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Effect of gamma-induced defects on the activator glow in $Lu_2SiO_5:Ce$ scintillator crystals

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Correlations were studied between the optical absorption (OA) spectra and the integral curves of thermal glow (TG) in 300–600 K after irradiation of $Lu_2SiO_5:Ce$ scintillation crystals with ^{60}Co gamma-quanta (1.17 and 1.33 MeV) at the dose rate 1.1 Gy/s in the dose range $70-5\cdot10^7$ Gy at 310 K and their gamma-luminescence (GL). There are intrinsic defects caused by technological process, such as neutral V_{O5}-centers with OA band at 193 nm and charged $\equiv Si-V_{O5}$ — 213 nm, $Lu1-F^+-Si$ — 238 nm, Ce^{3+}/Ce^{4+} — 263 nm, and Ce^{3+}/F — 295 nm centers. Irradiation to the dose $5\cdot10^4$ Gy resulted in decreasing in V_{O5}-center concentration, but did not influenced on others. While, after doses $> 5\cdot10^4$ Gy concentrations of all other mentioned defects grew. The observed recovery of OA at 193 nm and decrease in TG peak at 335 K with the ageing time (1, 3 and 10 hours) at 305 K, and also the correlated growth of OA at 238 nm and TG peak at 540 K after serial irradiations to doses from 70 to $2.3\cdot10^6$ Gy are due to releasing electrons from these color centers followed by radiative recombination at Ce1-centers. However Ce^{3+} GL yield decrease at 400 and 420 nm at doses $> 10^5$ Gy is possible related with increasing concentrations of $\equiv Si-V_{O4}$, $Lu1-F^+-Si$ and Ce^{3+}/F centers, which compete with Ce1 ones in trapping electrons. Thus, the upper limit for stable $Lu_2SiO_5:Ce$ gamma-scintillation is 10^5 Gy.

Keywords: $Lu_2SiO_5:Ce$, color centers, gamma-induced luminescence, scintillation dose limit.

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1. Introduction

Single crystals of lutetium oxyorthosilicate, doped with cerium ions $Lu_2SiO_5:Ce$ (LSO:Ce), are being actively studied as a very promising scintillation material, thanks to their high density (7.4 g/cm^3), short decay time (40 ns), high light output (26 000 photon/MeV), which is five times greater than the light output of the used $Bi_4Ge_3O_{12}$ (BGO) scintillators without activators, and a suitable radiation wavelength (410 nm) for photo-electric converters/radiation detectors [1–3]. LSO:Ce crystals were suggested for fast detection of γ- or X-rays in medical imaging (positron emission tomography PET, X-ray mammography), in nuclear physics and high-energy physics experiments (see, e.g., [4–8]).

The following is required in future experiments at the Large Hadron Collider (HL-LHC) by 2030: increase of accelerator luminosity to $(5-10)\cdot10^{34}\,cm^{-2}\cdot s^{-1}$, total luminosity to 3000 fb^{-1}, fluences of charged hadrons above 10^{14} p/cm^2 and fast neutrons to $5\cdot10^{15}\,cm^{-2}$, and ionization dose to 130 Mrad ($130\cdot10^4$ Gy) [7–10]. For this, scintillation crystals must have a high stability of optical transparency and gamma-luminescence at the specified radiation levels. Therefore, it was necessary to reveal the reason of radiation changes of the scintillation luminescence yield of LSO:Ce crystals and the limiting dose of its stability.

The authors of [7,11] studied the degradation of optical transparency in the ultraviolet and visible spectrum regions of LSO:Ce after irradiation with gamma quanta (from a ^{60}Co) source in the dose range of 10^2-10^6 Gy [11] and after the irradiation dose of $2\cdot10^3$ Gy [7]. The authors showed the stability of optical transmission in the spectral region of 300–600 nm at least up to the doses of 10^4 Gy, while after the dose of 10^6 Gy they found only a 7% decrease of transmission in the region of 420 nm and recovery of the initial state after thermal annealing of the color centers at 300°C (573 K) [11]. However, the mechanism of recovery to the initial state after annealing is not discussed in that paper. The authors of [7] described a series of optical absorption (OA) bands of 240, 306, 343, 376 and 416 nm observed after irradiation with the gamma dose of $2\cdot10^3$ Gy, regardless of Ce activator content in LSO, which are annealed at 300°C (573 K), and noted correlations with thermally-stimulated luminescence (TSL) from traps in the orthosilicate obtained in [12,13].

Growth defects form in the process of LSO:Ce crystal growing by the Czochralski method in an inert atmosphere — e.g., oxygen vacancies in sites (O5), which are not related to Si and have the lowest formation energy [14]. It means that these vacancies are due to a break of the Lu1–O5 bond, according to the detailed structural analysis performed earlier in [15]. The following was found in

LYSO : Ce crystals grown by the method of zone melting in the air: an increase of the 420 nm X-ray luminescence band and a decreased intensity of TSL peaks in the temperature range of 300–500 K depending on O2 content increase (1.4, 21 and 100%) [13]. This data indicates a possibility to control the number of initial defects which can change the crystal's optical properties. On the other hand, a purposeful action of penetrating radiation on a substance is an important method for the revelation of growth defects and controlled changing of their number.

The objective of this paper is to study kinetics (^{60}Co) of gamma-induced accumulation and annealing of optical defects in a wide range of gamma doses $70-5\cdot10^7$ Gy and mechanisms of their influence on the activator centers of luminescence in doped LSO : Ce.

2. Research objects and methods

The samples of LSO : Ce^{3+} single crystals (Ce concentration of 0.25 at.%) were grown by the Czochralski method in nitrogen atmosphere (N_2) containing 3000 ppm of oxygen (O_2) (Scintillation Materials Research Center, Department of Materials Science and Engineering, University of Tennessee, Knoxville, USA).

Strips sized 4 × 4 mm and 1 mm thick were prepared for optical studies. The samples were wrapped in aluminum foil to restrict the action of atmosphere on the surface and were irradiated at the Institute of Nuclear Physics of the Academy of Sciences of Uzbekistan by gamma-quanta of a ^{60}Co source with the energies of 1.17 and 1.33 MeV and the dose rate of 1.1 Gy/s in the dose range of $70-5\cdot10^7$ Gy at 310 K. To prevent possible photobleaching of the samples under exposure to daylight, they were kept in the aluminum foil from the start of irradiation till placement in the measurement cell of the spectral device.

Spectra of optical absorption (OA) before and after irradiation were measured at the temperature of 305 K using LAMBDA-35 (PerkinElmer) and SF-56 (LOMO) spectrophotometers in the spectral region of 190–1100 nm. One and the same sample was successively irradiated with the dose of 10^3 Gy and the OA spectrum was recorded each time. The time interval from irradiation stop till the start of spectrum measurements did not exceed 3 min. The integral dose was 10^4 Gy. The OA spectra after irradiations in the dose range of $5\cdot10^4-5\cdot10^7$ Gy were measured in three samples after a week.

