The Luminescence of the Praseodymium - doped Strontium Borate $Sr_4B_{14}O_{25}:Pr^{3+}$

Kudrjavtcev[1] D.P., Oseledchik[1] Yu. S., Prosvirnin[1] A.L., Svitanko[1] N.V., Petrov[2] V.V.

[1]The Zaporozhye State Engineering Academy, prospect Lenina 226, 69006 Zaporozhye, Ukraine, kudryvzev99@mail.ru.
[2]The Institute of Laser Physics, Siberian branch of Russian Academy of Sciences, 630090, Russia, Novosibirsk, ak. Lavrent'eva street 13.

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Abstract

The absorption and the luminescence spectra of the new Pr - doped strontium borate $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals were measured. The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal sample 5×5×9,6 mm^3 in size was used for investigation. It was found that the short - wave transparency edge of $Sr_4B_{14}O_{25}:Pr^{3+}$ is 227 nm. The longwave absorption edge of spectra corresponds to 3200 nm The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal simples were measured by a laser and lamp pump. A strong luminescence line was detected in the orange spectral range λ = 595 nm ($^1D_2 \rightarrow {}^3H_4$ transition). The polarizing dependence of the luminescence intensity out was determined.

Keywords: luminescence, strontium borate, praseodymium-ion.

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1.Introduction

The study of the luminescence of rare-earth ions Eu, Sm, Yb, Tm in polycrystalline Sr borates (SrB_4O_7, SrB_6O_{10}), obtained by the method of solid state synthesis, has attracted much attention. [1-4].

The luminescence of the Pr^{3+} ions in various matrixes was studied recently [5-8]. It was shown that the praseodymium crystal lasers have the greatest number of luminescence channels in comparison to other solid-state crystal lasers. They allow to receive generation in the visible, near and mid - IR ranges at room temperature with the usual flash - lamp pump techniques [5]. In particular, the generation in dark blue (λ = 479 nm, $^3P_0 \rightarrow {}^3H_4$, T = 300 K) [6], green (λ = 537,8 nm, $^3P_0 \rightarrow {}^3H_5$, T = 110 K) [7], orange (λ = 607,1 nm, $^3P_0 \rightarrow {}^3H_6$, T =300 K) [8] and red (λ = 719,7 nm, $^3P_0 \rightarrow {}^3F_2$, T = 300 K) [9] spectral ranges was received in the visible range.

The strontium tetraborate SrB_4O_7 (SrO * $2B_2O_3$), is a very suitable host lattice for the luminescent lanthanide ions [1-4]. This prompted us to investigate the praseodymium - doped new strontium borate crystals $Sr_4B_{14}O_{25}:Pr^{3+}$ ($4SrO*7B_2O_3$) which were grown in our laboratory [10]. In this paper the luminescence of the Pr^{3+} ions in a single crystal $Sr_4B_{14}O_{25}:Pr^{3+}$ and the absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ has been measured.

2. Crystal growth

The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals were obtained from the melts SrO - $2B_2O_3$ - x Pr_2O_3 where the ratio of the Pr_2O_3 to SrO was more than 0.2 mol%. The crystal structure of the $Sr_4B_{14}O_{25}:Pr^{3+}$ was determined by the X - ray HZG - 4A diffractometer. The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals

belong to the monoclinic crystal system with the space group C2/m. The unit cell parameters these crystals are a = 16.384 Å, b = 7.762 Å, c = 16.619 Å, β= 119.18°. The habit of crystals is presented on Fig. 1.

The International Tables for X - ray Crystallography of the International center for diffraction data do not contain data on the $Sr_4B_{14}O_{25}:Pr^{3+}$ compounds.

