

Defects and energy transfer in  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$ , doped with ions  $\text{Pr}^{3+}$ © E.S. Trofimova<sup>1,2¶</sup>, V.A. Pustovarov<sup>1</sup>, A.F. Zatsepin<sup>1</sup><sup>1</sup> Ural Federal University,  
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Luminescent properties of  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$  crystalline powders doped with  $\text{Pr}^{3+}$  ions upon excitation in the ultraviolet region of the spectrum are considered. In the temperature range 5–320 K, are considered. In the photoluminescence spectra, an intense glow corresponding to radiative interconfigurational  $5d \rightarrow 4f$ -electronic transitions, weak narrow lines of intra-configuration  $4f \rightarrow 4f$ -transitions, and also the emission of two types of crystal structure defects, are observed. Under pulsed electronic excitation, the temporal characteristics of emission associated with an impurity center and defects and the temperature dependence of the luminescence yield were studied. The processes of energy transfer between defects and an impurity center are discussed.

**Keywords:**  $5d \rightarrow 4f$  luminescence, energy transfer, decay kinetics, ion  $\text{Pr}^{3+}$ 

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## Introduction

Luminescent materials with nanosecond luminescence decay time attract the attention of researchers as potential materials for new fast scintillators. The short decay time of luminescence is important to ensure the possibility of registering fast processes and increasing the spatial resolution of detectors for ionizing radiations. Such scintillators are used as radiation detectors in various applicable scopes of medical equipment and industrial radiation monitoring means. One of the directions of research into new scintillation materials is considering substances doped with rare-earth metal ions, namely, ions exhibiting interconfigurational  $5d \rightarrow 4f$  luminescence, since such electronic transitions are characterized by short luminescence decay times. For the near ultraviolet and visible ranges, the use of  $\text{Ce}^{3+}$  ions or  $\text{Pr}^{3+}$ . In dielectric wide-bandgap crystals,  $\text{Pr}^{3+}$  ions exhibit a luminescence decay time two to three times shorter than in the same matrices doped with  $\text{Ce}^{3+}$  ions. For example, in  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Pr}^{3+}$  the luminescence decay time  $\text{Pr}^{3+}$  is about 20 ns [1], while the same time in  $\text{Lu}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  is near to 60 ns [2]. Due to this property,  $\text{Pr}^{3+}$  ions are attracting more and more attention of researchers as a dopant for fast scintillators. The best known and

well-researched are crystals doped with  $\text{Pr}^{3+}$  ions, such as  $\text{Y}_3\text{Al}_5\text{O}_{12}$ ,  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ ,  $\text{Y}_2\text{SiO}_5$ ,  $\text{Lu}_2\text{SiO}_5$  [3].

Among the families of matrices for new scintillation materials, phosphates can be singled out due to their excellent chemical and physical properties, the absence of hygroscopicity and the presence of a wide energy band gap. It have been published a sufficient number of works devoted to various phosphates doped with ions of  $\text{Pr}^{3+}$ , considered from the point of view of their applicability as scintillation

materials:  $\text{LuPO}_4$  [4],  $\text{Sr}_3\text{La}(\text{PO}_4)_3$  [5],  $\text{K}_3\text{Lu}(\text{PO}_4)_2$  [6],  $\text{KLuP}_2\text{O}_7$  [7],  $\text{LiSrPO}_4$  [8] and others.

In this work, one consider the luminescent properties of the  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7:\text{Pr}^{3+}$  microcrystalline powder, which was previously shown its potential applicability as a fast scintillator [9]. The material has properties that are of interest in this aspect: relatively high effective atomic number ( $Z_{\text{ef}} \approx 39$ ), high chemical stability, radiation stability, a wide band gap (by analogy with double phosphates of rare earth ions  $E_g = 7.3\text{--}9.5\text{ eV}$  [10]). It is also known the work that considers  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7:\text{Ce}^{3+}$  as an efficient energy converter [11].

In previous studies [9] the presence of luminescence spectra in  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7:\text{Pr}^{3+}$  emissions associated with defects in the crystal structure of  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$ , was found. Such defects form competing channels for the capture of charge carriers, channels for their radiative relaxation or nonradiative recombination. The purpose of present work is to study the spectroscopic manifestations of these defects, their influence on the processes of relaxation of electronic excitations of  $\text{Pr}^{3+}$  ions and features of energy transfer processes between defects and an impurity center.