Gamma-luminescence (GL) spectra were recorded at 310 K using a MDR-12 diffraction monochromator with a FEU-39 photomultiplier tube in the spectral region of 200–600 nm. The GL spectra up to the dose of $5\cdot10^5$ Gy were measured on one sample, while the subsequent doses of $5\cdot10^4-5\cdot10^7$ Gy were measured on three samples.

The integral peaks of thermal luminescence (TL) were recorded using a FEU-79 photomultiplier tube at the permanent heating speed of 0.25 K/s in the temperature range of 300–600 K with monitoring by means of a chromel-copel thermocouple.

The following was done for the interpretation of the effects of manifestation of the color centers and luminescence: successive annealing of the TL peaks for 20 min up to temperatures corresponding to the minimum values on the TL curves and subsequent cooldown in a furnace to 300 K, and then measurement of optical absorption spectra.

3. Results and discussion

The OA spectra of the non-irradiated samples of LSO : Ce have absorption bands in the UV spectrum region of 195 and 200 nm and a structureless wide band in the region of 205–250 nm, as well as the known bands of 260, 295 (Fig. 1, *a*, curve *1*), and 360 nm (Fig. 1, *b*, curve *1*) relation to ($4f \to 5d$) transitions of the Ce^{3+} ion. The measured OA spectrum in the non-irradiated sample of LSO : Ce is identical to the spectra published by other researchers earlier [12,16,17]. The authors of [12,16] ascribe the OA bands of 200, 220, 264, 295 and 356 nm to $4f \to 5d$ transitions in Ce^{3+} ions. It should be noted that the OA spectra of the non-irradiated nominally pure sample of yttrium orthosilicate YSO also has an OA band of 195 nm and a wider 200–250 nm (curve *6*), which is also present in the LSO crystal with the monoclinic structure C2/c with two non-equivalent metallic sites (Fig. 1, *a*, curve *1*). This means that the observed OA bands in the region of 190–250 nm do not depend on the presence of the Ce activator ion, that's why they are related to anion defects.

After ^{60}Co gamma-irradiation with the doses of 10^2 and 10^4 Gy there is a more noticeable decrease of the 195 nm OA band as compared to the spectral region of 200–250 nm (Fig. 1, *a*, curves *2* and *3*). This band increases after the doses of $5\cdot10^5$ and $5\cdot10^7$ Gy and reaches saturation (Fig. 1, *a*, curves *4* and *5*). Moreover, at the dose of $5\cdot10^5$ Gy there is a more distinct OA band in the region of 240 nm, and the 240, 260 and 290 nm OA bands quickly increase after the doses up to $5\cdot10^7$ Gy (Fig. 1, *a*, curves *4* and *5*). Thereat, these are no significant changes of the 360 nm OA band (Fig. 1, *b*, curves *1–5*). The breakdown of the OA spectra in Fig. 2 is based on the literature data [12,16,17], which gives the number and position of the bands, as well as on a discussion of the further nature of this bands further in the present article. This is necessary for a more precise analysis of the kinetics of change of the color centers after a gamma dose from 70 to $5\cdot10^7$ Gy.

Fig. 2, *a* shows the spectral dependences of absorption coefficient α (cm^{-1}) at the wavelength of ≤ 330 nm (≥ 3.75 eV) after irradiation with the dose of $5\cdot10^7$ Gy (curve *1*), for which a breakdown into Gaussian functions was performed. Six bands (G1–G6) with the maxima at 4.22 eV (293 nm), 4.7 eV (263 nm), 5.18 eV (238 nm), 5.8 eV (213 nm), 6.12 eV (202 nm) and 6.4 eV (193 nm) and FWHM (full width at half maximum) of 0.51, 0.52,

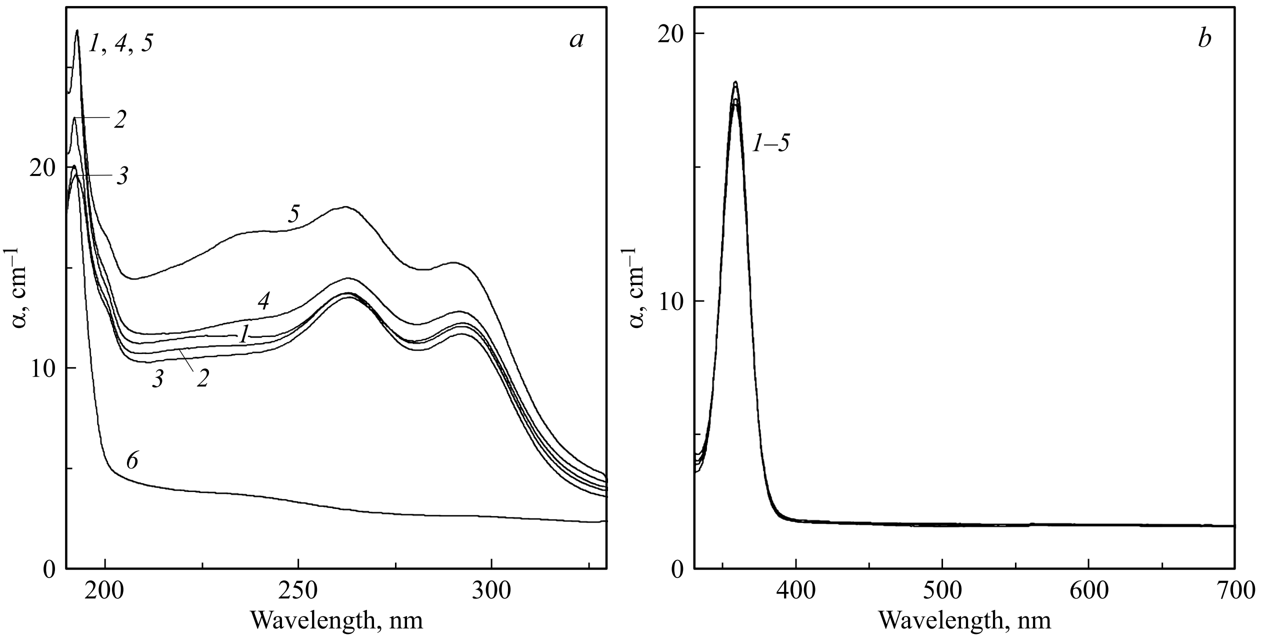

Figure 1. Absorption spectra of the activated LSO:Ce crystal in *a*) UV and *b*) visible regions: the initial one (curves *1*) and after irradiation with the dose of 10^2, 10^4, $5 \cdot 10^5$, $5 \cdot 10^7$ Gy (curves *2–5*, respectively), and the initial YSO crystal (curve *6*).

