A luminescence spectroscopy study of SrI$_2$:Nd$^{3+}$ single crystals

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ABSTRACT

The paper presents the results of a study on the luminescence of SrI$_2$:Nd$^{3+}$ single crystals grown by the vertical Bridgman method. The photoluminescence (PL) spectra of SrI$_2$:Nd crystals show characteristic lines corresponding to transitions in trivalent Nd$^{3+}$ ions, the most intense line at ca. 1070 nm is due to the radiative $^4$F$_{3/2} \rightarrow ^4$I$_{11/2}$ transitions. Efficient PL excitation in a crystal transparency band occurs due to optical $^4$F$_{3/2}$ transitions from the ground $^4$I$_{9/2}$ state, or the charge transfer transitions $^4$I$_{9/2}$ $\rightarrow $ Nd$^{3+}$. The paper discussed two new PL emission bands at 2.8 and 3.8 eV, associated with the lattice defects formed in SrI$_2$ crystal at introducing Nd$^{3+}$ impurity ions; two intense narrow PL excitation bands at 5.52 and 5.31 eV, originating from free and defect-bound excitons, respectively; an efficient channel of exciton energy transfer between the host lattice and defects. We calculated the $\beta(k)$ functions of distribution of the elementary relaxations over the reaction rate constants and explained on this basis the nonexponential PL decay kinetics in SrI$_2$:Nd$^{3+}$ crystal.

1. Introduction

Scintillation crystals are now an important part of many applications, including the detection of gamma radiation with high energy resolution to identify isotopes. Among the commercially available inorganic scintillators, LaBr$_3$:Ce is leading in the energy resolution of ca.2.6% at 662 keV [1–3]. Alkaline earth metal iodides represent another outstanding family of fluorescent crystals. In this series, SrI$_2$:Eu$^{3+}$ emits light in the Eu$^{3+}$ photoluminescence (PL) band ($\lambda$ = 435 nm, $\tau$ = 1.2 $\mu$s [4,5]), shows the highest light output (over 120 photons/keV [6]), excellent energy resolution (2.6% at 662 keV [7]), and a high proportionality of light yield [8]. Many research works were devoted to optimize a composition and improve the energy transfer processes in strontium iodide crystals. For instance, Gahane et al. [9] studied the luminescence of Eu$^{3+}$ ions in the matrices of KI - 2 BaI$_2$ and KI - 2 SrI$_2$ and CaI$_2$. The SrI$_2$(Ce/Na) system was studied in Refs. [6,8]. Other trivalent ions have not been tested in the SrI$_2$ system, while LaBr$_3$ crystals doped with Nd$^{3+}$ impurity ions have recently been developed and successfully applied in a fast LaBr$_3$:Nd$^{3+}$ scintillator with the PL lifetime of $\tau$ = 15 ns, light yield ca. 20 photons/keV and the energy resolution of 7.5% [10,11]. We are not aware of such publications on SrI$_2$:Nd, although SrI$_2$:Nd$^{3+}$ crystals can be considered as a model system to better understand the SrI$_2$ host lattice doped with heterovalent impurity ions of trivalent rare earth elements. There are important reasons to choose Nd$^{3+}$ impurity ions to study the problem. Indeed, as some of the rare earth elements, neodymium ion can be in the divalent or trivalent charge state. However, unlike the other rare earth elements, neodymium ion forms steady compounds, such as iodide, which is essential for doping by heterovalent impurity ions. The compensation of the excess charge in this case can be done by uncontrolled intrinsic lattice defects or intentionally introduced alkali metal ions. Note also that in addition to the above applications, the neodymium ions in various matrices are widely used in a variety of optical applications, such as the working material for lasers operating in the near infrared spectral range.

The main goal of this work is a study of luminescence properties of SrI$_2$:Nd single crystals using a time-resolved vacuum ultraviolet (VUV) spectroscopy technique upon selective excitation by synchrotron radiation in a broad energy range. The main attention was paid to the processes in the SrI$_2$:Nd host lattice and the energy transfer from the matrix to the Nd$^{3+}$ impurity ions. The present work does not include the detailed spectroscopic study of the processes occurring inside the Nd$^{3+}$ ions. The data on the spectroscopy of Nd$^{3+}$ ions have been published in numerous publications, such as Refs. [12–14]. In our study, these data were used to identify the Nd$^{3+}$ ions in the luminescence spectra of SrI$_2$:Nd$^{3+}$.

