomes slower.

#### IV. DISCUSSION

When we analyze the energy transfer from the  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ , we ignore the transfer from  $\text{Gd}^{3+}$  to  $\text{Ce2}^{3+}$  since the spectral overlap between  $\text{Gd}^{3+}$  emission band and  $\text{Ce2}^{3+}$  absorption band is very small (fig. 2). The rate equations for  $\text{Gd}^{3+}$  and  $\text{Ce1}^{3+}$ , after initial sharp excitation, are given by [10]:

$$\frac{dN_D^*}{dt} = -W_D^I N_D^* - W_{DA}^{II} N_D^* \quad \text{and} \quad (1)$$

$$\frac{dN_A^*}{dt} = -W_A N_A^* + W_{DA}^{II} N_D^* , \quad (2)$$

where  $N_D^*$  and  $N_A^*$  are the number of excited  ${}^6\text{I}_J$  multiplets and of excited acceptors ( $\text{Ce1}^{3+}$ ), respectively.  $W_{DA}^{II}$  is the effective transfer rate from the  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce1}^{3+}$ ,  $W_D^I$  is the decay rate of the lowest  ${}^6\text{I}_J$  multiplets including transitions to both ground  ${}^8\text{S}_{7/2}$  state and the excited  ${}^6\text{P}_J$  multiplets in an isolated  $\text{Gd}^{3+}$  ion, and  $W_A$  is the decay rate of the excited 5d level of  $\text{Ce1}^{3+}$ . The solution for  $N_A^*$ , then becomes:

$$N_A^*(t) = N_D^*(0) \frac{W_{DA}^{II}}{W_A - (W_D^I + W_{DA}^{II})} \times [\exp[-(W_D^I + W_{DA}^{II})t] - \exp[-W_A t]] , \quad (3)$$

where  $N_D^*(0)$  is the number of excited donors ( ${}^6\text{I}_J$  multiplets) created at  $t=0$ . Eq. (3) describes the  $\text{Ce1}^{3+}$  decay in the case where no  $\text{Ce1}^{3+}$  ions are created at  $t=0$ . In the current study of diluted GSO, we measured the decay of  $\text{Ce1}^{3+}$  emission ( $N_A^*$ ) and examined the decay rate of the excited  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$  ( $W_D^I + W_{DA}^{II}$ ) as a function of  $N_A$  and  $N_D$  using UV- and gamma-ray excitations.

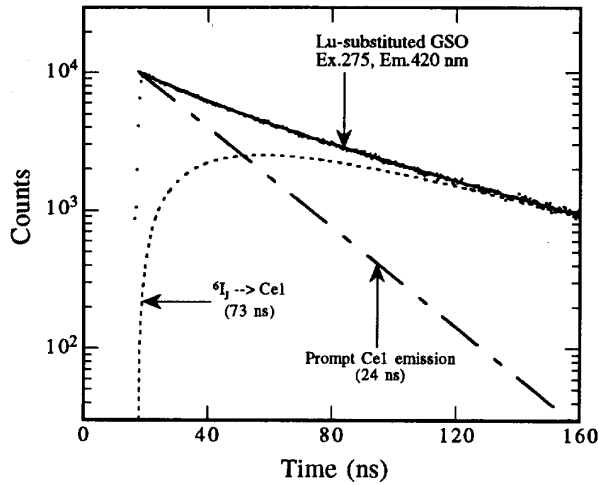


Fig. 5 The decay curve of Lu-substituted GSO (no. 9) excited at 275 nm (closed circles). The data are fit with eq. (4) (solid line) and decomposed into two curves, representing each term in eq.(4).

When GSO is excited with UV light at 275 nm, both  $Gd^{3+}$  and  $Ce^{3+}$  are excited. Thus, the decay curves of 10 diluted GSO samples excited at 275 nm were fit with the following equation:

$$N_A^*(t) = N_A^*(0) \exp\left(-\frac{t}{24}\right) + N_D^*(0) \frac{W_{DA}^{II}}{\frac{1}{24} - (W_D^I + W_{DA}^{II})} \times \{\exp[-(W_D^I + W_{DA}^{II})t] - \exp\left[-\frac{t}{24}\right]\}, \quad (4)$$

where the first term represents the direct emission from the Ce1 center (prompt Ce emission), and the second term represents the energy transfer from Gd to Ce (delayed Ce emission).  $N_A^*(0)$  is the number of excited acceptors at  $t=0$ . Fig. 5 shows, as an example, the decomposed decay curve of Lu-substituted GSO (no. 9) with UV excitation at 275 nm (emission at 420 nm), which was shown in fig. 3. The dashed line indicates the prompt emission of the Ce1 center and the dotted line represents the energy transfer from the  ${}^6I_J$  multiplets of Gd to Ce1. From figs. 3 and 5, it is clear that Lu-substituted GSO (no. 9), which has a slower build-up, has a slower decay rate of the  ${}^6I_J$  multiplets than undiluted GSO.

