Intrinsic trapping sites in rare-earth and yttrium oxyorthosilicates

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Similarity among the thermally stimulated luminescence glow curves of undoped Lu_2SiO_5 and Ce^{3+}-doped oxyorthosilicates possessing the monoclinic $C2/c$ structure strongly suggests the luminescence traps are intrinsic in origin. They are most likely associated with the configuration of oxygen ions in the vicinity of not only the Ce^{3+} ion, as suggested in previous work, but also the host lanthanide ion. The optical absorption spectrum of pristine Lu_2SiO_5 shows the presence of intrinsic absorption centers that are enhanced upon x irradiation as seen in other oxides containing oxygen related point defects. © *1999 American Institute of Physics.* [S0021-8979(99)06921-2]

Cerium activated oxyorthosilcates Lu_2SiO_5:Ce (LSO:Ce), Y_2SiO_5:Ce (YSO:Ce), and Gd_2SiO_5:Ce (GSO:Ce) have proved to be excellent scintillation phosphors because of their relatively high density, good light output, and fast decay time.[1–4] Although the $1/e$ decay time, τ, is fast (~ 40 ns) there is considerable afterglow, i.e., light emitted at times exceeding τ, that is deleterious in most imaging applications. The intensity of afterglow has been shown to exhibit sample-to-sample variability even among specimens extracted from the same boule.[5] Thermally stimulated luminescence (TSL) studies have established the existence of several glow peaks in LSO:Ce with the most intense one occurring just above room temperature (~ 375 K) and characterized by a thermal activation energy of ~ 1 eV, leading to the conclusion that TSL traps are responsible for the afterglow.[6–8] Recent results on related compounds, $LuAlO_3$:Ce and $YAlO_3$:Ce, have provided additional support for this conclusion.[9] Measurements of radioluminescence (RL) and TSL emission spectra in Ce-doped oxyorthosilicates have firmly established the Ce^{3+} ion as the luminescence center; however, identification of the trapping sites is lacking. Dorenbos *et al.*[7] have proposed a center-to-center recombination model to explain TSL in LSO:Ce whereby Ce^{3+} is the charge donor, recombination center, and trap-creating defect. The origin of these traps was described as an intrinsic property of LSO:Ce, most likely associated with specific configurations of oxygen ions around the central Ce^{3+} ion.

In the present work, we show that undoped LSO exhibits a glow curve similar to LSO:Ce. In fact, we find that YSO:Ce, YbSO:Ce, LSO:Ce, and LSO exhibit similar TSL glow curves, leading to the conclusion that oxyorthosilcates possessing the monoclinic $C2/c$ structure[10] are characterized by intrinsic glow peaks, which do not require the presence of Ce^{3+} ions for their formation. In support of this conclusion, we show that the TSL glow curve of GSO:Ce, which has the monoclinic $P2_1/c$ structure, is quite different from the LSO-type glow curve.

Emission spectra of all Ce-doped oxyorthosilicates are dominated by Ce^{3+} transitions, whereas the multiple line spectrum observed in undoped LSO is ascribed to transitions of low-level rare-earth impurities. Regardless of variations in the emission spectra, LSO and LSO:Ce, as well as other oxyorthosilicates with the $C2/c$ structure, exhibit similar glow curves. This strongly suggests that TSL traps are intrinsic and are likely associated with the configuration of oxygen ions in the vicinity of the host rare-earth ions. The presence of Ce^{3+} is not required to produce the characteristic glow curve of the $C2/c$-structured oxyorthosilicates.

All measurements on oxyorthosilicates were made on specimens of dimensions $2\times2\times1$ mm^3 grown by the usual Czochralski technique.[10] TSL glow curves were obtained with a Harshaw Model 3500 reader operating at a linear heating rate of 5 °C/s. RL and TSL emission spectra were measured by passing a portion of the emitted light through an optical fiber onto the entrance slit of a 1/4 m monochromator and collecting it with a charge-coupled device (CCD) detector. Optical absorption was measured at room temperature with a Cary 5E spectrophotometer.

In Fig. 1, we show the TSL results for LSO:Ce and undoped LSO following room temperature x irradiation (1.2×10^4 R). Although the integrated TSL intensity of undoped LSO is much lower than LSO:Ce, the positions of the peaks are nearly identical. Three peaks are easily resolved with maxima near 375, 430, and 490 K, with additional weak glow (shown more clearly in Fig. 3) at higher temperature, similar to the previously reported results.[7] TSL and RL emission spectra are identical and we show the RL spectra in Fig. 2. LSO:Ce emission is dominated by the very efficient $5d$ to $4f$ electronic transitions of the Ce^{3+} ion, whereas undoped LSO is characterized by several weak lines presumably associated with low-level rare-earth impurities. Similarity in the glow peak positions of the two samples strongly suggests that trapping sites responsible for these peaks are intrinsic to the structure and not dependent upon the Ce^{3+} substitutional impurity for their formation. The reduced TSL intensity of LSO relative to LSO:Ce may be due to the lack of an efficient scintillator ion (Ce^{3+}, e.g.) in the undoped LSO lattice.

