

Energy Transfer Mechanism in Pr-Doped SrF₂ Crystals

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Abstract—Results of investigation of energy transfer mechanism in SrF₂ crystals doped with Pr³⁺ ions are presented. Temperature dependences of 5d-4f and exciton emission in this material under X-ray excitation, and thermostimulated luminescence (TSL) in temperature range 80–300 K are studied. It has been established that in SrF₂-Pr³⁺ crystals the consecutive electron-hole capture mechanism of energy transfer takes place. Also we found that hole centers made a contribution to energy transfer from primary electrons and holes to Pr³⁺ ions.

Index Terms—Alkali-earth fluoride, energy transfer, praseodymium, rare earth, scintillation mechanism, scintillators, TSL.

I. INTRODUCTION

TRIVALENT praseodymium ions are perspective dopant for scintillation materials [1]. In previous experiments we have shown that crystals of SrF₂ doped with Pr³⁺ ions have a good temperature stability of light yield and could be used for well-logging application in contrast to the alkali-earth fluorides doped with Ce³⁺ ions [2]. However, light yield of strontium fluoride doped with Pr³⁺ is lower (about 11000–12000 ph/MeV [2]) than theoretical limit (about 35000 ph/MeV [1], [3]). One of the reasons for degradation of scintillation properties of the material consists in difference between mechanisms of energy transfer from created by ionizing radiation primary electrons and holes to rare earth ions. In Pr³⁺ doped alkali-earth fluorides consecutive capture of electrons and holes is the primary energy transfer mechanism [4]–[6]. Temperature dependences of 5d-4f emission under X-ray excitation and thermostimulated luminescence (TSL) at 80–300 K are studied to clarify this energy transfer.

II. EXPERIMENTAL METHODOLOGY

The crystals of SrF₂ doped with different concentrations of Pr³⁺ ions were grown in a graphite crucible by the Stockbarger method. PrF₃ impurity was added into raw materials in amount from 0.01 to few mol.%. Concentration of Pr³⁺ ions in crystals

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was controlled by the ISP-MS method using Finnigan Element 2 spectrometer. Samples of 8×10×2 mm dimensions were used.

The excitation was performed with an anode X-ray tube. The operating voltage of the tube was 25 kV, the current was 4 mA. We used grating vacuum monochromator VM-4 and solar-blind PMT FEU-142 for emission detection.

Luminescence decays and time-resolved spectra of these decays were measured under pulsed X-ray excitation performed with a X-ray tube based on MIRA (pulse duration is about 8 ns, energy in a pulse is about 100 keV). We used a grating monochromator MDR-2, a photomodule Hamamatsu H6780-04, and an oscilloscope Rigol DS1202CA with different input resistances for decay curves registration. Values of input resistors were 0.8, 2.8, and 10 kΩ.

Experiments were carried out in temperature interval 80–300 K. A sample was mounted in a vacuum cryostat. Chromel-alumel thermocouple with cold end compensator at 80 K was used to temperature control. The linear heating regime (10 K/min) was used to measure temperature dependences of emission and TSL curves.

III. RESULTS

A. Temperature Dependences of the Emission Intensity and Thermostimulated Luminescence (TSL)

The temperature dependences of X-ray excited 5d-4f emission of SrF₂ crystals doped with different concentrations of Pr³⁺ ions are shown in Fig. 1, dots. The intensities of the 5d-4f emission bands decrease several times as the temperature decreases from room temperature (RT) to 80 K (LNT). The intensity decreases are about 2.5 times in the SrF₂-0.015 mol.% Pr³⁺ crystal (Fig. 1(a), dots), about 2 times in SrF₂-0.15 mol.% Pr³⁺ (Fig. 1(b), dots), and about 1.5 times in SrF₂-1 mol.% Pr³⁺ (Fig. 1(c), dots). The intensity of exciton emission band measured at 290 nm slightly increases as the temperature decreases from RT to LNT (Fig. 2).