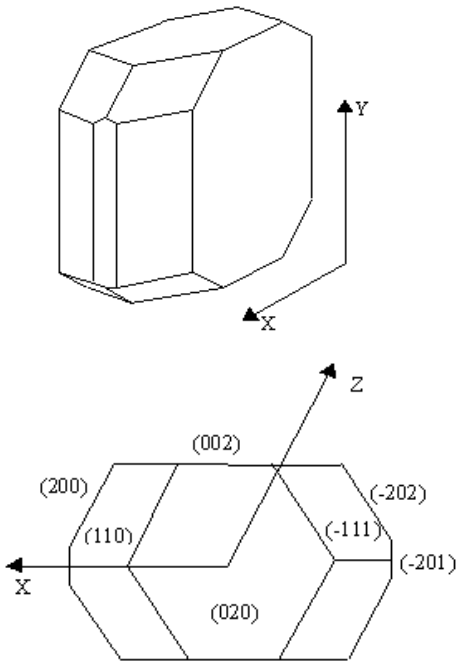

Fig. 1. The habits of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals.

The chemical compounds H_3BO_3, $SrCO_3$ and Pr_2O_3 with 99.5% purity were used to grow the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal. After the compounds were ground and mixed, they were put into the platinum crucible, melted and heated to 1050°C for 5 - 6 h. The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal was grown from the melt with Pr_2O_3/ SrO = 0.87 mol% by the TSSG method with pulling (modified Czochralski method) at the temperature 1015°C. The bulk crystals were 25 mm in diameter and more than 10 mm in length.

The praseodymium concentration in the grown crystals was measured by microprobe analysis (COMEKA COMEBAX). It was shown that the distribution of the activator concentration on a sample is nonhomogenous. The average segregation coefficient is 0,33. The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal boule was cut out with the dimension of 5 × 5 × 9,6 mm^3.

3. The absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ single crystal

The absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal sample were measured at room temperature with the Shimadzu UV 3101 PC spectrophotometer, the light was passed along the [100] direction. The absorption spectra is shown in Fig 2. The shortwave passband edge of the trasparency spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$

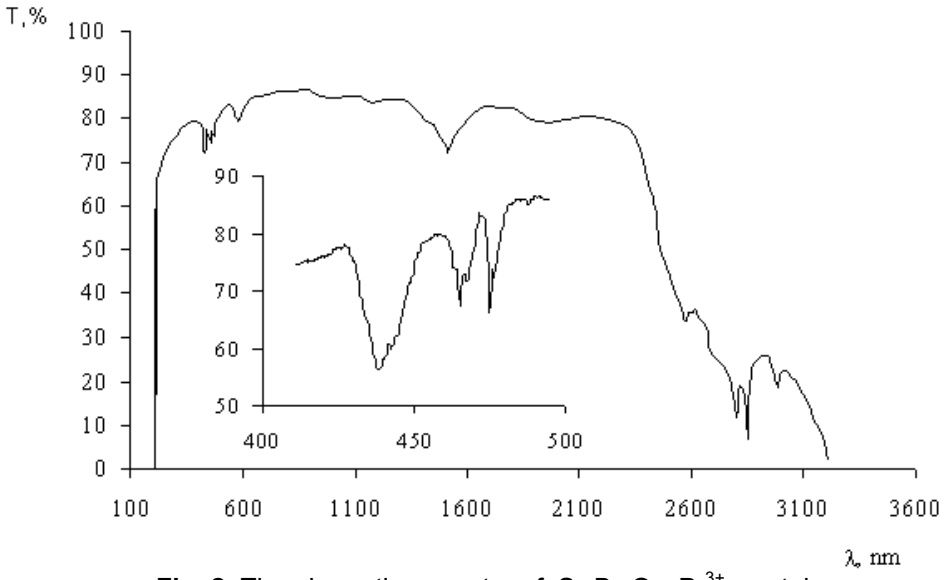

Fig. 2. The absorption spectra of $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal.

crystal are at 227 nm. The longwave absorption edge of spectra corresponds to 3200 nm. The form of the longwave edge of the spectrum has a complex structure. The absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal has three absorption peaks at the wavelength of 2750 nm, 2800 nm, 2935 nm, which do not correspond to the absorption lines of the Pr^{3+} - ions. Such a structure of the longwave transparency edge can be caused by matrix features. The absorption spectra contains eight peaks from 443 nm to 2320 nm, which corresponds to an electronic transition of the Pr^{3+} ion (Table 1). The absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ in the range (400 - 500) nm are submitted on the insertion (Fig 2). Fig. 3 shows the energy diagram of the Pr^{3+} with the registered electronic transitions.

4. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ single crystal

The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal were measured at room temperature when the $Sr_4B_{14}O_{25}:Pr^{+3}$ crystal sample was pumped by the radiation of Ar^+ - laser. The wavelength of filtered laser radiation was 488 nm, that correspond to the edge of

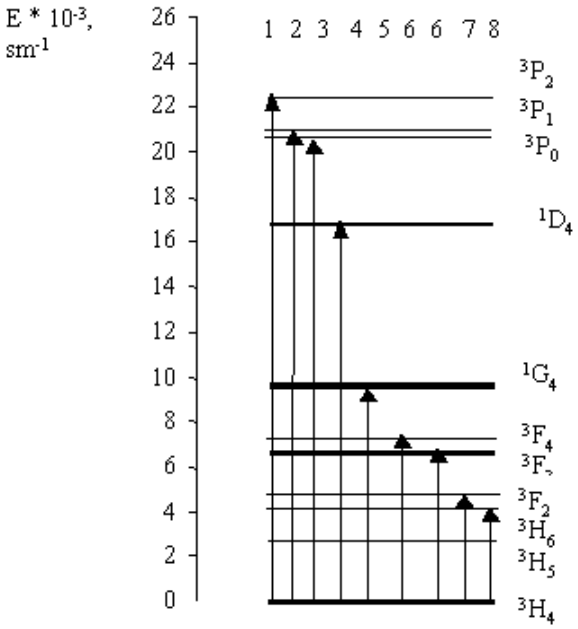

Fig. 3. The energy diagram of the Pr^{3+} ion.

Table 1. The electronic transitions of the Pr^{3+} - doped $Sr_4B_{14}O_{25}$ crystal.

№	λ, nm	Transition
1	443	$^3H_4 \rightarrow {}^3P_2$
2	470	$^3H_4 \rightarrow {}^3P_1$
3	482	$^3H_4 \rightarrow {}^3P_0$
4	585	$^3H_4 \rightarrow {}^1D_2$
5	1005	$^3H_4 \rightarrow {}^1G_4$
6	1504	$^3H_4 \rightarrow {}^3F_2$
7	1909	$^3H_4 \rightarrow {}^3F_3 + {}^3F_4$
8	2520	$^3H_4 \rightarrow {}^3H_6$

absorption line of the transition $^3H_4$ - $^3P_0$. The radiation linearly polarized by the Glan - prism was focused on the sample. The luminescence radiation was collected by the collimator and was analyzed by another one Glan - prism. The recording circuit contained the monochromator MDR 23, selective nanovoltmeter Unipan 232B, adjusted to the frequency of a mechanical modulator, and the recorder.

The pump was passed along the [100] direction.

Fig. 4 shows the luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal sample. It was not possible to register the luminescence peaks which correspond to transition $^3P_0$ - $^3H_4$ (dark blue spectral area) because the absorption transition $^3H_4$ - $^3P_0$ was not pumped.

The luminescence spectra in the orange - red spectral area (580 - 625) nm is shown in Fig. 5. The dependence of the luminescence intensity from polarization of the pump radiation and the luminescence polarization is submitted. From Fig. 5 we can see that luminescence peaks in (580 - 625) nm spectral area are stronger than in other spectral ranges. The luminescence intensities depend on different polarisation ($E \perp x$ and $E \parallel x$) of pump radiation.