## Objects and methods

The objects of study were nominally pure crystalline powders  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$  (SLuP) and SLuP, doped with  $\text{Pr}^{3+}$  ions at concentration of 1 mol.%. The crystals were obtained by high-temperature solid-phase synthesis with the participation of Dr. Qiufeng Shi (Taiyuan University of Technology, China). The objects were certified by X-ray diffraction diffraction. The obtained data correlate with

the available data of the ICSD database for  $\text{Sr}_9\text{In}(\text{PO}_4)_7$  (ICSD #59-722). The analysis showed that the object is characterized by a monoclinic phase, space group  $I2/a$ , and doping with  $\text{Pr}^{3+}$  ions at a concentration of 1 mol.% does not introduce significant changes in the crystal structure [9]. These data correspond to the description of the crystal structure of a family of compounds of the form  $\text{Sr}_9\text{A}(\text{PO}_4)_7$  ( $\text{A} = \text{Sc}, \text{Cr}, \text{Fe}, \text{Ga}, \text{In}$ ), which was detailed studied in [12]. In this crystal structure, the ions of  $\text{Pr}^{3+}$  can occupy both the positions of ions of  $\text{Sr}^{2+}$  (predominantly) and the positions of ions of  $\text{Lu}^{3+}$  by analogy with the data obtained for ions of  $\text{Ce}^{3+}$ ,  $\text{Eu}^{3+}$  in this matrix [11].

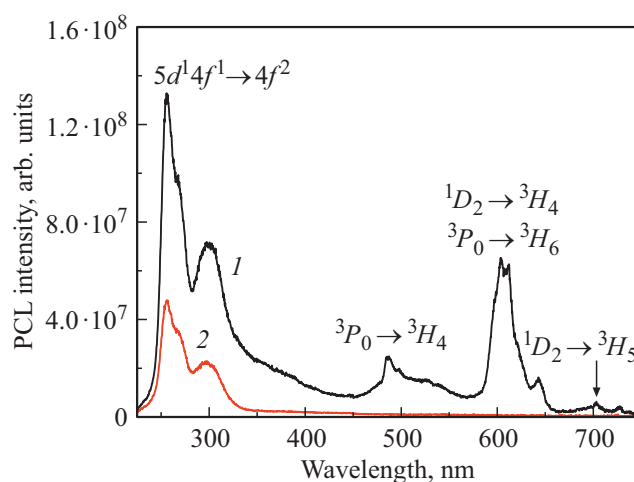
Photoluminescence (PL) spectra were studied using a spectrometer of series iXR320 by Horiba, equipped with a cooled CCD camera and an ozone-free xenon lamp. Additionally, in the far ultraviolet region, the PL excitation spectra were measured using a 400 W gas-discharge deuterium lamp (DDS-400), two DMR-4-type prismatic monochromators, and an R6358-10 photomultiplier detector (Hamamatsu). The PL excitation spectra were normalized to equal number of excitation photons with the application of Lumogen F Yellow, which has a constant quantum yield in the used spectral band.

The pulsed cathodoluminescence (PCL) kinetics at room temperature were measured using a MIRA-2D pulsed electron accelerator with IMA-2-150E electron tube ( $E = 150 \text{ keV}$ ,  $\text{FWHM} \sim 25 \text{ ns}$ ) at the Ural Federal University. The PCL spectra at temperatures 5 and 295 K were measured at the University of Tartu (Estonia) using a pulsed electron accelerator of the Radan-330 A type ( $E = 120 \text{ keV}$ ,  $\text{FWHM} = 200 \text{ ps}$ , frequency 5 Hz) as an excitation source and 0.3 m Andor Shamrock 303i monochromator with an MCP-PMT detector as a registration system. The „time windows“ method was used. The PCL spectra were measured in „fast“ (0–32 ns) and „full“ (0–2 ms) time windows.

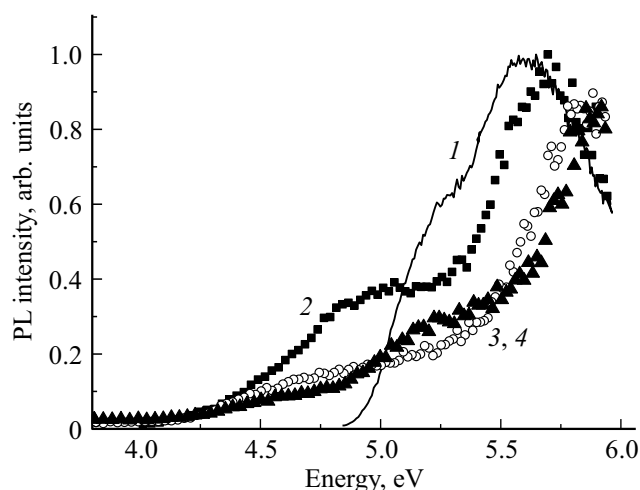
Roentgenoluminescence (RL) spectra were measured using the apparatus URS-55A (X-ray tube BSV-2, 30 kV, 10 mA, Cu-anode), monochromator LOMO MDR-23 and photomultiplier detector FEU-106. Thermoluminescence curves were recorded through a monochromator in the temperature range 88–350 K after X-ray irradiation at a temperature of  $T = 88 \text{ K}$  with a sample heating rate of 0.33 K/s.