After X-ray irradiation at 80 K thermostimulated luminescence (TSL) is observed. TSL glow curves at 5d-4f emission band are presented in Fig. 1, bold line. Strong TSL peaks are observed at around 151 K, and 243 K in SrF₂ doped with 0.015 mol.% Pr³⁺ (Fig. 1(a), bold line). The peaks at around 135 K and around 245 K are found in SrF₂-0.15 Pr³⁺ (Fig. 1(b), bold line). In the crystal doped with 1 mol.% of Pr³⁺ ions a weak glow peak is at around 130 K and strong TSL peak is at 245 K (Fig. 1(c), bold line). The first TSL peaks (Fig. 1, bold line, peak "1") are observed in all crystals in the temperature range when the 5d-4f emission intensity decreasing is found.

TSL glow curve at exciton emission band is added in Fig. 2, bold line. Two peaks are found at around 108 K and 130 K.

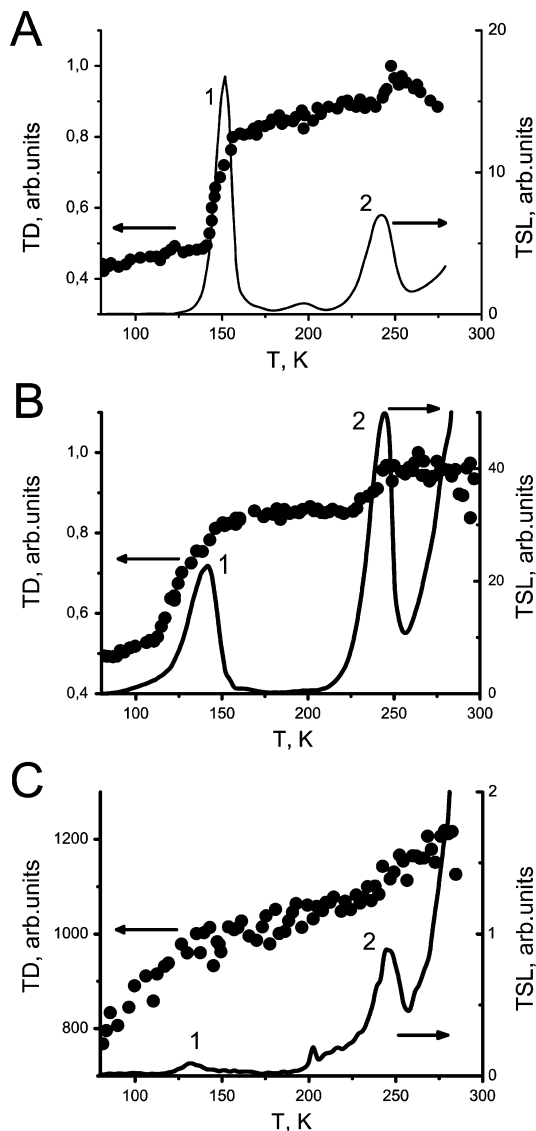


Fig. 1. Temperature dependence of normalized emission (TD), dots; and thermoluminescence (TSL), solid lines, of SrF₂ doped with 0.015 mol.% Pr³⁺ ions (A), 0.15 mol.% Pr³⁺ ions (B), and 1 mol.% Pr³⁺ ions (C) crystals measured at 235 nm. TSL peaks are marked as “1” and “2”.

An integral TSL curve (bold line) and normalized temperature dependence of 5d-4f emission intensity (dots) measured in SrF₂-0.015 mol.% crystals are shown in Fig. 3.

B. Luminescence Decay Kinetics

Long time decay kinetics of 5d-4f emission of Pr³⁺ ions are found in SrF₂-Pr³⁺ crystals at around room temperature. The decay curves measured at around RT at 235 nm are shown in Fig. 4(a), (b), (c). The luminescence kinetic can be approximated by the sum of four exponential decay curves in SrF₂-0.015 mol.%, and SrF₂-0.15 mol.%, and by the sum of three exponential decay curves in SrF₂-1 mol.% Pr³⁺. The decay times are 0.8, 1.4, 6.6, and 17 μ s in SrF₂-0.015 mol.% Pr³⁺ (Fig. 4(a)); 0.9, 1.1, 5.5, and 20 μ s in SrF₂-0.15 mol.% Pr³⁺ (Fig. 4(b)); and 0.9, 1.6, and 3 μ s in SrF₂-1 mol.% Pr³⁺ (Fig. 4(c)).