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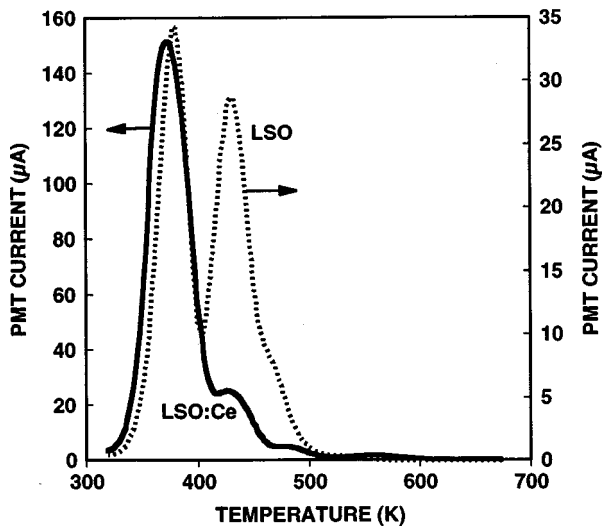

FIG. 1. X-ray-induced TSL glow curves of undoped and Ce-doped LSO taken by heating the samples at 5 °C/s. Note the different ordinate scales.

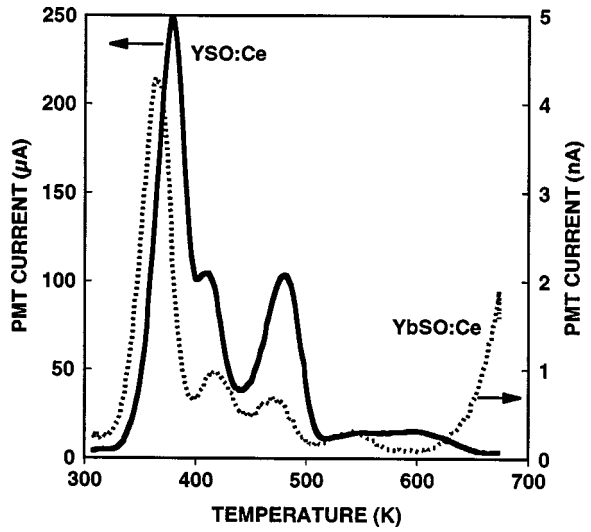

FIG. 3. X-ray-induced TSL glow curves of YSO:Ce and YbSO:Ce. Note the different ordinate scales. The sharp upturn above 650 °C for the weak YbSO:Ce TSL is due to blackbody radiation emanating from the silver sample holder.

To support the suggestion that TSL traps are intrinsic we measured TSL and emission spectra of YSO:Ce and YbSO:Ce subjected to the same exposure. Each of these specimens has the same monoclinic $C2/c$ structure as LSO, but the latter specimen does not exhibit intense luminescence due to quenching of the Ce^{3+} emission via a charge transfer mechanism.[11] Nevertheless, as shown in Fig. 3, they both exhibit glow curves that are similar to those of LSO:Ce and undoped LSO, shown in Fig. 1. The emission spectrum of YSO:Ce is identical to that of LSO:Ce (see Fig. 2), whereas emission from YbSO:Ce is quenched as mentioned above. Based on these results we conclude that the origin of the TSL traps is intrinsic defects most likely associated with the configuration of oxygen ions around the rare-earth ions. The important difference between our conclusion and that of Dorenbos *et al.*[7] is that the presence of Ce^{3+} ions is not necessary for the formation of traps. Host lanthanide ions also are perturbed by the neighboring oxygen configuration thus allowing formation of trapping sites.

Substitution of the larger Gd^{3+} ion into the rare-earth oxyorthosilicate lattice causes the crystal structure to change from the monoclinic $C2/c$ structure to the monoclinic $P2_1/c$ lattice.[10] Therefore, we expect GSO:Ce to exhibit a glow curve that is distinctively different from the LSO type, as confirmed by the result shown in Fig. 4.

Oxygen related defects in oxides, for example F-type centers, are usually enhanced by irradiation or thermochemical reduction as manifested by optical absorption changes in the ultraviolet and visible portions of the spectrum.[12] Accordingly, we measured the optical absorption spectra of x irradiated and pristine LSO and show the results in Fig. 5.