2. Experimental details

All the examined crystals, SrI$_2$ and SrI$_2$:Nd doped with the 2.5 mol.% Nd$^{3+}$ ions, were grown at the Institute of Geology and Mineralogy of Siberian Branch of Russian Academy of Sciences.
The size of grown crystals was 10×10×10 mm³. Samples were cut from a clean part of crystal boule, which was 25 mm in length. The sizes of the investigated crystals were 6×5×1.5 mm³; the largest surfaces studied were cleaved and parallel. The concentration of the Nd³⁺ impurity ions was chosen to make its luminescence comparable in intensity with the other PL emission bands found previously in SrI₂ crystals [16]. Data on the real structure of the grown crystals of strontium iodide were presented in a previous paper [16]. X-ray diffraction study showed that crystal structure parameters of SrI₂:Nd crystals have no significant deviations from that of pure SrI₂ presented in Ref. [17].

Because of hygroscopic nature of SrI₂ crystals, any contact with the atmospheric air leads to degradation of the sample surface that becomes cloudy due to the formation of crystalline hydrates. In this regard, each SrI₂:Nd sample after preparation was kept in an evacuated and sealed ampoule. In all our experiments the samples were removed from the ampoules, cleaved in an atmosphere of a dry hot air and immediately mounted in the sample holder attached to a He-flow cryostat with a fast vacuum pumping. Before starting the VUV experiments the samples were kept in a cryostat for 12 h at T = 90 °C in a vacuum not worse than 10⁻¹⁰ Torr. After that, we performed spectroscopic measurements in a vacuum better than 7 × 10⁻¹⁰ Torr.

The present study was carried out by the means of the low-temperature luminescence VUV spectroscopy with the time-resolution. The PL emission spectra in the energy range of Eᵣ from 1.2 eV to 5.0 eV and the PL excitation (PLE) spectra in the energy range of Eₓ from 3.7 eV to 20 eV (spectral resolution 0.32 nm) were recorded at the temperatures of 8 and 293 K at the SUPERLUMI experimental station of HASYLAB (DESY, Germany) [18] upon excitation with synchrotron radiation (SR). At the storage ring DORIS the full width at half maximum (FWHM) of synchrotron radiation pulses was 130 ps with the repetition period of 96 ns. Such pulses excitation enables the recording of spectra within a time-window correlated with the arrival of SR pulses. In the present experiments we recorded time-resolved spectra within two independent time-windows (TWs) set for detection of luminescence signal within 1.4–14.0 ns (TW1) and 52.5–72.5 ns (TW2) relative to the beginning of the SR pulse. Time-integrated (TI) spectra were recorded within the full time range available between two sequential excitation pulses, viz. 96 ns. The primary 2 m-vacuum monochromator, equipped with Al-grating was used for selective PL excitation with synchrotron radiation. The PL excitation spectra were corrected to an equal number of photons incident on the sample using sodium salicylate with the energy-independent quantum yield over the studied spectral range. The 0.3 m ARC Spectra Pro-300i monochromator equipped with an R6358P (Hamamatsu) photomultiplier were used as a registration system. The PL emission spectra were not corrected to the spectral sensitivity of the recording system.

The PL characteristics upon excitation in the visible and UV spectral region were measured at 293 K. The 1 kW xenon discharge lamp and the primary MDR-2 grating monochromator were used as an excitation source. The secondary SDL-1 spectrophotometer and the cooled FEU-83 photomultiplier tube were used as a registration system to record photoluminescence in the visible to near infra red spectral region. The PLE spectra were normalized to an equal number of photons incident on the sample, whereas the PL emission spectra are shown without correction.