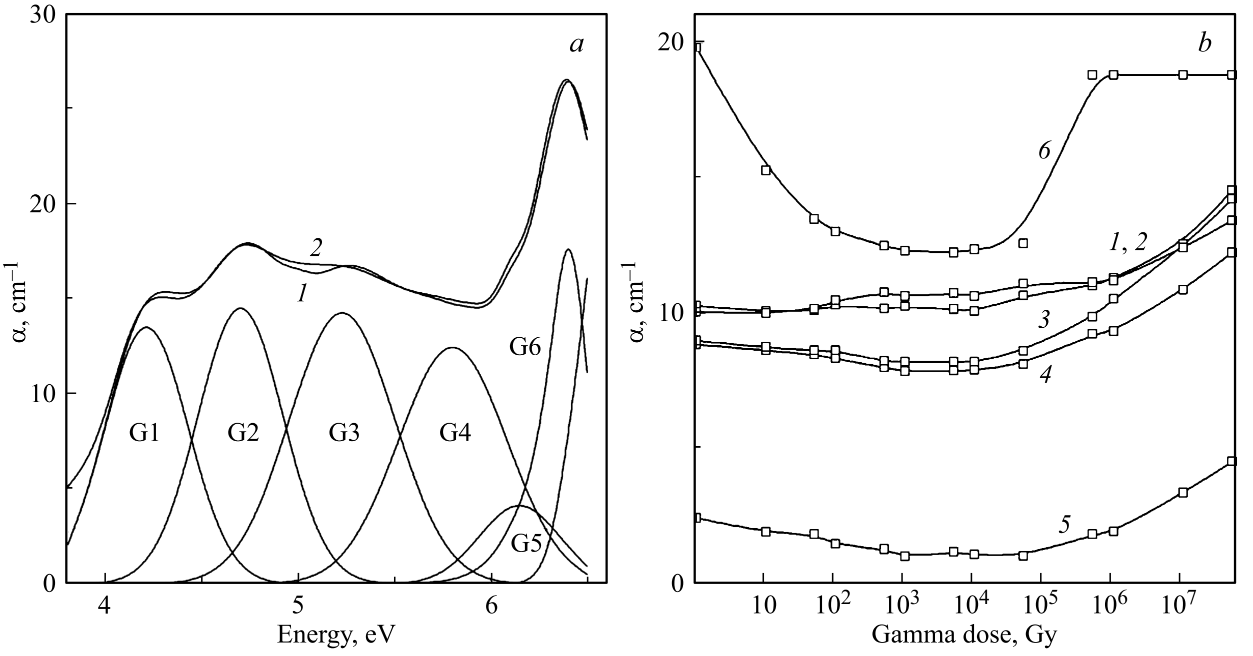

Figure 2. *a*) Absorption spectrum of LSO:Ce crystal after irradiation with the dose of $5 \cdot 10^7$ Gy (curve *1*), its Gaussian components (G1–G6) and their sum (curve *2*); *b*) dose dependences of the following absorption bands: 4.22, 4.7, 5.18, 5.8, 6.12 and 6.4 eV (curves *1–6*, respectively).

0.64, 0.65, 0.5 and 0.4 eV, respectively, are distinguished. Based on this, we have plotted the dose dependences of the maxima of the OA bands of 4.22 eV (293 nm), 4.7 eV (263 nm), 5.18 eV (238 nm), 5.8 eV (213 nm), 6.12 eV (202 nm) and 6.4 eV (193 nm) to determine the kinetics of their changes. Fig. 2, *b* shows the dose dependences of each Gaussian component.

It can be seen from Fig. 2, *b* that there is a significant decrease of the coefficient of the 193 nm OA band (curve *6*) with a gamma-dose increase to 10^4 Gy as compared to the 6.12 eV (202 nm), 5.8 eV (213 nm) and 5.18 eV (238 nm) bands (curves *5, 4, 3*). Thereat, the coefficients of the 4.7 eV (263 nm) and 4.22 eV (293 nm) bands do not change significantly up to the dose of $5 \cdot 10^5$ Gy (curves *2* and *1*).

With a further dose increase from 10^4 to $5 \cdot 10^5$ Gy, the 193 nm OA band increases with subsequent saturation to $5 \cdot 10^7$ Gy (curve *6*). We also observe an increase of the coefficients of the 6.12 eV (202 nm) (curve *5*), 5.8 eV (213 nm) (curve *4*) and 5.18 eV (238 nm) bands (curve *3*) from $5 \cdot 10^4$ Gy to the dose of $5 \cdot 10^7$ Gy. An increase of the coefficients of the 4.7 eV (263 nm) and 4.22 eV (293 nm) OA bands was noted at the dose of $> 10^6$ Gy (curves *2* and *1*).

The studies of reflection, excitation and luminescence spectra using synchrotron radiation in the energy range of 5−30 eV (248−41.3 nm), described in papers [18–20], as well as the data of X-ray photoelectron spectroscopy (XPS), indicate that the valence band consists of mixed Lu4f−O2p states, while the conduction band is formed by a Lu5d-state. The exciton luminescence about excitation band of 7.27 eV (170 nm) is conditioned by a O2p → Lu5d transition, the estimated band gap energy is 7.52 eV (165 nm) [18]. According to [7], oxygen vacancies can be included in the $O^{2-}-V_O$ charge-transfer transition, the energy of which must be higher than the optical transition energies of F^+- and F-centers [7]. Taking into account the detailed structural analysis performed in [15], the observed 6.4 eV (193 nm) OA band in the initial LSO : Ce samples (Fig. 1, *b*, curve *1*) is possibly conditioned by oxygen vacancies O5 in the Lu1−O5 bond ($Lu1-V_{O5}$) which are not bound to Si. The observed 5.8 eV (213 nm) OA band is also found in silicate and quartz glasses SiO_2 [21,22], which is ascribed to E'-centers (three-coordinated silicon ≡Si). Based on this and taking account the structural analysis in [15], we assume that the 213 nm OA band is possibly related to a complex defect $\equiv Si-V_{O4}-Lu1$. The 5.18 eV (238 nm) band observed in the OA spectrum (Fig. 1, *a*, curves *4* and *5*) according to [23] is related to the F^+-center (an oxygen vacancy which trapped one electron) and, possibly, is formed by the breakdown of the longest bond (0.26163 nm) in [15] Lu1−O2−Si with the formation of a charged vacancy V_{O2} — complex center $Lu1-F^+-Si$.