## Results and discussion

Fig. 1 shows the  $\text{SLuP:Pr}^{3+}$  PCL spectra measured in „fast“ (0–32 ns) and „full“ (0–2 ms) time windows at room temperature. The temporal resolution makes it possible to single out bands in the spectrum corresponding to fast interconfigurational  $5d \rightarrow 4f$  transitions in  $\text{Pr}^{3+}$  ions. Three types of spectral bands and lines are observed. First, these are short-wave bands associated with  $5d \rightarrow 4f$  transitions, namely, radiative interconfigurational transitions from states of a mixed  $5d^1 4f^1$ -electron configuration to multiplets  $^3H_J$



**Figure 1.** PCL spectra  $\text{SLuP:Pr}^{3+}$  measured in „full“ (0–2 ms, 1) and „fast“ (0–32 ns, 2) time windows,  $T = 295 \text{ K}$ .



**Figure 2.**  $\text{SLuP:Pr}^{3+}$  PL excitation spectra measured for  $5d \rightarrow 4f$  (265 nm, 1)- and  $4f \rightarrow 4f$ -transitions (600 nm, 2) and for defect emission (400, 500 nm, 3, 4),  $T = 295 \text{ K}$ .

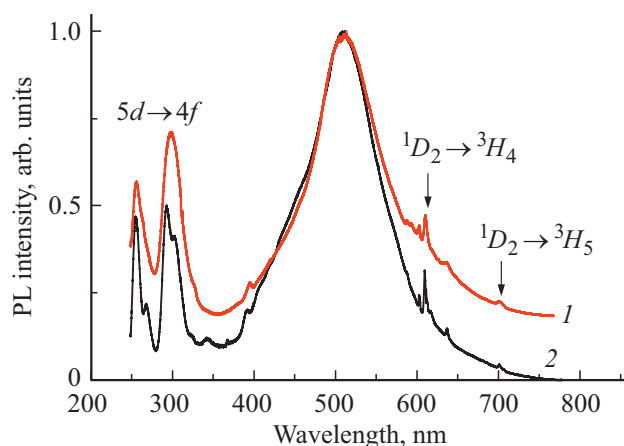
and  $^3F_J$  of the ground state of  $\text{Pr}^{3+}$  ions. They have fast nanosecond decay kinetics and therefore dominate the spectra measured in the „fast“ time window. In more details, this will be discussed below when considering the luminescence decay kinetics  $\text{SLuP:Pr}^{3+}$ . Secondly, the PCL spectrum recorded in the „full“ time window additionally contains lines associated with intraconfigurational  $4f \rightarrow 4f$  transitions in the  $\text{Pr}^{3+}$  ion. Thirdly, a sequence of bands are observed, the energy position of which does not allow them to be associated with the luminescence of  $\text{Pr}^{3+}$  ions, their maxima are located in the region of  $\sim 350$  and  $\sim 500 \text{ nm}$ . These bands can potentially be related to the emission of defects or autolocalized excitons (ALEs).

To obtain data on energy transfer, PL excitation spectra were measured (Fig. 2). In these spectra, measured for different lines and emission bands, four main groups can be distinguished. First, these are bands centered at 5.2