3. Experimental results and discussion

3.1. Undoped SrI₂ crystals

Undoped crystals of SrI₂ are transparent in a wide spectral range, the crystal transparency band has a short-wavelength edge at ca. 300 nm. Photoexcitation of undoped SrI₂ crystals at λᵣₓ = 350 nm (3.54 eV) and T = 293 K results in PL emission in the yellow spectral region, Fig. 1. The PL emission spectrum comprises of two broad bands at 2.2 and 2.9 eV (FWHM = 0.55 and 0.22 eV), respectively. The 2.2 eV band can be caused by crystal hydrates, that arose in the interaction of the SrI₂ surface with the water molecules as it was shown previously for SrI₂:Eu [16]. Spectroscopic parameters of the low-intensity 2.9 eV band are the same as for the 5d → 4f luminescence of Eu²⁺ in SrI₂ crystals. On the basis of spectroscopic data we suggest that the undoped SrI₂ crystals could contain traces of unintentionally introduced Eu²⁺ ions.

3.2. Luminescence spectroscopy of Nd³⁺ ions in SrI₂:Nd crystals

Deep red PL emission spectra. Luminescent properties of SrI₂:Nd crystals differ substantially from those of undoped SrI₂ crystals. The main difference lies in the manifestation of intense radiative transitions in Nd³⁺ impurity ions. Inset in Fig. 2 shows the energy diagram of trivalent Nd³⁺ ion composed on the basis of numerical data [12,13]. The spectroscopic properties of neodymium impurity ions in the present study were investigated in the visible and near infrared spectral region. Fig. 2 shows a fragment of the steady-state luminescence spectrum of SrI₂:Nd crystal recorded at T = 293 K in the spectral range of 925–1150 nm upon excitation at λᵣₓ = 330 nm. The dominant PL emission band at 1060–1080 nm and less intensive band at 975–990 nm correspond to the intra-configuration transitions from the lowest excited state ⁴F₃/₂ onto the levels of ⁴I₇/₂ and ⁴I₉/₂, respectively. These transitions are chosen as the most intense and informative because ⁴F₃/₂ manifold contains only two Stark levels, and ⁴I₉/₂ manifold contains five Stark levels and is the ground state of ⁴F₃/₂ shell in Nd³⁺ ion. Energy diagram (Fig. 2) suggests the possibility of other radiative transitions, but they have much lower PL intensities in comparison with the dominant PL emission band.
Let us discuss the possible prerequisites for introduction of Nd$^{3+}$ impurity ions into SrI$_2$ host lattice.

From a crystallographic point of view, SrI$_2$ belongs to the orthorhombic crystal system (space group Pbca), its unit cell contains eight formula units (24 atoms) and characterized by lattice parameters $a=1.522$, $b=0.822$, $c=0.790$ nm, and it has a specific weight $\rho=4.540$ g cm$^{-3}$ [17,21,22]. The SrI$_2$ unit cell contains eight equivalent Sr$^{2+}$ ions and two non-equivalent sets of eight I$^{-}$ ions. Such a lattice is not a cubic structure, and cannot be represented as a slightly distorted cubic structure. Such a lattice cannot be described in terms of cubic symmetry, or presented as a slightly distorted cubic structure. The observed splitting of $^{4}P$ PLE band (Fig. 3) also suggests non-cubic local symmetry of Nd$^{3+}$ sites in SrI$_2$ crystals. The ionic radii of Nd$^{3+}$ and Sr$^{2+}$ are 112.3 and 132 pm, respectively [23], which favors the heterovalent substitution of Sr$^{2+}$ host ion by Nd$^{3+}$ impurity ion. The compensation of the excess charge of the impurity ion in this case can be done by either alkali metal ions or structural lattice defects. In this case, the compensation of the excess charge of the impurity ion can be done by either monovalent alkali metal ions or structural lattice defects. However at this stage we should not exclude the possibility that Nd$^{3+}$ impurity ions can occupy interstitial voids in the SrI$_2$ host lattice.

It should be noted that we do not expect the introduction of divalent Nd$^{2+}$ ions into the SrI$_2$ host lattice. Indeed, despite the isovalent nature of Nd$^{2+}$ impurity ion, its ionic radius (143 pm) exceeds the radius of Sr$^{2+}$ host ion that requires considerable lattice distortion in the vicinity of the impurity ion. In addition, we have not detected the expected spectroscopic manifestations of the radiative $4f^1 5d-4f^2$ transitions in Nd$^{2+}$ ions. Such transitions have been previously observed in the form of a weak broad band at 560 nm in SrB$_2$O$_3$:Nd [24] and CaF$_2$:Nd [25].