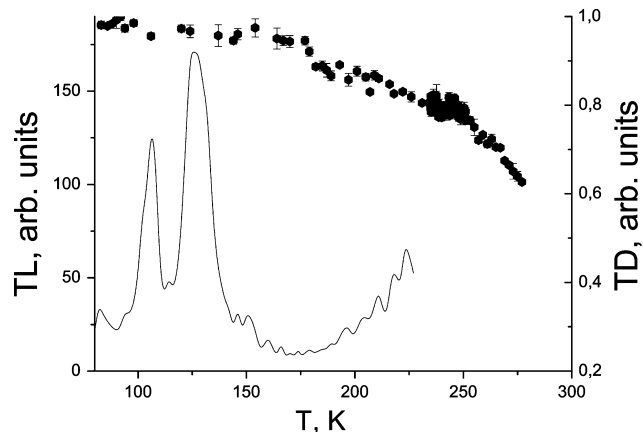


Fig. 2. Temperature dependence of normalized emission (TD) and thermoluminescence (TL) of SrF₂-0.15 mol.% Pr³⁺ crystals measured at 290 nm.

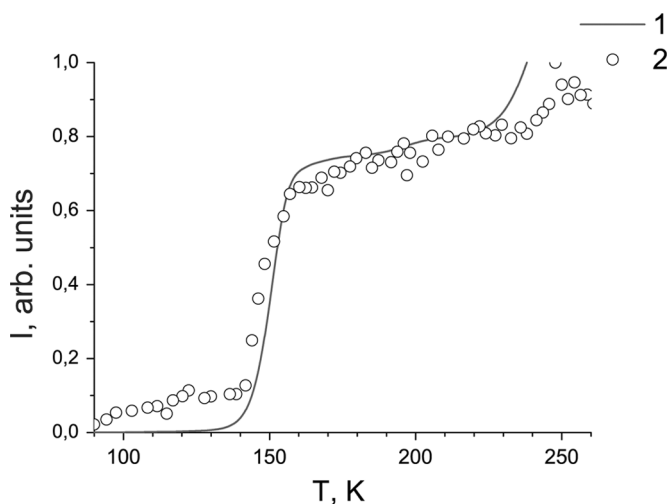


Fig. 3. Temperature dependence (dots, 2) of normalized emission and integral thermoluminescence (curve 1) of SrF₂-0.015 mol.% Pr³⁺ crystals measured at 235 nm.

We do not rule out possibility of the presence of longer decay time components. Unfortunately, those intensities were too weak to study decay kinetics in detail. The decay times are calculated and shown in Fig. 4(a), (b), (c). The first exponential decays (0.8–0.9 μ s) in all crystals are attributed to fast 5d-4f emission of Pr³⁺ ions (about 25 ns [6]). The intensities of these components are much higher than intensities of the slower ones.

Decay times of the 5d-4f luminescence kinetics depend on temperature. They become longer as the temperature decreases. The temperature dependences of different decay time components are shown in Fig. 5. All decay times are proportional to inverse temperature.

Time-resolved spectra of SrF₂-0.15 mol.% Pr³⁺ crystals measured in two time windows: 0–1 μ s, and 6–8 μ s are presented in Fig. 4(d). In all time windows complicated spectra were registered. Distinct emission bands at around 5.55 eV and 5.35 eV are observed. The position of the bands in the spectra coincides with those of the 5d-4f spectral lines observed under synchrotron radiation [6]. This allows us to ascribe these bands to the 5d-4f emission. The spectrum also shows a broad band with maximum at around 4.8 eV attributed to self-trapped

