Study of the energy band structure of Lu$_2$SiO$_5$:Ce$^{3+}$ single crystals by thermally stimulated luminescence method

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Abstract. Results of optical absorption spectroscopy and photoluminescence for Lu$_2$SiO$_5$:Ce$^{3+}$ (LSO) single crystals produced by modified Musatov method are reported. The energy structure of electron traps in LSO is studied by thermally stimulated luminescence method when the crystals are exposed to UV sources with different spectral and energy characteristics. The thermoluminescence glow curves allowed us to find a luminescence maximum corresponding to 300 K, which was not observed previously. The obtained results are interpreted taking into account the anisotropy of LSO and different energy of exciting photons.

1. Introduction

In recent two decades, owing to the rapid development of the high-energy physics and medicine, heavy scintillation materials, which are characterized by high both gamma-quanta absorption cross-section and quantum efficiency, and good temporal resolution as well, became necessary. The cerium-doped lutetium oxyorthosilicate Lu$_2$SiO$_5$:Ce$^{3+}$ (LSO) is a crystalline scintillator, which exhibits extremely well combined physical and luminescence properties. The LSO has the high density, and both effective atomic number and quantum efficiency, which result in the low radiation length and high conversion efficiency [1]. The luminescence maximum of LSO corresponds to the wavelength range of 400-450 nm; this fact determines the adequate coincidence with the spectral response of photomultiplier tube (PMT) applied now in scintillation detectors. Potentially, this material can substitute for NaI:Tl$^+$, which at present dominates among scintillation crystals. The substantial disadvantage of LSO consists in the afterglow, which worsens the time resolution of detectors and limits the application of the material. In accordance with the luminescence theory of crystalline materials, the afterglow phenomenon is related to the participation of electron traps (ET) in the luminescence process, which are defects that form metastable levels in the forbidden band and can radiationlessly trap electrons and release them for a long time [2]. There are phosphorescence models for the LSO in the literature, which take into account the conduction band [3] and ignore its [4]. However, at present, no comprehensive mechanism of phosphorescent transitions in LSO is available.

The subject of the present study is a LSO single crystal, the structure of which corresponds to the monoclinic (low-symmetry) crystal system (syngony) (point group symmetry 2/m, space group C2/c). There are two sites for Lu$^{3+}$ ions in the LSO crystal lattice: Lu$^I$ ion is locating in seven-oxygen-coordinated site (seven-apical coordination polyhedron) and Lu$^II$ ion is locating in six-oxygen-coordinated site (oxygen ions form a distorted octahedron). The pure Lu$_2$SiO$_5$ compound exhibits
common luminescence parameters; because of this, to reach the intense and rapid luminescence used in detecting high-energy particles, the material is doped with Ce$^{3+}$ activator. When doping, Ce$^{3+}$ ions substitute for Lu$^{3+}$ ions and, therefore, Ce$^{3+}$ ions can occupy the two aforementioned sites. The Lu and Ce elements correspond two opposite ends of the lanthanide row; therefore, their ionic radii are substantially different, namely, 0.86Å (Lu$^{3+}$) and 1.02Å (Ce$^{3+}$). Doped Ce$^{3+}$ ions are more likely to substitute for Lu ions in seven-oxygen-coordinated sites [5].

This work is a stage of investigations performed by us, which is aimed at the study of mechanisms of the efficient energy storage in LSO single crystals and at the finding of effects, which allow one to control the luminescence parameters of dielectric materials activated with rare-earth and transition metal ions. To study the luminescence properties and determine the luminescence mechanism, we apply the absorption spectroscopy and photoluminescence (PL) methods and thermally stimulated luminescence (TSL) using the exposition to different UV sources.

2. Experimental details

The optical-grade LSO single crystals studied in terms of the present work were grown along the direction perpendicular to the (31 ̅1) plane using the modified Musatov method without rotation; this ensures the preparation of perfect crystals [6]. The studies were performed using plate-like samples 2x10x10 mm in size (optical absorption spectroscopy) and cubic samples 10x10x10 mm in size (PL and TSL experiments), the faces of which correspond to the (31 ̅1) and (001) crystallographic planes. The optical absorption spectroscopy was performed at room temperature in a wavelength range of 180-800 nm using a UV-Vis-NIR Cary 5000 Varian (AgilentTech.) spectrometer.

Emission spectra were measured at 300 K with an original set-up [7] based on a MDR-23 monochromator and a FEU-100 PMT, which were mounted perpendicular to the exciting laser beam. The luminescence was excited using a YAG:Nd LTI-345 UV laser, which allows one to generate light pulses with the photon energy $h\nu=3.49$ eV.