The luminescence peaks which confirm to transitions $^3P_0 \rightarrow {}^3F_2$, $^3P_0 \rightarrow {}^3F_3$, $^3P_0 \rightarrow {}^3F_4$, $^1D_2 \rightarrow {}^3H_5$, $^1D_2 \rightarrow {}^3H_6$, $^1D_2 \rightarrow {}^3F_2$, $^3P_0 \rightarrow {}^1G_4$ are independent polarization of pump radiation .

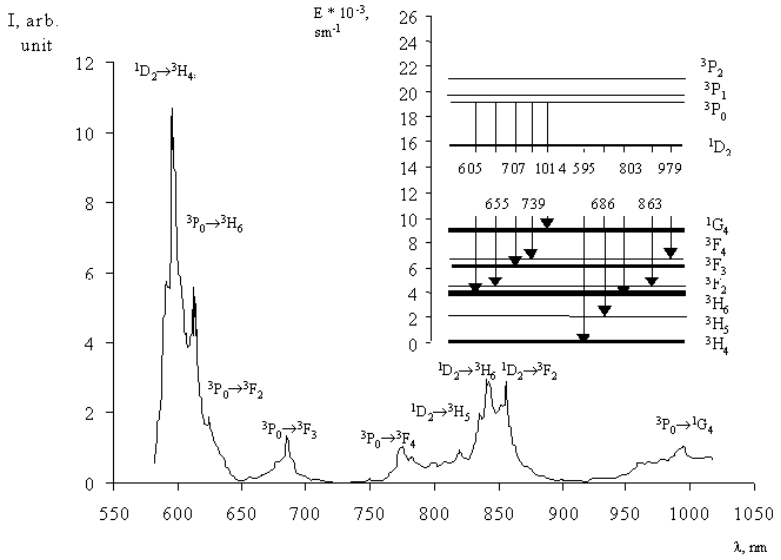

Fig. 4. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal under the Ar^+ - laser pump.

5. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal with the lamp pump

The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal simples were measured by the Hitachi spectrofluorimeter when the crystal simple was lamp pumped by absorption lines 440 nm, 470 nm, 485 nm and 585 nm. Fig. 6 shows the luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal when it was pumped by 440 nm lines. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal on the lamp pump in a range of 650-750 nm by excitation 440 nm was investigated with more accuracy and is presented on the insertion to fig. 6. The strongest luminescence peak is centered at 475 nm which conforms to the transitions $^3P_0 \rightarrow {}^3H_4$ of the Pr^{3+} - ions. The broad line of the luminescence is located at the wavelength at 540 nm ($^3P_0 \rightarrow {}^3H_5$ transitions). From Fig. 7 we can see the luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal when it was pumped by the 470 nm. The luminescence peak is centered at 540 nm and conforms to $^3P_0 \rightarrow {}^3H_5$ transitions of Pr^{3+}. The