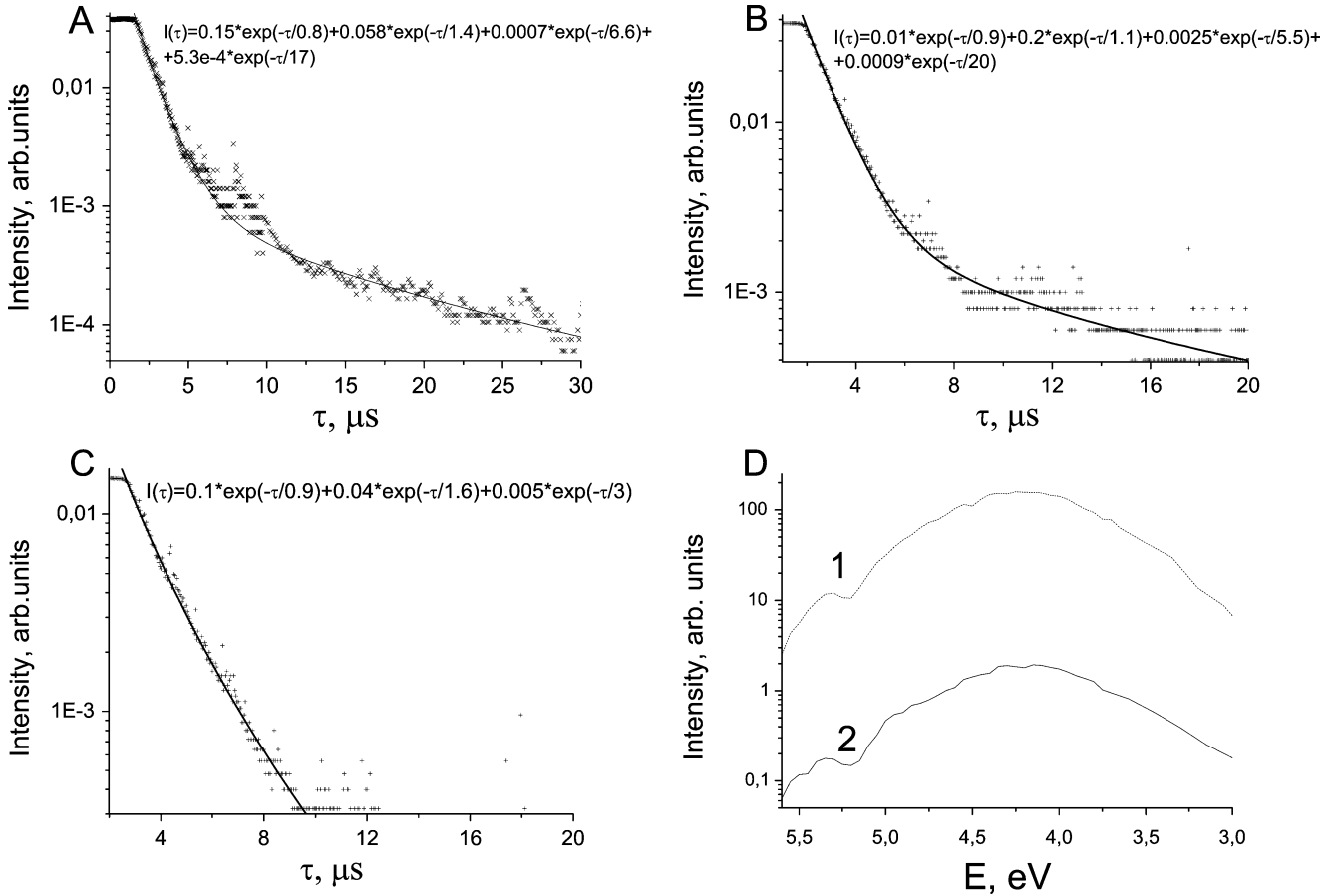


Fig. 4. 5d-4f luminescence decay curves of SrF₂ crystals doped with 0.015 mol.% (A), 0.15 mol.% (B) measured at around RT, and 1 mol.% (C) measured at around 300 K. All curves are approximated by sum of single exponential decays. The equations of approximation are given in labels in right parts of figures. In figure D time-resolved spectra of SrF₂-0.15 mol.% Pr³⁺ crystal measured in 0–1 μ s (1) and 6–8 μ s time windows is shown.

exciton luminescence [7]. In the crystals doped with other concentrations of % Pr³⁺ ions time-resolved spectra have the same bands, however, intensities of 5d-4f lines in SrF₂-0.015 mol.% Pr³⁺ are lower than in the crystals doped with higher activator concentrations.

