

# Selective laser spectroscopy of SrF<sub>2</sub> crystal doped with Pr<sup>3+</sup> ions

O.K. Alimov, M.E. Doroshenko, V.A. Konyushkin, A.G. Papashvili, V.V. Osiko

**Abstract.** SrF<sub>2</sub> crystals doped with Pr<sup>3+</sup> ions with concentrations corresponding to 0.5, 1.0 and 2.0 wt % of PrF<sub>3</sub> are studied by selective laser excitation. The absorption and luminescence spectra of Pr<sub>3</sub> ions are measured at a temperature of 77 K. Three types of tetragonal centres (C, E, S) with the point symmetry group C<sub>4v</sub> and three types of cluster centres (K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>) are found. Energy level diagrams of the <sup>3</sup>H<sub>4</sub>, <sup>3</sup>P<sub>1</sub> and <sup>3</sup>P<sub>2</sub> terms of Pr<sup>3+</sup> ions in SrF<sub>2</sub> crystals are plotted for the tetragonal (C) and cluster optical centres. The lifetimes of the tetragonal C centre [ $\tau(300\text{ K}) \sim 112\ \mu\text{s}$ ,  $\tau(77\text{ K}) \sim 108\ \mu\text{s}$ ] and cluster centres K<sub>1</sub> ( $\sim 43\ \mu\text{s}$ ), K<sub>2</sub> ( $\sim 7\ \mu\text{s}$ ) and K<sub>3</sub> ( $\sim 48\ \mu\text{s}$ ) are measured at 77 K for the first time.

**Keywords:** luminescence, Pr<sup>3+</sup>:SrF<sub>2</sub>, lifetime, luminescence decay kinetics, tetragonal centre, Stark splitting.

## 1. Introduction

The spectral-kinetic characteristics of fluoride crystals (CaF<sub>2</sub>, SrF<sub>2</sub>, CdF<sub>2</sub>, PbF<sub>2</sub> and BaF<sub>2</sub>) doped with trivalent rare-earth ions (RE<sup>3+</sup>) have been studied for more than 50 years. In studies [1–8], it was shown that RE<sup>3+</sup> ions in fluoride materials can form optical centres of different types (RE<sup>3+</sup>–F<sub>i</sub><sup>–</sup>)<sub>m</sub>. These are single and cluster centres (*m* is the number of rare-earth and interstitial fluorine ions in the cluster) with different optical properties.

Among the listed fluoride crystals, the SrF<sub>2</sub> crystal doped with Pr<sup>3+</sup> ions has a short phonon spectrum ( $\hbar\omega_{\text{max}} = 380\text{ cm}^{-1}$ ) and is a promising laser material for the red-green-blue (RGB) spectral range under blue ( $\lambda \approx 445\text{ nm}$ ) laser diode pumping, as well as a good luminophore for new-generation displays. Therefore, due to the practical importance of RE<sup>3+</sup>-doped SrF<sub>2</sub> crystals, it is of particular interest to study their spectroscopic properties.

In one of the basic studies of the spectroscopic characteristics of Pr<sup>3+</sup> ions in SrF<sub>2</sub> crystals at 4.2 K [9], the single optical C centre of Pr<sup>3+</sup> ions was found and a set of luminescent cluster centres was identified. The effect of charge compensators (F<sup>–</sup>, T<sup>–</sup>, and D<sup>–</sup>) on the formation of tetragonal centres (C<sub>4v</sub>) in Pr<sup>3+</sup>:SrF<sub>2</sub> and Pr<sup>3+</sup>:CaF<sub>2</sub> crystals was considered in [10]. In [11], it was shown that introduction of Sr<sup>2+</sup>, Ba<sup>2+</sup> and Ca<sup>2+</sup> impurities into these crystals leads to the appearance of

completely new optical centres with Pr<sup>3+</sup> ions. In a Pr<sup>3+</sup>:SrF<sub>2</sub> (0.05 wt %) crystal codoped with LaF<sub>3</sub> (1.0 wt %), the authors of [12] found one type of pair optical centres La<sup>3+</sup>–Pr<sup>3+</sup>, which forms as a result of substitution of the Pr<sup>3+</sup> ion by the optically inactive La<sup>3+</sup> ion in the Pr<sup>3+</sup>–Pr<sup>3+</sup> pair.

In the present work, we investigate the nature of formation of optical Pr<sup>3+</sup> centres in SrF<sub>2</sub> crystals by studying the spectral-kinetic characteristics of praseodymium ions by laser spectroscopy.