After the high-temperature annealing of the LSO : Ce sample at 1400°C in air atmosphere (14 h), the authors of [24] found an increased absorption in the region of 200−290 nm in relation to the initial sample due to an increase of the Ce^{4+}-center concentration, even if this does not lead to a noticeable decrease of the absorption band of Ce^{3+}-centers, and a decrease of the 265 and 297 nm bands of excitation of 400 and 420 nm luminescence of the Ce^{3+}-center [24]. Moreover, the 240 and 306 nm OA bands are also observed in the nominally pure LSO sample after gamma irradiation with the dose of $2 \cdot 10^3$ Gy, and the authors of [7] ascribe them to F-centers (an oxygen vacancy which trapped two electrons). We assume that the 4.7 eV (263 nm) and 4.22 eV (293 nm) absorption bands of Ce^{3+} ions in the spectral region of 250−300 nm are possibly overlapped by bands of other Ce^{4+}- and F-color centers, respectively. The formation of an F-center is possibly related to an oxygen vacancy in the $Lu-V_{O1}-Si$ bond (Lu−F−Si OA of 306 nm [7]) or $Ce-V_{O1}-Si$ (Ce−F−Si OA of 4.22 eV, 293 nm). Then these color centers with the specific OA bands of 4.7 eV (263 nm) and 4.22 eV (293 nm) are designated in a simplified form as Ce^{3+}/Ce^{4+}- and Ce^{3+}/F--centers, respectively.

The measured dose dependences (Fig. 2, *b*) of the absorption coefficients for the color centers, related to oxygen vacancies $Lu1-V_{O5}$ (the 6.4 eV, 193 nm band), $\equiv Si-V_{O4}-Lu1$ (5.8 eV, 213 nm), $Lu1-F^+-Si$ (5.18 eV, 238 nm), activation centers Ce^{3+}/Ce^{4+} (4.7 eV, 263 nm) and Ce^{3+}/F (4.22 eV, 293 nm), show that the existing growth defects are charged up to the irradiation dose of $5 \cdot 10^4$ Gy. An increased concentration of centers $\equiv Si-V_{O4}-Lu1$ (5.8 eV, 213 nm), $Lu1-F^+-Si$ (5.18 eV, 238 nm) and Ce^{3+}/F (4.22 eV, 293 nm) at the gamma doses of $\geq 10^5$ Gy means the generation of free electrons and additional vacancies V_{O4}, V_{O2} and V_{O1}, which can become competitors for the luminescent Ce^{3+}-center in the trapping of these electrons. We have recorded the GL spectra at 305 K (Fig. 3, *a*) in order to reveal the influence of the generated centers on the activator luminescence of Ce^{3+} in the LSO : Ce crystal. The intrinsic luminescence bands of 250 nm (excitons) and 315 nm (self-localized holes) in LSO orthosilicate, according to papers [19,6], are efficiently excited at ≤ 100 K. Then their contribution at 305 K is excluded.

As seen from Fig. 3, *a*, the GL spectrum of the LSO : Ce sample after the first 3 min of irradiation has a wide luminescence band in the energy region of 2 to 3.5 eV (curve *1*). It is known that photo- [24,25,26] and X-ray [27] quanta excite luminescence bands with the maxima of 3.1 and 2.95 eV, related to Ce1-centers, in this spectral region; 2.75 eV (curve *1*) — related to Ce2-centers (coordinated by six oxygen ions); these bands are conditioned by a $d \rightarrow f$ transition of Ce^{3+} ions. Then the GL spectra of the same sample were recorded with the time interval of 6 min up to the dose of 10^4 Gy. Then the GL spectra were recorded in three samples preliminarily irradiated with the doses of $5 \cdot 10^4$ and 10^5, 10^6 and $5 \cdot 10^7$ Gy, respectively. Taking into account the number of luminescence bands and their wavelengths in [24,25–27], our GL spectra were broken down into Gaussians after each gamma irradiation dose. After breakdown into Gaussian components, the known luminescence bands with the maxima of 3.1 eV (399 nm) (curve G1) and 2.95 eV (420 nm) (curve G2), related to Ce1-centers; 2.75 eV (450 nm) (curve G3) — to Ce2-centers, can be distinctly seen in Fig. 3, *a*. After breakdown of the GL spectra, obtained after each irradiation from 70 to $5 \cdot 10^7$ Gy, into Gaussian components, we plotted the kinetics of a change in intensity of the GL band components of 3.1 eV (399 nm), 2.95 eV (420 nm) and 2.75 eV (450 nm) which are shown in Fig. 3, *b*, curves *1–3*.

An interesting phenomenon is observed: with an increase of irradiation time up to the dose of $5 \cdot 10^4$ Gy, the intensities of the GL 3.1 eV (399 nm), 2.95 eV (420 nm) and 2.75 eV (450 nm) bands do not change, and start decreasing after the doses of $\geq 10^5$ Gy, that is, the

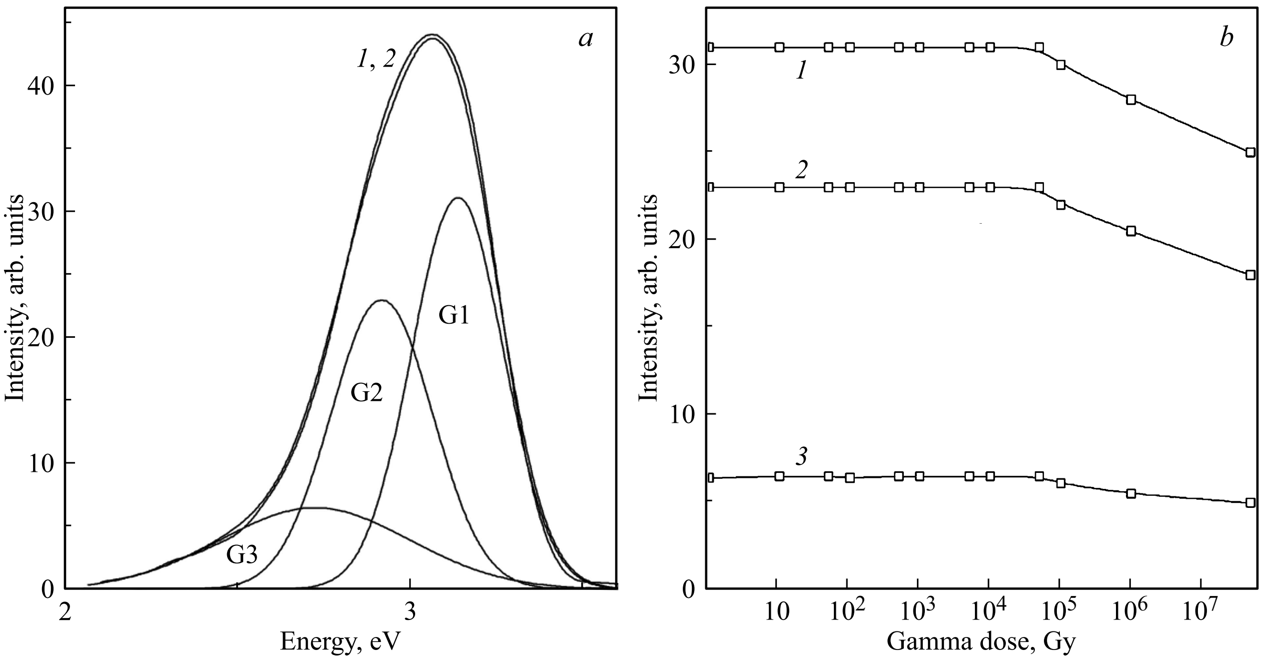

Figure 3. Gamma-luminescence spectrum of LSO : Ce crystal: *a*) the initial one (curve *1*), its Gaussian components (G1–G3) and their sum (curve*2*); *b*) dose dependences of the luminescence band: 3.1, 2.95 and 2.75 eV (curves *1–3*, respectively).