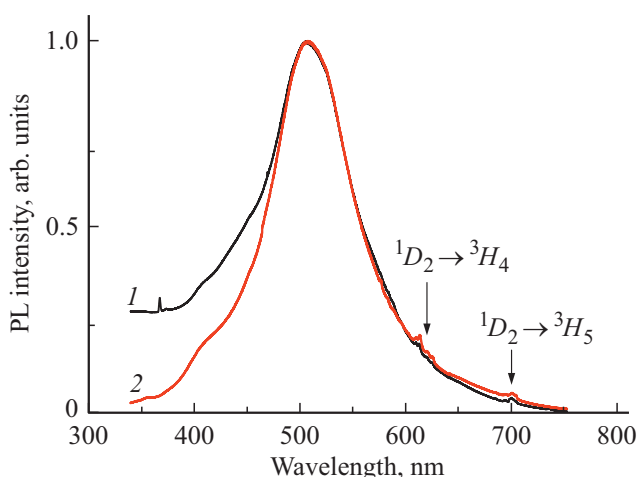
and 5.6 eV, which can be attributed to the intracenter excitation of ions  $\text{Pr}^{3+}$ . Transitions with this energy are primarily responsible for the excitation of the radiative  $5d \rightarrow 4f$  transitions of the  $\text{Pr}^{3+}$  ion, but also participate in the excitation of  $4f \rightarrow 4f$  transitions and emission in the region of 400 and 500 nm, which, while presumably, are associated with defects in the crystal structure. Secondly, it are distinguished bands centered at 4.6 and 5.0 eV, which are present in excitation spectra of  $4f \rightarrow 4f$  transitions and defect emission bands. These stripes are not associated with transitions in the  $\text{Pr}^{3+}$  ion, but can be attributed to intracenter excitation of defect emission. Then the presence of these bands in the PL excitation spectra of both defects and  $4f \rightarrow 4f$  transitions indicates the conduct of energy transfer between defects and  $\text{Pr}^{3+}$  ions. It should be noted that the energy transfer is carried out in both directions, i.e.  $\text{Pr}^{3+}$  luminescence excitation ( $4f \rightarrow 4f$  transitions) is observed upon intracenter excitation of defects, while defect excitation is possible upon intracenter excitation of  $\text{Pr}^{3+}$  ions.

When studying the PL excitation spectra, it is also important to estimate the Stokes shift in the material. This value is one of the key factors determining the conditions for the manifestation of fast  $5d \rightarrow 4f$  luminescence of  $\text{Pr}^{3+}$  ions in solids. These conditions were summarized in the work [13]: firstly, the value of the Stokes shift should not exceed the value of  $3000 \text{ cm}^{-1}$  ( $\sim 0.37 \text{ eV}$ ), secondly, the first (lowest) against energy transition  $4f^2 \rightarrow 4f^1 5d^1$  in the PL excitation spectra (or in absorption spectra) should be against energy below than level  $^1S_0$ . In  $\text{SLuP:Pr}^{3+}$  the Stokes shift is  $\sim 4600 \text{ cm}^{-1}$  (0.6 eV), and the band is  $4f^2 \rightarrow 4f^1 5d^1$  in the PL excitation spectra is limited in the region of low energies approximately in the region of  $45000 \text{ cm}^{-1}$ , while the level  $^1S_0$  is located in the region  $47000 \text{ cm}^{-1}$  (according to the data obtained for  $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  [14]). Thus, the conditions that ensure the predominant manifestation in the luminescence spectra of bands corresponding to fast interconfiguration  $5d \rightarrow 4f$  transitions  $\text{SLuP:Pr}^{3+}$  are partially met. It should be noted that it is not necessary to fulfill all the listed conditions simultaneously, since, for example, in  $\text{LaPO}_4$  Stokes, the  $\text{Pr}^{3+}$  luminescence shift is close to  $5000 \text{ cm}^{-1}$ , while its luminescence spectra are dominated by fast interconfigurational transitions  $\text{Pr}^{3+}$  [15].

Figure 3, *a, b* shows the PL spectra of  $\text{SLuP:Pr}^{3+}$  upon excitation by photons with a wavelength of  $\lambda_{\text{exc}} = 235 \text{ nm}$ . This wavelength corresponds to intracenter excitation of  $\text{Pr}^{3+}$  ions (transition  $4f^2 \rightarrow 4f^1 5d^1$ ). Under this excitation in the PL spectrum, the bands of  $5d \rightarrow 4f$  transitions appear (both to the ground state and to higher energy levels of the  $4f$  configuration in the longer wavelength region), lines of intraconfigurational  $4f \rightarrow 4f$  transitions (marked in the figure), and intense wide non-elementary band in the region the figure), and intense wide non-elementary band appears in the region 400–600 nm. Several bands can be distinguished in its composition, which allows us to make an assumption about the existence of several types of defects



**Figure 3.**  $\text{PLuP:Pr}^{3+}$  PL spectra measured upon excitation  $\lambda_{\text{exc}} = 235 \text{ nm}$  at temperature of 295 (1) and 5 K (2).

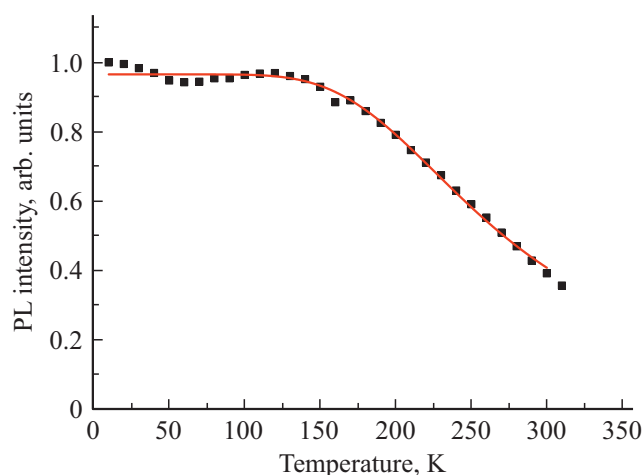


**Figure 4.** Normalized  $\text{SLuP:Pr}^{3+}$  PL spectra measured upon excitation  $\lambda_{\text{exc}} = 270 \text{ nm}$  at temperature of 5 (1) and 295 K (2).