## 2. Method of investigation

Strontium fluoride crystals were synthesised by the Bridgman–Stockbarger method. The concentrations of PrF<sub>3</sub> in the SrF<sub>2</sub> crystals were 0.5, 1.0 and 2.0 wt %. The SrF<sub>2</sub> crystal has the structure of simple fluorides and belongs to the class of cubic crystals with the Fm3m space group and the unit cell parameter  $a = 0.578\text{ nm}$  [13].

The optical absorption spectra were recorded on a Carry-5000 spectrophotometer at 77 and 300 K. Praseodymium ions in SrF<sub>2</sub> crystals were excited by the second harmonic of a tunable laser based on F<sub>2</sub><sup>+</sup> colour centres ( $\lambda_{\text{gen}} = 870\text{--}980\text{ nm}$ ). The second harmonic (435–490 nm) was generated in a non-linear LiIO<sub>3</sub> crystal. The F<sub>2</sub><sup>+</sup> colour centre laser was pumped by the second harmonic ( $\lambda_{\text{exc}} = 532\text{ nm}$ ) of a repetitively pulsed Nd:YAG laser ( $\Delta t = 15\text{ ns}$ ,  $f = 1.0\text{--}25\text{ Hz}$ ).

The luminescence was focused by a condenser onto the slit of an MDR-23 monochromator; as a detector, we used an FEU-79 photomultiplier. The luminescence spectra and the decay kinetics were recorded using a broadband Tektronix-TDS 3052B oscilloscope connected to a computer.

## 3. Results and discussion

Figure 1 presents the optical absorption spectra of Pr<sup>3+</sup>:SrF<sub>2</sub> crystals with different concentrations of praseodymium ions (0.5, 1.0 and 2.0 wt % of PrF<sub>3</sub>) measured at 77 K. The absorption spectrum of the <sup>3</sup>H<sub>4</sub>(1) → <sup>3</sup>P<sub>0</sub>, <sup>3</sup>P<sub>1</sub>(1) transitions contains two narrow spectral lines belonging to the single C centre with the maxima at 465 and 476.6 nm and a series of lines in the spectral range 480–481.5 nm corresponding to the cluster K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> centres [9]. The broad band at 482.6 nm is caused by the <sup>3</sup>H<sub>4</sub>(2, 3, 4) → <sup>3</sup>P<sub>0</sub> transitions from the excited Stark levels of the <sup>3</sup>H<sub>4</sub> term of the ground state, which are populated at 77 K ( $kT = 51\text{ cm}^{-1}$ ).

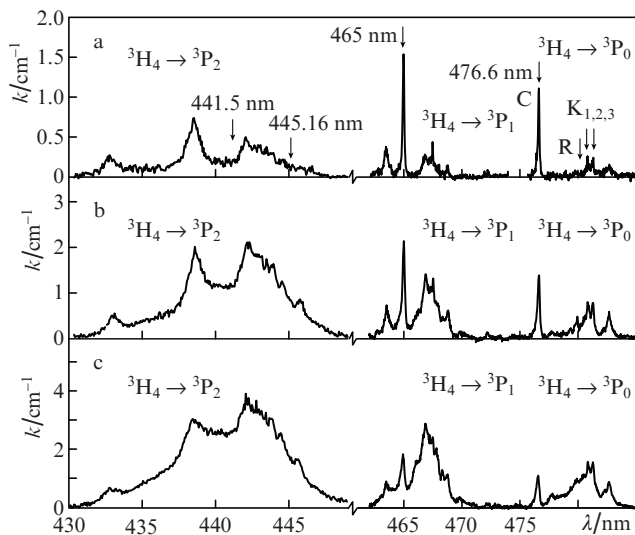
An increase in the concentration of Pr<sup>3+</sup> ions in the SrF<sub>2</sub> crystal corresponding to an increase in the PrF<sub>3</sub> concentration from 0.5 to 1.0 wt % and from 1.0 to 2.0 wt % leads to an increase in the absorption coefficients of the single C centre at  $\lambda = 465$  and 476.6 nm by 1.27 and 1.14 times, respectively.