concentration of Ce1 and Ce2 radiative centers decreases. A decrease of the yield of the 399, 420 and 450 nm luminescence bands after the maximum dose of $5 \cdot 10^7$ Gy, as compared to the yield after the threshold dose of $5 \cdot 10^4$ Gy, was approximately 21%, respectively. At the same time, an increase of the concentration of defect-related color centers is observed from the kinetics of change of the OA coefficients at $\lambda \leq 330$ nm after doses of $> 5 \cdot 10^5$ Gy: Lu1–V_{O5} (the 6.4 eV, 193 nm band), $\equiv$Si–V_{O4} (5.8 eV, 213 nm), Lu1–F^+–Si (5.18 eV, 238 nm), activator Ce^{3+}/Ce^{4+} (4.7 eV, 263 nm) and Ce^{3+}/F (4.22 eV, 293 nm) (Fig. 2, *b*). Consequently, it can be assumed that Ce^{3+} ions in the field of ^{60}Co gamma-quanta act as deep traps for holes trapped from the valence band

$$Ce^{3+} + h\nu \rightarrow Ce^{4+}. \quad (1)$$

When an electron is trapped from the conduction band and goes from the excited state to the ground $4f$-state, the $(Ce^{3+})^*$ ion emits a quantum

$$Ce^{4+} + e_c^- \rightarrow (Ce^{3+})^* \rightarrow h\nu. \quad (2)$$

This mechanism will be effective if there is no direct recombination of electrons and holes or their trapping by other defects. As noted above, the eigen luminescence bands of 250 and 315 nm during GL measurement at 305 K are not excited. Thus, a decrease of the GL yield of activator luminescence of Ce^{3+} (centers Ce1 and Ce2) after the dose of $\geq 10^5$ Gy (Fig. 3, *b*, curves *1–3*), is apparently related to an increased concentration of competing additional vacancy centers Lu1–F^+–Si (5.18 eV, 238 nm) and Ce^{3+}/F (4.22 eV, 293 nm) which trap thermalized electrons. In this respect, it was further interesting to study the relation between these gamma-induced centers and the known TL peaks [12,27–29] in the temperature range of 300–600 K. The spectral composition of the TL peaks was determined; it contains a 420 nm band related to $5d \rightarrow 4f$-transitions of Ce^{3+}, and the activation energy parameters and frequency factors were also determined [12].

Fig. 4, *a* gives the integral curves of TL of the activated LSO : Ce irradiated by the same dose of $2 \cdot 10^2$ Gy at 305 K, recorded in the temperature range of 300–600 K, after 3 min and 1, 3 and 10 h (curves *1–4*, respectively). The OA spectra, measured before and after (the above-mentioned holding times) measurement of the TL curves up to 600 K, are shown in Fig. 4, *b*, curves *1–7*. The TL curves usually contain five peaks: 1-st — 335, 2-nd — 390, 3-rd — 440, 4-th — 475 and 5-th — 540 K (Fig. 4, *a*, curve *1*). A comparison of the TL curves (Fig. 4, *a*) and the OA spectra (Fig. 4, *b*) has revealed the following: i) the amplitude of the most intensive TL peak of 335 K, measured in 3 min of holding after irradiation (curve *1*), significantly decreases with an increase of holding time to 1 h (curve *2*) and 3 h (curve *3*) at 300 K, and after 10 h this TL peak is virtually absent (Fig. 4, *a*, curve *4*). As distinct from this peak, the high-temperature TL peaks of 390, 440, 475 and 540 K do not depend on holding time (Fig. 4, *a*), that is, these traps are stable at 300 K; ii) the coefficient of the 193 nm OA band in the OA spectrum after the dose of $2 \cdot 10^2$ Gy decreases significantly (curve *2*) as compared to the initial sample (curve *1*) (Fig. 4, *b*). It increases after holding for 1 h (curve *3*) and 3 h (curve *5*) at 300 K, while

