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Intrinsic trapping sites and ion-lattice coupling parameters of cerium-doped lutetium oxyorthosilicate

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ABSTRACT

Cerium-doped lutetium oxyorthosilicate (LSO:Ce) is an excellent scintillator due to its fast decay time (~ 40 ns), excellent brightness ($>3\times$ bismuth germanate), and high density (7.4 gm/cm^3). However, the luminescence process in this technologically important scintillator is not well understood. Elucidation of electronic traps and their role in scintillator afterglow is lacking and fundamental ion-lattice coupling parameters have not been established. From thermally stimulated luminescence and emission spectra data on several oxyorthosilicates we show the traps to be intrinsic and uniquely associated with the $C2/c$ crystal structure. Temperature dependent optical absorption measurements reveal prominent Gaussian bands at 3.432 eV (peak a), 3.502 eV (peak b), 4.236 eV (peak c) and 4.746 eV (peak d). The second moments are well described by the usual linear coupling model yielding the Huang-Rhys parameter and vibrational quantum energies for each peak. Oscillator strengths of the $4f \rightarrow 5d$ transitions are calculated from Smakula's formula and knowledge of the cerium distribution between the two crystallographically inequivalent sites. From the known correlation between average Ce-ion-ligand distance and oscillator strength we conclude that peak a is correlated with the seven-oxygen-coordinated site, and peaks b, c and d are associated with the six-oxygen-coordinated site.

Keywords: Lutetium oxyorthosilicate, scintillator, thermally stimulated luminescence, optical absorption

1. INTRODUCTION

The favorable scintillation properties of rare-earth based oxyorthosilicates activated with cerium are well known and have been thoroughly discussed in the literature.¹⁻³ LSO:Ce is particularly interesting because it exhibits excellent light yield ($>3\times$ bismuth germanate), relatively high density (7.4 gm/cm^3), and fast decay time (~ 40 ns). The results of various experimental studies, including thermally stimulated luminescence (TSL),⁴⁻⁶ optical absorption,^{7,8} and emission spectra,⁹ have established the important role of Ce ions in the LSO:Ce scintillation process. Incorporation of these activator ions into the host lattice occurs via substitution for the Lu^{3+} ions during crystal growth. The LSO structure is monoclinic with space group $C2/c$, and exhibits two crystallographically inequivalent rare-earth sites coordinated with six or seven oxygens. Introduction of Ce is therefore expected to yield a similar lattice with Ce^{3+} ions occupying two distinctly different sites. Based on excitation and emission spectra data, Suzuki *et al.*⁹ have shown that LSO:Ce emission is characterized by two bands, the first consisting of maxima at 393 and 427 nm, and the second with maxima at 460 nm. They arbitrarily labeled the site responsible for the double-peaked emission as Ce1, and the other as Ce2. Furthermore, for temperatures exceeding about 80 K, they showed that Ce2 emission was very weak and obscured by the more intense emission from site Ce1. The characteristic room temperature spectrum of LSO:Ce is the double-peaked emission from site Ce1, which is attributed to electronic deexcitation from the lowest crystal-field split level of the $5d$ manifold to the spin-orbit split $4f$ doublet. A simplified energy level diagram of the Ce^{3+} ion consists of the excited state $5d$ level, comprised of five lines with energy spacing approximately 0.35 eV, and the $4f$ doublet ground state with energy splitting approximately 0.25 eV.¹⁰ The correlation of sites Ce1 and Ce2 with absorption bands and the appropriate oxygen coordination has not been established. In the present work we use temperature-dependent optical absorption data to extract fundamental ion-lattice parameters in LSO:Ce, including vibrational quantum

energy and ion-lattice coupling magnitude (Huang-Rhys parameter), as well as oscillator strengths of the absorption bands. From the known correlation between oscillator strength and metal-ion-ligand spatial separation in similar materials, we correlate the absorption bands in LSO:Ce with their respective coordination numbers.

An unwanted characteristic of LSO:Ce is afterglow, *i.e.*, light emitted at times exceeding a few scintillator decay lifetimes. For imaging applications this is especially deleterious. Thermally stimulated luminescence studies have shown that LSO:Ce is characterized by the presence of several glow peaks, the main one occurring near 375 K. These peaks result from thermal release of charges that have been trapped at defect sites within the lattice. Because the main TSL glow peak occurs very near room temperature it has been suggested that it is responsible for the unwanted afterglow.^{4,6} However, identification of the defect responsible for this trapping site has not been established. Dorenbos *et al.*⁵ have proposed a center-to-center recombination model for TSL in LSO:Ce whereby Ce^{3+} is the charge donor, recombination center, and trap-creating defect. In this model the traps are considered to be intrinsic in origin and likely associated with specific configurations of oxygen ions around the central Ce^{3+} ions. In the present work we examine the TSL glow curve of LSO:Ce and compare it to glow curves of other similar oxyorthosilicates. The results support the conclusion that the traps are intrinsic and associated with the oxygen configuration not only near the Ce^{3+} ions, but near the host lanthanide ions as well. In other words, promulgation of an appropriate trapping model does not require the presence of Ce^{3+} ions.