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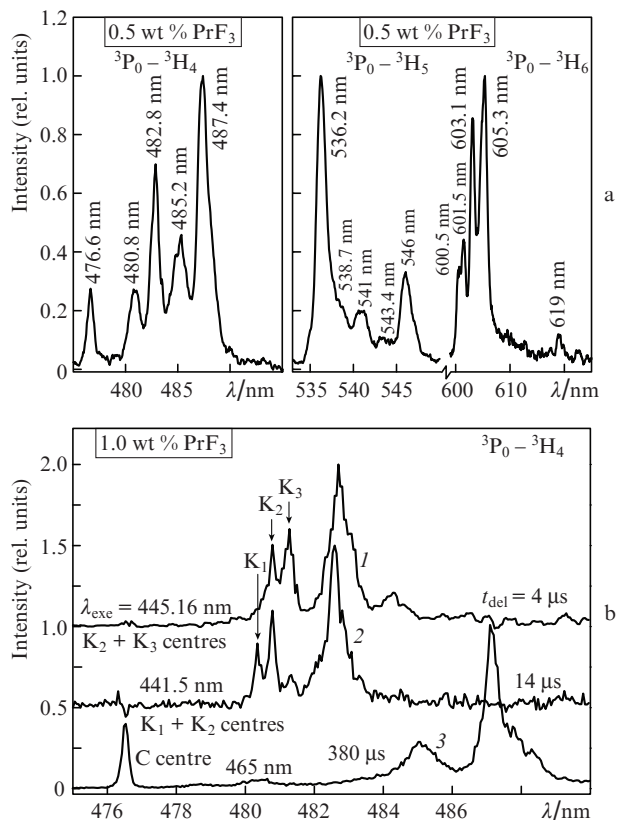
**Figure 1.** Absorption spectra of Pr<sup>3+</sup>:SrF<sub>2</sub> crystals with praseodymium concentrations corresponding to (a) 0.5, (b) 1.0 and (c) 2.0 wt % of PrF<sub>3</sub> measured at 77 K (the arrows show the excitation wavelengths  $\lambda_{\text{exc}}$  and the spectral positions of the C, K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> centres).

However, a further increase in the PrF<sub>3</sub> concentration to 2.0 wt % decreases these absorption coefficients by 1.14 times. In the case of the cluster K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> centres, an increase in the Pr<sup>3+</sup> concentration corresponding to an increase in the PrF<sub>3</sub> concentration from 0.5 to 2.0 wt % increases their absorption coefficients by 6.8 times.

The absorption bands of the  $^3\text{H}_4 \rightarrow ^3\text{P}_2$  transition of Pr<sup>3+</sup> ions in the SrF<sub>2</sub> crystal are broadened (Fig. 1) compared to the bands of the  $^3\text{H}_4(1) \rightarrow ^3\text{P}_1(1)$  and  $^3\text{H}_4(1) \rightarrow ^3\text{P}_0$  transitions. This is caused by several factors: First, by electron–phonon interaction, which causes the broadening of the Stark lines of Pr<sup>3+</sup> ions and overlapping of the Stark lines of different praseodymium optical centres. Second, by the optical centre symmetry, which determines the number of Stark levels (in the case of low-symmetry centres, the number of Stark levels for the  $^3\text{P}_2$  term is five), by the magnitudes of splitting of the  $^3\text{H}_4$  and  $^3\text{P}_2$  terms and by the population of excited Stark levels of the ground  $^3\text{H}_4$  state at a given temperature (77 K).

Figure 2a shows the luminescence spectra of a Pr<sup>3+</sup>:SrF<sub>2</sub> crystal measured upon broadband excitation by a KGM-12-100 lamp at a temperature of 77 K. The radiation in the spectral range 260–440 nm, which was used for excitation of Pr<sup>3+</sup> ions at the  $^3\text{H}_4(1) \rightarrow ^3\text{P}_2$  transition, was separated by an UFS-6 optical filter. The luminescence lines were observed in the blue (487 nm, transition  $^3\text{P}_0 \rightarrow ^3\text{H}_4$ ), green (536 nm, transition  $^3\text{P}_0 \rightarrow ^3\text{H}_5$ ), and red (605 nm, transition  $^3\text{P}_0 \rightarrow ^3\text{H}_6$ ) spectral regions. The broadband lamp radiation allows one to excite all types of Pr<sup>3+</sup> optical centres in the Pr<sup>3+</sup>:SrF<sub>2</sub> crystal and observe the entire luminescence spectrum of all optical centres. The number of lines in the luminescence spectrum is determined by the set of luminescent centres of Pr<sup>3+</sup> ions in the SrF<sub>2</sub> crystal, by the number of Stark levels of the  $^3\text{H}_j$  and  $^3\text{P}_0$  terms responsible for the luminescence, and by temperature.

