

Luminescence kinetics of crystals LSO co-doped with rare-earth elements

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The effect of lutetium oxyorthosilicate (LSO) crystals co-doping with rare-earth elements (Ce, Yb) on the luminescence energy and kinetic parameters has been studied. A significant decrease of light storage (afterglow drop by 10^2) is observed at the certain concentrations of activators ($C_{Ce} \sim 0.1$ at. %, $C_{Yb} \sim 0.5$ at. %). Herein, the luminescence spectral composition and high light yield value are retained, and stability of output characteristics for LSO(Ce, Yb) is improved considerably.

Изучено влияние активирования кристаллов оксиортосиликата лютеция LSO редкоземельными элементами (Ce, Yb) на энергетические и кинетические параметры люминесценции. Показано, что при определенных концентрациях активирующих примесей ($C_{Ce} \sim 0,1$ ат. %, $C_{Yb} \sim 0,5$ ат. %) наблюдается существенное снижение светозапасания (уровень послесвечения уменьшается примерно в 10^2) при сохранении спектрального состава излучения и высокого световыхода с одновременным значительным улучшением стабильности выходных характеристик кристаллов LSO(Ce, Yb).

Crystals of Ce doped rare earth (RE) oxyorthosilicates are promising scintillators with high light yield and nanosecond decay times. Cerium doped lutetium oxyorthosilicate $\text{Lu}_2\text{SiO}_5(\text{Ce})$, LSO(Ce), is among these materials [1, 2]. However, high afterglow level (several per cent in the millisecond range) narrows the application range for this material in some branches, such as radiation introscopy, where this parameter is critical. The afterglow is usually attributed to oxygen vacancies [3].

One of the possible ways to improve output parameters of a scintillator is its co-doping with ions having specific features. For instance, positive results were obtained for CsI(Tl) doped with Eu or Sm [4–6], A_2B_6 based scintillators doped with Sm [7], nanocrystalline luminophors based on LSO with Yb and Dy dopants [9]. The effect of co-doping with Sc, La, Gd, Y on properties

of bulk single crystal scintillator LSO(Ce) was studied in [10], however, no remarkable influence of these optically inactive elements on the luminescence light yield and decay was discovered.

Yb ions, as well as Eu and Sm ones, possess stable valency 2+, thus, these ions can capture charge carriers (electrons in our case) which give rise to afterglow in crystals. Then the captured carriers may annihilate by nonradiative means, or call a longer-time afterglow (accompanied by a decrease of short-time afterglow). These factors were decisive at choice of co-dopant for LSO(Ce) crystals. This work is aimed at studies of luminescence characteristics and output parameters stability in bulk LSO(Ce, Yb) as functions of co-activator concentration.

Activated bulk LSO(Ce, Yb) crystals of 30 mm in diameter and 30 to 60 mm length were obtained by the Czochralski technique

using iridium crucibles in Ar atmosphere with O₂ admixture. Rare-earth oxides Lu₂O₃, Yb₂O₃, CeO₂, SiO₂ of at least 4N purity mixed at stoichiometric proportions were used as starting materials for crystal growing. The post-growth annealing of the ingots was carried out in inert atmosphere at 1500°C. Samples of 10×10×2 mm³ and 10×10×0.5 mm³ size with polished 10×10 faces were cut out from the crystals for measurements of light yield, afterglow kinetics, thermostimulated luminescence (TSL), and luminescence spectra. Concentration of Ce and Yb in crystals was controlled by AES method (see, for example [11]).

The afterglow level $\eta(t)$ of crystals after X-ray irradiation was determined using procedures described in [7, 8], and calculated as

$$\eta(t) = [I(t)/I_0] \cdot 100, [\%], \quad (1)$$

where I_0 is the crystal luminescence intensity at X-ray irradiation; $I(t)$, afterglow intensity after the irradiation is over. The thermostimulated luminescence parameters were determined using the procedure [9] at temperature change rate about 5 K/min. The afterglow kinetics after X-ray irradiation ($D_x = 5$ R) was measured using a specialized measurement setup [8]. The residual afterglow at UV irradiation was determined after irradiation by DRT-250 Hg lamp during 5 min. 20 s after the irradiation was over, a FD-288 photodiode was mounted at the sample, and its output current was registered by a B7-35 voltmeter. X-ray luminescence spectra of samples were studied using a KSVU-8 measurement complex.

