

## Mechanisms of charge interactions in co-doped $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ crystals

*A.Masalov, O.Viagin, I.Ganina, Yu.Malyukin*

Institute for Scintillation Materials, STC "Institute for Single Crystals",  
National Academy of Sciences of Ukraine,  
60 Lenin Ave., 61001 Kharkiv, Ukraine

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The influence of co-doping with  $\text{Dy}^{3+}$  and  $\text{Yb}^{3+}$  ions on luminescence and scintillation characteristics of  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$  crystal has been investigated. It was shown that the introduction of co-dopants with different donor-acceptor properties with respect to charge carriers affects significantly the charge interactions in the crystal and allows controlling the thermoluminescence and afterglow. The mechanisms of the free charge carrier recombination in co-doped crystals have been proposed. According to these mechanisms, dysprosium ( $\text{Dy}^{3+}$ ) ions act as the hole traps and promote increasing of the energy storage effect. Ytterbium ions ( $\text{Yb}^{3+}$ ) are acceptors of electrons and produce the additional channel of charge carrier recombination that reduces the energy storage level in  $\text{LSO}:\text{Ce},\text{Yb}$ .

Исследовано влияние соактивирования ионами  $\text{Dy}^{3+}$  и  $\text{Yb}^{3+}$  на люминесцентные и сцинтилляционные свойства кристалла  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ . Показано, что введение соактиваторов с различными донорно-акцепторными свойствами по отношению к носителям заряда значительно влияет на зарядовые взаимодействия в кристалле и позволяет управлять величиной послесвечения и термолюминесценции. Предложены механизмы рекомбинации носителей заряда в соактивированных кристаллах, согласно которым ионы  $\text{Dy}^{3+}$  играют роль ловушек дырок, и способствуют, таким образом, увеличению эффективности запасаения энергии в  $\text{LSO}:\text{Ce},\text{Dy}$ , а ионы  $\text{Yb}^{3+}$  являются акцепторами электронов и создают в кристалле дополнительный канал рекомбинации носителей заряда, что приводит к снижению уровня запасаения энергии в  $\text{LSO}:\text{Ce},\text{Yb}$ .

### 1. Introduction

Nowadays, doped oxide crystals are used successfully as luminescent materials in laser and scintillation systems and medical diagnostic devices. Such crystals exhibit a high chemical and radiation resistance and wide transparency range. The cerium doped rare-earth oxyorthosilicates, in particular,  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$  ( $\text{LSO}:\text{Ce}$ ) stand out in the doped oxide crystal family. This scintillator is used mainly in modern positron emission tomographs [1]. However,  $\text{LSO}:\text{Ce}$  crystal shows an effect undesirable in scintillators, an effective energy storage, that can be observed as an afterglow or thermoluminescence [2]. It was shown that a high after-

glow level of  $\text{LSO}:\text{Ce}$  is caused by the effective charging of electron traps [3–5]. Due to the fact that the lowest excited  $5d$  level of  $\text{Ce}^{3+}$  ion is located close to the bottom of the conduction band, the dopant ion can undergo ionization, and transport of electrons to trapping centers occurs through the conduction band. For example, it was established in [3] that if producing electron traps in a confined crystal volume by a strongly focused laser beam, the photostimulated luminescence can be observed at a distance of 400  $\mu\text{m}$  from the focusing spot. This experiment demonstrates clearly that the electron diffusion to traps and back to recombination centers involves the band states of  $\text{Lu}_2\text{SiO}_5$ . Since doped rare-earth ions and