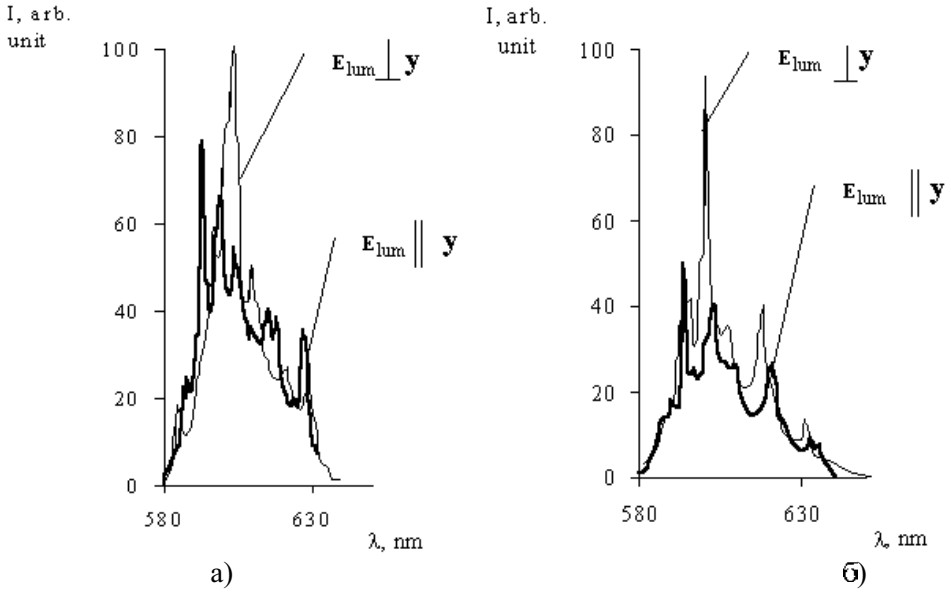

Fig. 5. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal in the range 580 nm - 640 nm а) $E_{pump} \perp y$, б) $E_{pump} \parallel y$, the pump was along on axis **x.**

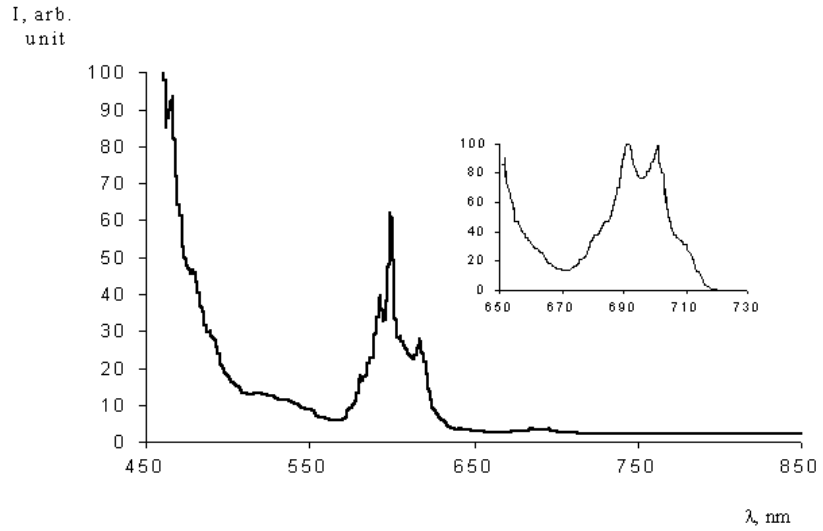

Fig. 6. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$crystal at the lamp pump by the excitation 440 nm.

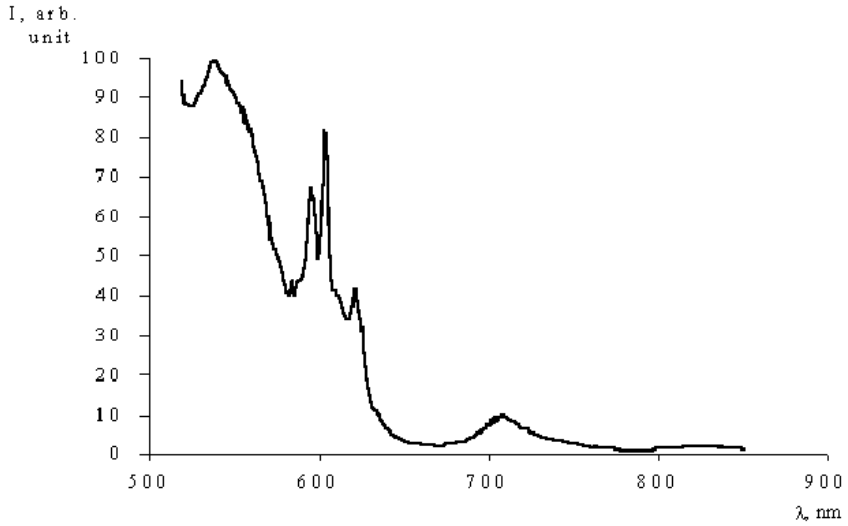

Fig. 7. The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal at the lamp pump by the excitation 470 nm.

luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal when it was pumped by the 482 nm lines are similar to the luminescence spectra when it was pumped by the radiation of Ar^+ - laser (Fig. 4). The luminescence of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal when the crystal was lamp pumped by the 585nm is very weak. Fig. 8 shows the energy diagram of the Pr^{+3} - ion transitions.