The decay rates ( $W_D^I + W_{DA}^{II}$ ) of the  ${}^6I_J$  multiplets of  $Gd^{3+}$  for 10 samples are displayed with the data previously taken for

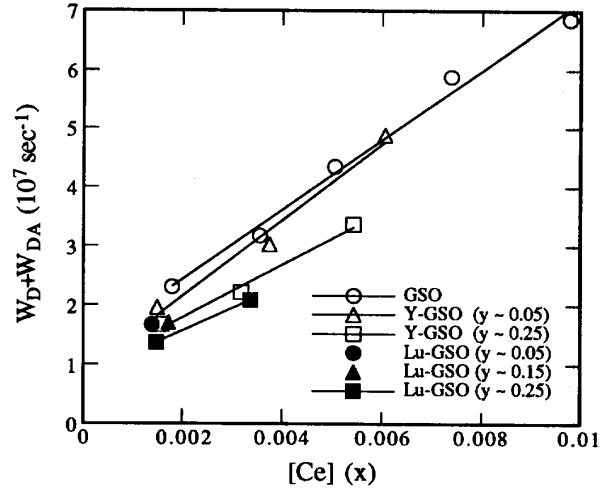


Fig. 6 The decay rates of the  ${}^6I_J$  multiplets obtained from UV-excited decay curves. The measured samples are undiluted GSO ( $y = 0$  and  $x$  varies from 0.0018 to 0.0098) and diluted GSO (crystal no. 1 ~ 10).

undiluted GSO ( $y = 0$ ) as a function of Ce concentration (fig. 6, column 5 in table I). Although the concentration of trivalent Ce was not measured, we assume that the  $Ce^{3+}$  concentration is proportional to the total Ce concentration obtained from chemical analysis. The decay rates ( $W_D^I + W_{DA}^{II}$ ) are fit with a straight line for a group of samples which have approximately the same Gd concentration. The decay rates of the diluted GSO samples which have the same Gd concentration linearly increase as the Ce concentration increases, in agreement with the functional dependence of the effective transfer rates  $W_{DA}^{II}$ .

All the straight lines intercept the vertical axis at about  $1 \times 10^7 \text{ sec}^{-1}$ . This indicates that  $W_D^I$ , which is independent of Ce concentration, is about  $1 \times 10^7 \text{ sec}^{-1}$ . Since the lowest state of the  ${}^6I_J$  multiplets, i.e.,  ${}^6I_{7/2}$  usually has a decay rate of the order of  $10^3 \sim 10^4 \text{ sec}^{-1}$  [15], the large value of  $W_D^I$  obtained from the fitting may represent the energy transfer rate from Gd to impurity centers or to quenching centers, whose contribution is not taken into account in deriving eq. (4). The existence of quenching centers such as  $Gd^{3+}$  traps (or perturbed  $Gd^{3+}$  ions) in Gd compounds has been previously reported [16], [17]. In fact, when a lightly Ce-doped GSO crystal was cooled to 11 K, we observed very strong emission at 318 nm (fig. 7). This wavelength is slightly longer than the peak wavelength of unperturbed  $Gd^{3+}$  ions (excited  ${}^6P_{7/2}$  level) and can be attributed to the perturbed  $Gd^{3+}$  ions or  $Gd^{3+}$  traps. The emission at 318 nm disappeared when the temperature was raised above 60 K.

