Migration-enhanced energy transfer from host to dopant in Sr_2CeO_4:Eu crystal

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The strontium oxycerate blue phosphor (Sr_2CeO_4) belongs to a particular class of optical materials with luminescence governed by optical transitions associated with the electron charge transfer. The uniqueness of its crystallographic structure including a chain-like sequence of luminescence centers favors the effective transfer of electron excitation energy from the matrix to impurity centers. Sr_2CeO_4 samples, both pure and activated with various Eu^{3+} concentrations have been synthesized by Pechini citrate-gel method. The luminescence spectra and luminescence decay curves of Sr_2CeO_4 and Sr_2CeO_4:Eu^{3+} have been investigated. The experiments carried out have revealed the excitonic mechanism of electron excitation energy transfer from the crystal matrix to the doping europium ions.

Бело-голубой люминофор оксицерата стронция Sr_2CeO_4 принадлежит к особому классу материалов, люминесценция которых определяется оптическими переходами, связанными с электронным переносом заряда. Уникальность его кристаллической структуры, цепочкоподобное расположение люминесцентных центров позволяет реализоваться эффективному переносу энергии электронного возбуждения от матрицы к примесным центрам. Цитратным методом Печини синтезированы образцы чистого и активированного ионами Eu^{3+} люминофора Sr_2CeO_4. Исследованы спектры люминесценции и затухания люминесценции Sr_2CeO_4 и Sr_2CeO_4:Eu^{3+}. Проведенные эксперименты показали экситонный механизм переноса энергии электронного возбуждения от кристаллической матрицы к примесным ионам европия.

Charge-transfer (CT) transitions of rare-earth (RE) ions have been known for a long time [1−3] and systematically investigated recently [4−6]. In CT transitions, an electron is transferred from an external ligand to the $4f^n$ shell of the RE ion. However, such a transition involves a considerable reorganization of the charge density distribution around the metal ion along with transfer of one electron. Some states that arise at such a transition are stable and can relax to the ground state with a photon emission (CT luminescence). Despite the fact that the properties of CT transitions are used in some applications [7, 8], they are insufficiently studied as compared to $4f^n$−$4f^n$ and $4f^n$−$4f^{n-1}5d$ transitions.

The range of compounds that possess the CT luminescence is restricted. In 1979, Nakazawa was the first who report of CT luminescence for phosphates and oxysulphides activated with Yb^{3+} ions [9]. Later, it was demonstrated that Yb-related CT luminescence is a common phenomenon for a wide range of matrices [10, 11]. Most of RE elements do not demonstrate this luminescence type due to the non-radiative relaxation from the CT state to the excited states of $4f$ or $5d$ configuration. In ytterbium-containing compounds, the CT state is situated higher in energy than the excited $4f$-state and lower than $5d$ states, so CT luminescence can be observed. In 1998, Danielson et al. reported an unusual luminescence of inorganic oxide compound Sr_2CeO_4. UV ex-

cited blue-white luminescence of this compound was attributed to the CT transition involving Ce^{4+} ions [12, 13]. The structure of the compound reveals a strong anisotropy defined by a set of one-dimensional chains of contiguous CeO_6 octahedrons along [001] direction with a spatial period of 3.597 Å [12]. In [14–16], RE doped Sr_2CeO_4 crystal was studied. However, the experimental data obtained were interpreted very contradictory that does not allow an unambiguous judgement of the energy transfer mechanisms from the CT complex to the doping RE ions. In [14], the exchange mechanism of energy transfer was stated, but this is not confirmed by the experimental data. The authors [15] have concluded that the energy transfer occurs under involvement of CT states of dopant ions only (Eu^{3+}–O^{2-}, Sm^{3+}–O^{2-}). Nevertheless, the crystal excitation into states located lower in energy than CT states of dopant ions also causes the energy transfer. Moreover, the authors [15] state that the doping with impurity ions does not effect the luminescence decay time of the Sr_2CeO_4 crystal. However, it was found [16] that the doping with RE ions (Eu, Ho, Tm, Er) decreases the luminescence decay time of the Sr_2CeO_4 crystal and the energy is transferred directly to the $4f^n$ states of doping RE ions.