TSL glow curves (intensity as a function of temperature) were measured in a temperature range of 125-570 K at heating rates of 4.5÷10 K/min using a VUP-5-based vacuum setup. This setup is equipped with a SZS-22 light filter (the transmission band is 400-600 nm) and a FEU100 PMT. Before the heating, the crystals were exposed with UV light from either a DDS30 low pressure deuterium lamp or a DRL400 high pressure mercury lamp at exposition times of 10, 15, 20, and 30 min.

3. Results and discussion

3.1. PL parameters

Optical transmission spectra of LSO plate-like samples (figure 1) demonstrate the stable high transmittance in the visible wavelength range (400÷800 nm), which confirms the optical-grade quality of the single crystals, and the decrease in the transmittance in the UV wavelength range, which is typical of the absorption of crystalline Lu$_2$SiO$_5$ matrix with Ce$^{3+}$ activator. The linear approximation of the characteristic absorption edge (figure 1, see inset) allowed us to calculated the band gap energy $E_g$, which, according to the sample orientation, is 6.22 eV (001), 6.19 eV (31 ̅1), and 6.26 eV (undirected samples) at $\Delta E_s = \pm 0.005$ eV; these results agree well with the literature data [8,9].

To analyze the Ce$^{3+}$ activator absorption bands at 200÷400 nm, the transmission spectra were transformed into absorption spectra (figure 2). In this case, we use the well-known Bouguer-Lambert-Beer law (1) and the relationship (2) between the wavelength $\lambda$ and photon energy:

$$\frac{I}{I_0} = \exp[-\alpha \cdot l]$$

$$h\nu = \frac{hc}{\lambda}$$
where \( I_0 \) and \( I \) are the intensities of incident and transmitted light, respectively; \( \alpha \) is the absorbance of a material; and \( l \) is the sample thickness.

Emission spectra (figure 2) measured for the cubic LSO samples differing in the orientation (from herein, excitation face/ PL response face) were obtained by transformation of the dependences \( I(\lambda) \) into \( I(h\nu) \) by equation (3) to satisfy the luminous flux conservation condition \( dF = Idh\nu = Id\lambda. \)

\[
I(h\nu) = I(\lambda) \frac{h^2}{c}
\]

The approximation of absorption and emission spectra with the Gaussian function allowed us to identify four absorption and thee emission bands (figure 2), the position of which is almost unchanged (within the measurement error) with changing orientation of samples (table 1). The absorption bands correspond to optical transitions in Ce\(^{3+}\) ions \([8,9]\) occupied two nonequivalent crystallographic sites Ce\(^1\) (at 3.47, 4.2, and 4.7 eV) and Ce\(^2\) (at 3.74 eV). The emission spectra demonstrate bands at \( \approx 2.96 \) and \( \approx 3.13 \) eV (related to Ce\(^1\)) and at \( \approx 2.70 \) eV (related to Ce\(^2\)), which were reported in \([9,10]\).

**Figure 1.** Transmission spectra measured for the LSO plates; inset shows the linear approximation of the characteristic absorption band edge.

**Figure 2.** Absorption (blue line) and emission (red line) spectra measured for plate (001) and cubic (001)/(31\(^\overline{1}\)) LSO samples, respectively. Green lines are results obtained with Gauss peak fitting of the spectra.

**Table 1.** Results of Gauss peak fitting of absorption and emission bands for LSO samples.

| Absorption face | Absorption maximum\(^a\) (eV) | PL response face | Emission maximum\(^b\) (eV) |
|-----------------|-------------------------------|------------------|-----------------------------|
|                 | \( h\nu_{a1} \) | \( h\nu_{a2} \) | \( h\nu_{a3} \) | \( h\nu_{a4} \) | \( h\nu_{e1} \) | \( h\nu_{e2} \) | \( h\nu_{e3} \) |
| (001)           | 3.47 | 3.72 | 4.20 | 4.70 | (31\(^\overline{1}\)) undirected | 2.69 | 2.95 | 3.13 |
|                 |      |      |      |      | (001) undirected            | 2.72 | 2.97 | 3.12 |
| (31\(^\overline{1}\)) | 3.47 | 3.74 | 4.20 | 4.70 | (001) undirected          | 2.68 | 2.95 | 3.12 |
|                 |      |      |      |      | (31\(^\overline{1}\)) undirected | 2.71 | 2.98 | 3.13 |
| undirected      | 3.47 | 3.78 | 4.20 | 4.70 | (001)                        | 2.72 | 2.97 | 3.12 |
|                 |      |      |      |      | (31\(^\overline{1}\))       | 2.69 | 2.96 | 3.13 |

\(^a\) \( \Delta h\nu_{a}=0.02 \) eV.