Visible and near-UV PL emission spectra. In the visible and near-ultraviolet (UV) spectral region, the PL emission spectrum of SrI$_2$: Nd crystal contains broad bands that cannot be associated with the radiative transitions in neodymium ions. Fig. 4 shows the time-integrated (TI) PL emission spectra of SrI$_2$: Nd crystal, measured in the energy range of 2.0–4.5 eV. Profile of PL spectrum depends on the excitation energy $E_{\text{ex}}$. At $E_{\text{ex}}=5.29$ eV, the low-temperature PL emission spectrum consists of two intense broad bands at 3.3 and 3.75 eV, and two well-defined shoulders at 2.2 and 2.5 eV. At $E_{\text{ex}}=5.39$ eV the PL emission spectrum changed in profile. In this case, the low-temperature PL emission spectrum consists of broad bands at 2.45 and 3.25 eV, and shoulders at 2.2 and 3.75 eV. At room temperature, the PL emission spectrum consists of a broad complex band at 2.6 eV, which shows a gradual decrease in intensity of high-energy slope from 2.6 to 4.5 eV. Decomposition of PL emission spectrum has identified five principal elementary Gaussian bands labeled as $g_1$–$g_5$. Fig. 4. A set of these bands describe all the observed PL emission spectra shown in Fig. 4. The difference between these spectra is only in the relative intensities of the elementary bands. Comparison of the band parameters (Table 1) indicates that the low temperature PL emission spectrum is dominated by two bands of $g_4$ and $g_5$, which together are responsible for more than half of the light sum. However, the ratio of their contributions depends on the excitation energy. At $E_{\text{ex}}=5.29$ eV, $g_5$-band has the highest intensity in PL emission spectrum and determines ca.35% of the light sum. At $E_{\text{ex}}=5.39$ eV, $g_4$-band dominates and determines ca. 42% of the light sum, whereas the contribution of $g_5$-band is reduced by more than three times. At room temperature, the PL emission spectrum is determined by the contribution of the other two bands of $g_4$ and

![Fig. 2. PL emission spectrum recorded for SrI$_2$:Nd crystal at T=293 K upon excitation at $\lambda_{\text{ex}}=330$ nm (3.76 eV). Inset shows the Nd$^{3+}$ energy diagram composed using numerical data [12,13].](image)

![Fig. 3. PLE spectrum recorded for SrI$_2$:Nd crystal at T=293 K monitoring emission at 1070 nm. Labels indicate the lines of the identified transitions from the ground $^4$H$_{9/2}$ state to labeled excited levels in Nd$^{3+}$ ion.](image)

3.3. Luminescence spectroscopy of lattice defects in SrI$_2$: Nd crystals
The common feature of these spectra is that in all cases the most intense PL maximum of the PL spectrum ($E_m$) is observed in the total light sum of the PL emission spectrum ($I_m$). Percentage contribution of the elementary band into the total light sum of the PL emission spectrum ($S$) is being responsible for the PL emission bands: the higher intensity is observed in the PLE spectrum recorded monitoring emission at the other bands ($E_m > 5$ eV) – Fig. 5a. In the 6–10 eV energy range, PLE efficiency is not high, but it is different for different PL bands: the higher intensity is observed in PLE spectrum recorded monitoring emission at $E_m > 5.26$ eV, Fig. 5b.

Fig. 5. PLE spectra recorded for SrI$_2$:Nd crystal at 8 (a–c) and 293 K (d) monitoring time-integrated emission at $E_m$. The vertical arrow indicates the position of $E_m$ according to the data [16]. Inset shows an enlarged fragment of PLE spectrum in the energy range from 5 to 6 eV.

Isolated low-intensity bands at 4.30 and 4.95 eV, which are observed only in the PLE spectrum for $E_m = 3.87$ eV, are due to charge-transfer transitions $1^− \rightarrow$ Nd$^{3+}$, Fig. 5a. In the 6–10 eV energy range, PLE efficiency is not high, but it is different for different PL bands: the higher intensity is observed in PLE spectrum recorded monitoring emission at $E_m = 3.26$ eV, Fig. 5b.