Conclusion

The absorption and the luminescence spectra of the strontium borate crystals $Sr_4B_{14}O_{25}:Pr^{3+}$ were measured.

The $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals was grown in our laboratory and belong to the monoclinic crystal system with space group C2/m.

The transparency range of $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals is λ=227–3200nm. The absorption spectra contains eight peaks from 443 to 2320 nm, which corresponds to the electronic transition of the Pr^{3+} ion. The absorption spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystal has absorption peaks at the wavelengths of 2750nm, 2800nm, 2935nm, which do not correspond to the absorption lines of the Pr^{3+} - ions.

The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals measured at room temperature by excitation of the Ar^+ - laser.

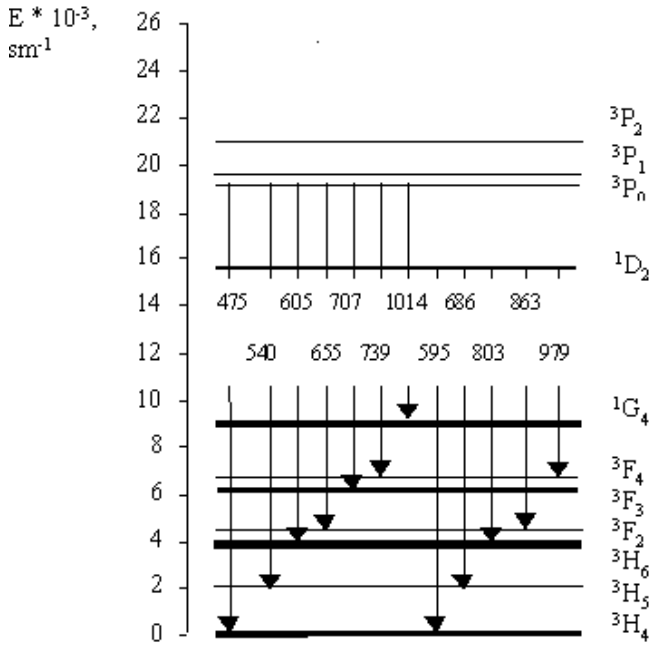

Fig. 8. The energy diagram of the Pr^{3+} ion with all registered electronic transition (vertical arrow).

The luminescence line 595 nm ($^1D_2 \rightarrow {}^3H_4$ transition), 605 nm ($^3P_0 \rightarrow {}^3H_6$), 640 nm ($^3P_0 \rightarrow {}^3F_2$), 775 nm ($^3P_0 \rightarrow {}^3F_3$), 820 nm ($^1D_2 \rightarrow {}^3H_5$), 843 nm ($^1D_2 \rightarrow {}^3H_6$), 860 nm ($^1D_2 \rightarrow {}^3F_2$), 997 nm ($^3P_0 \rightarrow {}^1G_4$) were registered. The polarizing dependence of the luminescence intensity was investigated. A strong line of the luminescence in the orange spectral area 595 nm ($^1D_2 \rightarrow {}^3H_4$) was detected.

The luminescence spectra of the $Sr_4B_{14}O_{25}:Pr^{3+}$ crystals was measured at room temperature by lamp excitation (Hitachi - spectrofluorimeter) in all absorption line The same luminescence line and additionally lines 475 nm ($^3P_0 \rightarrow {}^3H_4$), 540 nm ($^3P_0 \rightarrow {}^3H_4$) were detected by the lamp pump.

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