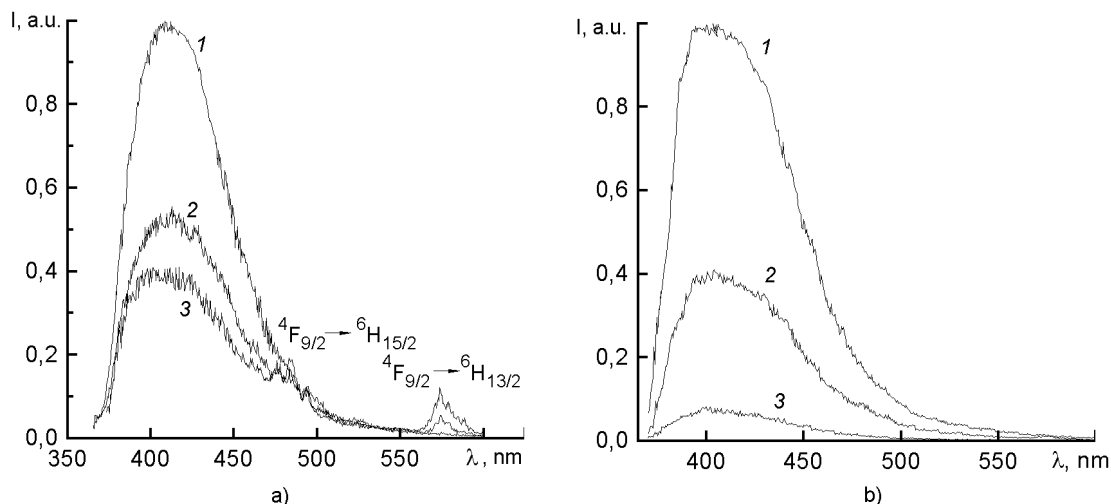


Fig. 1. Luminescence spectra of LSO:Ce,Re,  $\lambda_{exc} = 325$  nm,  $T = 300$  K. a) 1 — LSO:Ce, 2 — LSO:Ce,Dy (0.5 at.%), 3 — LSO:Ce,Dy (5 at.%); b) 1 — LSO:Ce, 2 — LSO:Ce,Yb (0.1 at.%), 3 — LSO:Ce,Yb (0.5 at.%).

electron traps in a LSO:Ce crystal are independent subsystems, the energy storage efficiency can be modified by the crystal codoping with other rare-earth elements showing pronounced donor or acceptor properties with respect to the charge carriers. The codoping can promote the enhancement of the charge carrier recombination process, competing with the trapping one, or, conversely, reduce the recombination rate.

## 2. Experimental

Dysprosium (Dy) and ytterbium (Yb) ions were chosen as co-dopants. The choice was motivated by characteristic valence states of the ions, and estimation of the ground  $4f$  and excited  $5d$  levels position of these ions relatively to bands of  $\text{Lu}_2\text{SiO}_5$ . The trap type (electron or hole) is defined by the ion level position. There is a simple and reliable model that makes it possible to determine the absolute positions of ground and excited states of lanthanides in dielectric crystals [6, 7]. In accordance with this model, if the positions of  $4f$  and  $5d$  levels of  $\text{Ce}^{3+}$  ion in a crystal host are known, the level positions of other lanthanides in the same host can be reconstructed [7]. Using this model, the level positions for  $\text{Dy}^{3+}$  and  $\text{Yb}^{3+}$  ions in the  $\text{Lu}_2\text{SiO}_5$  host have been determined.

The experimental samples were synthesized by the sol-gel technique from the corresponding lanthanide oxides [8]. The concentration of cerium was constant in all samples (1 at.%), while the concentration of co-dopants was varied within the 0.1–5 at.% range. The luminescence spectra were meas-

ured using an automated spectrofluorimeter based on a MDR-23 grating monochromator. The photoluminescence (PL) was excited by the radiation of a He–Cd laser operating at a wavelength of  $\lambda = 325$  nm. The PL decay curves were measured in the time-correlated single photon counting mode [9]. During these measurements, the PL was excited by the fourth harmonic of a YAG:Nd laser ( $\lambda = 266.5$  nm) operated in active longitudinal mode locking.

