Photostimulated Luminescence and Thermoluminescence of LSO Scintillators

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Abstract

Photostimulated luminescence (PSL) and thermoluminescence (TL) from five $Lu_{2(1-x)}Ce_{2x}(SiO_4)O$ (LSO) crystals with different light outputs is reported. Optical irradiation into the Ce^{3+} absorption bands causes the appearance of a broad absorption band near 280 nm which is ascribed to Ce^{4+}. In addition, a tail is observed extending beyond 700 nm. Optical irradiation into this tail (PSL) or heating of the crystal (TL) results in Ce^{3+} emission. It is shown that both PSL and TL are due to the same traps. In addition, an anti-correlation is found between the light output under gamma-ray irradiation and the trap concentration in the crystal. The nature of the recombination centers responsible for the low light output in some crystals is not clear. Annealing experiments suggest that the traps and the recombination centers may be related to oxygen vacancies.

I. INTRODUCTION

$Lu_{2(1-x)}Ce_{2x}(SiO_4)O$ (LSO) is known as a fast and intense scintillator. The decay of the scintillation pulse is almost a single exponential with a decay time of about 40 ns and the light output can be as high as 28000 phot/MeV (75% of NaI(Tl)) [1]. The scintillation decay time is close to the decay times of the two Ce^{3+} centers (Ce1 and Ce2) present in the crystal [2]. This shows that the Ce^{3+} ions are excited on a very short time scale after the capture of a radiation quantum and that energy transfer from excited Ce^{3+} ions to quenching centers is negligible.

In our laboratory, we have grown several $Lu_{2(1-x)}Ce_{2x}(SiO_4)O$ crystals. For the best crystals, the previous paragraph applies. But for some crystals, the light output is considerably lower than the value of 28000 phot/MeV. This can not be explained by a lower Ce^{3+} emission efficiency for two reasons: 1) in optical excitation experiments we have found that the Ce^{3+} emission intensity per photon absorbed by Ce^{3+} is about the same for all crystals and 2) the scintillation decay time in low light output crystals is only 25% smaller than in high light output crystals. Thus, the low light output in some crystals is due to a poor energy transfer from free electrons and holes to Ce^{3+}. It is noteworthy that undoped $Lu_2(SiO_4)O$ has only very weak emission, even at 11 K,

which suggests that in $Lu_{2(1-x)}Ce_{2x}(SiO_4)O$, the Ce^{3+} ions are excited directly by electrons and holes and not by some intermediate center intrinsic to the host material. Then, the light output of the LSO crystal is determined by the amount of electrons and holes that can reach the Ce^{3+} ions before being trapped or annihilated at recombination centers.

In order to obtain some insight into the nature of the traps and recombination centers present in the LSO crystals, we investigated samples from four crystal boules with different light outputs. It is known that ionizing radiation or UV radiation fills traps that can be subsequently observed in a thermoluminescence (TL) experiment [3]. For this reason, we investigated the TL of our samples. In addition, we performed photostimulated luminescence (PSL) measurements in order to relate the TL to the optical properties of our samples.

II. EXPERIMENTAL

$Lu_{2(1-x)}Ce_{2x}(SiO_4)O$ crystals were grown by the Czochralski technique. The raw materials were 99.99% pure Lu_2O_3, SiO_2, and CeO_2. After mixing and pressing the raw materials into pellets, they were melted in an iridium crucible which was inductively heated. The furnace assembly was located in a sealed chamber and crystal growth was carried out under a continuous flow of N_2 + 3000 ppm O_2. As grown, the crystal boules were typically ~ 20 mm in diameter and ~ 40 - 60 mm long.