Pure and Eu^{3+} activated Sr_2CeO_4 crystals were synthesized by the Pechini citrate-gel method [17]. Solutions of Sr, Ce and Eu nitrates were mixed in the stoichiometric ratio. A citric acid solution in ethylene glycol was added to the mixed nitrate solution. The mixture of solutions was heated at 80°C under continuous stidding during 10–20 hours that resulted in the removal of nitric acid excess and rise of the solution pH. During this time, water was also removed from the solution and a gel was formed as a result of the polycondensation reaction. Then the gel was subjected to hydrolysis and precipitation took place. The precipitate obtained was dried at 110–120°C, dehydrated at 550°C during 4 hours and annealed at 950°C during 10 hours with intermediate particle size reduction. As a result, the monophase white powder Sr_2CeO_4:Eu^{3+} was obtained where the dopant concentration was varied within the 0.1–10 at.% range. The optically excited emission spectra were recorded using an automatic spectrofluorimeter on the base of a MDR-25 grating monochromator. The luminescence of pure and Eu-doped Sr_2CeO_4 crystals was excited by a He–Cd laser
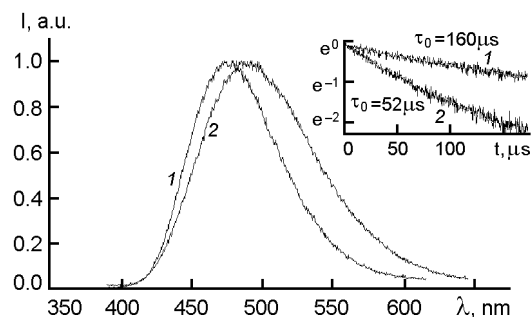

Fig. 1. Luminescence spectra of Sr_2CeO_4 (λ_{exc} = 325 nm). The inset represents Sr_2CeO_4 luminescence decay curves (λ_{exc} = 354.4 nm), *1* — 80K, *2* — 300K.

(λ_{exc} = 325 nm). The luminescence decay curves were recorded by the time-correlated single-photon counting method [18]. The excitation scheme based on a third harmonic (354 nm) of a YAG:Nd laser operating in the Q-switching mode was used. The luminescence spectra and decay lifetimes were measured at both liquid nitrogen and room temperatures.

The Sr_2CeO_4 crystal luminescence spectrum is characterized by a wide band ranged from 390 to 650 nm peaked at 485 nm (Fig. 1). As it was shown in [12], this spectrum is associated with CT transitions. For all known crystals, the CT luminescence is an allowed transition with decay constant of about 50 ns [19, 20], while the decay time of Sr_2CeO_4 luminescence is in microsecond range (see the inset in Fig. 1). The authors [13] ascribe such a long lifetime to the transition of excited electron from oxygen ion to cerium one with electron spin flip resulting in formation of excited triplet state. However, the transition from the excited triplet state to the ground singlet one is forbidden. The considerable increase of luminescence decay time from 52 μs at T = 300 K up to 160 μs at T = 80 K (Fig. 1) is associated with the well-known fact of the CT transition temperature quenching.

Thus, Sr_2CeO_4 crystals belong to a small group of crystals which luminescence properties are governed not by impurity optical centers, but regularly arranged luminescent elements. The main feature of such a luminescent system is the interaction of its regular optical centers, which promotes spatial delocalization of excitation energy. Such an interaction will favor the efficient excitation energy transfer from the matrix

to extrinsic centers emitting in other spectral ranges.

As an extrinsic center, europium ion was chosen due to its stable valency 2+ and possibility to substitute isomorphically Sr^{2+} ions. A similar situation is realized in ortho-silicates and ortho-phosphates, where doping Eu^{2+} ion substitutes strontium ion and efficiently emits in the blue-green spectral range [21]. Such a situation was expected to be observed in Sr_2CeO_4. However, already at the concentration of europium ions of 0.5 at.% with respect to strontium ones, the efficient luminescence of Eu^{3+} was observed (Fig. 2). The fact that the luminescence is associated with Eu^{3+} is confirmed by the pronounced multiplet structure of the luminescence spectrum, whereas the luminescence of Eu^{2+} is characterized by a broad structureless band. At room temperature, the extrinsic luminescence decay time is 634 µs that is also evidence of Eu^{3+} luminescence. The activated crystals were synthesized both in air atmosphere and in vacuum. The synthesis in vacuum must promote the formation of Eu^{2+} state. However, it should be noted that in both cases the luminescence spectrum is the same. So, the doping Eu ion seems to be located in both cerium and strontium positions in pairs, thus equalizing the space charge.