The energy gap between the lowest excited  $5d$  level of  $\text{Ce}^{3+}$  ion and the bottom of the conduction band is about 0.45 eV [4]. The value of this gap is larger than  $kT$  at room temperature (0.025 eV). Nevertheless, photocurrent experiments revealed an effective thermal ionization of  $\text{Ce}^{3+}$  under excitation to the lowest  $5d$  level at 300 K [5]. This was explained by the fact that the lowest of the five levels of  $\text{Ce}^{3+}$  is overlapped with the crystal exciton band. Therefore, after excitation of the dopant, an exciton-like state  $\text{Ce}^{4+}-e^-$  is formed having the thermal ionization barrier comparable with the  $kT$  value. The laser excitation energy used in our experiments (3.8 eV) is sufficient to provide thermal ionization of electrons and subsequent traps charging.

## 3. Results and discussion

Fig. 1a shows the luminescence spectra of LSO:Ce,Dy at the excitation into the absorbance band of  $\text{Ce}^{3+}$ . The spectra represent the combination of the well-known band of  $\text{Ce}^{3+}$   $5d \rightarrow 4f$  interstate transitions

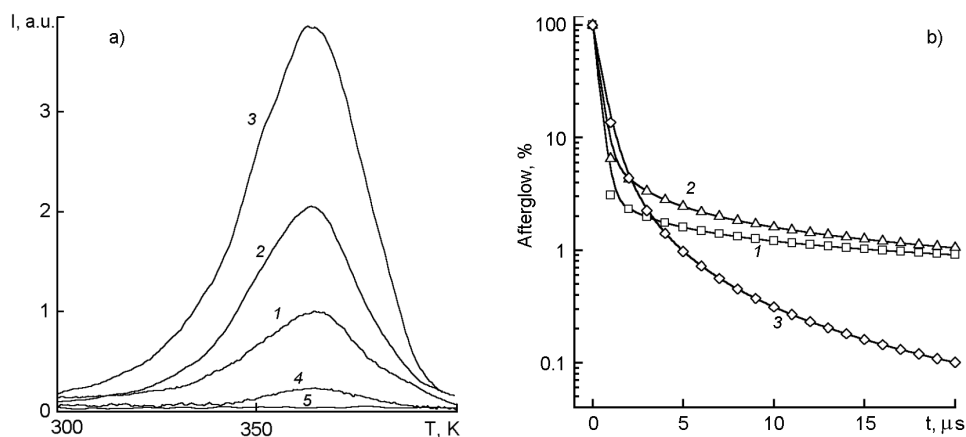


Fig. 2. a) Thermoluminescence spectra of co-doped crystals ( $\lambda_{reg} = 410$  nm). LSO:Ce TSL intensity has been taken as a unit. 1 — LSO:Ce, 2 — LSO:Ce,Dy (0.5 at.%), 3 — LSO:Ce,Dy (5 at.%), 4 — LSO:Ce,Yb (0.1 at.%), 5 — LSO:Ce,Yb (0.5 at.%); b) The afterglow curves of LSO:Ce,Re at X-ray excitation.

with  $\lambda_{max} = 410$  nm and  $Dy^{3+} 4f^5 \rightarrow 4f^5$  intrastate transitions in the 460–600 nm range. The increase in dysprosium concentration causes a decrease in cerium luminescence intensity and an increase in dysprosium  $4F_{9/2} \rightarrow 6H_{15/2}$  and  $4F_{9/2} \rightarrow 6H_{13/2}$  luminescence intensity. The luminescence spectrum of LSO:Ce,Yb consists of the  $Ce^{3+}$  luminescence band only (Fig. 1b). Similarly to the LSO:Ce,Dy crystal, the increase in  $Yb^{3+}$  concentration causes the  $Ce^{3+}$  luminescence decrease. Though both co-dopants quench cerium luminescence, they affect the energy storage in LSO:Ce in different ways. All oxyorthosilicates of lanthanides show the energy storage effect to a greater or lesser extent [10, 11]. It was shown in some works [10–12] that the main electron traps in oxyorthosilicates are oxygen vacancies created by oxygen atoms not bound directly to the silicon ones.