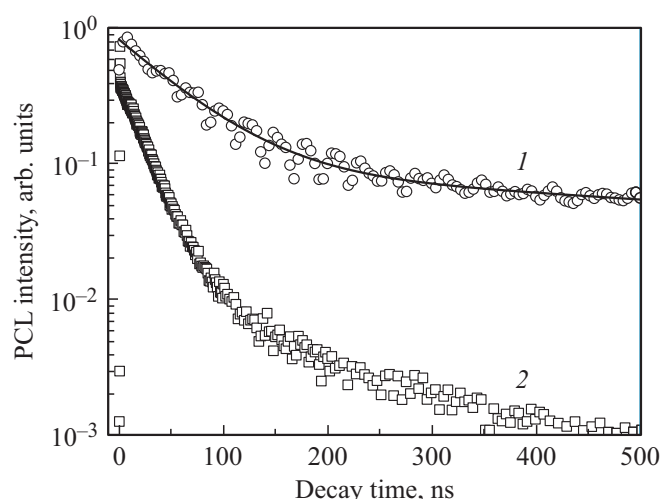
that generate emission in this spectral region. It should be emphasized that in the previously studied  $\text{SLuP}$  samples doped with  $\text{Pr}^{3+}$  ions with a higher concentration (5 mol.%), the relative intensity of the bands associated with the glow of  $\text{Pr}^{3+}$  ions, was higher compared to a similar glow of defects [9]. This indicates that the concentration of defects is not determined by the introduction of  $\text{Pr}^{3+}$  impurity ions into the crystal lattice of  $\text{SLuP}$ .

It should be noted two properties of luminescence associated with defects in a given object. Firstly, the intensity of PL and PCL in the region 400–600 nm increases with decreasing temperature (below, the temperature dependence of the luminescence yield in this region will be considered). Secondly, since the luminescence under consideration manifests itself in the PL spectrum upon intracenter excitation of the  $\text{Pr}^{3+}$  ion, there is energy transfer?the impurity center  $\rightarrow$  defect?.

To additionally confirm the hypothesis about the conduct processes of energy transfer from the defect to impurity



**Figure 5.** Temperature dependence of the  $\text{SLuP:Pr}^{3+}$  PL yield on the wavelength  $\lambda_{\text{em}} = 500$  nm (defect). The solid line represents the curve approximations by the Mott's formula (1).



**Figure 6.** PCR decay kinetics  $\text{SLuP:Pr}^{3+}$  for 270 nm emission bands ( $5d \rightarrow 4f$ -transitions) (2) and 500 nm (defect) (1),  $T = 295$  K.

ions, the PL spectra of  $\text{SLuP:Pr}^{3+}$  were measured upon excitation  $\lambda_{\text{exc}} = 270$  nm (presumably this is an intracenter excitation of defects). upon excitation  $\lambda_{\text{exc}} = 270$  nm (presumably this is intracenter excitation of defects). The obtained spectra are shown in (Fig. 4). Indeed, under such excitation, in addition to a broad band containing defect emission bands, the PL spectrum contains lines corresponding to  $4f \rightarrow 4f$  transitions of the  $\text{Pr}^{3+}$  ion (marked in the figure). It is also important to note that at low temperatures ( $T = 5$  K) the luminescence intensity of defects increases, and a new band appears in the wavelength.

range shorter than 400 nm. Similar band was also observed in the PCL spectra, presented above (Fig. 1).