We denote the four crystal boules investigated in this study by A, B, C, and D, where A has the highest light output, B the next highest, etc. The Ce concentration was measured by ICP mass spectrometry by X-ray Assay Laboratories, Don Mills, Ontario: x=0.00066 (A), 0.0021 (B), 0.0014 (C) and 0.00064 (D). Small samples were taken from the boules. For optical absorption measurements polished samples were taken from each of the boules. For thermoluminescence measurements four unpolished chips of about 3x3x1 mm^3 were taken. From boule A, which turned out to be inhomogeneous, an additional unpolished 3x3x1 mm^3 sample was taken. Optical absorption measurements were carried out using a Hitachi U-3210 spectrophotometer. Thermoluminescence measurements were carried out using the Harshaw model 2000-A thermoluminescence detector and the
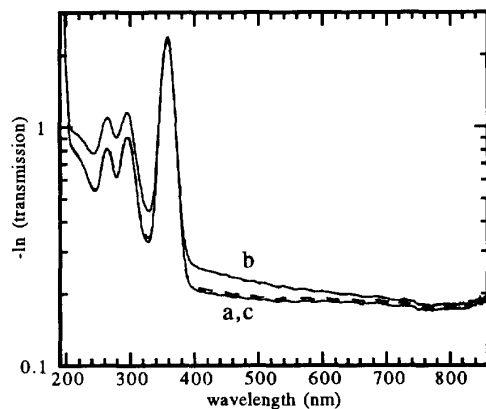
Figure 1. Optical absorption spectrum of a 0.49 mm thick sample from boule D. Curve a shows the spectrum after heating the sample to 460 °C. Curve b is taken after an additional 8 minutes irradiation with a Hg lamp (surface irradiation dose $\sim 10^{18}$ photons/cm^{2}, with wavelength mainly <350 nm). Curve c (dashed) is measured after an additional 11 minute irradiation at wavelengths >500 nm (surface irradiation dose $\sim 10^{19}$ photons/cm^2).

Figure 2. The difference between the absorption curves b and a in figure 1.

model 2000-B automatic integrating picoammeter coupled to a personal computer through a Fluke 8840A digital multimeter. Optical excitation experiments were carried out using a Spex Fluorolog-2 spectrofluorometer. The exciting beam was incident perpendicular on the sample surface; emission was recorded at 22.5° relative to the exciting beam. All spectra were corrected for the equipment's detection efficiency. For annealing the unpolished 3x3x1 mm^3 samples were placed on a larger LSO piece resting on Ir wires in an alumina boat that was placed in a programmable Lindberg furnace.

III. RESULTS

We performed optical and TL measurements on the samples from the four boules. First, PSL and other optical properties of these samples are presented. Next, TL measurements are discussed.

A. PSL and other optical properties

In figure 1, the optical absorption spectrum of a polished sample from boule D is shown. Curve a is measured after heating the sample to 460 °C, thereby emptying several traps and eliminating afterglow. At 357, 294, 263 and 216 nm we observe Ce^{3+} absorption bands. At wavelengths shorter than 200 nm the absorption edge of the host lattice is observed. Curve b is taken after irradiation with a Hg lamp, which mainly emits at wavelengths where Ce^{3+} absorption is prominent. Clearly, this irradiation causes additional absorption features. After the measurement of curve b, the
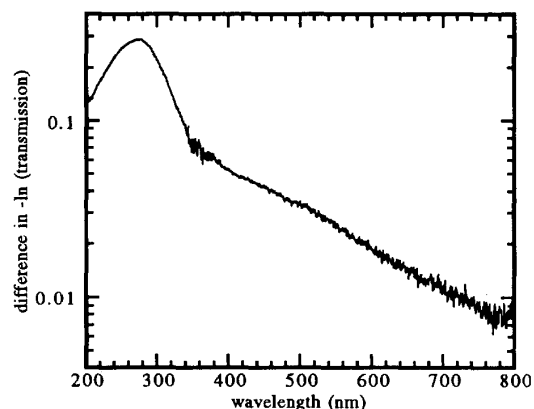
sample was irradiated with a W lamp having a 500 nm cut-off filter. As evident in figure 1, this treatment restored the original absorption spectrum.