For the same Ce concentration, the decay rates ( $W_D^I + W_{DA}^{II}$ ) decrease as the Gd concentration decreases (fig. 6). This

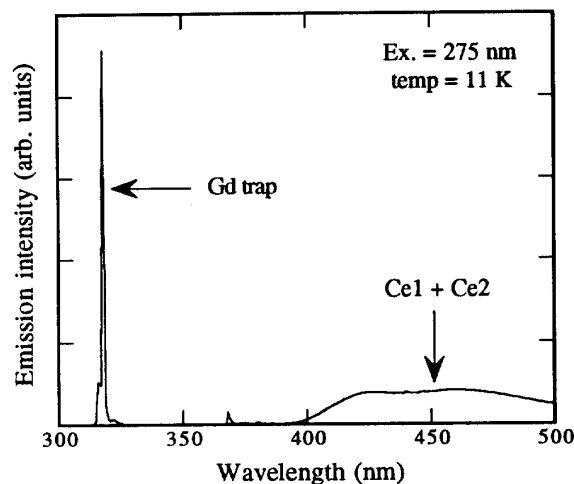


Fig. 7 Emission spectrum of  $(\text{Gd}_{0.99}\text{Ce}_{0.00035})_2(\text{SiO}_4)\text{O}$ .

dependence of the decay rates on the Gd concentration, as previously stated, suggests that the donor decay is in stage (3), since the transfer rates from Gd to Ce in stages (1) and (2) are independent of the Gd concentration. This dependence also suggests that the dilution of Gd causes the longer migration time through the Gd and results in the slower energy transfer to Ce. Although we do not know the nature of the Gd-Gd and the Gd-Ce interactions in GSO, we attempted to correlate the decay rates with Gd concentration by plotting the decay rates vs. the product of Ce concentration and Gd concentration,  $[\text{Ce}] \times [\text{Gd}]$  (fig. 8). The decay rates depend linearly on the  $[\text{Ce}] \times [\text{Gd}]$  product, suggesting that both Gd-Gd and Gd-Ce interactions for the excited  ${}^6\text{I}_J$  multiplets are dipole-dipole in nature.

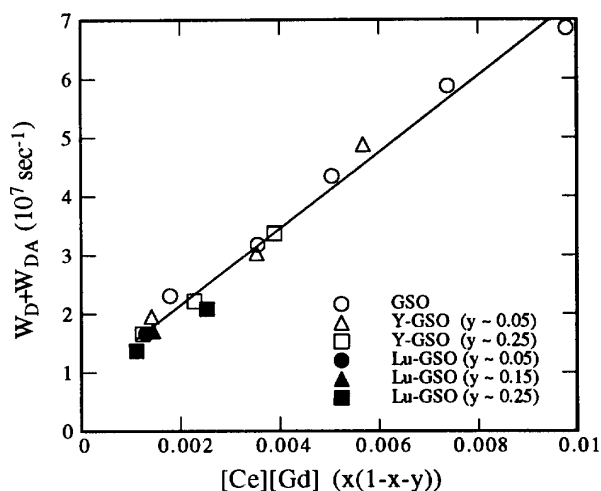


Fig. 8 The same decay rates as in fig. 4, but displayed as a function of  $[\text{Ce}] \times [\text{Gd}]$ .

We fit the gamma-ray excited decay curves [4] with the following equation:

$$\begin{aligned}
 N_A^*(t) = & N_A^*(0) \exp\left(-\frac{t}{24}\right) \\
 & + N_D^{I*}(0) \frac{W_{DA}^{II}}{\frac{1}{24} - (W_D^I + W_{DA}^{II})} \\
 & \times \left\{ \exp\left[-(W_D^I + W_{DA}^{II})t\right] - \exp\left[-\frac{t}{24}\right] \right\} \\
 & + N_D^{P*}(0) \frac{W_{DA}^{PI}}{\frac{1}{24} - (W_D^P + W_{DA}^{PI} + W_{DA}^{P2})} \\
 & \times \left\{ \exp\left[-(W_D^P + W_{DA}^{PI} + W_{DA}^{P2})t\right] - \exp\left[-\frac{t}{24}\right] \right\} \quad (5)
 \end{aligned}$$

which is based on the assumption that after gamma rays are absorbed in the crystal, excited  $\text{Ce}^{3+}$  ions,  $(\text{Ce}^{3+})^*$ , and excited  $\text{Gd}^{3+}$  ions,  $(\text{Gd}^{3+})^*$ , are immediately created. We assume that the build-up of the gamma-ray excited decay is due to the energy transfer from  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ , and that the slow decay is due to the transfer from  ${}^6\text{P}_J$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  and  $\text{Ce}^{2+}$ , whose decay equation is not shown. We thus ignore the energy transfer from other excited states of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$  in this simple model of the scintillation processes. Thus, the first term in eq. (5) indicates the prompt emission from Ce1, the second term represents the Ce1 emission through the  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$ , and the third term represents the Ce1 emission through the  ${}^6\text{P}_J$  multiplets.  $N_A^*(0)$ ,  $N_D^{I*}(0)$ , and  $N_D^{P*}(0)$  are the populations of excited Ce1, of the excited  ${}^6\text{I}_J$  multiplets, and of the excited  ${}^6\text{P}_J$  multiplets, at  $t=0$ . The last two terms indicate the delayed Ce1 emission. The curves from the fit of the decay of crystal (no. 8) is shown in fig. 9 (the  $y=0.16$  curve of fig. 4).