2. EXPERIMENT

2.1. Sample characterization

Single-crystal samples of LSO:Ce of varying dimensions were used in TSL and optical absorption measurements. Specimens were cut from boules that had been grown by the Czochralski method. Cerium concentration in the melt was 0.25 at. % relative to Lu^{3+} , but because the Ce ion is much larger than Lu (1.034 vs 0.848 Å) there was a much smaller Ce content in the extracted crystal. Assuming a crystal-to-melt distribution coefficient of 0.22² implies a Ce concentration of 0.055 at. %. A single crystal of cerium-doped gadolinium oxyorthosilicate (GSO:Ce), which was used in TSL experiments, was obtained from Hitachi Chemical Company; the stated cerium concentration in the melt was 0.25 at. % relative to Gd^{3+} . The crystal-to-melt coefficient for GSO:Ce is 0.6¹¹, thus yielding a Ce concentration of 0.15 at. %.

Samples used in TSL experiments had typical dimensions $2 \times 2 \times 1 \text{ mm}^3$, whereas the specimen utilized for optical absorption had dimensions $1 \text{ cm}^2 \times 0.065 \text{ cm}$ thickness. This latter sample was optically polished to obtain parallel opposing faces with an rms surface roughness of 0.7 nm.

2.2. Optical measurements

Thermally stimulated luminescence glow curves were obtained in the interval 300 – 650 K with a Harshaw Model 3500 reader operating at a linear heating rate of 5 K/s. Glow peaks were induced by x irradiating (50 kV, 40 mA) the samples to a total dose in air of 120 Gy. Room temperature emission spectra were recorded during continuous x-ray excitation by passing a portion of the emitted light through an optical fiber and onto the entrance slit of a 1/4 m monochromator and collecting it with a charge-coupled-device detector. Emission spectra were not corrected for nonlinearities of the spectrophotometer.

Optical absorption measurements were made with a Cary 5E spectrophotometer modified to accommodate an optical cryostat for acquiring data in the interval 10 – 300 K. Data were taken at 10 and 20 K, and at each 20-K interval thereafter up to 300 K. Sample temperature was measured with a carbon-glass resistor and controlled to within $\pm 2 \text{ K}$ of each set point by a LakeShore Cryotronics Model 340 temperature controller. After reaching each set point, and prior to making the optical absorption measurement, the sample was maintained at that value for 10 min to ensure that thermal equilibrium had been attained. Raw data were acquired as absorbance and plotted as decadic absorption coefficient α ($\alpha = 0.434\kappa$, where κ is the absorption coefficient to base e) vs energy.

3. RESULTS AND DISCUSSION

3.1. Optical absorption

Optical absorption spectra of LSO:Ce taken at 300 K (solid line) and 10 K (dotted line) are shown in Fig. 1. Each spectrum exhibits four prominent peaks with maxima near 3.4, 4.2, 4.7, and 5.7 eV. Above approximately 100 K a small additional peak appears near 6.2 eV, and below approximately 100 K an additional peak is resolved near 3.8 eV. The peaks are all attributed to Ce^{3+} absorption. Note that the band edge occurs near 6.5 eV. Careful analysis of the absorption spectrum shows the main band near 3.4 eV to be comprised of two closely spaced bands as indicated in Fig. 2. Utilizing a Levenberg-Marquardt nonlinear least-squares fitting procedure we found that all bands in the spectrum were well described by a Gaussian profile.

FIG. 1. Representative optical-absorption spectra of LSO:Ce. Data were taken at 300 K (solid line) and 10 K (dotted line).

Results of spectral analyses yield four peaks with maxima at 3.432 ± 0.002 eV (peak a), 3.502 ± 0.002 eV (peak b), 4.236 ± 0.0002 eV (peak c), and 4.746 ± 0.0002 eV (peak d). The absorption spectra are in excellent agreement with the excitation spectra data of Suzuki *et al.*⁹ A comparison of the present absorption data with their excitation spectra suggests that absorption peak a is correlated with site Ce2, and peaks b, c, and d are associated with site Ce1.