In figure 2, we show the difference between curves b and a in figure 1. This difference is the absorption induced by the Hg lamp irradiation. Figure 2 shows a broad absorption band peaking at 276 nm ($36 \cdot 10^3$ cm^{-1}) which has a FWHM width of 105 nm ($15 \cdot 10^3$ cm^{-1}). Spectra similar to those shown in figure 1 and 2 were obtained for polished samples from the other boules, but the magnitude of the difference spectra is smaller for these samples.

Figure 3 shows the excitation spectrum of a polished sample from boule A, which was irradiated with the Hg lamp. The emission from Ce^{3+} is recorded at 428 nm wavelength. The excitation spectrum resembles the absorption spectra of figure 1. At wavelengths shorter than 400 nm Ce^{3+} excitation bands are visible, whereas at wavelengths longer than 400 nm a "tail" is observed extending beyond 700 nm. The PSL spectrum, obtained when exciting into this tail using 504.5 nm wavelength light, is shown in figure 4 (curve b).

Also in figure 4 is the afterglow spectrum, recorded when using no exciting light and taken prior to the PSL spectrum (curve a). The shape of both spectra is almost identical, a small difference being due to decay of the emission intensity during the measurement of curve b (from short to long wavelengths). Results on samples from boules B, C and D are similar. The spectral shape differed somewhat from boule to boule (indicating different relative emission intensities due to Ce1 and Ce2 centers-see [2]), but the spectral shape of the afterglow was always almost identical to that of the PSL.

The above shows that Hg lamp irradiation induces the absorption features shown in figure 2 and the excitation properties related to it, whereas light with a wavelength larger than 500 nm reduces this absorption. This suggests that the
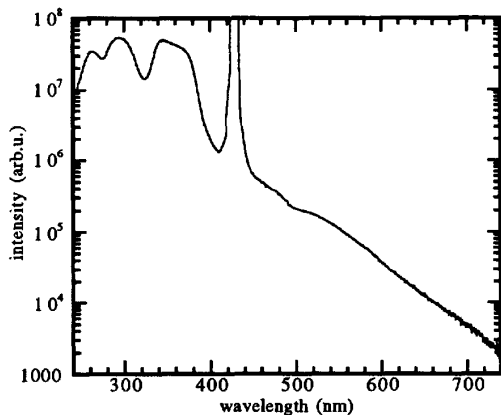
Figure 3. Excitation spectrum of a 1.57 mm thick polished sample from boule A after 3 minutes irradiation with the Hg lamp (accumulated surface dose is ~10^{18} photons/cm^2). The emission wavelength is 428 nm. In order to eliminate second order features, beyond 450 nm a cut-off filter was used.
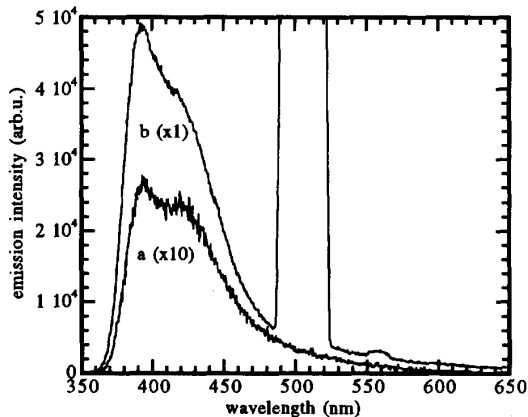

Figure 4. Afterglow spectrum of an unpolished sample from boule A (curve a, multiplied by 10 for clarity). Also shown is the spectrum obtained under the same circumstances, but when additionally exciting the crystal with 504.5 nm light (curve b). The structure at 560 nm is an artifact.