The decay rates of the  ${}^6\text{I}_J$  multiplets ( $W_D^I + W_{DA}^{II}$ ) and those of the  ${}^6\text{P}_J$  multiplets ( $W_D^P + W_{DA}^{PI} + W_{DA}^{P2}$ ) calculated from the gamma-ray excited decay curves are shown (table I). The decay rates of the  ${}^6\text{I}_J$  multiplets agree well with the decay rates obtained with UV excitation for lightly diluted GSO ( $y \leq 0.16$ ) (table I). However, the differences in the decay rates between UV- and gamma-ray excitation become larger for more heavily diluted crystals ( $y \sim 0.25$ ). The reasons for this difference are not clear.

In fig. 4, the concentration-dependence of the build-ups and the slow components on Gd is shown. Since the Ce concentration is about the same for these samples, the contribution of the prompt Ce1 emission to the total emission is approximately the same [4]. Thus, the decrease in the amount of build-up with increasing Gd concentration is due to the increase of the transfer rate from the  ${}^6\text{I}_J$  multiplets of  $\text{Gd}^{3+}$  to  $\text{Ce}^{3+}$ . Similarly, the slow component, which is due to the

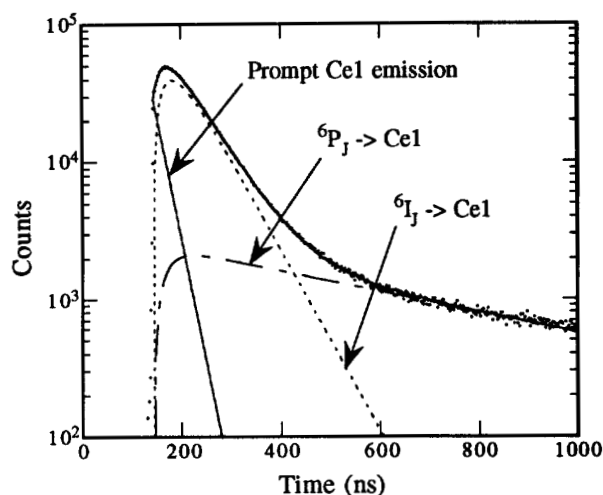


Fig. 9 The gamma-ray excited decay curve of crystal (no. 8). The data are fit with eq. (5) and decomposed into three curves.

energy transfer from the  ${}^6P_J$  multiplets of  $Gd^{3+}$  to  $Ce^{3+}$ , becomes shorter as the Gd concentration increases.

The decay rates of the  ${}^6I_J$  multiplets calculated from the UV-excited decay curves depend linearly on the  $[Ce] \times [Gd]$  product (fig. 8), which agrees with our assumption that the  $Y^{3+}$  and  $Lu^{3+}$  ions are optically inactive in this UV region and simply increases the average Gd-Gd distances. However, the decay rates of the  ${}^6I_J$  multiplets obtained from the gamma-ray excited decay curves of the heavily diluted GSO are much longer than the decay rates from UV-excited decay curves. Since for undiluted GSO the decay rates between UV- and gamma-ray excitation agree [4], the longer decay rates obtained with gamma-ray excitation for diluted GSO must be related to the substitution of Y and Lu. Lempicki et al. [18] reported the presence of the slow energy transfer to the  $Ce^{3+}$  in the gamma-ray excited decay curve of  $YPO_4:Ce$ . Although they didn't observe slow decay components for  $LuPO_4:Ce$ , the substitution of Y and Lu into GSO may introduce other channels which slowly transfer energy to either  $Gd^{3+}$  or  $Ce^{3+}$  when diluted GSO is exposed to ionizing radiation.