IV. DISCUSSION

During cooling a sharp decrease of 5d-4f emission intensity is found at 154 K in SrF₂-0.015 mol.% Pr³⁺ (Fig. 1(a), dots), 145 K in SrF₂-0.15 mol.% Pr³⁺ (Fig. 1(b), dots) and 139 K in SrF₂-1 mol.% Pr³⁺ (Fig. 1(c), dots). The intervals of the emission decrease are correlated with thermoluminescence peaks marked as “1” in Fig. 1. The thermoluminescence peaks at 100–250 K refer to delocalization of self-trapped holes [8]. There are V_k centers (100–120 K), and different types of V_{kA} centers—self-trapped holes captured near RE³⁺ ions. Some types of V_{kA} centers are stable even at room temperature [9]. Activation energies and frequency factors of the glow peaks “1” and “2” in Fig. 1 are calculated by using (1):

$$I(T) = \exp\left(\frac{-E}{k_B T} - \int B \exp\left(\frac{-E}{k_B T}\right) dT\right) \quad (1)$$

where E is activation energy of TSL peak, B is frequency factor, k_B is Boltzmann constant, and T is temperature.

The parameters of TSL peaks are the following:

- the peak “1” has an activation energy $E = 15 \pm 0.03$ eV and a frequency factor $B = 7 \cdot 10^{11} \text{ s}^{-1}$;
- the peak “2” has $E = 0.63 \pm 0.03$ eV, $B = 6 \cdot 10^{11} \text{ s}^{-1}$.

Fig. 3 compares normalized integral TSL and temperature dependence of 5d-4f emission. These seem to be in rough agreement. Therefore, the TSL ties with 5d-4f emission. Notice that integral TSL curve gives us information about light sum emitting on heating up to a current temperature. Thus, the correlation between TSL curve and temperature dependence of the emission intensity can be associated with participation of charge carrier traps in recombination process under X-ray excitation in SrF₂-Pr³⁺ crystals.

There are two possibilities of the recombination process. The first process is when an electron captured by Pr³⁺ ion and then recombines with coming self-trapped hole. The second is inverse process, i.e., the hole is trapped by Pr³⁺ ion. This center is called V_{kA} center—self-trapped hole neighbor Pr-ion. Afterwards, recombination of the coming electron and the captured hole occurs. In the both processes the recombination energy passes to excitation of the 4f-5d transitions in Pr³⁺.

If the process 2 occurred, the emission decrease at maximum TSL peak would be attributed to localization of electron in a trap. Thus, the decreasing emission intensity shall account for the electronic trap destruction.