absorption features in figure 2 are caused by Ce^{3+} excitation. In order to prove this, for an unpolished 3x3x1 mm^3 sample from boule A, we first bleached the absorption feature by irradiating the crystal with 504.5 nm light. Next, during several seconds we irradiated the crystal with monochromatic light (resolution: 3 nm FWHM). The accumulated surface light dose was ~10^{14} to ~10^{16} photons/cm^2, depending on the wavelength used. After this treatment, we excited the crystal with 504.5 nm light of a fixed intensity and measured the intensity of the resulting Ce^{3+} emission (PSL) at 400 nm. The PSL intensity was divided by the accumulated surface light dose. We call the quantity obtained in this way, the PSL creation efficiency. The PSL creation efficiency as a function of irradiation wavelength is shown in figure 5. Also shown in figure 5 is the excitation spectrum of the Ce^{3+} emission for this crystal. The correspondence of the PSL creation efficiency with the Ce^{3+} excitation spectrum is clear. This means that the tail in the excitation spectrum (cf figure 3) is caused by Ce^{3+} excitation and the energy storage processes following it. For wavelengths shorter than 340 nm, there is some difference between the two sets of data in figure 5, indicating that the PSL creation efficiency is also governed by some other process.

B. TL and its relation to PSL

For the five unpolished samples we measured the TL after irradiating with the Hg lamp for 8 minutes. In order to avoid differences in the irradiated crystal volume from sample to sample because of differences in sample size, during irradiation an aluminum plate with a 1 mm diameter hole in it was placed on the crystals resulting in the same light dose for each crystal: ~10^{17} photons, corresponding to a surface accumulated light dose of ~10^{18} photons/cm^2. At this dose, a large fraction
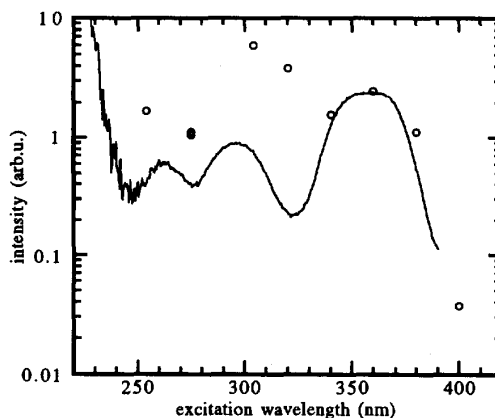
Figure 5. The PSL creation efficiency for the highest light output 3x3x1 mm^3 sample from boule A (circles). For comparison, the excitation spectrum recorded at 400 nm emission wavelength and using the same experimental setup is shown (solid curve).

of the traps responsible for the TL are expected to be filled, because the integrated TL intensity was not much different from that seen after only 3 minutes Hg lamp irradiation. The TL intensity after 8 minutes was between 2% (highest light output sample) and 45% (lowest light output sample) higher than after 3 minutes irradiation.

In figures 6 and 7 the TL spectra obtained after 8 minutes Hg lamp irradiation are shown for the highest light output unpolished sample from boule A and the unpolished sample from boule D, respectively. The spectrum in figure 6, curve a is similar to that reported earlier by Dorenbos et al. [3]. The spectrum in figure 7, curve a, is much broader and more
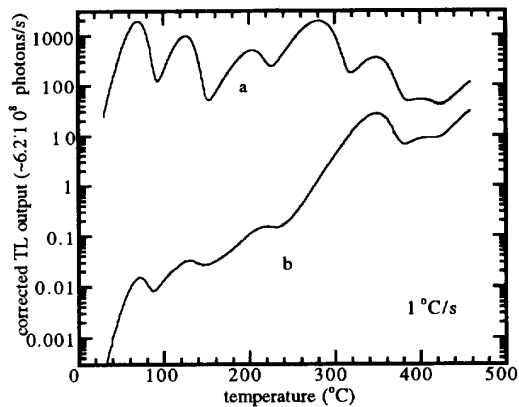
Figure 6. Corrected TL spectra for the highest light output unpolished sample from boule A. Curve a shows the TL spectrum measured after 8 minutes irradiation with the Hg lamp. Curve b shows the TL spectrum measured after 8 minutes irradiation with the Hg lamp, followed by a 16 minutes bleach using 504.5 nm light (accumulated surface dose ~10^{19} photons/cm^2). The heating rate is 1 °C/s.
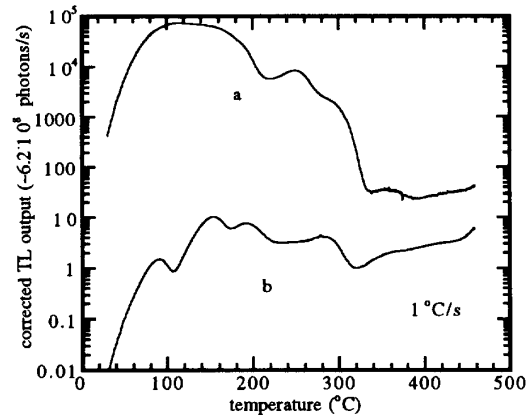
Figure 7. Corrected TL spectra for the unpolished sample from boule D. Curve a shows the TL spectrum measured after 8 minutes irradiation with the Hg lamp. Curve b shows the TL spectrum measured after 8 minutes irradiation with the Hg lamp, followed by a 59 minutes bleach using 504.5 nm light (accumulated surface dose ~10^{19} photons/cm^2). The heating rate is 1 °C/s.