Analysis of the results of work [9] shows that the number of Stark levels responsible for the excitation (transition  $^3\text{H}_4 \rightarrow ^3\text{P}_1$ ) and luminescence ( $^3\text{P}_0 \rightarrow ^3\text{H}_4$ ) spectra measured at 4.2 K does not coincide with the calculated values even for the individual optical C centre. This is caused both by the point symmetry



**Figure 2.** (a) Luminescence spectra of a Pr<sup>3+</sup>:SrF<sub>2</sub> crystal (transitions  $^3\text{P}_0 \rightarrow ^3\text{H}_4$ ,  $^3\text{H}_5$ ,  $^3\text{H}_6$ ) measured under lamp excitation at  $T = 77$  K and (b) luminescence spectra of the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition for three excitation wavelengths  $\lambda_{\text{exc}}$  and different delay times  $t_{\text{del}}$ .

group of the optical centres (C, K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>) and by the small Stark splitting of terms, which is responsible for the overlap of the Stark lines belonging to optical centres of different types.

The composition of Pr<sup>3+</sup> centres in SrF<sub>2</sub> crystals was determined by selective laser excitation [14]. For excitation, we used the second harmonic of a tunable F<sub>2</sub><sup>+</sup> colour centre laser. Figure 2b shows the luminescence spectra of a Pr<sup>3+</sup>:SrF<sub>2</sub> (1.0 wt % PrF<sub>3</sub>) crystal measured at 77 K. The excitation of Pr<sup>3+</sup> ions was performed at the wavelengths of the  $^3\text{H}_4(1) \rightarrow ^3\text{P}_0$ ,  $^3\text{P}_1$ ,  $^3\text{P}_2$  transitions, and the luminescence was recorded at the wavelength of the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition.

From Fig. 2b, one can see that the positions of lines in the luminescence spectra of the  $^3\text{P}_0 \rightarrow ^3\text{H}_4$  transition depend on the excitation wavelength. The luminescence spectra excited at three excitation wavelengths – 445.16 nm [curve (1)], 441.5 nm [curve (2)] and 465 nm [curve (3)] – differ from each other. The different positions of lines (or groups of lines) in the spectra recorded upon excitation at different wavelengths and at different delays  $t_{\text{del}}$  from the laser excitation instant allow us to suggest the presence of different types of optical centres in the Pr<sup>3+</sup>:SrF<sub>2</sub> crystal. The positions of luminescence lines peaking at 480.4, 480.8 and 481 nm [Fig. 2b, curves (1, 2)] coincide with the data of [9]. These lines correspond to the  $^3\text{P}_0 \rightarrow ^3\text{H}_4(1)$  transitions of the cluster optical centres K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub>. The broad intense band with a complex structure and a maximum at 482.6 nm [Fig. 2b, curves (1, 2)] is caused by the transitions from the  $^3\text{P}_0$  term to the excited Stark levels of the  $^3\text{H}_4(2, 3, \dots)$  term of the ground state.

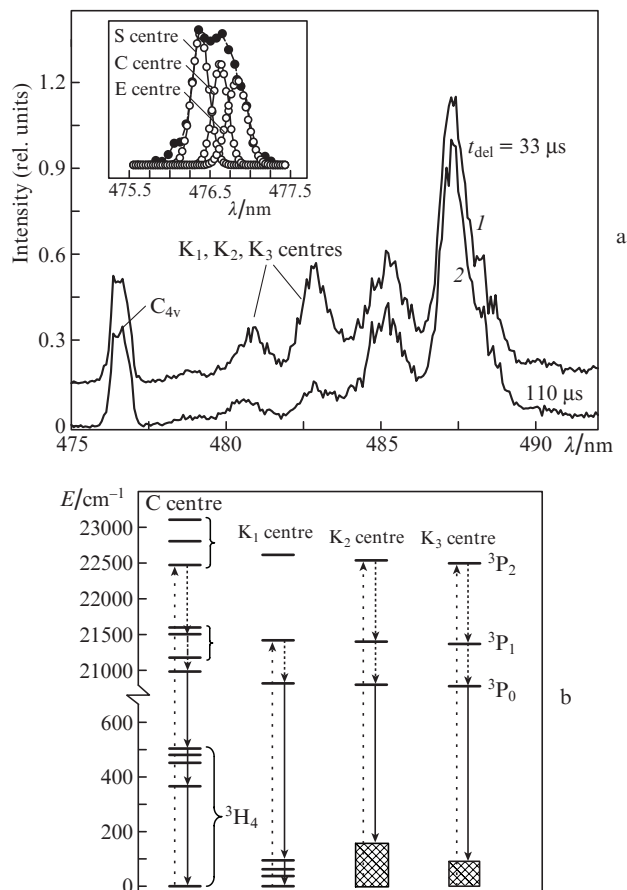
In the case of excitation of praseodymium ions at the wavelength  $\lambda_{\text{exc}} = 465$  nm corresponding to the  $^3\text{H}_4 \rightarrow ^3\text{P}_1$