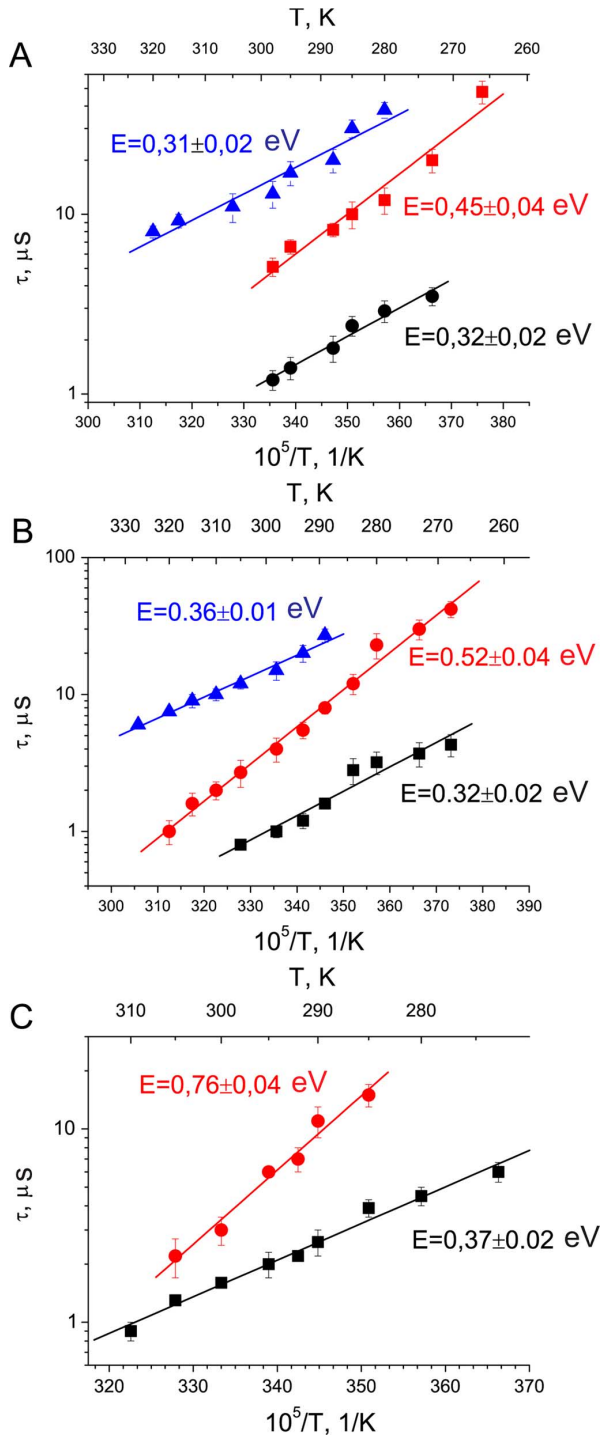


Fig. 5. Temperature dependences of long decay time components of 5d-4f Pr³⁺ emission in SrF₂ doped with 0.015 mol.% (A), 0.15 mol.% (B) 1 mol.% (C) of Pr³⁺ ions. Values of activation energy shown here were calculated by the temperature dependences of decay time.

However, low temperature TSL peaks in fluorides doped with rare earth ions are attributed to hole centers [9], [10], [8], [11]. Temperature of maximum and activation energy of the glow peaks “1” and “2” (Fig. 1, bold lines) calculated by (1) are similar to the ones reported in [9], [10], [8], [11]. Therefore, the emission decrease is due to self-trapping holes. That is the first evidence, that the process 1 occurs in the SrF₂-Pr³⁺ crystals.

The TSL peak at around 130–150 K is related to V_{kA} centers, i.e., a self-trapped hole neighbor Pr³⁺. TSL peak at around 240 K is attributed to other configuration of V_{kA} centers [9]. Here and elsewhere these centers are called $V_{kA'}$ centers.

Next evidence that the process 1 takes place is the value of activation energy of falling intensity of 5d-4f emission (Fig. 1, dots). A rough estimate can be made using the simple equation (2):

$$I = B \exp\left(\frac{-E_f}{k_B T}\right) \quad (2)$$

where E_f is activation energy of falling 5d-4f emission, and I is intensity of 5d-4f emission at the current temperature T . The activation energy calculated by using (2) is about 0.10–0.17 eV (Fig. 1, dots), that is the same order of magnitude of activation energy of V_{kA} centers calculated by TSL curves (Fig. 1, peak “1”).