intense. The measurement of curves a in the figures was started within a few minutes after the end of the excitation. The TL spectra for samples from boules A and B all look similar to those in figure 6; those for the sample from boule C are similar to those in figure 7. All spectra in the figures 6 and 7 were corrected for the temperature dependence of the Ce^{3+} emission [4]. This was done by multiplying the measured TL spectrum by the factor $[1+\exp(13-\{4616.3/T\})]$, where the temperature T is in Kelvin.

In addition to the TL spectra obtained after irradiation with the Hg lamp, figures 6 and 7 also show the TL spectra after PSL-bleaching with 504.5 nm light. During this bleaching process, we recorded the Ce^{3+} emission intensity at 400 nm. During the PSL-bleaching, the Ce^{3+} emission intensity decreased by a factor of about 900 for the sample from boule A and 2000 for the sample from boule D. The shape of the tail in the excitation spectrum at 400 nm emission wavelength (cf figure 3) was unchanged by the PSL bleaching at 504.5 nm; only its intensity decreased. As figures 6 and 7 show, after the PSL-bleaching, the TL signal is much lower than before the PSL-bleaching. This means that the majority of the traps giving rise to the TL also give rise to the PSL and therefore have absorption at 504.5 nm.

We have also measured the PSL after the TL measurements shown by the curves a in figures 6 and 7. The PSL intensity was about the same as after the 504.5 nm bleach described above, i.e. very low. This means that the majority of the centers giving rise to the PSL and the tail in the excitation spectrum (cf figure 3) also give rise to a TL signal. Together with the conclusion of the preceding paragraph, this means that mainly, the centers giving rise to the PSL are identical to

the traps giving rise to the TL. Our results on the samples from boules B and C are similar, so this conclusion holds for all of the boules investigated.

C. The relation between TL and light output

For the five unpolished samples, we measured the light output under ^{137}Cs gamma irradiation (662 keV), and we determined the integral of the TL curves between room temperature and 460 °C. The result is shown in figure 8. One can clearly see the anti-correlation between the TL intensity and the light output.

We also did annealing experiments on our samples. The samples were annealed in a heating cycle starting with an initial heating at 3.3 °C/min. from room temperature to 1550 °C, followed by 5 hours constant temperature of 1550 °C, after which the temperature was lowered to room temperature again at a rate -3.3 °C/min.. In the first annealing cycle the sample was surrounded by a 98% Ar/2% H$_2$ atmosphere. After measurements on these annealed samples, a similar annealing cycle was performed, but in a 99.5% pure O$_2$ atmosphere.