Our results (Figs. 4 and 5, Table 1) in combination with the earlier data on SrI$_2$:Eu luminescence [16] allow us to make reasonable assumptions about the nature of $g_1$–$g_5$ bands. According to spectroscopic parameters, two of the lower-energy bands $g_1$ and $g_2$ are comparable to the PL emission bands from crystal hydrates, which result from the interaction of the SrI$_2$ surface with water molecules. Low-temperature band $g_4$ is comparable to the 3.4 eV luminescence band [16], which is due to radiative annihilation of self-trapped excitons in the SrI$_2$ crystal. The remaining two elementary bands $g_3$ and $g_5$ cannot be compared with the data on SrI$_2$ (Fig. 1) and previous results on SrI$_2$:Eu [16]. These PL emission bands should be attributed to the presence of Nd$^{3+}$ impurity ions in the SrI$_2$ host lattice.

In our opinion, the narrow PLE peak at 5.31 eV (Fig. 5a) is due to a creation of excitons in the vicinity of the defect complexes consisting of Nd$^{3+}$ impurity ion and associated defect, which is needed to compensate for the excess charge of the trivalent impurity. Spectroscopic parameters of this peak are close to that

$$g_3$$, which together provide more than 70% of the light sum, Table 1.

**PLE spectra.** Fig. 5 shows PLE spectra recorded at 8 and 293 K monitoring time-integrated emission of different PL bands at $E_m$. The common feature of these spectra is that in all cases the most efficient PL excitation occurs in a rather narrow energy range from about 5 to 6 eV. At other excitation energies, the luminescence intensity is quite low. PLE spectrum recorded monitoring emission at $E_m = 3.87$ eV is the most structured, it consists of two partially overlapped intense narrow bands with sharp peaks at 5.31 and 5.52 eV (FWHM = ca.0.15 eV). The low-energy slope of the PLE spectrum is characterized by the cut-off energy of ca. 5.15 eV. The high-energy slope exhibits a pronounced local minimum at 5.75 eV. PLE spectra recorded monitoring emission at the other bands (Fig. 5b–d) are less structured, and their low-energy tails extend down to the low-energy region up to 4.5 eV. The position of the maximum intensity in these spectra varies slightly for different experimental conditions. At $T = 8$ K peaks in PLE spectra are located at 5.19 eV ($E_m = 2.43$ eV) and 5.50 eV ($E_m = 3.26$ eV). At room temperature, PLE maximum is located at 5.26 eV ($E_m = 2.58$ eV).

$$\text{Table 1}$$ Parameters of the $g_1$–$g_5$ elementary bands being responsible for the PL emission spectra recorded for SrI$_2$:Nd crystals, energy position ($E_m$, full width at half maximum (FWHM), band intensity normalized to 100 conventional units at the observed maximum of the PL spectrum ($I_m$), percentage contribution of the elementary band into the total light sum of the PL emission spectrum ($S$), exciting photon energy ($E_{ex}$), and temperature ($T$).

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$g_5$, which together provide more than 70% of the light sum, Table 1.

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Isolated low-intensity bands at 4.30 and 4.95 eV, which are observed only in the PLE spectrum for $E_m = 3.87$ eV, are due to charge-transfer transitions $1^− \rightarrow$ Nd$^{3+}$, Fig. 5a. In the 6–10 eV energy range, PLE efficiency is not high, but it is different for different PL bands: the higher intensity is observed in PLE spectrum recorded monitoring emission at $E_m = 3.26$ eV, Fig. 5b.

Our results (Figs. 4 and 5, Table 1) in combination with the earlier data on SrI$_2$:Eu luminescence [16] allow us to make reasonable assumptions about the nature of $g_1$–$g_5$ bands. According to spectroscopic parameters, two of the lower-energy bands $g_1$ and $g_2$ are comparable to the PL emission bands from crystal hydrates, which result from the interaction of the SrI$_2$ surface with water molecules. Low-temperature band $g_4$ is comparable to the 3.4 eV luminescence band [16], which is due to radiative annihilation of self-trapped excitons in the SrI$_2$ crystal. The remaining two elementary bands $g_3$ and $g_5$ cannot be compared with the data on SrI$_2$ (Fig. 1) and previous results on SrI$_2$:Eu [16]. These PL emission bands should be attributed to the presence of Nd$^{3+}$ impurity ions in the SrI$_2$ host lattice.