The spectral composition of X-ray luminescence for a LSO crystal at different dopant concentrations is shown in Fig. 1. The luminescence spectra are characterized

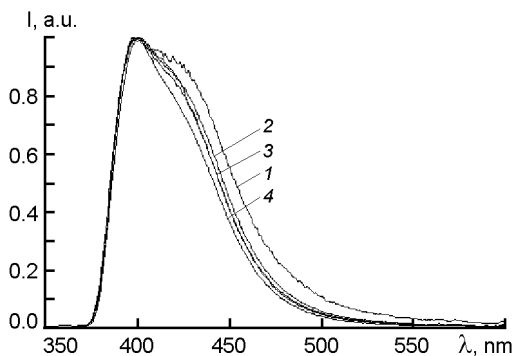


Fig. 1. X-ray luminescence spectra: 1, LSO (0.1 % Ce, 0.5 % Yb); 2, LSO (0.1 % Ce, 0.1 % Yb); 3, LSO (0.1 % Ce); 4, LSO (0.1 % Ce, 0.05 % Yb).

by long-wavelength widening depending on Yb concentration. The observed widening of long-wavelength luminescence edge (see Fig. 1) certifies an intensity redistribution for the band near 450 nm corresponding to six-fold oxygen coordinated Ce³⁺ (CeO₆ polyhedra) at the quenching of CeO₇ luminescence near 410 nm [12].

Other basic characteristics of studied crystals, such as concentrations of dopants C_{Ce} , C_{Yb} , respective light output S_0 , afterglow level η at $t = 100$ ms after irradiation termination are presented in Table.

The light output of the doped LSO decreases gradually with increasing Yb concentration; S_0 drops sharply at $C_{Yb} > 0.5$ mol. %. The afterglow level η in LSO(Yb,Ce) also decreases at C_{Yb} change up to 0.5 at. %, and stabilizes at $C_{Yb} > 0.5$ %. Different trends in $\eta(t)$ dependences for different samples (Fig. 2) also should be noted. In Yb-containing crystals, the afterglow level drop is less pronounced at times shorter than 3 ms, and takes place generally after 10 ms.

Table. Characteristics of LSO based crystals

No	Crystal	C_{Ce} , at. %	C_{Yb} , at. %	S_0 , a.u.	Afterglow level, η (%) after 100 ms
1	Undoped LSO	<0.001	<0.001	0.55	2.03
2	LSO(Ce)	0.1	<0.001	1	3.01
3	LSO(Ce,Yb)	0.1	0.05	0.94	0.478
4	LSO(Ce,Yb)	0.1	0.1	0.77	0.165
5	LSO(Ce,Yb)	0.1	0.5	0.72	0.017
6	LSO(Ce,Yb)	0.1	2	0.36	0.025

*nominally undoped LSO obtained from oxides Lu₂O₃ and SiO₂ 4N purity (99.99 %) contains Ce as an uncontrolled admixture at the level about 10⁻³-10⁻⁴ at. %.

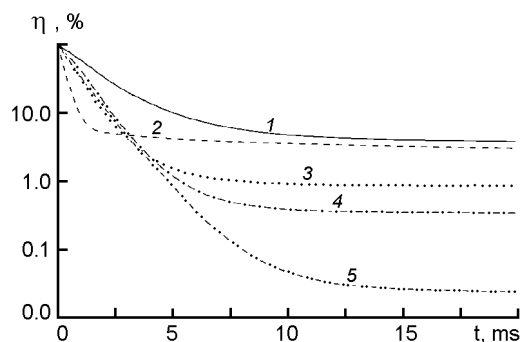


Fig. 2. Kinetics of LSO afterglow after X-ray irradiation: 1, undoped LSO; 2, LSO (0.1 % Ce); 3, LSO (0.1 % Ce, 0.05 % Yb); 4, LSO (0.1 % Ce, 0.1 % Yb); 5, LSO (0.1 % Ce, 0.5 % Yb).

Thus, at the optimal concentration ($C_{Yb} \sim 0.5$ mol. %), LSO doped scintillators with afterglow level lower by 2 orders of magnitude in comparison with undoped samples can be obtained. At the same time, the light output decrease is acceptable (not exceeding 28 %).

The stability of output parameters under ionizing radiation is another important feature of scintillators. Our results show that LSO(Ce,Yb) crystals with optimal concentration $C_{Yb} = 0.5$ mol.% possess the highest stability of light yield on X-ray irradiation dose D_x .