Fig. 5 shows the temperature dependence of the PL yield of  $\text{SLuP:Pr}^{3+}$ , measured at the radiation wavelength

$\lambda_{\text{em}} = 500$  nm (emission of defect). Two important conclusions can be drawn from obtained data. Firstly, temperature quenching of defect-related luminescence begins at relatively high temperatures (above 130 K). Secondly, the obtained dependence is well approximated by the well-known Mott's formula, traditionally used to describe the process of intracenter quenching:

$$I = \frac{I_0}{1 + A \exp(-E_A/kT)}, \quad (1)$$

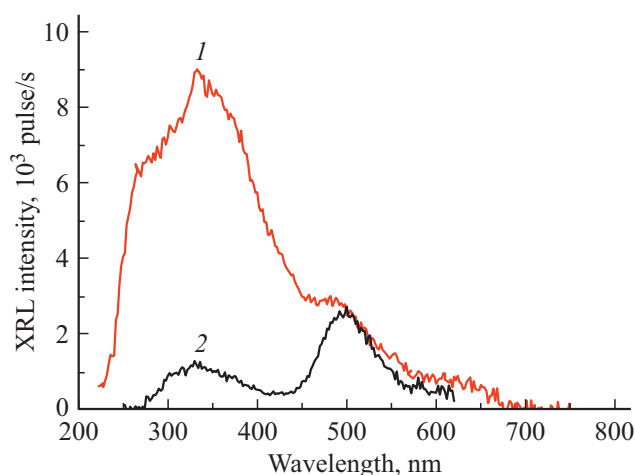
where  $A$  is a normalization factor equal to the ratio of the probabilities of nonradiative and radiative transitions;  $E_A$  is activation energy of thermal quenching;  $k$  is Boltzmann's constant. The calculated value of the activation energy of thermal quenching  $E_A$  was 0.095 eV, and the ratio of the probability of nonradiative and radiative transitions  $A$  was about 50. A satisfactory approximation of this dependence and low values of  $E_A$  and  $A$  indicate that the thermal quenching processes most likely occur inside the center and are not associated with energy transfer to other centers.

Fig. 6 shows the decay kinetics of  $\text{SLuP:Pr}^{3+}$  PCL measured at room temperature as for  $\text{Pr}^{3+}$  luminescence ( $\lambda_{\text{em}} = 265$  nm,  $5d \rightarrow 4f$ -transitions) and for the defect in the region 500 nm. Both PCL decay kinetics can be satisfactorily approximated by the two-exponential law:

$$I = I_1 \exp\left(\frac{-t}{\tau_1}\right) + I_2 \exp\left(\frac{-t}{\tau_2}\right) + I_0, \quad (2)$$

where  $\tau_1$ ,  $\tau_2$  are damping constants,  $I_0$  characterizes the contribution of the slow components of the micro-millisecond range. the contribution of the slow components of the micro-millisecond range. For  $5d \rightarrow 4f$  transition in the  $\text{Pr}^{3+}$  ion, the calculated PCL decay times were  $\tau_1 = 10$  ns and  $\tau_2 = 51$  ns, for PCL defect  $\tau_1 = 47$  ns,  $\tau_2 = 180$  ns, the proportion of slow components does not exceed 3%. Although the contribution of the  $\tau_2 = 51$  ns component is less than  $10^{-2}$ , the presence of such a relatively „slow“ component in the luminescence decay kinetics associated with  $5d \rightarrow 4f$  -transitions in the  $\text{Pr}^{3+}$  ion, indicates the occurrence of slow carrier recombination processes and the presence of „small“ charge carrier trapping centers.

At the same time, the nanosecond lifetime of the excited state of the defect is apparently due to the temperature quenching of its intracenter luminescence, which follows from the temperature dependence of the PL yield (Fig. 5). However, it cannot be excluded the presence of a more complex structure of the energy states of the defect. Since the crystals under study contain elements of the crystal structure i.e. complexes  $(\text{PO}_4)^{3-}$ , which are structural analogues of quartz, one can put forward some assumptions about the nature of intrinsic defects, based on data on defects in the crystal structure of  $\text{SiO}_2$  [16] or  $\text{AlPO}_4$  [17]. Most likely, such defects can be oxygen-deficient centers (oxygen-deficient centers — ODC), namely, a three-coordinated phosphorus atom (analogous to  $E'$ -centers in  $\text{SiO}_2$ ). Such a center is formed when



**Figure 7.** RL spectra of nominally pure SLuP measured at temperatures 88 (1) and 295 K (2).

a hole is localized in an oxygen vacancy and will be a radical ion  $(\text{PO}_3)^{2-}$ . These centers were found in quartz using the electron paramagnetic resonance (EPR) method, but their luminescence in  $\text{SiO}_2$  is not observed [16]. However, the difference in the electron density distribution in  $\text{Si}-\text{O}-\text{Si}$  bonds for  $\text{SiO}_2$  and  $\text{M}-\text{O}-\text{P}$  ( $\text{M}=\text{Sr}, \text{Lu}$ ) for SLuP can lead to a change in the adiabatic potentials of the luminescence center. In this case, the nanosecond components of the PCL decay kinetics of the defect will be formed by allowed transitions from singlet states to the ground state of the ODC luminescence center  $S_2 \rightarrow S_0$  and  $S_1 \rightarrow S_0$ , and the glow of the microsecond range corresponds to the forbidden transition from the triplet state  $T_1 \rightarrow S_0$  [17]. However, it should be noted that the presence of radical ions of the  $(\text{PO}_3)^{2-}$  type in the crystals under study requires proof by EPR.

