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# Diffusion-controlled excitation annihilation in $Sr_2CeO_4$ crystal

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The contribution from interaction between regular optical centers in $Sr_2CeO_4$ crystal structure to the migration process of electronic excitation energy has been demonstrated. The $Sr_2CeO_4$ crystals have been synthesized by the Pechini citrate method. The luminescence decay process has been studied as a function of the laser radiation density. Parameters of excitation mobility have been estimated. It is shown that the migration in strontium-cerium oxide is rather weak; during its lifetime, the excitation migrates over the 4 chain sites in the arrangement of the optical centers.

Показан вклад взаимодействия регулярных оптических центров в кристаллической структуре $Sr_2CeO_4$ в процесс миграции энергии электронного возбуждения. Образцы $Sr_2CeO_4$ синтезированы цитратным методом Печини. Исследованы кривые затухания люминесценции $Sr_2CeO_4$ в зависимости от плотности лазерного излучения. Определены параметры подвижности возбуждения. Показано, что миграция в церате стронция относительно слабая, за время жизни возбуждение преодолевает 4 узла цепочки в системе оптических центров.

An effective light absorption in the UV spectral region is among requirements to the materials intended for display and lighting techniques [1]. From this point of view, compounds, which possess optical transitions governed by the electron charge transfer are very promising [2]. Strontium-cerium oxide $Sr_2CeO_4$, where the bluish-white luminescence is caused by the radiative relaxation in the charge transfer complex $Ce^{4+}$–$O^{2-}$, belongs to such materials [3].

The $Sr_2CeO_4$ crystal structure belongs to the $Sr_2PbO_4$ structure type and is characterized by a strong anisotropy defined by a set of linear chains of trans edge-sharing $CeO_6$ octahedrons running in parallel to [001] direction with a spatial spacing of 3.597 Å [4]. Thus, a $Sr_2CeO_4$ crystal pertains to the group of compounds with luminescence properties governed by the regularly located luminescence elements rather than by impurity optical centers. Interaction between such regular optical centers must promote the energy spatial delocalization and efficient transport of excitation to the doped centers.

In europium activated $Sr_2CeO_4$:$Eu^{3+}$ crystal, a strong temperature dependence of the nonradiative energy transfer rate from the crystal host to the doping ions was revealed that was explained by the electron excitation migration in the crystal [5]. In the present short communication, we develop the idea stated in our previous work [5] and report the determination results of excitation mobility parameters in $Sr_2CeO_4$ crystal.

It is known that electronic excitations may annihilate when interacting [6, 7]. In experiments, the annihilation could be observed at a high excitation density. The increase of excitation density in a crystal causes the reduction of spacing between the excited centers. The excitation migration facilitates the excitation approach with subsequent annihilation, and, consequently, causes a shortened excitation lifetime [8].

$Sr_2CeO_4$ samples were synthesized by one of the sol-gel methods, namely, the Pechini citrate one [9]. A citric acid solution in ethylene glycol was added to the mixture of the Sr and Ce nitrate solutions. The obtained mixture was heated at 80°C during 10 h that results in the removal of excess nitric acid, the solution pH increase and a gel formation. The next synthetic stage involves the gel hydrolysis. The obtained precipitate was dried and then dehydrated during 4 h at 550°C and annealed during 10 h at 1000°C with intermediate grinding. X-ray structure analysis indicates the single crystalline phase of $Sr_2CeO_4$.

The luminescence decay curves were recorded by the time-correlated single-photon counting method [10]. Luminescence was excited by fourth harmonic (266 nm) of a YAG:Nd laser operated in the *Q*-switching mode. A standard optical cryostat was used for low temperature measurements. The laser radiation intensity was measured by a IMO-2N power meter. The magnitude of light flux hitting the sample was controlled by UV optical filters. For quantitative assessment of the annihilation rate, the equation describing a bimolecular quenching process was applied [11]:

$$\frac{d\rho}{dt} = -\frac{1}{\tau_0}\rho - \frac{1}{2}\gamma\rho^2, \qquad (1)$$

where $\rho$ is the excitation density; $\tau_0$, the luminescence decay time; $\gamma$, the annihilation rate.