Fig. 2a presents thermoluminescence spectra of the co-doped crystals. The thermoluminescence was registered in the maximum of cerium luminescence (410 nm) after the crystals irradiation within the cerium absorption band. In the case of the optical excitation in the impurity absorption band, intrinsic electronic states of  $Lu_2SiO_5$  host are not excited and only  $Ce^{3+}$  ions act as electron donors charging electron traps. Fig. 2a shows that the increase in  $Dy^{3+}$  concentration causes the increase in thermoluminescence intensity of LSO:Ce,Dy crystal. However, in contrast to LSO:Ce,Dy, the intensity of LSO:Ce,Yb thermoluminescence

decreases as compared to LSO:Ce and is not observed at  $Yb^{3+}$  concentration of 0.5 at.%.

The stored light sum is correlated with the afterglow of crystals. Fig. 2b shows afterglow curves of crystals under X-ray excitation. The co-dopant ions cause different effect on luminescence intensity of LSO:Ce crystal in the millisecond range.  $Dy^{3+}$  increases the slow decay component contribution, while co-doping by  $Yb^{3+}$  decreases this one. At the initial section of LSO:Ce,Yb afterglow curve, a somewhat increased intensity as compared to LSO:Ce is observed. When measuring the afterglow, a Si-photodiode having the maximal spectral response at 970 nm is used as a photodetector. Therefore, the higher afterglow level of LSO:Ce,Yb in the 0–3 ms range could be caused by the infrared luminescence of  $Yb^{3+}$  ions with characteristic decay time of about 900 ms.

Basing on experiments and calculations of lanthanides energy levels in  $Lu_2SiO_5$  host, the mechanisms of free charge carrier recombination can be proposed. Fig. 3 shows the probable recombination processes in co-doped crystals. After the excitation, an electron from cerium ion is thermally ionized in the conduction band and the dopant valency changes to 4+. The intensity of cerium absorption spectrum does not change with the increasing a laser irradiation dose. Thus, the concentration of  $Ce^{3+}$  ions is constant, i.e.  $Ce^{4+}$  is reduced rapidly by trapping of the electron from the valence band with the hole formation therein.