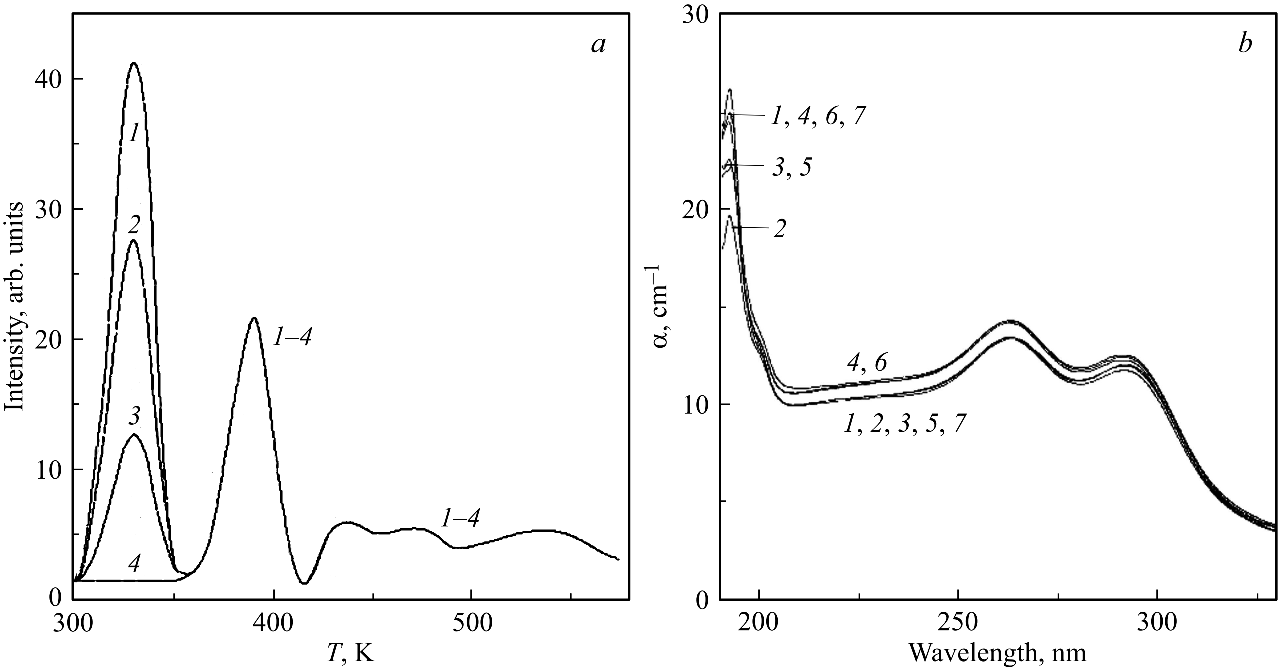

Figure 4. *a*) Thermal luminescence curves for the LSO:Ce crystal measured after irradiation with the dose of $2 \cdot 10^2$ Gy after 3 min and 1, 3 and 10 h — curves *1–4* respectively; *b*) absorption spectra in the UV region: the initial one (curve *1*), spectra measured after 1 h (*3*), 3 h (*5*), 10 h (*7*) and measured after heating to 600 K in 1 h (*4*), 3 h (*6*) after irradiation with the dose of $2 \cdot 10^2$ Gy (*2*).

after holding for 10-h its absorption coefficient reached the level of the initial non-irradiated sample (curve *7*) (Fig. 4, *b*), because the corresponding trap becomes empty at 335 K. Charged defects possibly transform into the chargeless state by the gradual liberation of electrons and subsequent recombination with a hole Ce^{4+} center. This process causes an increase of the concentration of neutral $Lu1{-}V_{O5}$-centers (chargeless state of an electron trap) located around the central Ce^{3+} or Lu^{3+} ion. The significant afterglow in LSO after gamma-excitation is related to the presence of an electron trap (TL peak of 335 K) according to [30]. Thus, the formation of the TL peak of 335 K and the decrease of the 193 nm OA band coefficient after irradiation, as well as the recovery of the 193 nm OA band and disappearance of the TL peak of 335 K after 10-hour holding at 305 K can possibly explain the afterglow mechanism, related to the recovery of the electron trapping centers (the 6.4 eV, 193 nm OA band).

Subsequent irradiation with doses in the range of $10^5{-}5 \cdot 10^7$ Gy were performed on three different samples. In order to distinguish the stable centers only, OA spectra were measured one week after each irradiation. That's why the observed increase of the 6.4 eV (193 nm) OA band coefficient (Fig. 2, *b*, curve *6*) is related to the recovery of the neutral $Lu1{-}V_{O5}$-center in the course of electron liberation from a color center (the 193 nm OA band). The observed slight increase of OA in the region of 200 to 290 nm (Fig. 4, *b*, curves *4* and *6*) after heating to 600 K (after taking of the TL curves) is possibly related to the transformation of more complex defects.

However, the coefficient of the 360 nm OA band, related to the $4f \rightarrow 5d$ transition in Ce1-centers, did not change after the different holding times of 1, 3 and 10 h at 305 K or after heating to 600 K after irradiation with the dose of $2 \cdot 10^2$ Gy. Then we revealed a relation between the gamma-induced color centers and charge carrier traps, which can condition a decrease of the activator Ce^{3+}-GL after irradiation with the doses of $> 10^5$ Gy (Fig. 3, *b*).

The OA spectra and TL curves were measured 5 min after gamma-irradiation with the high dose of $2.3 \cdot 10^6$ Gy. Fig. 5, *a* shows the OA spectra of the initial LSO:Ce sample (curve *1*), after irradiation with the dose of $2.3 \cdot 10^6$ Gy (curve *2*), after heating to 600 K (for TL removal and trap depletion) of the sample irradiated with the dose of $2.3 \cdot 10^6$ Gy (curve *3*), and after the additional small doses of 70, 200 and 10^4 Gy (curves *4–6*, respectively) for trap filling. After irradiation with $2.3 \cdot 10^6$ Gy there is an increase of the coefficients of the 238 nm OA bands by 15%, 263 nm by 8% and 295 nm by 6% (curve *2*) as compared to the values in the initial sample (curve *1*). The TL curves in Fig. 5, *b* after the high dose of $2.3 \cdot 10^6$ Gy (curve *1*), as distinct from the TL curve after the low dose of $2 \cdot 10^2$ Gy (Fig. 4, *a*, curve *1*), along with the known TL peaks of 335, 390, 440, 475 and 540 K [12,27–29], have an additional TL peak of about 373 K (Fig. 5, *b*, curve *1*). After taking of the TL curves of the sample irradiated with the dose of $2.3 \cdot 10^6$ Gy, the OA spectrum (Fig. 5, *a*, curve *3*) had a decreased coefficient of the 238 nm OA band — the $Lu1{-}F^{+}{-}Si$-center, while the coefficients of the 263 — Ce^{3+}/Ce^{4+} and 295 nm OA bands — Ce^{3+}/F