Together with instability of LSO light yield on dose D_x , that is, $S = f(D_x)$, dependence of η on D_x , that is $\eta_{t=fix} = f(D_x)$, is also observed (Fig. 4). It is worth to note that at the chosen irradiation mode (X-ray source, $U_a = 100$ kV), a monotonous increase of afterglow level is observed for all LSO-based crystals. At the same time, the η value drops with increasing irradiation dose D_x for other crystals, for example, CsI(Tl).

To determine the light collection mechanism and light output instability in co-doped LSO, dependences of TSL and afterglow after UV-irradiation were studied. The plots of afterglow intensity after UV-irradiation (Fig. 5) decrease gradually and have the same trend as $\eta = \eta(t)$ curves obtained at X-ray irradiation.

TSL spectra demonstrate clearly (Fig. 6) that co-doping with Yb causes a substantial change of carrier trap concentration being depleted in the temperature range 100–450 K (activation energies $E_a = 0.2$ –0.9 eV).

Ce doping results in a substantial decrease of shallow and deep trap number. The

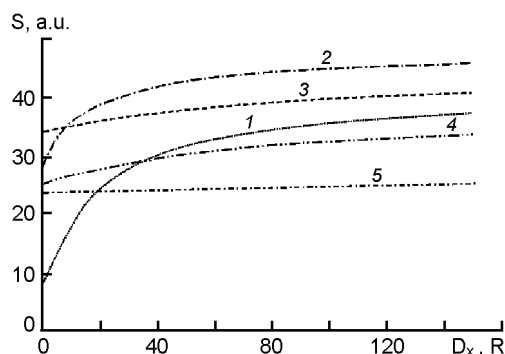


Fig. 3. Dependences of light yield S on X-ray irradiation dose D_x : 1, undoped LSO; 2, LSO (0.1% Ce); 3, LSO (0.1 % Ce, 0.05 % Yb); 4, LSO (0.1 % Ce, 0.1% Yb); 5, LSO (0.1 % Ce, 0.5 % Yb). $U_a = 100$ kV, $I_a = 1$ mA.

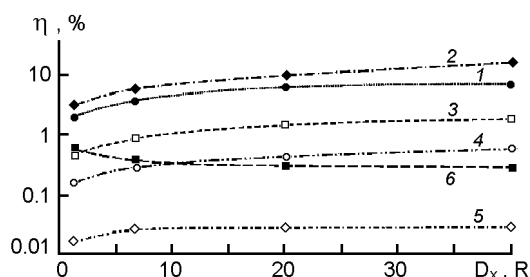


Fig. 4. Dependences of afterglow level $\eta(t = 100$ ms) of LSO and CsI(Tl) on preliminary irradiation dose D_x : 1, undoped LSO; 2, LSO (0.1 % Ce); 3, LSO (0.1 % Ce, 0.05 % Yb); 4, LSO (0.1 % Ce, 0.1 % Yb); 5, LSO (0.1 % Ce, 0.5 % Yb); 6, CsI(Tl).

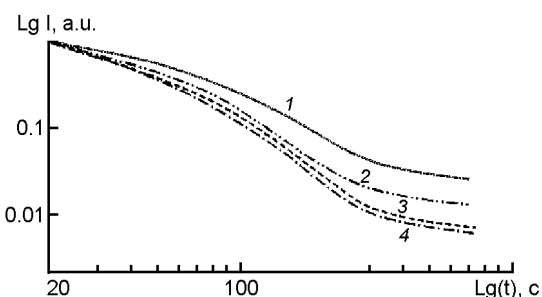


Fig. 5. Afterglow kinetics after UV-irradiation: 1, undoped LSO; 2, LSO (0.1 % Ce); 3, LSO (0.1 % Ce, 0.05 % Yb); 4, LSO (0.1 % Ce, 0.1 % Yb).

peak at 120 K ($E_a = 0.23$ eV) disappears at Yb addition, and the intensity of high temperature peaks at 340 and 400 K ($E_a = 0.61$ and 0.87 eV, respectively) decreases significantly. At Yb concentration increasing up to 0.1 at. %, the intensity redistribution is observed be-