In our opinion, the narrow PLE peak at 5.31 eV (Fig. 5a) is due to a creation of excitons in the vicinity of the defect complexes consisting of Nd$^{3+}$ impurity ion and associated defect, which is needed to compensate for the excess charge of the trivalent impurity. Spectroscopic parameters of this peak are close to that
for the exciton peak at 5.52 eV in PLE spectrum (Fig. 5a). Defect-bound exciton can relax by transferring energy to both the Nd$^{3+}$ impurity ion and associated charge-compensating defect. The presence of the 5.52 eV peak in PLE spectrum indicates the existence of an effective channel of exciton energy transfer from the matrix to the defect complexes. From Fig. 5a it follows that PLE efficiency of the Nd$^{3+}$ luminescence is much higher for excitonic channel than that for the charge-transfer transitions. PL emission band $g_5$ is efficiently excited in the entire investigated temperature range of 8–293 K, and it should be attributed to the luminescence of the charge-compensating defect. At the same time, the spectroscopic properties of the low-temperature PL emission band $g_5$ is similar to those of $g_{51}$-band, which is due to radiative annihilation of self-trapped excitons in SrI$_2$. This allows us to discuss the possible connection of PL emission band $g_5$ with radiative annihilation of self-trapped excitons in the vicinity of the discussed defect complexes in the SrI$_2$:Nd host lattice.

### 3.4. Decay kinetics and time-resolved spectra

**PL decay kinetics in nanosecond time-range.** Fig. 6 shows the PL decay kinetics curves recorded for SrI$_2$:Nd crystals at $T=8$ and 293 K monitoring emission at $E_{ex}=5.29$ and 5.39 eV upon excitation at $E_{ex}=5.29$ and 5.39 eV. A significant portion of the light sum is due to the inertial components of the micro- and millisecond decay time-range shown in our measurements in the form of a constant level—pedestal, Table 2. In all cases, the observed PL decay kinetics is not single-exponential, and it corresponds to the empirical relationship [26]

$$I(t) = I_0 + A \exp\left[-\frac{(t - \tau_0)}{\tau}\right],$$

where $I_0$ is a pedestal, taking into account the contribution of the inertial components; $A$ is the amplitude of the exponential component; $\tau_0$ is the approximation parameter that has the dimension of time; $0 < \beta \leq 1$ is a constant. Table 2 shows the results of the approximation.

The exponential term in Eq. (1) corresponds to the Kohlrausch relaxation function (’stretched exponent’), which is equivalent to a superposition of single-exponential components. Distribution of elementary relaxations through the reaction rate constants $k$ is described by a continuous function $H(k)$ [26].

$$\frac{I(t)-I_0}{A} = \int_0^\infty H(k) \exp(-kt) \, dk.$$  

Fig. 7 showed the distribution functions $H(k)$, which have been calculated for the PL decay kinetics. These functions comprise two broad asymmetric peaks at 9.6 and 10.8 ns, corresponding to the curves recorded monitoring emission at low-temperature PL band ($E_{em}=3.87$ eV) upon excitation at $E_{em}=5.29$ and 5.39 eV, respectively. In the extreme case when $\beta = 1$, the Kohlrausch function becomes the ordinary exponent and peak in the distribution tends to the Dirac delta-function $H(k) = \delta(k-1/\tau_0)$. This case is realized in our measurements at room temperature, where the PL decay kinetics is approximated by the sum of two exponential components with lifetimes $\tau_0 = 0.5$ and 25 ns, Figs. 6 and 7 and Table 2.

Table 2 shows also the values of average decay time $\tau$, calculated from formula [26]

$$\tau = \tau_0 \frac{\Gamma(2/\beta)}{\Gamma(1/\beta)}.$$  

**Table 2**

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* Kinetics was approximated by the sum of two exponential components.
where \( \Gamma \) is the Gamma function. For the exponent \( \gamma = 0.5 \), the average decay time \( \tau = 6 \Omega_0 \), which corresponds exactly to the position of the maximum in the \( H(k) \) distribution, Fig. 7.