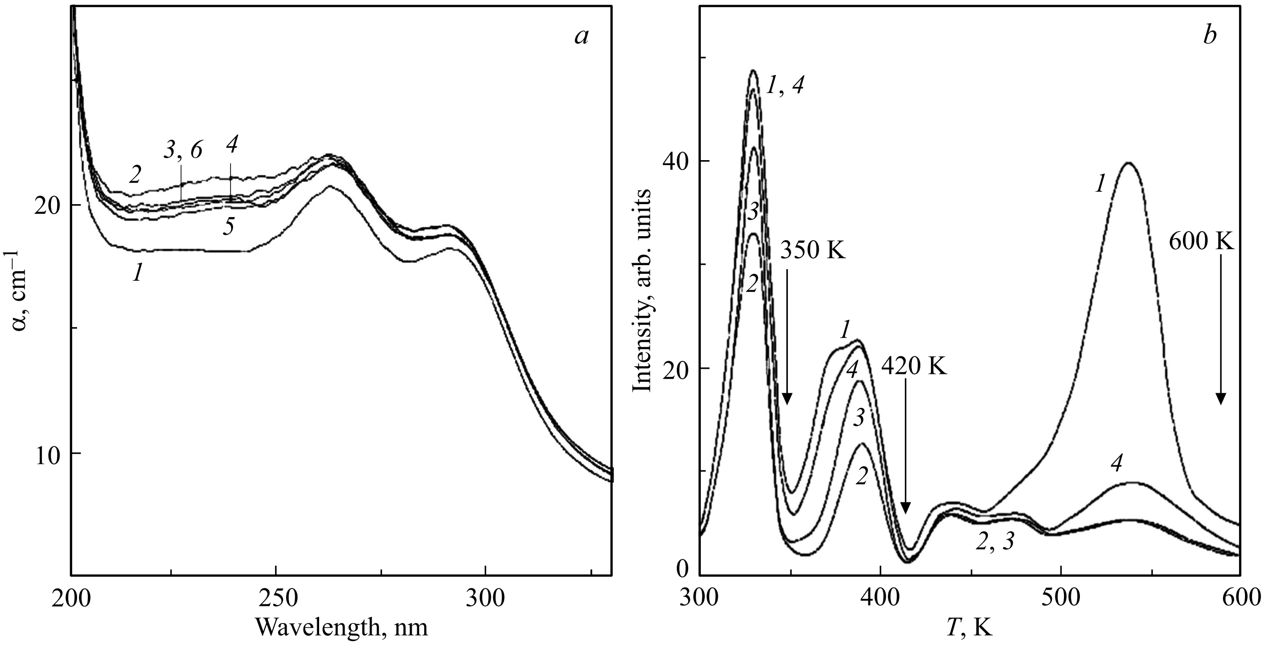

Figure 5. *a*) Absorption spectra of the activated LSO:Ce crystal in the UV-region: the initial one (curve *1*), after irradiation with the dose of $2.3 \cdot 10^6$ Gy (*2*) and heating to 600 K during TL measurement (*3*) and subsequent gamma-irradiation with the following doses: 70, 200 and 10^4 Gy — curves *4–6* respectively. *b*) TL curves for the LSO:Ce crystal: after irradiation with the dose of $2.3 \cdot 10^6$ Gy (*1*) and subsequent gamma-irradiation with the doses of 70, 200 and 10^4 Gy — curves *2–4* respectively.

did not change. These processes can be characterized as follows: when heat energy is transmitted to electrons released from traps (color centers), they undergo radiative recombination with holes on the Ce^{4+}-centers according to reaction (2). Thereat, the defects, generated by the gamma-dose of $2.3 \cdot 10^6$ Gy, where charge localization is possible, can remain. The color centers can be populated by carriers under the subsequent irradiation of this sample with the dose of $< 2.3 \cdot 10^6$ Gy. For this, the sample irradiated with the gamma-dose of $2.3 \cdot 10^6$ Gy and heated to 605 K (upon removal of TL), was then irradiated with the small gamma-dose of 70 Gy. As a result, the OA spectrum (Fig. 5, *a*) has interesting features related to the fact that, instead of an increase of the 238 nm OA band coefficient, there is a slight decrease of its coefficient after the small doses of 70 and 200 Gy (curves *4* and *5*), but its increase after the next dose of 10^4 Gy (curve *6*) up to the value for the sample irradiated with the dose of $2.3 \cdot 10^6$ Gy and heated to 605 K (curve *2*). At the same time, the intensity of the TL peaks of 335, 390 and 540 K increases in the TL curves (Fig. 5, *b*) when the dose of 70, 200 and 10^4 Gy is added (curves *2–4*). After the dose of 10^4 Gy, an additional new TL peak of 373 K (curve *4*), which increases up to the dose of $2.3 \cdot 10^6$ Gy (curve *1*), is found near the TL peak of 390 K. Moreover, the intensities of the TL peaks of 335 and 390 K at the irradiation dose of 10^4 Gy reach saturation and increase of the TL peak of 540 K up to the irradiation dose of $2.3 \cdot 10^6$ Gy. However, the TL peaks of 440 and 475 K do not change.

A comparison of the OA spectra (Fig. 5, *a*) and TL curves (Fig. 5, *b*) shows that the observed TL peaks in the temperature range of 300–600 K (Fig. 4, *a*) after irradiation up to the dose of 10^4 Gy, according to [12,28,29] are related to the growth oxygen vacancies generated in the technological process. A comparison of the LYSO:Ce orthosilicate crystals, grown in an atmosphere with a different oxygen content (O_2), has shown that its increase causes a decrease of the intensities of the above-mentioned TL peaks in the temperature range of 300–500 K [13], that is, these peaks are related to oxygen vacancies in the orthosilicate matrix. Indeed, an increase of the 238 nm OA coefficient — Lu1–F^+–Si-center observed after the irradiation dose of $> 10^4$ Gy (Fig. 1, *a*, curves *4* and *5* and Fig. 2, *b*, curve *4*) correlates with an increase of the amplitude of the 540 K TL peak (Fig. 5, *b*, curves *4* and *1*). Consequently, the 238 nm OA band of the Lu1–F^+–Si-center is related to one of the electron traps.

Then we studied the thermal fading of the gamma-irradiation-induced absorption bands which characterize the charge carrier trapping centers (color centers). For this purpose, we performed successive annealing of the TL peaks for 20 min up to the temperatures which corresponds to the minimum values on the TL curves (marked with arrows in Fig. 5, *b*), followed by cooldown to 300 K.

Fig. 6, *a* shows the absorption spectra taken before and after annealing for 20 min at the temperatures of 350, 420 and 600 K of the LSO:Ce sample irradiated with the dose of $5 \cdot 10^7$ Gy (Fig. 6, *a*, curves *1–6*). A slight increase of optical absorption (curves *3* and *4*) is observed