We suggest that two mechanisms of consecutive electron-hole capture are possible. In the first one, electron is captured by Pr³⁺ ion, forming Pr²⁺ center, and then the “hot” hole is captured by the Pr²⁺ ion with formation of excited Pr^{3+*} center and the following 5d-4f emission. This is “prompt” consecutive capture [12]. In other mechanism, “hot” hole is not captured by Pr²⁺ ion, but it becomes self-trapped forming different types of V_{kA} centers. Then the self-trapped hole is thermally released from the trapping center and captured by Pr²⁺ ion with the following emission as well as in the “prompt” process. This mechanism is called “delayed” consecutive capture. A contribution of the second mechanism can be estimated by the value of the 5d-4f emission decrease. The contribution is about 30–60% in the crystals doped with 0.01 mol.% – 1 mol.% Pr³⁺ ions, i.e., a considerable part of holes arrives to Pr²⁺ ions via V_{kA} centers.

The presence of the “delayed” energy transfer mechanism should result in availability of long decay time in 5d-4f Pr³⁺ emission at room and higher temperatures. Indeed, the hole lifetime in a trap is described by

$$\tau = \frac{1}{B} \exp\left(\frac{E}{k_B T}\right) \quad (3)$$

where B is frequency factor, E is deep of a trap, T is temperature and k_B is Boltzmann constant. At low temperatures the lifetime of a hole in a trap is significantly long than registration time. The lifetime in the trap decreases with increasing temperature, it is in microsecond span at room temperature. After releasing the hole recombines with an electron in Pr³⁺ ion.

Three long decay time components are observed in 5d-4f emission of Pr³⁺ ions in the crystals of SrF₂-0.015 mol.% Pr³⁺ and SrF₂-0.15 mol.% Pr³⁺. They are shown in Fig. 5. Decay times of these components have exponential dependences on inverse temperature. Activation energies calculated on temperature dependences of decay times are presented in the figure. Two components having the similar activation energies in the crystals doped with 0.015 mol.% and 0.15 mol.% of Pr³⁺ ions could be assigned with energy transfer from V_{kA} centers located at different distances from the recombination centers (Fig. 5, triangles; and $E = 11$ eV; Fig. 5, squares). A reasonable question is why there are only two related lifetimes and not more. We suppose that components with longer decays can exist. However,

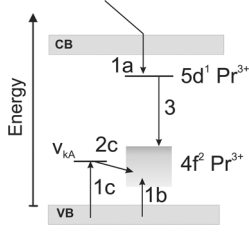


Fig. 6. Schematic illustration of electron-hole energy transfer process in SrF₂ crystal doped with Pr³⁺ ions.

these components have extremely low intensities and too long decay times, thus the ones cannot be measured. The third component (Fig. 5, circles) is attributed to $V_{kA'}$ centers [9] (TSL peaks “2”, Fig. 1, solid line).

In contrast to SrF₂-Pr³⁺ doped with lower concentrations, only two lifetimes are observed in the crystals doped with 1 mol.% of Pr³⁺ ions. Activation energies calculated using (3) differ. One of the energies is assigned to energy transfer from V_{kA} centers ($E = 0.37$ eV) and the other one is assigned to the transfer from $V_{kA'}$ centers ($E = 0.76$ eV). The presence of only two components in the luminescence kinetic is explained by decreasing average distances between a hole and recombination center due to distance reduction between Pr³⁺ ions with increasing activator ion concentration. The half Pr-Pr distance is near 16 Å at the level of 0.1 molar % and near 10 Å at the level of 1 molar %. The second cause is a diminish of deposit of V_{kA} centers to the energy transfer as the Pr³⁺ concentration increases, but the role of $V_{kA'}$ centers in transfer process increases. This directly follows from the comparison of intensities of the glow peak “1” and the peak “2” (Fig. 1(c)). Therefore, only one life time in luminescence kinetic attributed to V_{kA} centers can be measured. Other lifetimes, if they exist, have extremely low intensity and can not be detected.

The temperature dependence of long decay time of 5d-4f emission is a further proof of occurrence of the above described energy transfer mechanism. The energy transfer processes are illustrated by a scheme (Fig. 6) presenting band gap of SrF₂-Pr³⁺. 5d and 4f levels are located into the band gap of the crystal. Initially, Pr³⁺ ion captures electron from conduction band (1a) forming Pr²⁺ ion. Then the Pr²⁺ ion can trap a “hot” hole (1b) with following recombination. Only this mechanism occurs at low temperatures and it depends on Pr ion concentration in the crystal. The probability of the “hot” hole capturing increases progressively with Pr doping. The mechanism is called “prompt” consecutive electron-hole capture.