transition, the luminescence spectrum of the  ${}^3P_0 \rightarrow {}^3H_4$  transition [Fig. 2b, curve (3)] exhibits spectral lines of the single optical centre C (lines of the cluster  $K_1$ ,  $K_2$  and  $K_3$  centres are absent). The authors of [10, 11] define this centre as tetragonal with the point group  $C_{4v}$ . Since the tetragonal centre belongs to an intermediate symmetry group, the local crystal field of this symmetry only partially removes degeneration from the  ${}^3H_4$  term of  $Pr^{3+}$ , and the luminescence spectrum [Fig. 2b, curve (3)] of the  ${}^3P_0 \rightarrow {}^3H_4$  transition reveals only four Stark levels. In the case of low-symmetry cluster centres  $K_1$ ,  $K_2$  and  $K_3$ , degeneration from the  ${}^3H_4$  term should be completely removed and the luminescence spectrum of the  ${}^3P_0 \rightarrow {}^3H_4$  transition should contain all the nine Stark levels. However, the spectrum recorded in [9] at a temperature of 4.2 K showed only six levels. The absence of the total set of calculated Stark levels responsible for the luminescence spectra of the  ${}^3P_0 \rightarrow {}^3H_4$  transition is obviously related to the weak Stark splitting of the  ${}^3H_4$  term due to a weak local crystal field, because of which the Stark lines overlap. An increase in temperature to 77 K causes an additional effect, namely, broadening of the spectral lines due to electron–phonon interaction, which also leads to an overlap of lines and, hence, to a decrease in their number.

The luminescence spectra of the  ${}^3P_0 \rightarrow {}^3H_4$  transition of the  $Pr^{3+} : SrF_2$  (0.5 wt %  $PrF_3$ ) crystal measured at 77 K upon excitation at a wavelength of 463.5 nm (transition  ${}^3H_4 \rightarrow {}^3P_1$ ) are shown in Fig. 3a. One can see that, at a small time delay from the laser excitation pulse ( $t_{del} = 33 \mu s$ ), the shape of the luminescence spectrum [Fig. 3a, curve (1)] is similar to the shape of the luminescence spectrum recorded upon lamp excitation (see Fig. 2a, left curve). An increase in the delay time to  $t_{del} = 110 \mu s$  [Fig. 3a, curve (2)] leads to a decrease in the intensity of luminescence bands peaking at 480.8 and 483 nm, which belong to the cluster  $K_1$ ,  $K_2$  and  $K_3$  centres (their positions are shown in Fig. 3a). In this case, the spectrum becomes very similar to the luminescence spectrum of the single C centre [Fig. 2b, curve (3)].

The inset in Fig. 3a presents a fragment of the luminescence band in the spectral range 475.5–477.5 nm, which consists of at least three luminescence lines of the  ${}^3P_0 \rightarrow {}^3H_4$  transition. Approximation of this band by a Gaussian function allowed us to separate three luminescence lines peaking at wavelengths of 476.36, 476.65 and 476.9 nm. These lines obviously belong to three different tetragonal centres with the point symmetry group  $C_{4v}$ . The complex shape of the luminescence band in this region is caused by a distortion of the local environment of the tetragonal centre, which changes the crystal field strength and causes formation of three types of tetragonal centres. In [9], these centres are named C, E and S (Fig. 3a).

Analysis of the absorption, luminescence excitation (transitions  ${}^3H_4 \rightarrow {}^3P_0$ ,  ${}^3P_1$ ), and luminescence (transition  ${}^3P_0 \rightarrow {}^3H_4$ ) spectra allowed us to plot a diagram of the Stark levels of the  ${}^3P_2$ ,  ${}^3P_1$ ,  ${}^3P_0$  and  ${}^3H_4$  terms of  $Pr^{3+}$  ions in the  $Pr^{3+} : SrF_2$  (1 wt %  $PrF_3$ ) crystal (Fig. 3b). The arrows show the luminescence excitation and luminescence channels for the single (C) and cluster ( $K_1$ ,  $K_2$ ,  $K_3$ ) centres of  $Pr^{3+}$  ions. The diagram contains an incomplete set of the Stark levels of the  ${}^3P_2$ ,  ${}^3P_1$  and  ${}^3H_4$  terms of  $Pr^{3+}$  ions for the single and cluster centres. The luminescence bands corresponding to the transitions to the Stark levels of the ground state (term  ${}^3H_4$ ) for the low-symmetry  $K_1$ ,  $K_2$  and  $K_3$  cluster centres are concentrated mainly around 482.5 nm (transition  $P_0 \rightarrow {}^3H_4$ ) and are poorly resolved. The positions of these levels are shown on the diagram by dashed rectangles. The authors of