Fig. 2 shows that the increasing activator concentration causes the luminescence intensity redistribution between the matrix and the activator. In Fig. 2, the luminescence intensity is normalized to the europium intensity at $\lambda = 615.5$ nm. It is seen that at 10 at.% of europium ions, the matrix luminescence is completely quenched and the luminescence intensities of individual multiplets of europium ions is unmonotonous. So, the luminescence of multiplet at 467 nm increases at the first stage and then decreases passing the maximum at 1 at.% (Fig. 2). Such intensity variation is associated most probably with the effective cross-relaxation between europium ions that causes the quenching of doped ions luminescence [22].

The luminescence excitation spectrum of activated Sr_2CeO_4 crystals recorded in europium luminescence lines was identical to the pure Sr_2CeO_4 crystal excitation spectrum, so the fraction of europium ions excited directly by the laser radiation is small and the main luminescence is due to the excitation energy transfer from the Sr_2CeO_4 matrix. To ascertain the mechanism of crystal matrix luminescence quenching, the donor
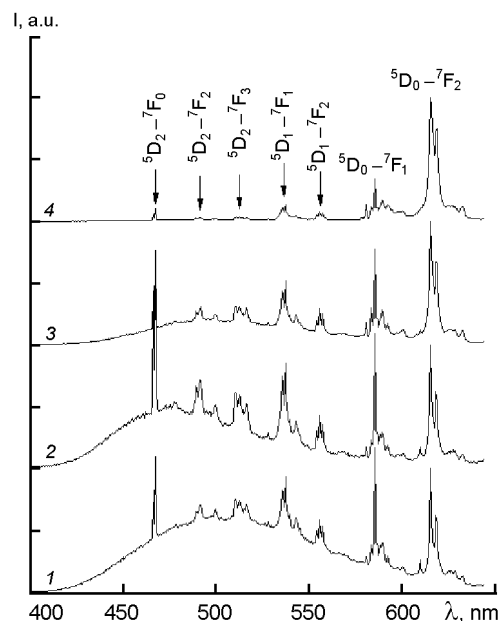

Fig. 2. Luminescence spectra of $Sr_2CeO_4{:}Eu^{3+}$ at various doping ion concentrations, $\lambda_{exc} =$ 325 nm, $T = 300$ К. 1 — 0.5 at.%, 2 — 1 at.%, 3 — 2 at.%, 4 — 10 at.%.

luminescence decay was studied as a function of the activator concentration. The crystal luminescence was excited by a pulse UV source ($\lambda_{exc} = 354.4$ nm) and the luminescence decay was collected at 450 nm, where the Eu^{3+} luminescence is not observed (Fig. 2). The luminescence decay curves are presented in Fig. 3a. The same ones were also measured at nitrogen temperature. Fig. 3a indicates that the increase in the doping ion concentration causes a shape change of the donor luminescence decay curve that evidences the non-radiative energy transfer to the dopant ion. To determine the luminescence decay law, the quenching functions $Ln(-Ln(I/I_0) + t/\tau_0)$ vs $Ln(t)$ were plotted (Fig. 3b), where τ_0 is the luminescence decay time of pure Sr_2CeO_4 crystal ($\tau_0 = 53.4$ µs). The plots allow the index of the quenching function to be determined [23]. Fig. 3b shows that the quenching function index does not depend on the dopant concentration and is equal to *0.5* that indicates the Foerster resonance energy transfer mechanism. The quenching function can be presented as $P(t) = \gamma(t)^{1/2}$, where $\gamma = (16\pi/3)^{1/2}C_{DA}^{1/2}C_A$, where C_{DA} is the microparameter of energy transfer; C_A, the acceptor concentration. The transfer rate γ is characterized by a nearly linear dependence on the dopant concentration in the 0.5–2 at.% concentration range (Table). The
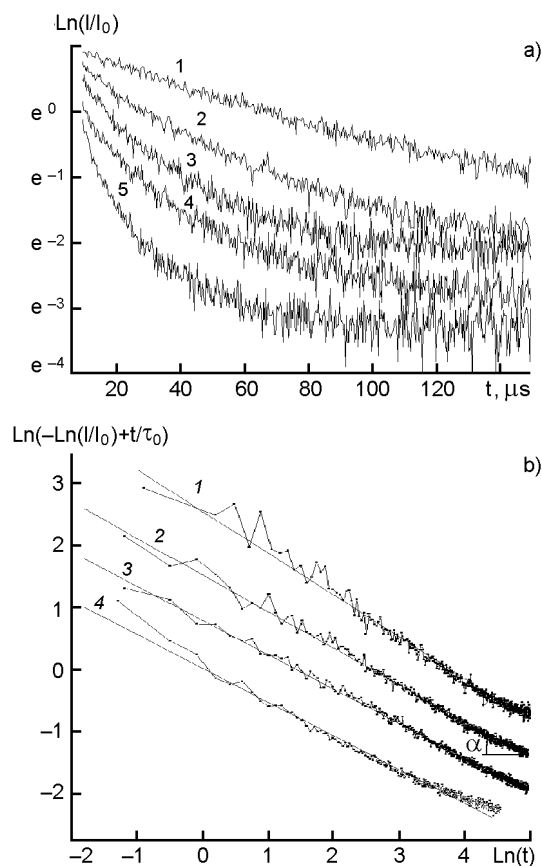
Ln(I/I_0)