Trivalent lanthanides having ground states located close to the valence band top

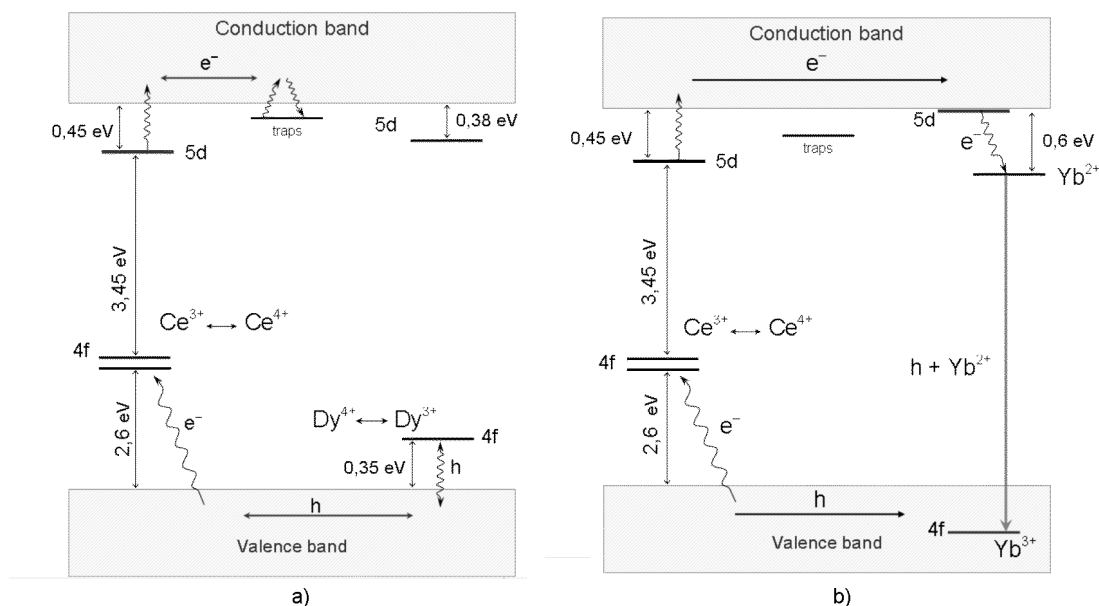


Fig. 3. Mechanisms of charge carrier recombination in co-doped LSO crystals. a)  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}, \text{Dy}^{3+}$ ; b)  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}, \text{Yb}^{3+}$ .

may trap holes therefrom. Therefore, as dysprosium possesses valence states 3+ and 4+, and  $\text{Dy}^{3+}$  ground state is located about 0.35 eV above the valence band top, dysprosium acts as a hole trap and changes valence to 4+. Then, thermally activated holes recombine with the conduction band electrons on cerium ions that cause delayed luminescence. The  $\text{Yb}^{3+}$  ion shows one of the largest electronegativity values among lanthanides. Since 5d states of  $\text{Yb}^{3+}$  are located just under the bottom of the  $\text{Lu}_2\text{SiO}_5$  conduction band, electrons in the conduction band can be trapped by  $\text{Yb}^{3+}$  ions with  $\text{Yb}^{2+}$  formation. The ionized cerium ions will be reduced to  $\text{Ce}^{3+}$  due to electron trapping from the valence band. The holes formed will recombine with the  $\text{Yb}^{2+}$  ions and transfer those back to valence state 3+. Thus, the introduction of ytterbium ions provides an additional channel of the free charge carrier recombination.

As mentioned above, LSO:Ce co-doping quenches the cerium luminescence. To ascertain the origin of  $\text{Ce}^{3+}$  luminescence quenching in LSO:Ce,Dy and LSO:Ce,Yb, the cerium luminescence decay was studied at the variation of the co-dopant concentration. Introduction of  $\text{Dy}^{3+}$  or  $\text{Yb}^{3+}$  ions into the LSO:Ce crystal causes a modification of cerium decay curves that indicates the non-radiative energy transfer between  $\text{Ce}^{3+}$  and co-dopant ions. The analysis of LSO:Ce,Dy and LSO:Ce,Yb luminescence decay curves

reveals the one-step Forster resonance energy transfer mechanism. It is known that the efficiency of the Forster mechanism depends on the overlap integral of the emission and absorption spectra of the interacting ions. For  $\text{Ce}^{3+}$  and  $\text{Dy}^{3+}$  ions, the overlap integral has a nonzero value, whereas spectral bands of  $\text{Ce}^{3+}$  and  $\text{Yb}^{3+}$  ions do not overlap. At the same time, the cerium luminescence quenching rate depends heavily on the  $\text{Yb}^{3+}$  concentration. So, the  $\text{Yb}^{3+}$  ions are not energy acceptors, but are involved in the formation of quenching centers.

Both cerium and ytterbium luminescence quenching was observed in different crystal hosts doped with  $\text{Yb}^{3+}$  and  $\text{Ce}^{3+}$  ions that is associated with the formation of charge transfer complex  $\text{Yb}^{2+}-\text{Ce}^{4+}$  [13–15]. The formation of such a complex explains cerium luminescence quenching as a result of the reduction of the amount of luminescence centers. However, as a rule, the distance between  $\text{Yb}^{2+}$  and  $\text{Ce}^{4+}$  ions at which such a complex can be formed is a few Angstroms. In accordance with the Monte-Carlo simulation, even at the ytterbium concentration of 0.5 at.%, the fraction of Ce–Yb pairs with a distance between metal ions of 5 Å is no more than 8 % from all dopant ions. Furthermore, the existence of this complex does not explain the deviation of  $\text{Ce}^{3+}$  luminescence decay curves from the exponential law. The energy position of the  $\text{Yb}^{2+}-\text{Ce}^{4+}$  complex can be estimated from

the difference between cerium and ytterbium ionization potentials [16]. Using data  $I(\text{III})_{\text{Yb}} = 25.8$  eV and  $I(\text{III})_{\text{Ce}} = 20.16$  eV [17], we obtain the value of 218 nm.