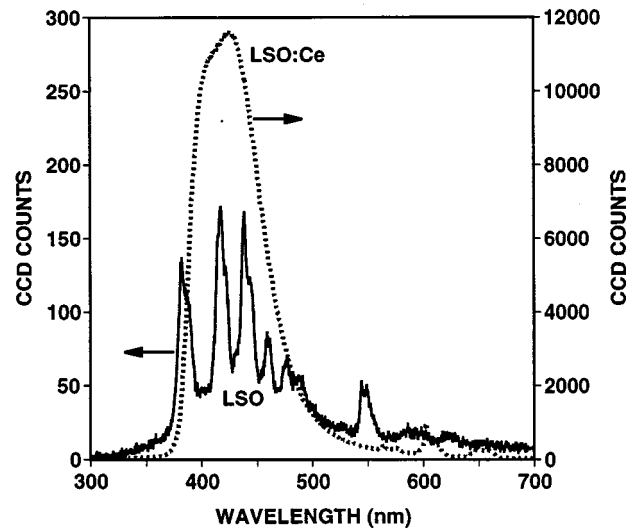

FIG. 2. Typical emission spectra (uncorrected) of undoped and Ce-doped LSO.

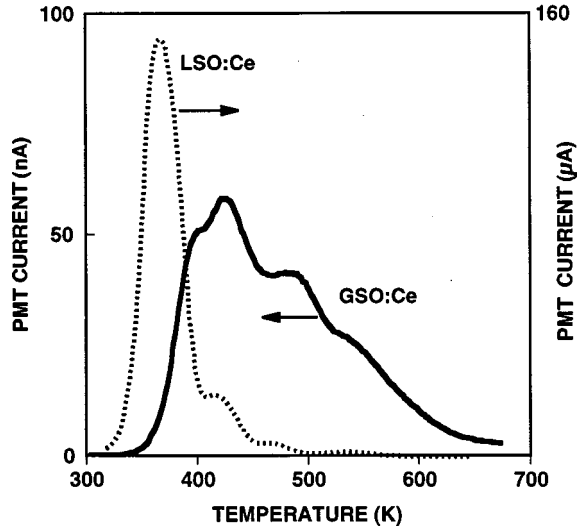

FIG. 4. Representative x-ray-induced TSL glow curve of GSO:Ce shown along with the glow curve of LSO:Ce for comparison.

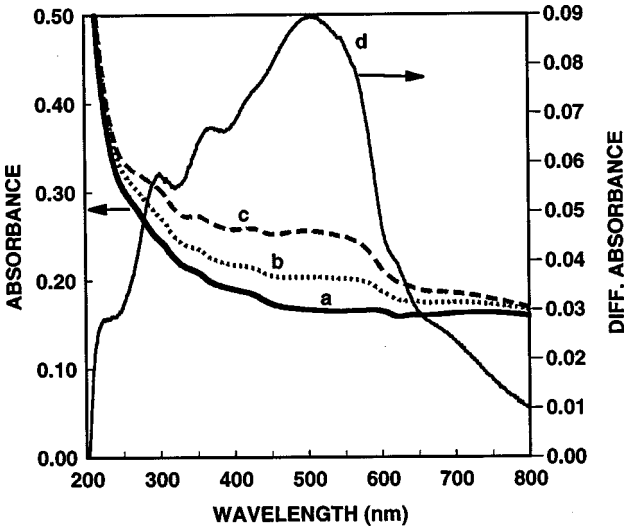

FIG. 5. Optical absorption spectra of pristine and x-irradiated LSO. (a) Pristine spectrum; (b) following 1 min x irradiation, (c) following 30 min x irradiation, and (d) difference spectrum obtained by subtracting (c) from (a). Note the different ordinate for curve d.

Absorption of the unirradiated sample is shown by curve a; curves b and c correspond to absorption following 1 and 30 min x-ray exposures (1.2×10^4 R/min) at room temperature. Curve d is the absorption difference obtained by subtracting spectrum c from spectrum a. Although relatively weak in intensity, several peaks are observed in the spectrum of the pristine sample, which are enhanced by x irradiation. We have not observed similar radiation-induced behavior in LSO:Ce, presumably due to the dominance of the well-known, strong absorption of the Ce^{3+} ion.[13] Nevertheless, the present results indicate the existence of inherent defects that can be enhanced by irradiation, typical of oxygen related defects in other oxides.

Summarizing, we have shown that TSL glow curves of undoped and Ce^{3+}-doped oxyorthosilicates with the $C2/c$ structure are similar, providing strong evidence for the intrinsic nature of the traps. They are most likely associated with the configuration of oxygen ions in the vicinity of not only the Ce^{3+} ion, as suggested by Dorenbos *et al.*,[7] but the host lanthanide ions as well. Therefore, development of an appropriate trapping model for these materials does not require the presence of Ce^{3+} ions. Optical absorption spectra of undoped LSO shows the presence of intrinsic absorption centers that are enhanced upon x irradiation and reminiscent of oxygen related point defects in oxides.

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