At higher temperatures, for example at room temperature, the self-trapped holes play an important role in energy transfer mechanism to Pr³⁺ ions. As pointed above, the traps are V_{kA} -type centers. In this case, the “hot” hole is self-trapped (1c) instead of having been captured by Pr²⁺ ion (1b). Next, the hole is thermally released from the trap and captured by the Pr²⁺ ion. This mechanism is called “delayed” consecutive electron-hole transfer. The recombination process (1a→1c→2c→3) depends on temperature. It starts at temperatures higher than the ones of releasing holes. In our case, these temperatures are around 150 K and 243 K tied with V_{kA} .

The increase of efficiency contribution of this mechanism with temperature explains the growth of 5d-4f emission intensity with temperature and exponential dependence of long component of decay time on temperature. Unfortunately, the presence of “delayed” consecutive electron-hole capture in SrF₂-Pr³⁺ crystals degrades light yield of the crystals, because the time of the “delayed” transfer is significantly longer than registration time of a standard spectrometric amplifier with shaping time not exceed 10 μs and, consequently, we cannot completely collect all light from the crystal.

In the first approximation, light yield is determined by [12]

$$LY = 10^6 \frac{SQ}{\beta E_g} \quad (4)$$

where S is efficiency of energy transfer to luminescence center, Q is quantum efficiency of luminescent center, constant β is equal to 2.5 [13]. If Q and S are equal to 1, then the highest light yield is observed and the light yield is determined only by number of electron-hole pairs. If “delayed” energy transfer occurs in scintillator, the factor S in (4) is less than 1. In the case of SrF₂-Pr³⁺ scintillator the contribution of “delayed” energy transfer can be calculated by the emission intensity decrease. The contribution of delayed energy transfer is about 60% in the crystals doped 0.015 mol.% of Pr³⁺ ions, 50% in SrF₂-0.15 mol. Pr³⁺, and 30% in SrF₂-1 mol. Pr³⁺. In the previous experiments [6] we found that maximal light yield was in SrF₂-0.045 mol.% Pr³⁺ and SrF₂-0.1 mol.% Pr³⁺. At higher concentration we saw concentration quenching of Pr³⁺ luminescence. Therefore, the factor S is between 0.5–0.6 for SrF₂-Pr³⁺ scintillator. In other words, the presence of “delayed” energy transfer mechanism reduces a light yield of SrF₂-Pr³⁺ by 40–50%.

How can the influence of this mechanism on light yield be diminished? In LuAG-Pr³⁺ crystals traps also take part in energy transfer process. However, they are shallow electron traps (not hole) [14]. In the referred paper, the authors applied an interesting decision called “band-gap engineering”. It was co-doping LuAG-Pr³⁺ with Ga³⁺ impurity thereby decreased a band gap. After co-doping the energy levels of shallow electron traps were found in conduction band and the influence of “delay” transfer mechanism was reduced.

In SrF₂-Pr³⁺ crystals, we have another type of traps: hole traps. They appear in the crystal after Pr³⁺ ion doping. These traps belong to Pr³⁺ centers. Thereby, it is difficult to exclude the influence of these traps on energy transfer mechanism in SrF₂-Pr³⁺ crystals. This fact can set a fundamental limit of light yield of SrF₂-Pr³⁺ scintillator.

V. CONCLUSION

In SrF₂-Pr³⁺ crystals, consecutive capture of electron forming Pr²⁺ center and then hole with following recombination is major luminescence mechanism. At room temperatures two compete processes are found. There are “prompt” electron-hole capture, when the activator ion traps consequently electron and hole, and “delayed” electron-hole capture, when the activator ion catches the electron and the hole coming to the activator via hole traps (V_{kA}). Herewith, the efficiency of the second process is a higher in SrF₂-Pr³⁺ crystals.

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