Let us now consider why undiluted GSO, which is currently used in oil-well logging application [19], [20], is a relatively good scintillator. In order to do this, we also consider the role of Gd in the scintillation processes of undiluted GSO. As discussed above, the Gd introduces additional channels in the excitation process of  $Ce^{3+}$ , which is, without the Gd, promptly excited by recombination of holes and electrons and immediately emits photons with a single exponential decay of ~24 ns. However, the energy transfer from the  ${}^6P_J$  and  ${}^6I_J$  multiplets of excited  $Gd^{3+}$  to  $Ce^{3+}$  lengthens the scintillation decay of GSO, though the high Gd concentration in GSO slightly shortens the migration

time through the Gd sublattice. The existence of energy sinks such as  $Ce^{3+}$  and Gd traps fortunately accelerates the energy transfer and contributes to the shortening of the scintillation decay. We can, thus, decrease the scintillation decay time by adding Ce or quenching centers such as Gd traps to GSO. The high concentrations of Gd, Ce and quenching centers are essential factors and all contribute to the shortening of the scintillation decay of GSO, as seen in fig. 8.

For maximizing the emission intensity, the existence of Gd is again not ideal. The Gd introduces Gd traps, which release their acquired energy to the lattice at elevated temperatures (> 60 K) (see fig. 7). On the other hand, the existence of  $Ce^{3+}$ , if its concentration level is low, is considered to be preferable because its quantum efficiency at room temperature is high (~0.9 for Ce1). However, as the total Ce concentration increases, the concentration of Ce2, which has low quantum efficiency (~0.1) at room temperature (see fig. 1), also increases. Because of its low quantum efficiency, Ce2 unfortunately acts as a quenching center at room temperature and reduces the total light output.

From the above discussion, it is not clear that the existence of Gd in GSO is particularly favorable. We see that only a very unique combination of Gd, Gd traps, Ce1 and Ce2 makes GSO a relatively good scintillator. If we could remove Gd from GSO, we might improve the scintillation properties. It is interesting to note that Ce-doped lutetium oxyorthosilicate  $Lu_2(SiO_4)O:Ce$  (LSO) [21], [22] behaves like GSO without Gd might behave, when it is excited by gamma-ray radiation. The crystal structure of LSO (C2/c) is different than that of GSO (P2<sub>1</sub>/c). As a result, the temperature dependences of two  $Ce^{3+}$  centers in LSO are worse than those in GSO, and the band structures of two  $Ce^{3+}$  centers in LSO are different than those in GSO. However, its decay curve can be described by a simple summation of single exponential decays of Ce1 (~32 ns) and Ce2 (~47 ns) centers [23], and its light output is three times as high as that of GSO. Apparently, the slow energy transfer and trap emission observed for GSO have not been seen for LSO which does not have the  $Gd^{3+}$  ions. If one could grow a p-type (P2<sub>1</sub>/c) cerium-doped rare earth oxyorthosilicate crystal free from energy transferring and trapping centers such as  $Gd^{3+}$  ion, the scintillation properties of this crystal might be much superior to those of GSO and LSO.

Future work on GSO should be directed toward the better understanding of the energy transfer from ionizing radiation to  $Ce^{3+}$  and  $Gd^{3+}$  centers, since the energy capture processes of  $Ce^{3+}$  and  $Gd^{3+}$  are still not clear.

## V. SUMMARY

The decay rate of the  ${}^6I_J$  multiplets of  $Gd^{3+}$  was investigated for Y- or Lu- substituted GSO using UV- and gamma-ray excitations. The decay rates obtained with two different excitation methods for lightly diluted GSO samples agree and suggest that the migration through the Gd slows down with the substitution of Y or Lu and leads to a delay in

the overall transfer rate from Gd to Ce. The decay rates obtained from UV excitation have a linear dependence on the product  $[Ce] \times [Gd]$ , which suggests that both Gd-Gd and Gd-Ce interactions for the excited  $^6I_7$  multiplets have dipole-dipole character. The decay rates obtained with UV excitation have a term independent of the Ce concentration, which suggests the existence of impurity centers or quenching centers. We, in fact, observe strong emission which is different than regular  $Gd^{3+}$  emission and attribute it to a Gd trap. A large difference in the decay rates between UV- and gamma-ray excitation was observed for heavily diluted GSO, which suggests that the substitution of Y and Lu introduces other channels of energy transfer when the diluted GSO is excited by gamma-ray radiation. We found that the high concentrations of Gd, Ce and quenching centers are essential in producing the fast scintillation decays. However, we also found that the high concentrations of Gd and Ce introduce quenching centers such as a Gd trap and  $Ce_2$ , and result in lower light output than might otherwise be achieved.

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