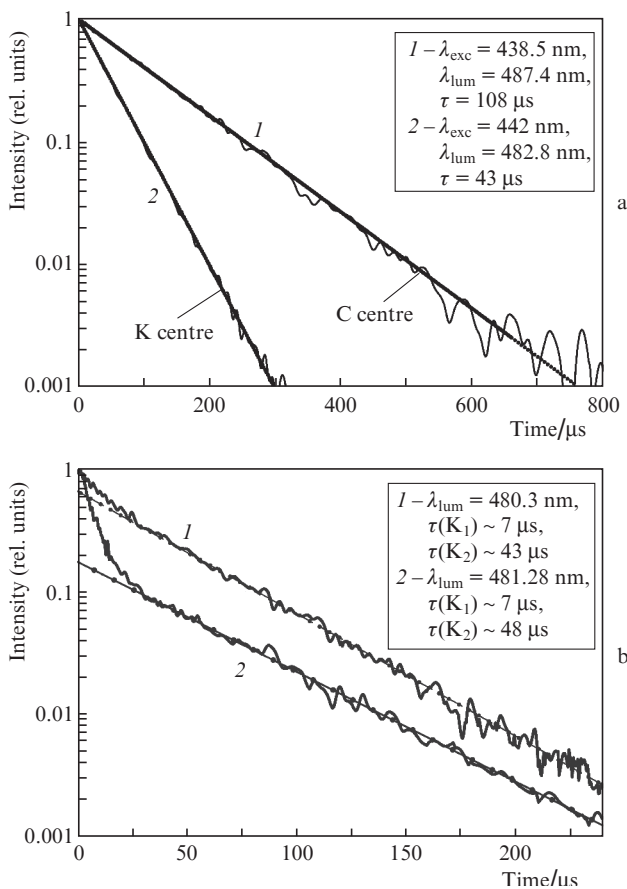
**Figure 3.** (a) Luminescence spectra of a  $Pr^{3+} : SrF_2$  crystal measured at  $\lambda_{exc} = 463.5$  nm and  $T = 77$  K (the inset shows the approximation of the luminescence band in the range 475.5–477 nm by three Gaussian curves) and (b) energy level diagram (terms  ${}^3P_0$ ,  ${}^3P_1$ ,  ${}^3P_2$ ,  ${}^3H_4$ ) for the C,  $K_1$ ,  $K_2$  and  $K_3$  centres of  $Pr^{3+}$  ions in the  $Pr^{3+} : SrF_2$  crystal (dashed rectangles correspond to the positions of the Stark levels of the  $K_1$ ,  $K_2$  and  $K_3$  centres [9]).

[9] failed to determine the positions of all the Stark centres for the cluster  $K_1$ ,  $K_2$  and  $K_3$  centres even at a temperature of 4.2 K. The energies of the Stark levels for the  ${}^3P_0$ ,  ${}^3P_1$  and  ${}^3H_4$  terms determined at 4.2 and 77 K coincide with an accuracy of  $\pm 5 \text{ cm}^{-1}$ .

By the double selection method [14], we measured the lifetimes of the single C centre and the cluster  $K_1$ ,  $K_2$  and  $K_3$  centres of  $Pr^{3+}$  ions in the  $Pr^{3+} : SrF_2$  (0.5 wt %  $PrF_3$ ) crystals at temperatures of 77 and 300 K. The decay kinetics of the 487.4-nm luminescence (transition  ${}^3P_0 \rightarrow {}^3H_4$ ) of the C centre upon excitation of  $Pr^{3+}$  ions at the  ${}^3H_4 \rightarrow {}^3P_1(1)$  transition ( $\lambda_{exc} = 465$  nm) at room temperature is exponential with a lifetime of 122  $\mu s$ . At a temperature decreased to 77 K, the luminescence decay is also described by an exponential law and the lifetime decreases to  $\tau \sim 108 \mu s$ . The difference between the lifetimes of  $Pr^{3+}$  ions in  $SrF_2$  crystals measured at 300 K ( $\tau \sim 122 \mu s$ ) and 77 K ( $\tau \sim 108 \mu s$ ) is about 9%. The observed luminescence quenching of single C centres with a decrease in temperature to 77 K is probably caused by electronic excitation energy migration over the donor ( $Pr^{3+}$ ) subsystem and is described by a diffusion mechanism [14, 15].

