

Light Emission Mechanism of $\text{Lu}_2(\text{SiO}_4)\text{O}:\text{Ce}$

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Abstract

Lutetium oxyorthosilicate $\text{Lu}_2(\text{SiO}_4)\text{O}$ has two crystallographically independent lutetium sites. When it is doped with Ce, the dopant Ce is assumed to occupy two different sites and thus the existence of two activation centers (called "Ce1" and "Ce2") was proposed. UV and gamma-ray excited spectra clearly indicate that two activation centers exist in cerium-doped lutetium oxyorthosilicate $\text{Lu}_2(\text{SiO}_4)\text{O}:\text{Ce}$ (LSO).

I. INTRODUCTION

Ce-doped lutetium oxyorthosilicate (LSO) was recently introduced as a potential single crystal scintillator [1], which has a high density, high effective atomic number for efficient gamma-ray detection, reasonably high light output and fast scintillation decay time, compared with conventional scintillators such as $\text{NaI}(\text{Tl})$ and bismuth germanate $\text{Bi}_4\text{Ge}_3\text{O}_{12}$.

The host material $\text{Lu}_2(\text{SiO}_4)\text{O}$ is one of the oxyorthosilicates $\text{RE}_2(\text{SiO}_4)\text{O}$ (RE = rare earth) [2] which display two different structure types. One structure type is stable for the large rare earths, La to Tb, and forms the monoclinic structure of space group $P2_1/c$. The rare earths in this structure occupy two crystallographically different sites. One site has an oxygen coordination number of 7 and the other site has 9. The other structure type includes the smaller rare earths, Dy to Lu, and has the monoclinic structure of space group $C2/c$ [3]. The rare earths in this group have 6 or 7 oxygen ligands. $\text{Lu}_2(\text{SiO}_4)\text{O}$ belongs to the latter group, namely, the monoclinic structure $C2/c$.

When $\text{RE}_2(\text{SiO}_4)\text{O}$ is doped with Ce, the Ce substitutes for the host rare earth and exists as Ce^{+3} ion. The Ce^{+3} ion has one electron in the 4f shell, and the light emission is based on the electronic transition from the lowest 5d energy level to two 4f ground levels, which have an energy separation of $\sim 2253 \text{ cm}^{-1}$ from the spin-orbit interaction [4]. The typical decay time of Ce^{+3} is of the order of tens of nanoseconds [5]. Since there are two crystallographically independent rare earth sites in

$\text{RE}_2(\text{SiO}_4)\text{O}$, it is reasonable to assume that there are also two Ce^{+3} sites in $\text{RE}_2(\text{SiO}_4)\text{O}:\text{Ce}$. In fact, our previous study [6] revealed that Ce-doped gadolinium oxyorthosilicate $\text{Gd}_2(\text{SiO}_4)\text{O}:\text{Ce}$ (GSO), which has the $P2_1/c$ structure type, has two Ce sites and that these two activation centers contribute to the emission excited by gamma-ray radiation. Although LSO has a different structure ($C2/c$) than GSO ($P2_1/c$), it also has two crystallographically independent lutetium sites. Thus it is natural to assume that there are also two Ce^{+3} sites, i.e., two activation centers in LSO. The two-activation-center model has been investigated for its applicability in describing the scintillation mechanism in LSO.

II. EXPERIMENT

The LSO single crystal used in this study was grown by the Czochralski technique in our laboratory using raw materials with purities of at least 99.99%. Iridium wire was used as a seed. The Ce concentration in the melt from which the crystal was grown was 0.125% relative to the lutetium content. However, because of the large difference in the ionic radius between the Lu^{+3} ion (0.848 Å) and the Ce^{+3} ion (1.034 Å), the distribution coefficient of Ce in the crystal is very small. The Ce concentration in the crystal was analyzed by X-ray Assay Laboratories to be 0.0258% relative to Lu. The calculated distribution coefficient of Ce in LSO is thus ~ 0.2 , in contrast with the greater distribution coefficient ~ 0.56 of Ce in GSO [7]. The structure of this crystal was analyzed by the powder x-ray diffraction method. The result confirmed that LSO had a monoclinic C structure.

The experimental equipment has been described in detail elsewhere [6]. Excitation and emission spectra between 11 and 300 K were measured with a SPEX Fluorolog-2 spectrofluorometer equipped with a helium refrigerator. For temperatures above 300 K, an LS-100 (Photon Technology International, Inc.) spectrophotometer equipped with a resistively heated copper sample holder was used. Decay time data were obtained by operating the LS-100 in a pulsed mode. Low temperature decay data were obtained by sample immersion in organic solvents frozen by liquid nitrogen. Decay data above room temperature were obtained with the same heated copper sample holder.