To study the issue of the origin of defects and the possibility of manifestation of ALE luminescence, the RL spectra of nominally pure  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$  were measured at room temperature and  $T = 88 \text{ K}$  (Fig. 7). At room temperature in the RL spectra, one can clearly distinguish at least two bands with maxima at 330 and 500 nm. It should be noted that the same emission bands that are observed here in the RL spectra of the SLuP matrix were also observed in the PCL spectra of  $\text{SLuP:Pr}^{3+}$  (Fig. 1), which indicates their identical nature. In other words, the luminescence in these spectral regions is associated with the luminescence of defects in the SLuP crystal lattice and is not associated with possible defects formed in the crystal lattice upon the introduction of  $\text{Pr}^{3+}$  ions.

At low temperatures, the RL yield in the ultraviolet region increases sharply, the 350 nm band dominates in the spectrum, and a short-wavelength shoulder is observed in the region of 290 nm. Potentially, luminescence in this region of the spectrum can be associated with the manifestation of ALE. There are literature data on ALE luminescence in some phosphates: for example, in  $\text{YPO}_4$

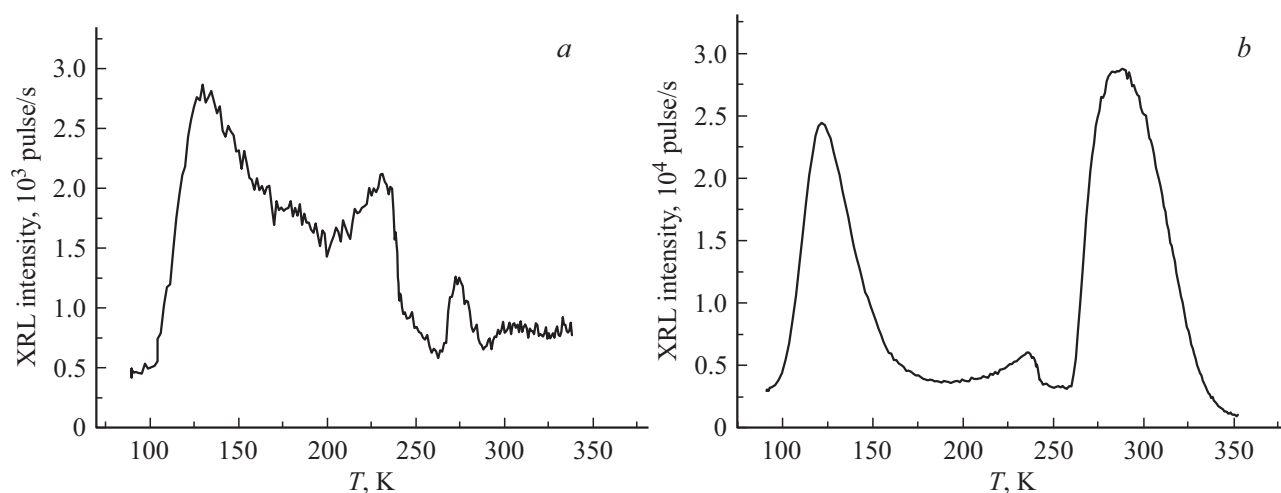
the ALE emission in the PL spectrum is in the region  $\sim 23800 \text{ cm}^{-1}$  ( $\sim 450 \text{ nm}$ ) [18], in  $\text{LiY}(\text{PO}_4)_3$  is in the region  $\sim 22600 \text{ cm}^{-1}$  ( $\sim 470 \text{ nm}$ ) [19], in  $\text{LiMgPO}_4$  is in the region  $\sim 350 \text{ nm}$  [20], in  $\text{AlPO}_4$  the ALE emission band has a maximum at 2.95 eV (420 nm) [17]. However, to interpret the 350 nm band as an ALE emission in the studied wide-bandgap  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$ , it is necessary to measure the PL excitation spectra up to region of the fundamental absorption edge and interband transitions in the vacuum ultraviolet region. Literature data on estimates of the minimum energy of interband transitions  $E_g$  are missing. However, in complex double phosphates containing lanthanide ions, such as  $\text{REPO}_4$ ,  $\text{A}_3\text{RE}(\text{PO}_4)_2$  ( $\text{RE}$  is rare earth ion,  $\text{A}$  is alkali metal ion) [12], or related compound  $\text{Ca}_9\text{Lu}(\text{PO}_4)_7$  [21] minimal energy of interband transitions is estimated as  $E_g = 7.3\text{--}9.5 \text{ eV}$ . Therefore, the available experimental and literature data are not yet sufficient to conclude that the band in the 350 nm region in the RL or PCL spectra is related to the ALE emission in the matrix  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$ .