Figure 4a [curve (1)] presents the luminescence decay kinetics for the  ${}^3P_0 \rightarrow {}^3H_4$  transition ( $\lambda_{lum} = 487.4$  nm) of the C centre at 77 K upon excitation at the wavelength  $\lambda_{exc} = 438.5$  nm corresponding to the  ${}^3H_4 \rightarrow {}^3P_2$  transition of  $Pr^{3+}$

ions. The luminescence decay is described by an exponential law with  $\tau = 108 \mu\text{s}$ , similar to the case of excitation at  $\lambda_{\text{exc}} = 465 \text{ nm}$  [transition  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_1(1)$ ]. The luminescence of cluster centres with  $\lambda_{\text{lum}} = 482.8 \text{ nm}$  (transition  ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$ ) excited at  $\lambda_{\text{exc}} = 442 \text{ nm}$  (transition  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$ ) also decays according to an exponential law, the lifetime being  $\tau \sim 43 \mu\text{s}$  [Fig. 4a, curve (2)]. The lifetimes of Pr<sup>3+</sup> ions in SrF<sub>2</sub> crystals measured at different luminescence and excitation wavelengths differ by 2.5 times, which points to the presence of at least two types of optical centres in Pr<sup>3+</sup>:SrF<sub>2</sub> crystals [Fig. 4a, curves (1, 2)], one of which is the C centre and the other (with  $\tau \sim 43 \mu\text{s}$ ) corresponds to one of the K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> centres.



**Figure 4.** (a) Luminescence decay kinetics of Pr<sup>3+</sup> ions in a Pr<sup>3+</sup>:SrF<sub>2</sub> (0.5 wt % PrF<sub>3</sub>) crystal for the excitation wavelengths  $\lambda_{\text{exc}} = 438.5$  and  $442 \text{ nm}$  and the recording wavelengths  $\lambda_{\text{lum}} = 487.4$  and  $482.8 \text{ nm}$ , as well as (b) luminescence decay curves for Pr<sup>3+</sup> ions in a Pr<sup>3+</sup>:SrF<sub>2</sub> (1.0 wt % PrF<sub>3</sub>) crystal in the case of excitation at  $\lambda_{\text{exc}} = 445.15 \text{ nm}$  and recording at  $\lambda_{\text{lum}} = 480.3$  and  $481.28 \text{ nm}$ .

The lifetimes of the cluster K<sub>1</sub>, K<sub>2</sub>, K<sub>3</sub> centres were measured for a Pr<sup>3+</sup>:SrF<sub>2</sub> crystal with 1.0 wt % of PrF<sub>3</sub> at 77 K. The recording wavelengths were chosen from the luminescence spectrum of the  ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4(1)$  transition (see Fig. 2b). The measured luminescence kinetics for this crystal is shown in Fig. 4b. The excitation of Pr<sup>3+</sup> ions was performed at the  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$  transition ( $\lambda_{\text{exc}} = 445.15 \text{ nm}$ ), and the luminescence decay kinetics was recorded at  $\lambda_{\text{lum}} = 480.3$  and  $481.28 \text{ nm}$ , which correspond to the luminescence peaks of the cluster K<sub>1</sub> and K<sub>3</sub> centres. [Note that the K<sub>2</sub> centres also luminesce in this wavelength region (see Fig. 2b).] The decay curve of luminescence at  $\lambda_{\text{lum}} = 480.3 \text{ nm}$  is approximated by two expo-

nents, with decay times  $\tau \sim 7$  and  $43 \mu\text{s}$  [Fig. 4b, curve (1)]. The decay curve of luminescence at  $\lambda_{\text{lum}} = 481.28 \text{ nm}$  is also approximated by two exponents, with lifetimes  $\tau \sim 7$  and  $48 \mu\text{s}$  [Fig. 4b, curve (2)]. The luminescence with  $\tau \sim 7 \mu\text{s}$  [curves (1) and (2)] corresponds to the K<sub>2</sub> centre, while the luminescence with  $\tau = 43$  and  $48 \mu\text{s}$  belongs to the K<sub>1</sub> and K<sub>3</sub> centres, respectively.