a)

Eu^{3+} concentra-tion, at.%	$\gamma \cdot 10^{-3}$, $s^{-1/2}$	
	$T = 300$ K	$T = 80$ K
0.5	0.181	0.0102
1.0	0.270	0.0169
2.0	0.306	0.0302
10	0.566	0.0774

Ln(−Ln(I/I_0)+t/τ_0)

b)

Fig. 3. (a) Sr_2CeO_4:Eu^{3+} luminescence decay curves at various doping ion concentrations, $\lambda_{exc} = 354.4$ nm, $T = 300$ K; (b) Luminescence quenching functions plotted in coordinates $Ln(-Ln(I/I_0) + t/\tau_0)$ vs $Ln(t)$.

transfer rate deviation from the linear law at high doping ion concentrations is correlated with the luminescence spectra. As is seen from Fig. 2, at the Eu^{3+} concentrations exceeding 1 at.%, the quenching of "blue" multiplets begins. Such a deviation confirms the assumption about the cross-relaxation occurrence in the europium subsystem.

Thus, the matrix luminescence quenching is concluded to be a result of Forster resonance energy transfer between donors and acceptors distributed randomly within the crystal volume. However, in Sr_2CeO_4, cerium ions are ordered along 1D chains [12] that supposes the excitonic mechanism of the luminescence quenching. Both Forster and excitonic mechanisms are characterized by the root law of electronic excitation quenching [23, 24]. The main distinction of the excitonic mechanism is a strong temperature dependence of exciton mobility.

For the Forster mechanism, the quenching rate does not depend on temperature, because it is governed by the spectral overlap integral, which is proportional to the overlap between the donor emission spectrum of the donor and the acceptor absorption one. RE ions are characterized by a weak influence of electron-phonon interactions on the optical properties. So, the temperature decrease can cause only a partial spectral line narrowing, while the area under the spectral transition line remaining unchanged. Taking into account the broad luminescence band of Sr_2CeO_4 that weakly depends on temperature (Fig. 1) and the retention of the resonance coincidence of luminescence and absorption bands of the donor and the acceptor, we can conclude that the temperature decrease should not affect significantly the probability of the electron excitation transfer from the donor to the acceptor. However, the experiments carried out at nitrogen temperature point that the transfer rate decreases almost by an order of magnitude at the same concentration of the doping ions (Table). This in possible if excitation is transferred on the doping ion due to the excitation migration along the crystal chain. In this case, the exciton diffusion constant depends strongly on temperature and is governed by the activation law [25].

The experiments carried out have demonstrated the excitonic mechanism of electron excitation energy transfer from the crystal matrix to the doping europium ions. The energy transfer efficiency allows us to expect that Sr_2CeO_4 crystal structure could form a base for development of luminescence materials emitting in various spectral ranges.

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Міграційно-прискорене перенесення енергії від матриці до активатора в кристалі Sr$_2$CeO$_4$:Eu

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Біло-блакитний люмінофор оксицерату стронцію Sr$_2$CeO$_4$ належить до особливого класу матеріалів, люмінесценція яких визначається оптичними переходами, пов'язаними з електронним переносом заряду. Унікальність його кристалічної структури, ланцюжкове розташування люмінесцентних центрів забезпечує ефективне перенесення енергії електронного збудження від матриці до домішкових центрів. Цитратним методом Печіні синтезовано зразки чистого й активованого іонами Eu^{3+} люмінофора Sr$_2$CeO$_4$. Досліджено спектри люмінесценції й загасання люмінесценції Sr$_2$CeO$_4$ і Sr$_2$CeO$_4$:Eu^{3+}. Проведені експерименти підтвердили екситонний механізм перенесення енергії електронного збудження від кристалічної матриці до домішкових іонів європію.