From a physical point of view, the observed distribution of the rate constants indicates a static distribution in the properties of the nearest environment of the luminescent center. This means that the processes occurring in one center will not affect the processes in other centers. The value \( \gamma = 0.5 \) has been previously observed in the processes of diffusion-controlled quenching of the luminescence through the contact reactions [27,28], and in processes of diffusionless resonance energy transfer through the dipole–dipole mechanism in various three-dimensional systems [29–31]. Two mechanisms of energy transfer to quenching centers were found for Nd\(^{3+} \) ions in YAG matrix [32]. At short decay times, a one-step energy transfer to randomly distributed quenching sites dominates, whereas energy migration to sinks consisting of cross-relaxing Nd ions dominates at long decay times. Under short-pulse excitation the luminescence decay is nonexponential for concentrations greater than about 1 at % whereas at long-pulse excitation single exponential lifetimes occur even at Nd concentrations of a few percents [32]. The origin of the quenching centers can be attributed to the presence of large amount of hydroxyl groups [33], or the nanosecond kinetics of nonradiative relaxation of highly quenched levels of Nd\(^{3+} \) ions [34]. The luminescence quenching can also occur due to quasidiffusion and stepwise migration in a disordered medium [35].

**Time-resolved PL and PLE spectra.** Fig. 8 shows the time-resolved photoluminescence spectra of SrI\(_2\):Nd crystals recorded in the energy range of 2.0–4.5 eV. In the low-energy spectral region, where \( g_1 \)–\( g_3 \) bands are located, the TW1 and TW2 spectra are identical in profile, so they are normalized to match the intensity in this spectral region. In the energy region where \( g_4 \) and \( g_5 \) bands are located, the time-resolved spectra TW1 and TW2 are different in profile. The difference of normalized spectra TW1 and TW2 gives an idea about the spectrum for the fast component of the PL decay kinetics. From Fig. 8 it follows that the spectrum of the fast component covers the \( g_4 \) and \( g_5 \) PL emission bands. This confirms indirectly our assumptions about the excitonic mechanism of energy transfer and the origin of the emission bands.

Fig. 9 shows PLE spectra recorded monitoring time-resolved emission at different PL bands. A common feature of all the spectra is the low PL intensity upon excitation in the energy range of interband transitions at \( E_{ex} > E_g \). In combination with high photoluminescence intensity upon excitation at the fundamental absorption region \( E_{ex} < E_g \) (exciton region), this indicates a high mobility and a high value of the diffusion length for electron excitations. At energies \( E_{ex} > E_g \), the mean free path of photons in the crystal becomes comparable with the diffusion length of the electronic excitations, most of which can reach the surface and contribute to the surface energy losses due to non-radiative recombination. In addition, it indicates the insignificant role of the electron–hole recombination in the photoluminescence excitation in the SrI\(_2\):Nd crystal.

In the energy range of \( E_{ex} < 2.5E_g \), the TW1 and TW2 spectra are identical in profile. Some minor differences are observed only at \( E_m = 3.87 \) eV (Fig. 9a) in the TW2 spectrum. With further increase in the excitation energy, we observed a slow monotonic increase in the PL intensity of the TW1 spectrum, while the PL intensity in the TW2 spectrum remains virtually unchanged. The lifetime of the fast component of the PL decay kinetics which leads to the observed increase in the intensity, is much greater than the excitation pulse duration. Therefore, the observed increase in the luminescence intensity in the TW1 spectrum at \( E_{ex} > 2.5E_g \) cannot be attributed to instrumental reasons, such as increasing the contribution of the scattered light from the PL excitation channel. The most significant increase in the PL intensity in the TW1 spectrum occurs at \( E_m = 3.26 \) eV (Fig. 9b). This PLE spectrum relates mainly to the excitation of the PL emission band \( g_6 \), which is due to radiative annihilation of self-trapped excitons in SrI\(_2\) crystal. Unfortunately, the excitation energy range in our study

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**Fig. 8.** The time-resolved (TW) PL emission spectra recorded in the energy range of 2.0–4.5 eV for SrI\(_2\):Nd crystal at 8 (a, b) and 293 K (c) monitoring emission at time-window TW1 (1) and TW2 (2) upon excitation at \( E_{ex} = 5.29 \) (a) and 5.39 eV (b). Curve (3) corresponds to the difference of normalized spectra TW1 and TW2.