III. RESULTS

GSO has two crystallographically independent Gd^{+3} sites and the existence of two activation centers (Ce1 and Ce2) was proposed for the following reasons [6]:

(1) When GSO was excited with UV light, two different decay times, two types of excitation spectra and two types of emission spectra were observed.

(2) The absorption spectra have two types of Ce^{+3} absorption bands whose wavelengths correspond to the excitation bands of two different Ce^{+3} sites.

(3) The temperature-dependence of the decay times is identical with the temperature-dependence of the emission efficiencies between 11 and 300 K for each Ce^{+3} luminescence center.

(4) There exist, in fact, two crystallographically independent sites of the Ce^{+3} ion in GSO.

The confirmation of the two-activation-center model for GSO was that the gamma-ray excited emission spectra could be duplicated by adding the appropriately weighted UV-excited emissions of Ce1 and Ce2 at all temperatures between 11 and 300 K.

By analogy with GSO, UV excited emission and excitation spectra were examined for LSO. Similar to GSO, two types of excitation and emission spectra were obtained with UV-excitation. Fig. 1 shows two excitation spectra at 11 K which have emission wavelengths of 390 nm (marked "1") and 500 nm (marked "2"). The excitation spectrum "1" has excitation bands at 263, 296 and 356 nm, while spectrum "2" has excitation bands at 326 and 376 nm.

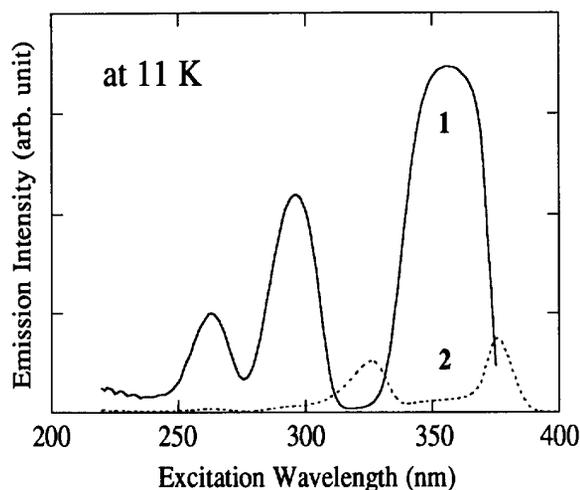


Figure 1. Excitation spectra of LSO at 11 K. The excitation spectra were measured at the two emission wavelengths of 390 nm (solid curve) and 500 nm (dashed curve).

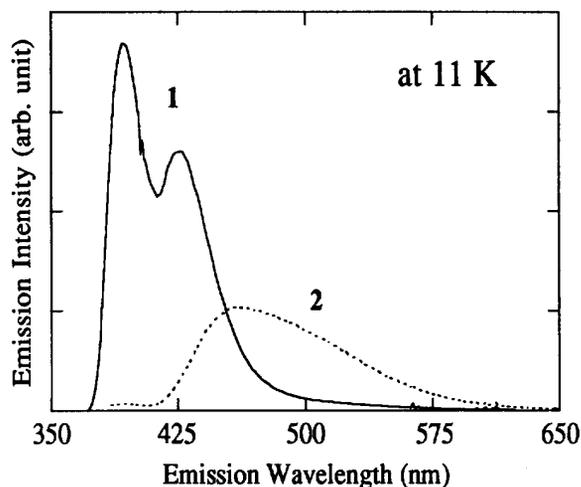


Figure 2. Emission spectra of LSO at 11 K. The two emission spectra have excitation wavelengths of 356 nm (solid line) and 376 nm (dashed line).

The measurements of emission spectra were made using excitation wavelengths corresponding to the strongest and lowest excitation bands in spectra "1" and "2" of Fig. 1, i.e., 356 and 376 nm. Fig. 2 displays two emission spectra excited at 356 nm (marked "1") and 376 nm (marked "2"). The spectrum "1" has two emission peaks at 393 and 427 nm, showing the characteristic transition of the Ce^{+3} ion from the 5d level to the two 4f ground states. The spectrum "2" has an emission peak at 460 nm, for which the Ce^{+3} doublet structure cannot be seen.

Since there are two crystallographically independent sites of the Ce^{+3} ions, it is reasonable to attribute the two types of excitation and emission spectra to the two Ce^{+3} sites in LSO. For convenience, we will refer to these centers as Ce1 and Ce2. We arbitrarily designate Ce1 as the center responsible for excitation bands at 263, 296 and 356 nm (curve "1" in Fig. 1) and Ce2 as the center responsible for excitation bands at 326 and 376 nm (curve "2" in Fig. 1). It follows that the emissions at 393 and 427 nm are due to Ce1 (curve "1" in Fig. 2), and the emission at 460 nm is due to Ce2 (curve "2" in Fig. 2).