\(^b\) \( \Delta h\nu_{e}=0.03 \) eV.
3.2. Thermally stimulated luminescence

It follows from absorption bands parameters of Ce$^{3+}$ in LSO that, the efficient excitation energy storage is possible in using gas-discharge UV-radiation lamps; the position of luminescence bands allows us to record the TSL glow curves in using sufficiently simple equipment, namely, optical glasses and a PMT.

When using the TSL method, the heating rate of sample affects substantially the recorded curves. Because of this, we performed the measurements at different heating rates ($\mu$). Data obtained at a heating rate of 4 K/min are characterized by a low signal-to-noise ratio that impedes the data processing. At heating rates of above 10 K/min, the thermal destruction of samples takes place, which manifests itself in the appearance of triboluminescence flashes. The heating rate $\mu=7$ K/min allows us to obtain intense curves without the triboluminescence.

The TSL glow curves obtained after exposition to the deuterium lamp radiation (figure 3) at different exposition times $\tau_{exp}$ demonstrate two TSL maxima at $\sim 403$ K (I) and $\sim 345$ K (II), which are well understood [4,9]. As in previously reported studies, no TSL peak was found in the low-temperature range (100÷300 K). The ratio of intensities of peaks I and II is 1:4; the intensities increase as the exposition time increases from 4 to 20 min (figure 3, see inset). In this case, the structure and positions of maxima change insignificantly. The use of the mercury lamp leads to the appearance of an additional peak in the TSL glow curves (figure 4), which corresponds to 300 K (III) and was not previously reported in the literature.

![Figure 3](image-url)  
**Figure 3.** TSL glow curves of LSO, in increasing order of intensity, UV (the deuterium lamp) exposure times of 4, 10, 15, and 20 min. The curves were recorded at a heating rate of 7 K/min. Inset shows the proportional increase in the TSL peak intensity with increasing exposure time.

![Figure 4](image-url)  
**Figure 4.** TSL glow curves measured for LSO after exposure to Hg lamp light (top curve) and deuterium lamp light (bottom curve). Green lines are results obtained with asymmetric Gauss peak fitting.

| UV source, $\tau_{exp}$, $\mu$ | Peak | Experimental data | Literature data [4,9] |
|-------------------------------|------|-------------------|----------------------|
|                               | $T_{\text{max}}$ (K) | $E_i$ (eV) | $\ln[s]$ (Hz) | $E_i$ (eV) | $\ln[s]$ (Hz) |
| D lamp, 20 min, 6.5 K/min      | I    | 403±4            | 1.18±0.04           | 30.9±0.7   | 1.17, 1.45   | 30.5, 29.5   |
|                               | II   | 344±3            | 0.92±0.02           | 28.4±1.0  | 0.98, 1.21  | 29.3, 32.4  |
| Hg lamp, 4÷7 min, 7 K/min      | I    | 400±1            | 1.12±0.03           | 30.7±0.2  | 1.17, 1.45  | 30.5, 29.5  |
|                               | II   | 345±2            | 0.96±0.04           | 30.0±1.6  | 0.98, 1.21  | 29.3, 32.4  |
|                               | III  | 298±3            | 0.88±0.01           | 32.2±0.3  | –, –        | –, –        |

*Table 2 – Parameters of electron traps*
The obtained curves were approximated with the asymmetric Gaussian function:

\[ y = y_0 + \frac{\sqrt{2} \Delta}{\sqrt{\pi} (w_1 + w_2)} \exp \left[ -\frac{(x - x_0)^2}{2w_{1,2}^2} \right] \]  

To calculate parameter of ETs, we used peak shape method, which is based on the linear approximation (equation (5)) of the temperature dependence of the intensity of emission I(T) due to the trap emptying on coordinates ln[I(T)/S(T)] – 1/T:

\[ \ln \frac{I(T)}{n} = -\frac{E_i}{kT} + \ln \frac{s}{\mu} \]  

where \( n \) is the number of filled ETs, which is proportional to the area \( S(T) \) under the high-temperature portion of TSL peak; \( E_i \) is the depth or activation energy of ET; and \( s \) is the frequency factor. Results of the calculation are given in table 2 in comparison with the literature data.