**Fig. 9.** PLE spectra recorded for SrI\(_2\):Nd crystal at 8 (a, b, c) and 293 K (d) monitoring emission at \( E_m \) in time-windows TW1 (1) and TW2 (2).
was only up to 20 eV, which is not enough to determine the reason of increase in the PLE intensity in the TV1 spectra. We have no reason to discuss in this paper the possibility of manifestation of the photon multiplication effect in SrI₂:Nd crystals. We can only note that in SrI₂:Eu crystals such effect was observed earlier in the PLE spectra recorded monitoring emission at 2.85 eV (Eu²⁺), or 2.40 eV (crystalline hydrates) upon excitation in the energy range up to 40 eV [16]. The photon multiplication effect has been observed previously also in many alkali halides [36], binary oxides [37], nonlinear optical crystals [38–40]. Photon multiplication aspect in SrI₂:Nd crystals are a separate topic and could be origin of a special investigation. At this stage we can only say that SrI₂:Nd crystals exhibit mobile electronic excitations. Extremely low PLE intensity in the energy range from 1.9 to 3.3 eV (Fig. 9) is due to the high probability of migration for electronic excitations, which can easily reach the sinks of nonradiative relaxation.

4. Conclusions

We reported the results on the luminescence spectroscopy study of SrI₂:Nd crystals performed by the methods of luminescence VUV spectroscopy with a time resolution at 8 and 293 K. The main conclusions are as follows.

(1) Trivalent Nd³⁺ impurity can be introduced into the SrI₂ crystal lattice during the growth of these crystals by the vertical Bridgman method. The ratio of the ionic radii of Nd³⁺ and Sr²⁺ favors the heterovalent substitution of regular Sr²⁺ cation sites by the Nd³⁺ impurity ions. Compensation of the excess charge of the impurity ion in this case can be carried out by alkali metal ions or structural lattice defects. However, we cannot exclude the possibility that the Nd³⁺ impurity ions can also occupy the interstitial voids.

(2) The results obtained by luminescence spectroscopy revealed the presence of trivalent Nd³⁺ impurity ions in the SrI₂ crystal lattice. At the same time, our results did not reveal the presence of divalent Nd²⁺ in the SrI₂:Nd crystal. This can be explained by the fact that divalent Nd²⁺ cannot be stabilized in the SrI₂ lattice due to the presence of an insulating SrI₂ lattice.

(3) Two elementary PL bands at 2.8 and 3.8 eV we attribute to the presence of Nd³⁺ impurity ions in SrI₂ host lattice. The g₂ band emission is attributed to the luminescence of a lattice defect, possibly to the luminescence of the charge compensating defect, located in the vicinity of Nd³⁺ impurity ion. The g₂ band is presumably associated with radiative annihilation of self-trapped excitons in the defective areas of the SrI₂:Nd crystal.

(4) SrI₂:Nd crystals provide an efficient channel for exciton energy transfer from the matrix to the defect complexes discussed above. Two narrow intense peaks at 5.31 and 5.52 eV in the PLE spectrum of the intrinsic emission of SrI₂:Nd crystal is due to the creation of excitons in the vicinity of the defect complexes, and in a defect-free region of the crystal, respectively.

(5) The PL decay kinetics recorded for SrI₂ crystal monitoring emission at g₄ and g₂ bands upon excitation through the PLE excitonic bands, exhibits a nonexponential profile. Analysis of the PL decay kinetics using Kohlrausch function and restoring the distribution function H(k) using the inverse Laplace transform, showed the presence of two broad asymmetric peaks at 9.6 and 10.8 ns in the distribution of the reaction rate constants, which indicate the presence of a static distribution on the properties of the nearest environment of the luminescent center. All these observations do not encourage the development of Nd³⁺ doped strontium iodide as a scintillation crystal without additional doping by monovalent impurity ions.

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