The absorbance of another charge transfer complex  $\text{Yb}^{3+}-\text{O}^{2-}$  is observed in the same spectral range. Since a metal ion in oxyorthosilicates is always surrounded with oxygen ions, the probability of the  $\text{Yb}^{3+}-\text{O}^{2-}$  complex formation is much higher than that of  $\text{Yb}^{2+}-\text{Ce}^{4+}$  one. So, the absorption in the 200–230 nm spectral range is associated just with the charge transfer from oxygen to ytterbium. This conclusion agrees well with the LSO:Ce,Yb diffuse reflection spectra. The spectra reveal a broad band ( $\sim 3600$   $\text{cm}^{-1}$ ) with the maximum centered at  $\lambda = 215$  nm, which intensity increases with increasing ytterbium concentration. In our experiments, however, the luminescence was excited by a lower energy than the absorption one of both charge transfer complexes. Therefore, a nonradiative energy transfer in LSO:Ce,Yb cannot be realized to these ytterbium containing charge transfer complexes. It is known that in the same crystal host, the  $\text{Yb}^{2+}$  absorption spectrum is located in the region of  $\text{Ce}^{3+}$  luminescence [18]. In this case, in the LSO:Ce,Yb crystal,  $\text{Yb}^{2+}$  ions, which are formed as a result of electron trapping by  $\text{Yb}^{3+}$  ion, will act as energy acceptors.

#### 4. Conclusion

Thus, the incorporation of the co-dopant ions with different donor-acceptor properties with respect to charge carriers affects significantly the charge interactions in  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$  crystal, and allows the energy storage efficiency to be controlled. According to the proposed mechanisms of free charge carriers recombination in LSO:Ce,Dy and LSO:Ce,Yb crystals, the  $\text{Dy}^{3+}$  ions act as hole traps and promote the increase of the energy storage effect;  $\text{Yb}^{3+}$  ions are acceptors of electrons and produce an additional channel of charge carrier recombination that reduces the energy storage level in

LSO:Ce,Yb. The co-doping makes it possible to expand the LSO:Ce application field and to use it, for example, in dosimetry where an efficient energy storage is necessary or in scan systems where scintillators with a low afterglow level and high time resolution are required. Taking into consideration the fact that the introduction of co-dopants results in quenching of cerium luminescence, it is possible to select the optimum of the dopant/co-dopant concentration ratio for specific applications.

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## **Механізми зарядових взаємодій у співактивованих кристалах $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$**

***А.Масалов, О.Вягін, І.Ганіна, Ю.Малюкін***

Досліджено вплив співактивування іонами  $\text{Dy}^{3+}$  і  $\text{Yb}^{3+}$  на люмінесцентні та сцинтиляційні властивості кристала  $\text{Lu}_2\text{SiO}_5:\text{Ce}^{3+}$ . Показано, що введення співактиваторів з різними донорно-акцепторними властивостями стосовно до носіїв заряду значно впливає на зарядові взаємодії у кристалі і дозволяє керувати величинами післясвітіння й термолюмінесценції. Запропоновано механізми рекомбінації носіїв заряду у співактивованих кристалах, згідно з якими іони  $\text{Dy}^{3+}$  відіграють роль пасток дірок і сприяють, таким чином, збільшенню ефективності запасання енергії в  $\text{LSO}:\text{Ce},\text{Dy}$ , а іони  $\text{Yb}^{3+}$  є акцепторами електронів і створюють у кристалі додатковий канал рекомбінації носіїв заряду, що приводить до зниження рівня запасання енергії в  $\text{LSO}:\text{Ce},\text{Yb}$ .