After the first annealing experiment, in Ar/H$_2$ atmosphere, the absorption spectra did not show large differences to those measured before annealing. In contrast to this, the scintillation light output was much less than before annealing and the TL intensity was higher. This is indicated in figure 8. After the second annealing experiment, in O$_2$ atmosphere, the absorption in the <350 nm wavelength region was markedly increased. On the average, the scintillation light output was slightly higher after the second annealing than before the two annealing cycles and the TL intensity was slightly lower. No annealing cycle altered the light output ordering of the
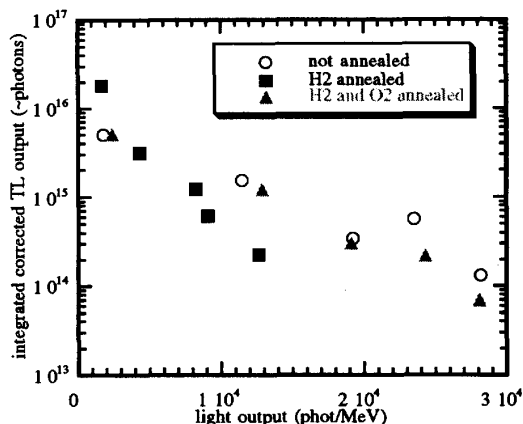
Figure 8. The light output and the integral of the corrected TL curve for the five unpolished samples. Before the TL measurement a 1 mm diameter circle of the samples was irradiated with the Hg lamp for 8 minutes (accumulated light dose through the circle: ~10^{17} photons). Shown are the results before annealing, after the Ar/H_2 anneal and after the additional O_2 anneal. For each annealing stage, the data points pertain to the samples (from the left to the right): D, C, B, A(lower light output), A(highest light output).

samples: it remained A(highest)>A(lower)> B>C>D.

connected to PSL as well as to TL. Hence, the tail is ascribed to the emptying of traps, maybe involving transitions from trap levels below the conduction band to energy levels in the conduction band. Glow curve analysis shows that the traps observed in the TL spectra in figure 6 have a depth between 1.0 and 1.7 eV, so photons with a wavelength <1200 nm may be able to empty the traps, which is consistent with the wavelength position of the tail in the absorption spectrum.

Finally, we address the relation between the TL intensity, i.e. the concentration of traps, and the scintillation light output. The mere presence of traps in a crystal is not a reason in itself for expecting a low scintillation light output. As soon as the traps are filled, the light output may be high again. But we never observed any variation of the light output of our crystals as a function of the concentration of filled traps. This means that a low light output is not caused by the traps, but by non-radiative recombination centers accompanying them (except of course if the traps are also non-radiative recombination centers). In this view, both traps and non-radiative recombination centers would have a common cause, e.g. disorder in the lattice. We note that after annealing in Ar/H_2 atmosphere, the light output was less than before annealing and after annealing in O_2 atmosphere it was slightly higher. This suggests that oxygen vacancies may be involved in the reduction of the light output.

IV. DISCUSSION AND CONCLUSIONS

We give an explanation for the results presented in this paper. We note that the interpretation is preliminary: more research is necessary to support our interpretation.

First, we consider the absorption band at 276 nm in figure 2. The position and the width of this band are similar to those observed for Ce^{4+} and other 4+ charged rare earth ions in several oxide lattices [5,6]. The fact that extra absorption at wavelengths <350 nm appears after annealing in an O_2 atmosphere supports the assignment of the 276 nm absorption band to Ce^{4+}. Then figures 2 and 5 tell us that if Ce^{3+} is excited, apparently Ce^{4+} can be created. This can be understood when realizing that, for instance, in $Y_3Al_5O_{12}$ crystals [7], the Ce^{3+} 5d levels are close to or higher than the bottom of the conduction band. This situation might be present in $Lu_2(SiO_4)O$ as well. Then, if Ce^{3+} is excited into a 5d state, the 5d electron can enter the conduction band, leaving behind a Ce^{4+} ion.

Second, we consider the absorption tail in figure 2, which is connected to the excitation tail in figure 3, and which extends from 400 nm to beyond 700 nm. The tail is probably not composed of many less broad absorption bands, each belonging to a particular center, because then we would expect bleaching at 504.5 nm to result in some kind of hole burning. Instead, no change was observed in the shape of the tail when bleaching with 504.5 nm light. We have shown that the tail is

V. ACKNOWLEDGEMENTS

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