If the lowest excited level of the Ce^{+3} ions, i.e., the lowest 5d level for each site is excited by UV light, both the decay time $\tau(T)$ and luminescence efficiency $\eta(T)$, which are functions of temperature, should satisfy the characteristic fluorescence relation [8]

$$\tau(T) / \tau(0) = \eta(T) / \eta(0)$$

By comparing the temperature-dependence of the decay time and luminescence efficiency from these lowest 5d levels to the 4f ground state level, it is theoretically possible to test the existence of two luminescence centers. But, it was difficult to

measure the luminescence efficiency of Ce2 above 80 K as the broadening of the Ce1 excitation band over the Ce2 excitation band becomes significant and the Ce2 emission was no longer resolved from the Ce1 emission above 80 K. In the discussion below, for the Ce2 center we present only the decay time at 77 K. And for Ce1 center both the decay time and luminescence efficiency are displayed as a function of temperature.

The decay time of Ce1 and Ce2 has been measured at 77 K. The decay curves were obtained by excitation into the lowest 5d level. The pulse shape of the N₂ flash lamp, which has about a 6 ns duration and a long decaying tail, was deconvoluted from the decay data that were then fit with a single exponential. The excitation and emission wavelengths were chosen to minimize overlap of the emission curves of the two Ce sites. The decay curve of Ce1 has excitation and emission wavelengths of 358 and 400 nm, respectively. The decay curve of Ce2 has excitation and emission wavelengths of 381 and 480 nm, respectively. The calculated decay times are 32 ns for the Ce1 and 54 ns for the Ce2.

Fig. 3 shows the decay time (Ex.358, Em.400 nm) and luminescence efficiency (Ex.356 nm) of Ce1 as functions of temperature with the excitation into the lowest 5d level of Ce1. The rollover point of the decay time is near 300 K. This trend in the temperature-dependence of the decay time is similar to the behavior of the luminescence efficiency.

IV. DISCUSSION

The temperature-dependence of decay time and luminescence efficiency in GSO were shown for each center [6]. In GSO the temperature-dependence of Ce1 was different than that of Ce2 so that it was clear that there were two activation centers in GSO. In LSO, however, the spectra of Ce2 cannot be well

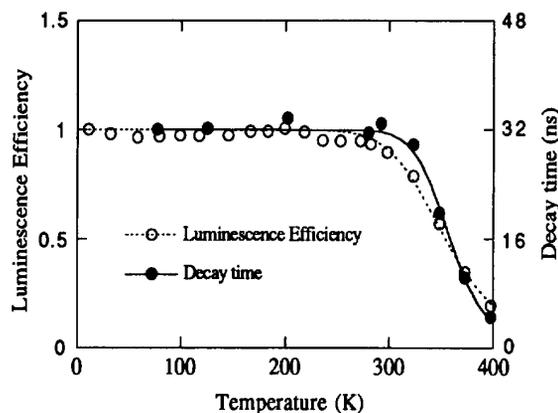


Figure 3. The decay time (filled circle) and the luminescence efficiency (open circle) of Ce1 in LSO as functions of temperature. The emission intensity and decay time obtained at each temperature was normalized to the intensity at 11 and 77 K, respectively.

resolved above 80 K and the existence of Ce2 cannot be confirmed.

However, the fact that the gamma-ray excited emission curve can be simulated by the UV excited emissions of Ce1 and Ce2 supports the existence of two activation centers. For the emission spectrum at 11K, where the two Ce emissions are clearly resolved, the gamma-ray (²⁴¹Am) excited emission spectrum can be reproduced by adding the emission spectra of Ce1 and Ce2 in a ratio of 55:45. This agreement supports our assumption that there are two activation centers in LSO.

V. SUMMARY

Two types of excitation and emission spectra with UV-excitation were shown at 11 K for LSO. Since there are two crystallographically independent lutetium sites in LSO, the existence of two Ce activation centers (two-activation-center model) was proposed. The existence of two different decay time constants of the order of tens of nanosecond, which are characteristic for fast Ce emission, were shown at 77 K. Although the temperature-dependence of the decay time and the luminescence efficiency could not be measured for the Ce2, the fact that the gamma-ray excited emission can be reconstructed from a weighted combination of the Ce1 and Ce2 emission spectra supports the two-activation-center model for LSO.

VI. REFERENCES

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