3.2. Ion-lattice coupling parameters

The ground-state energy level of an impurity ion in a host lattice can be described as a classical quantum-mechanical harmonic oscillator with quantum energy spacing $\hbar\omega$. Assuming identical vibrational frequencies of the ground and excited state, this model predicts that the width of the impurity absorption band, taken as full width at half maximum as a function of temperature, obeys the relation

$$W(T) = W(0) \left[\coth \left(\frac{\hbar\omega}{2kT} \right) \right]^{1/2}. \quad (1)$$

For a Gaussian line shape this is written

$$W(T) = \hbar\omega \left[8S \ln 2 \coth\left(\frac{\hbar\omega}{2kT}\right) \right]^{1/2}, \quad (2)$$

where S is a dimensionless measure of the ion-lattice coupling magnitude, often referred to as the Huang-Rhys factor.

FIG. 2. 10-K absorption spectrum (solid line) of LSO:Ce with Gaussian fits (dotted lines).

FIG. 3. Temperature dependence of absorption-band widths a,b,c, and d.

The filled symbols in Fig. 3 are the temperature-dependent widths of the four prominent absorption bands. Errors are smaller than the plot symbols. The solid lines represent best fits of the data to Eq. (2) with the extracted parameters given in Table I.

TABLE I. Electron-lattice coupling parameters.

Peak	$W(0)$ (eV)	ω (10^{13} s^{-1})	S
a	0.105	2.74	6.1
b	0.156	3.85	6.8
c	0.242	4.06	14.7
d	0.297	5.17	13.7

S values for peaks c and d are more than twice as large as those characterizing peaks a and b, indicating that their excited-state energy levels are considerably more diffuse. Systems characterized by $S > 5$ are in the strong-coupling regime and exhibit a large Stokes shift, which for LSO is ~ 0.50 eV.

3.3. Oscillator strengths

For Gaussian absorption bands the oscillator strength f is given by Smakula's formula

$$Nf = 8.7 \times 10^{16} \text{ cm}^{-3} \frac{n}{(n^2 + 2)^2} \alpha_{\text{max}} W, \quad (3)$$

with concentration of absorbing centers N , index of refraction n , maximum absorption α_{max} and full width at half maximum W . From the measured absorption, index of refraction (1.82), and known concentration of Ce^{3+} , we compute oscillator strengths of the four bands a, b, c, and d. Although the Ce^{3+} concentration is 0.055%, it is not uniformly distributed between the two inequivalent cerium sites. Based on integrated emission intensities, Naud *et al.*¹² found the ratio of respective site concentrations to be $[\text{Ce1}]/[\text{Ce2}] = 4.11$. Accordingly, we assign the Ce distribution as 80% to site Ce1 and 20% to site Ce2, thus yielding concentrations $[\text{Ce1}] = 4.290 \times 10^{18} \text{ cm}^{-3}$ and $[\text{Ce2}] = 1.073 \times 10^{18} \text{ cm}^{-3}$. Computed oscillator strengths, shown in Fig. 4, indicate a weak temperature dependence for peaks b, c, and d, but a relatively strong dependence for peak a. Recall that peak a is associated with site Ce2, whereas the other peaks are associated with site Ce1.

FIG. 4. Temperature dependence of absorption band oscillator strengths.

Williams *et al.*¹³ have previously noted that variations in f are correlated with the average Ce^{3+} -ion-ligand distance; in general, a smaller separation corresponds to a smaller f value relative to the free-ion value. The present data show that f values of peaks b, c, and d are similar in magnitude and 3-6 times smaller than that of peak a, thus implying a larger Ce-ligand distance for the latter site. Because the Ce-ligand distance is greater for the seven-oxygen-coordinated site than the six-oxygen site we suggest that absorption peak a is correlated with the seven-oxygen-coordinated site and the remaining peaks are correlated with the six-oxygen site. That is, peak a is associated with site Ce2 and peaks b, c, and d are correlated with site Ce1.

3.4. Glow curves

Figure 5 shows the TSL glow curves of undoped LSO and LSO:Ce following room-temperature x-ray excitation (120 Gy in air). Each one exhibits three peaks with maxima near 375, 430, and 490 K, and additional weak emission at higher temperature. Similarity in the two specimens' glow-peak temperatures suggests that trapping sites responsible for these peaks are not dependent upon cerium content for their formation. To pursue this hypothesis we measured TSL glow curves of several other Ce-doped oxyorthosilicates, including Y_2SiO_5 , Yb_2SiO_5 , $\text{Lu}_{1.8}\text{Y}_{0.2}\text{SiO}_5$, and Gd_2SiO_5 , and compared the results. All glow curves are strikingly similar with the exception of GSO:Ce. The main glow peak in this latter material occurs near 405 K rather than 375 K, as shown in Fig. 6. Although the shift is relatively small, we attribute it to the difference between crystal structure of GSO:Ce and the other oxyorthosilicates investigated in this work. GSO is a monoclinic structure with $P2_1/c$ symmetry, whereas the others are characterized by the monoclinic $C2/c$ structure. As proposed by Dorenbos *et al.*⁵, the origin of the TSL traps in LSO:Ce is intrinsic and likely associated with the specific configuration of oxygen ions around the central Ce^{3+} ion. This suggestion implies that a change in crystal structure ought to affect the local trap environment and produce a slightly different glow curve, as observed in the present work. Our current results suggest that the traps are intrinsic and are likely associated with the oxygen ion configuration around the host lanthanide ion, as well as the impurity Ce^{3+} ion. In other words, Ce^{3+} presence is not required to produce the characteristic glow curve of the $C2/c$ -structured oxyorthosilicates.