In addition to the luminescence of defects, an alternative competing channel that determines the yield of recombination radioluminescence of impurity centers in wide-bandgap dielectrics is the capture of charge carriers in traps. The efficiency of such a process can be successfully controlled by studying thermally-stimulated luminescence (TSL). This method allows one to calculate the parameters of charge carrier traps. Fig. 8 shows the thermoluminescence curves of SLuP and  $\text{SLuP:Pr}^{3+}$  after they were irradiated with X-rays at temperature of  $T = 88 \text{ K}$  during TSL observation at wavelengths corresponding to emission centers of 350 nm in SLuP and  $5d \rightarrow 4f$ -transitions (265 nm) in the  $\text{Pr}^{3+}$  ion in  $\text{SLuP:Pr}^{3+}$ . Thermoluminescence curves of both objects show TSL peaks in practically the same temperature ranges, the main TSL peaks lie in the region of 124 and 286 K. The high TSL yield in  $\text{SLuP:Pr}^{3+}$  indicates that there is effective capture of charge carriers in traps and recombination of delocalized charge carriers at the  $\text{Pr}^{3+}$  impurity center. The parameters of trapping centers (order of the process kinetics, activation energy, frequency factor) were calculated by the methodology described in the work [22]. The calculation methodology is based on the use of general order kinetics. For the main TSL peaks 124 and 286 K, the results of calculating the activation energy in  $\text{SLuP:Pr}^{3+}$  give the values 0.12 and 0.8 eV, respectively, and the shape of the peaks is described by second-order kinetics, which indicates a high probability recapture of delocalized charge carriers in traps. For second-order kinetics, the frequency factor was not calculated.

## Conclusions

In present work, the spectroscopic properties of  $\text{Pr}^{3+}$  ions and crystal structure defects in  $\text{Sr}_9\text{Lu}(\text{PO}_4)_7$  micropowders:  $\text{Pr}^{3+}$ , were studied. Luminescent methods were used for excitation of objects by photons in the ultraviolet range, X-





**Figure 8.** SLiP thermoluminescence curves ( $\lambda_{\text{em}} = 350$  nm) (a) and SLuP:Pr<sup>3+</sup> ( $\lambda_{\text{em}} = 265$  nm) (b), irradiated with X-rays at  $T = 88$  K.

rays and a pulsed electron beam, as well as methods of low-temperature thermal activation spectroscopy. Crystals doped with Pr<sup>3+</sup> ions at a concentration of 1 mol.% show intense luminescence associated with fast interconfigurational  $5d \rightarrow 4f$  transitions in the Pr<sup>3+</sup> ion in the ultraviolet range. In addition, weak narrow lines of intraconfigurational  $4f \rightarrow 4f$  transitions are observed in the luminescence spectra, as well as the emission of two types of defects in the crystal structure. The temporal characteristics of the PCL of the impurity center and defects, as well as the processes of energy transfer between defects and the impurity center, are studied. Energy transfer is observed in both directions. Presumably, the nature of intrinsic defects formed during the synthesis of crystals is associated with the presence of oxygen-deficient centers (ODCs). Thermoluminescent studies show a high concentration of charge carrier trapping centers that form an alternative channel for the recombination luminescence of an impurity center. The data obtained complement the information available in the literature on the spectroscopy of impurity Pr<sup>3+</sup> ions, energy transfer processes, and intrinsic defects in the crystal lattice of phosphates.

Although the presence of defects as centers of radiative recombination of charge carriers, as well as a high concentration of charge carrier trapping centers, limit the luminescence yield of the impurity center, the relatively high intensity and short decay times of radiative  $5d \rightarrow 4f$  transitions in Pr<sup>3+</sup> ions are the positive qualities of SLuP:Pr<sup>3+</sup> in terms of suitability for use as a scintillation material.

Further studies of the impurity center excitation efficiency should include the study of luminescence excitation spectra in the region of interband transitions in the vacuum ultraviolet region, including the use of synchrotron radiation. To suppress the effect of crystal structure defects and charge carrier traps on the recombination luminescence yield of the Pr<sup>3+</sup> center, it may be useful to study the luminescence properties of SLuP:Pr<sup>3+</sup> when co-doped with alkaline earth metal ions, as has been observed for other phosphates [23].

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## Conflict of interest

The authors declare that they have no conflict of interest.

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