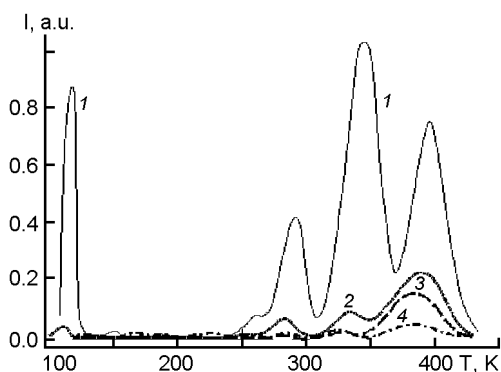


Fig. 6. TSL of LSO-based crystals: 1, undoped LSO; 2, LSO (0.1 % Ce); 3, LSO (0.1 % Ce, 0.05 % Yb); 4, LSO (0.1 % Ce, 0.1 % Yb).

tween the peak at 400 K attributed to deep traps being associated to oxygen vacancies, and peaks at $T < 360$ K caused by carrier delocalization from traps with the energies up to 0.7 eV at non-silicon-bound oxygens [13]. The increased intensity of TSL peaks at 0.55 and 0.7 eV can be attributed to formation of new traps at oxygens surrounding Yb.

Comparing the results in Figs. 2 and 3, one can note a correlation between light output instability and light storage. No TSL peaks are observed at Yb concentration $C_{Yb} \geq 0.5$ %.

Energy of optical (UV) photons is insufficient to initiate radiation-stimulated processes (Schottky and Frenkel defect formation) in these crystals. Therefore, it may be assumed that in case of both UV and X-ray irradiation, the afterglow is due not only to recharging of existing defects. A very heavy dependence of light output for samples with non-optimized concentration of co-dopant (Yb) on the preliminary irradiation dose may certify a contribution from radiation-stimulated processes resulting in additional luminescence center formation by sub-threshold mechanism [8, 14]. The increase of afterglow in LSO-based samples with preliminary irradiation dose also confirms the existence of such processes. The decrease of CsI(Tl) afterglow intensity in the same conditions may be ascribed by partial filling of carrier traps governing the afterglow in crystals of this type.

The afterglow level decrease and other effects observed for LSO crystals with the optimal co-dopant concentration may be ascribed to both crystal-chemical and electro-physical factors. The addition of an isoelectronic (isoelectronic) dopant (Yb) into LSO(Ce) crystals results in suppression of genetic

defects, that is, improvement in the crystal lattice perfection due to the mechanisms described in [15] is possible. At the same time, Yb may act as an isoelectronic acceptor that neutralizes the non-compensated charge of traps defining light storage in crystals [4–7, 9].

Basing on the presented data, the following mechanism of radiative and non-radiative processes in codoped LSO crystals may be presented. After formation of electron-hole pairs in LSO:Ce, electrons can be captured by deep traps alongside with recombination with holes. Those traps cause an intense afterglow after irradiation termination and are manifested by TSL peaks at temperatures from 250 K and higher.

Trivalent Yb has a one of the highest electronegativities among lanthanide ions [16], and Yb^{3+} 5b levels intersect with LSO conduction band. Thus, an electron situated in the conduction band may be captured by with formation of Yb^{3+} . The holes from valence band will recombine with Yb^{2+} ions and transfer them back into trivalent state. Thus, addition of Yb provides an additional channel of carrier recombination and decreased number of electrons captured on traps. Ytterbium itself does not contribute to the working luminescence band of the scintillator, because in matrices of complex oxides, it glows in IR band or in red part of visible band (see, e.g., [17]).

Thus, doping of LSO by Ce and Yb at optimal concentrations ($C_{Ce} \sim 0.1$ at. %, $C_{Yb} \sim 0.5$ at. %) can provide a scintillation material with afterglow level less than 0.02 % after 20–100 ms and high light yield. The LSO co-doping, besides of improvement of scintillation characteristics, increases substantially the radiation stability of output parameters for this scintillator.

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Кінетика люмінесценції кристалів LSO, допованих рідкісноземельними елементами

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Вивчено вплив активування кристалів оксіортосилікату лютецію LSO рідкісноземельними елементами (Ce, Yb) на енергетичні та кінетичні параметри люмінесценції. Показано, що при певних концентраціях активуючих домішок ($C_{Ce} \sim 0,1$ ат. %, $C_{Yb} \sim 0,5$ ат. %) спостерігається істотне зниження світлозапасання (рівень післясвітіння зменшується приблизно в 10^2 разів) при збереженні спектрального складу випромінювання та високого світлового виходу з одночасним значним поліпшенням стабільності вихідних характеристик LSO(Ce, Yb).