4. Discussion

It is known that the electron states of the top of the valence band and the bottom of the conduction band in the LSO belong to the 2p- and 5d-electron states of O\(^{2-}\) and Lu\(^{3+}\) ions, respectively. Therefore, the variations of the \( E_g \) value obtained from the position of characteristic absorption edge mainly are due to the anisotropy of the density of electron states of anion-cation pairs O\(^{2-}\)-Lu\(^{3+}\) in the crystal matrix, in which the distance between ions, depending on the direction, is from 2.16 to 2.62 Å [11]. According to intracenter transition theory [2], the anisotropy of absorbed \( h\nu_{a1=2} \) and emitted \( h\nu_{c1=3} \) quanta energy also is determined by the crystal environment of Ce\(^{3+}\) ion. However, to determine such an interrelation, experiments should be performed at low temperatures (below 100 K), which ensure the low error of determination of spectral band parameters.

The characteristics of UV radiation of sources used in the present study for TSL experiments differ substantially. The low-pressure deuterium lamp gives the continuous UV radiation spectrum; the radiation intensity decreases as the wavelength decreases, and the radiant intensity is 1.8 mW/sr. The radiation of high-pressure mercury lamp is characterized by intense UV-range lines with the photon energies of up to 6.5 eV and the radiant intensity of 310 mW/sr. Thus, based on the absorption spectroscopy data for the LSO, the mercury lamp radiation not only can ensure the excitation of Ce\(^{3+}\) activator but also leads to the ionizing of it accompanied by the electron transfer to the conduction band \( (h\nu_{a1=2}+\text{Ce}^{3+}=\text{Ce}^{4+}+e^-) \) and to the band-band transitions accompanied by the formation of electron-hole pairs. The analysis of the TSL data obtained in using the aforementioned UV radiation sources allows us to assume that traps responsible for the observed maxima are different in origin. Indeed, traps I and II, which take place in all experiments, are related to either the Ce\(^{3+}\) luminescence centre or objects associated with it, whereas traps III, the luminescence of which takes place only in using the mercury lamp, are related to states localized near the bottom of the conduction band of LSO. In any case, the study of the nature of found ET’s is a matter of further investigations. No maxima at temperatures of above 400 K, which were indicated previously in [4,9], were found because the observation of them is possible only in using the high-energy radiation (X-ray or \( \gamma \) radiation).

The comparison of the obtained results of the absorption spectroscopy and photoluminescence with the TSL data allows us, in using data of [3,11], to construct schematic diagram of energy levels, which determine the luminescence mechanism in the single-crystal LSO (figure 5). The absorption of quanta with energies of 3.47-4.70 eV are realized by Ce\(^{3+}\) ion at the expense of electron transitions between doublets of ground 4f and excited 5d states. As the exciting quantum energy increases up to 5.83 eV, the ionizing of the luminescence centre to the Ce\(^{4+}\) state and the electron transfer to the conduction band take place. Further, the electron trapping with traps both localized near the conduction band bottom (trap III) and associated with Ce\(^{3+}\) (traps I, II) is possible. The final stage of luminescence process in the LSO is preceded by the electron release from traps and radiationless electron transitions from the conduction band and top 5d levels of Ce\(^{3+}\) to the bottom 5d level. The photon emission corresponds to the electron
transitions from $5d$ levels to the $4f$ ground-state doublet with energies of 2.96, 3.12 eV (Ce$^{3+}$) and 2.70 eV (Ce$^{4+}$). Thus, we can conclude that the photoluminescence in the LSO has not only the intra-centre mechanism; the conduction band and trap states localized near the conduction band participate in the excitation energy storage.

### Figure 5
Simplified energy diagram of luminescence transitions in the single-crystal LSO. Vertical arrows correspond to radiation (solid) and radiationless (dotted) electron transitions.

## 5. Conclusions
The spectral characteristics of Ce$^{3+}$ doping-activator in the LSO single crystals grown by the modified Musatov method, have been studied. The band gap energy was found to depend on the optical beam direction in the crystal; the dependence is due to the crystal anisotropy. No anisotropy was found for the centroids of absorption and luminescence bands of Ce$^{3+}$. The parameters of electron traps participating in the luminescence were determined by TSL method. Traps characterized by a depth of 0.88 eV were found for the first time; they make a contribution to the TSL process when the crystal is exposed to the more intense radiation produced by the high-pressure mercury lamp. Using the obtained data, a model of the energy structure levels determining the luminescence process in the LSO has been constructed.

### Acknowledgments
This study was supported by the Russian Foundation for Basic Research (project no 18-32-00656 mol a “Investigation of the relationship between optical-luminescent and mechanical phenomena caused by reversible ionization of the Ce$^{3+}$ activator in Lu$_2$SiO$_5$:Ce$^{3+}$ single crystals”).

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