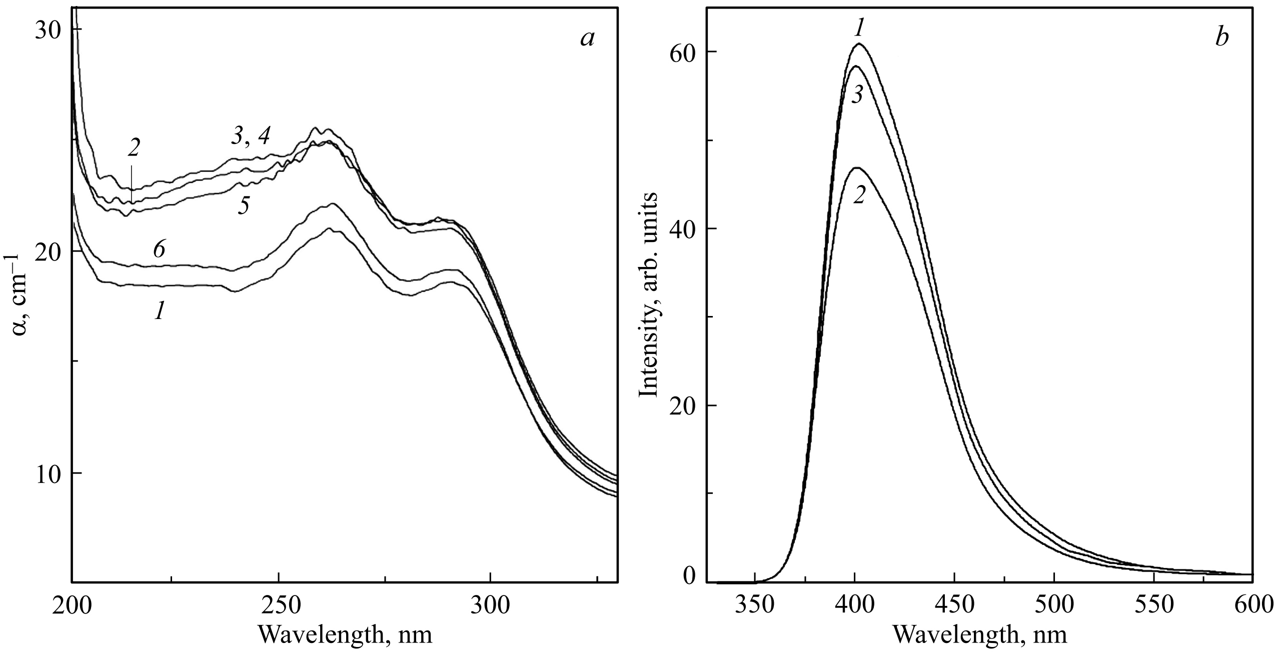

Figure 6. *a*) Absorption spectra in the UV-region of the activated LSO : Ce crystal: the initial one (curve *1*), after gamma-irradiation with the dose of $5 \cdot 10^7$ Gy (curve *2*), after annealing at the temperatures of 350, 420, 600 and 773 K — curves *3–6*, respectively. *b*) Gamma-luminescence spectra of the LSO : Ce crystal: the initial one (curve *1*), after gamma-irradiation with the dose of $5 \cdot 10^7$ Gy (*2*) and after annealing at 773 K (*3*).

in the spectral region of < 280 nm after annealing at 350 and 420 K. This behavior is also confirmed in paper [7], where, regardless of the presence of the Ce activator in the LSO sample gamma-irradiated with the dose of $2 \cdot 10^3$ Gy, a decrease of absorption in the visible region and its increase in the UV-region is observed after annealing at 100°C (373 K). Apparently, this is due to the following processes: a part of the thermally liberated electrons undergo radiative recombination with Ce^{4+} hole centers, while the other part is trapped by deeper traps. Such deep electron traps can be Lu1–F^+–Si-centers, characterized by the 238 nm OA band, the coefficient of which after annealing at 350 and 420 K slightly increases (curves *3* and *4*), while, on the contrary, it decreases after annealing at 600 K (curve *5*). The OA band in the visible region of 400–500 nm after gamma-irradiation of the LSO sample 10 mm thick, described in [11,7], is, in our opinion, related to the detected additional TL peak of 375 K after the dose of 10^4 Gy, which increases with dose buildup to $2.3 \cdot 10^6$ Gy (Fig. 5, *b*, curves *4* and *1*). Due to the small thickness (1 mm) of our samples as compared to the thickness of the 10-mm samples, irradiated with doses up to 10^6 Gy in [11, 7], we did not find an OA band in the region of 410–500 nm even after the higher dose of $5 \cdot 10^7$ Gy, though the obtained concentration of this color center in our experiment was higher. After the highest dose of $5 \cdot 10^7$ Gy, the induced Lu1–F^+–Si, Ce^{3+}/Ce^{4+} and Ce^{3+}/F centers after annealing for 20 min at 600 K are not annealed completely, because of the maintained high coefficients of the 238, 263 and 295 nm OA bands (Fig. 6, *a*, curve *5*), as compared to the original sample (curve *1*). These defects are almost completely annealed at the temperatures of ≥ 773 K (Fig. 5, *a*, curve *6*), then this must affect the change of the GL yield of the activator Ce^{3+}-center. Indeed, there is an increase in the intensity of the GL yield (Fig. 6, *b*, curve *2*) to the GL level of the non-irradiated LSO : Ce sample (Fig. 6, *b*, curve *1*). This is due to the fact that the radiation-induced interstitial oxygen diffuses at the annealing temperature of ≥ 773 K to the nearest induced anionic vacancy and recombines (healing of the Frenkel pair in the anionic sublattice).

4. Conclusion

We have performed a comparative study of optical properties (absorption and luminescence) of lutetium orthosilicate crystals activated with cerium ions LSO : Ce, before and after gamma-irradiations (^{60}Co) in the dose range of 70–$5 \cdot 10^7$ Gy at 310 K.

Origination of an own neutral V_{O5}-center, admittedly in the place of a non-bridging oxygen in the Lu1–O5 bond, with a typical absorption band of 193 nm and a TL peak of 335 K, is related to the technological process. The growth defects also include mutually overlapping bands of Ce^{3+}/Ce^{4+} at 263 nm as well as Ce^{3+}/F at 295 nm.

It is shown that intensities of the 399 and 420 nm (Ce1-centers) and 450 nm GL bands (Ce2-centers) do not change under ^{60}Co gamma-irradiation at 310 K in the dose range of 70 to $5 \cdot 10^4$ Gy. Higher doses of > $5 \cdot 10^4$ Gy cause a decrease of intensity of this GL bands of the activator Ce^{3+}-center due to defect generation in the LSO:Ce crystal structure: i) $\equiv$Si$-V_{O4}$ (OA 213 nm) in the place of O4 in the $\equiv$Si$-$O4 bond, ii) break of the longest bond (0.26163 nm) Lu1$-$O2$-$Si with the formation of a charged vacancy O2 — a complex center Lu1$-F^+-$Si (238 nm OA) and iii) Lu1$-$F$-$Si or Ce1$-$F$-$Si (295 nm OA). These assumptions are based on the detailed structural analysis in [15]. These color centers start competing with the luminescent Ce^{3+}-center in electron trapping. The upper limit of gamma-scintillator stability is the irradiation dose of 10^5 Gy.

It is shown that the most intensive 335 K TL peak (accountable for scintillator afterglow) is related to the electron trapping on Lu1$-V_{O5}$ (the 193 nm OA decreases).

The Lu1$-F^+-$Si complex center (238 nm OA) is characterized by an intensive (after irradiation) TL peak of 540 K.

The additional TL peak of 375 K after the dose of 10^4 Gy and its increase up to the dose of $5 \cdot 10^7$ Gy is related to a color center in the visible region and does not depend on the presence of the Ce activator; this is possibly due to a break of the short (~ 0.23 nm) Lu1$-$O1$-$Si bond and the formation of a charged vacancy O1 — a Lu1$-$F$-$Si complex center.

The induced color centers at the irradiation dose of $5 \cdot 10^7$ Gy with typical OA bands — 238 nm-Lu1$-F^+-$Si-center, 263 — Ce^{3+}/Ce^{4+} and 295 — Ce^{3+}/F after heat treatment at 773 K (20 min) in air are fully annealed, which results in an increase of activator GL of Ce^{3+} in the gamma-field up to a state after the minimum dose of 200 Gy. This means that irradiation-induced vacancies are healed by interstitial oxygen (healing of a Frenkel pair in the anionic sublattice).

The most intensive TL peak at 335 K, which deteriorates the response rate, can be eliminated by stopping the gamma-irradiation for 10 h or by increasing the scintillator operating temperature to 360 K.

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Conflict of interest

The authors declare that they have no conflict of interest.

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