FIG. 5. TSL glow curves of undoped and Ce-doped LSO. Note the different ordinate scales.

The inherent assumption in this conclusion is that *undoped* LSO does not contain Ce^{3+} as an unintentional impurity. Measuring radioluminescence spectra of undoped LSO and Ce-doped LSO can check this because the latter should exhibit the usual band emission characteristic of Ce^{3+} ions. Results of this experiment are shown in Fig. 7. LSO:Ce emission is indeed dominated by the efficient $5d \rightarrow 4f$ electronic transitions of the Ce^{3+} ion, whereas undoped LSO is characterized by several weak lines. These lines may be due to unknown low-level impurities or to a very low concentration of cerium.

Electron-spin-resonance spectroscopy did not detect any resonance signals in the undoped specimen, but revealed several lines in the cerium-doped sample. Given the sensitivity of the spectrometer, $\sim 10^{12}$ spins/cm³, we conclude that any unintentional cerium impurity must be less than about 1 ppb.

FIG. 6. A comparison of TSL glow curves of LSO:Ce and GSO:Ce.

FIG. 7. Room-temperature radioluminescence spectra of undoped LSO and cerium-doped LSO.

Oxygen related defects in oxides (*e.g.* F centers) usually exhibit changes in their optical absorption spectrum upon irradiation. Accordingly, we measured the optical absorption spectra of pristine and x irradiated LSO and display the results in Fig. 8. Curve a depicts the absorption of the unirradiated sample and curves b and c represent radiation-induced absorption following doses of 120 and 3600 Gy (in air) at room temperature. The difference absorption, obtained by subtracting curve c from curve a, is given in the figure by curve d. Several radiation-induced peaks are observed in the spectrum of pristine LSO. Similar radiation-induced absorption in LSO:Ce has not been observed because of the strong absorption of the Ce^{3+} ions. Nevertheless, the present results clearly indicate the existence of intrinsic defects that can be enhanced by irradiation, typical of oxygen related defects in oxides.

FIG. 8. Optical absorption spectra of undoped LSO. (a) Pristine spectrum; (b) 120 Gy (in air); (c) 3600 Gy (in air); and (d) difference absorption obtained by subtracting curve (c) from curve (a). Note the different ordinate for curve (d).

4. CONCLUSIONS

Optical absorption of LSO:Ce has been measured in the temperature interval 10 – 300 K and Gaussian bands with maxima at 3.432 ± 0.002 eV (peak a), 3.502 ± 0.002 eV (peak b), 4.235 ± 0.0002 eV (peak c), and 4.746 ± 0.0002 eV (peak d) have been observed. The temperature dependence of the band widths is well described by the linear coupling model, which yields Huang-Rhys parameters (S) and vibrational quantum energies. All peaks are characterized by $S > 5$ indicating strong coupling between the impurity Ce^{3+} ion and lattice vibrations.

Using reported values for the cerium distribution between the two crystallographically inequivalent sites in LSO, oscillator strengths of the four major absorption bands were computed. Peaks b, c, and d exhibited weak temperature dependence with typical f values ranging from approximately 0.003 to 0.004, whereas peak a was characterized by a much stronger temperature dependence and a larger f value, approximately 0.012 to 0.018. Using previously published information, which showed a correlation between the average Ce^{3+} -ion-ligand distance and oscillator strength, we conclude that absorption peak a is correlated with the seven-oxygen-coordinated site, and peaks b, c, and d are associated with the six-oxygen site.

TSL glow curves of undoped and cerium-doped oxyorthosilicates having the $C2/c$ structure are similar, whereas GSO, with the $P2_1/c$ structure exhibits a different glow curve. These results suggest that traps responsible for these glow peaks are intrinsic and most likely associated with the configuration of oxygen ions in the vicinity of not only the Ce^{3+} ion, but the host lanthanide ions as well. An appropriate trapping model for these oxyorthosilicates does not require the presence of Ce^{3+} .

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