The estimation of the initial concentration of excited centers was estimated using the following equation [12]:

$$\rho_0 = \frac{N_0(1 - e^{-1})}{\Delta S \cdot \Delta l}, \qquad (2)$$

where $N_0$ is the number of emitted photons; $\Delta S$, the irradiated area of the sample; $\Delta l = 1/K$, the average depth of the exciting beam penetration; $K$, the extinction coefficient. As the samples under study were compacted powders, it is necessary to take into account the laser beam scattering from a sample surface. The Kubelka-Munk theory that describes a relation between absorbed, reflected, and scattered light energy for powder materials [13] was used to determine the amount of scattered energy. The values of the extinction ($K$) and reflection ($R$) indices for $Sr_2CeO_4$ at 266 nm (0.4 and 0.08, respectively) were taken from [14, 15].

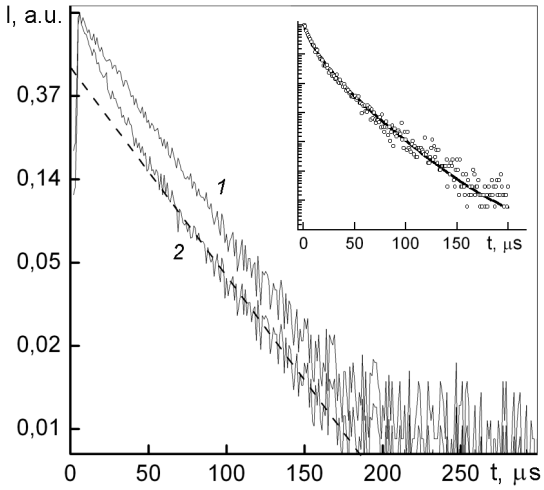


Fig. The luminescence decay curves for a $Sr_2CeO_4$ crystal at different initial excitation densities: $10^{18}$ cm$^{-3}$ (*1*), 2 — $10^{20}$ cm$^{-3}$ (*2*). Inset: fitting of curve 2 by the solution of equation (1).

Using these data, the scattering coefficient ($S$) was calculated.

Figure shows the $Sr_2CeO_4$ luminescence decay curves at different initial excitation densities. At 300 K, the decrease of the luminescence decay time becomes observable if the excitation density exceeds $\rho_0 \sim 10^{20}$ cm$^{-3}$. According to the calculations basing on crystallographic data [4], at such an excitation density, the average distance between the excited centers in $Sr_2CeO_4$ crystal does not exceed 10 Å. The extrapolation of the exponential part of decay curve *2* to $t = 0$ allows the amount of unquenched centers to be estimated (Fig.). $\gamma = 2.65 \cdot 10^{-16}$ cm$^3$/s was calculated from the experimental data fitting by the solution of equation (1) (see inset in Fig.). The annihilation rate $\gamma$ and the diffusion coefficient $D$ are interrelated as $\gamma = 4\pi D R_A$, where $R_A$ is the annihilation radius [16]. Taking $R_A = 10$ Å (the average distance between excited centers), we obtain $D = 2 \cdot 10^{-10}$ cm$^2$/s and the excitation mean-square track length $l = \sqrt{2\tau_0 D} \sim 12$ Å. It should be noted that at 80 K, the decrease in $Sr_2CeO_4$ luminescence decay time was observed even at the excitation density of $5 \cdot 10^{20}$ cm$^{-3}$. This result agrees with our previous work [5] and is explained by the shortening of the excitation track length.

Thus, the excitation energy migration in $Sr_2CeO_4$ has been confirmed. The annihilation rate estimation shows that the excita-

tion migrates over the over 12 Å or 3–4 chain sites during its lifetime, taking the spatial period to be 3.597 Å. It could be concluded that despite the regular arrangement of luminescent centers in strontium-cerium oxide, the excitation mobility is rather weak. It is associated with the charge transfer in the crystal, i.e. the excitation preferred localization on $CeO_6$ octahedrons as a result of significant electron density redistribution in the excited state.

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## Дифузійно-контрольована анігіляція збуджень у кристалі $Sr_2CeO_4$

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Продемонстровано внесок взаємодії регулярних оптичних центрів у кристалічній структурі $Sr_2CeO_4$ до процесу міграції енергії електронного збудження. Зразки $Sr_2CeO_4$ синтезовано цитратним методом Печіні. Досліджено криві загасання люмінесценції $Sr_2CeO_4$ залежно від густини лазерного випромінювання. Визначено параметри рухливості збудження. Показано, що міграція у цераті стронцію відносно слабка, за час життя збудження долає 4 вузли ланцюжка у системі оптичних центрів.