Let us consider the effect of cross-relaxation quenching on the lifetimes of the cluster K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> centres of Pr<sup>3+</sup> ions in SrF<sub>2</sub> crystals. We measured the luminescence decay kinetics of Pr<sup>3+</sup> ions in a SrF<sub>2</sub> crystal with 3 wt % of LaF<sub>3</sub> and 1 wt % of PrF<sub>3</sub> at 77 K. It is known [4, 5, 12] that the introduction of LaF<sub>3</sub> into SrF<sub>2</sub> crystals leads to a total or partial substitution of Pr<sup>3+</sup> ions by optically inactive La<sup>3+</sup> ions and to a change in the lifetime of cluster optical centres of Pr<sup>3+</sup> ions, as well as affects the concentration ratio between the K<sub>1</sub>, K<sub>2</sub>, and K<sub>3</sub> centres. In the case of excitation of the  ${}^3\text{H}_4 \rightarrow {}^3\text{P}_2$  ( $\lambda_{\text{exc}} = 442 \text{ nm}$ ) transition of Pr<sup>3+</sup> ions in the SrF<sub>2</sub> crystal containing 3 wt % of LaF<sub>3</sub> and 1 wt % of PrF<sub>3</sub>, the luminescence decay kinetics at the  ${}^3\text{P}_0 \rightarrow {}^3\text{H}_4$  transition ( $\lambda_{\text{lum}} = 482 \text{ nm}$ ) is described by a sum of two exponents with lifetimes  $\tau(\text{K}_2) \sim 17.5 \mu\text{s}$  and  $\tau(\text{K}_3) \sim 47.5 \mu\text{s}$ . Comparison of these lifetimes with the lifetimes of the same centres in the Pr<sup>3+</sup>:SrF<sub>2</sub> crystal with 1.0 wt % of PrF<sub>3</sub> [ $\tau(\text{K}_2) \sim 7 \mu\text{s}$  and  $\tau(\text{K}_3) \sim 48 \mu\text{s}$ ] shows that the lifetime of the K<sub>2</sub> centre in the crystal with La<sup>3+</sup> ions considerably increases, while the lifetime of the K<sub>3</sub> centre changes only slightly, within the experimental error. The increase in the K<sub>2</sub> centre lifetime from  $\tau \sim 7 \mu\text{s}$  in the Pr<sup>3+</sup>:SrF<sub>2</sub> (1.0 wt % PrF<sub>3</sub>) crystal to  $\tau \sim 17.5 \mu\text{s}$  in the SrF<sub>2</sub> crystal with 3 wt % of LaF<sub>3</sub> and 1 wt % of PrF<sub>3</sub> allows us to conclude that cross-relaxation quenching in the K<sub>2</sub> centre is weaker in the mixed crystal, in which the lifetimes of the cluster K<sub>1</sub> and K<sub>3</sub> centres do not change.

## 4. Conclusions

Three types of tetragonal centres – C, E, and S with the point symmetry group C<sub>4v</sub> – and three low-symmetry cluster centres K<sub>1</sub>, K<sub>2</sub> and K<sub>3</sub> are found in the Pr-doped SrF<sub>2</sub> crystal for the first time at a temperature of 77 K by selective laser excitation. A diagram of the Stark levels of the  ${}^3\text{H}_4$ ,  ${}^3\text{P}_1$  and  ${}^3\text{P}_2$  terms of Pr<sup>3+</sup> ions in the SrF<sub>2</sub> crystal is drawn for the tetragonal and cluster optical centres. The lifetimes of the tetragonal C centre at 77 and 300 K [ $\tau(300 \text{ K}) \sim 122 \mu\text{s}$ ,  $\tau(77 \text{ K}) \sim 108 \mu\text{s}$ ] and of cluster centres at 77 K [ $\tau(\text{K}_1) \sim 43 \mu\text{s}$ ,  $\tau(\text{K}_2) \sim 7 \mu\text{s}$ ,  $\tau(\text{K}_3) \sim 48 \mu\text{s}$ ] are measured for the first time. It is shown that the lifetime of the K<sub>2</sub> centre in the SrF<sub>2</sub> crystal is determined by cross-relaxation quenching. Substitution of Pr<sup>3+</sup> ions by optically inactive La<sup>3+</sup> ions in SrF<sub>2</sub> crystals does not change the lifetime of the cluster K<sub>1</sub> and K<sub>3</sub> centres, but increases the lifetime of the K<sub>2</sub> centre (to  $\tau \sim 17.5 \mu\text{s}$ ) due to suppression of cross-relaxation quenching.

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