The spectroscopy of $4SrO•7B_2O_3:RE^{3+}$ ($RE = Eu^{3+}, Pr^{3+}, Nd^{3+}$) glasses

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Abstract

In this paper the spectroscopic properties of boron glasses $4SrO•7B_2O_3:RE^{3+}$ ($RE = Eu^{3+}$, Pr^{3+}, Nd^{3+}) are described. The transmissions and luminescence spectra are presented. The earlier known absorption bands of Eu^{3+}, Pr^{3+} and Nd^{3+} are detected. The luminescence of$4SrO•7B_2O_3:Pr^{3+}$ (under the laser pumping), $4SrO•7B_2O_3:Eu^{3+}$ (under the light-emitting diode pumping) is investigated. All the transmissions and luminescence lines are characterized.

Keywords: luminescence, strontium borate glasses, praseodymium ion, neodymium ion, europium ion.

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1. Introduction

Many works have been devoted to searching for and investigations of new laser glasses [1-3]. The interest to the laser glasses has increased during recent 10 years because of appearance and application of fibre lasers and amplifiers for the needs of digital information technologies [4,5]. One of the main parameters of laser glasses, which influences directly the working term of glass lasers, is the thermal coefficient of the refractive index β_T. It has been shown that boron glasses have worse thermooptical properties than the phosphate and fluoride glasses [6], though they have negative or zero thermal coefficient of refractive index (i.e., the effect of thermo-focusing is absent) [6]. This is especially typical for the glasses that contain cation modifiers with large ion radius and small charge. The aforesaid information leads to conclusion that boron glasses have a limited application (when compare to industrial and commercial glasses), attracting instead a permanent fundamental interest.

This paper is devoted to the studies of spectroscopy properties of $4SrO•7B_2O_3:RE^{3+}$ ($RE = Eu^{3+}, Pr^{3+}, Nd^{3+}$) glasses, which continue the cycle of works on the investigation of crystallization system $SrO - B_2O_3$ and the optical properties of new single crystals $4SrO• 7B_2O_3:RE^{3+}$ [7,8].

2. Experiment

The following samples were used for the experiments:

1. $4SrO•7B_2O_3:Pr^{3+}$ (ι=7 mm, the doping concentration $C_1Pr^{3+} = 1.7\times10^{20}$ cm^{-3}, $N_2Pr^{3+} = 3.5\times10^{20}$ cm^{-3});
2. $4SrO•7B_2O_3: Nd^{3+}$ (ι=2 mm, $CNd^{3+} = 1.04\times10^{21}$ cm^{-3});
3. $4SrO•7B_2O_3: Eu^{3+}$ (ι=7 mm, $CEu^{3+} = 1.7\times10^{20}$ cm^{-3}).

The glass samples for the investigation have been prepared in the following way. The boron and strontium oxides according to the ratio 4:7 have been melted in the resistance furnace at 1030~1050°C in the platinum cruci-

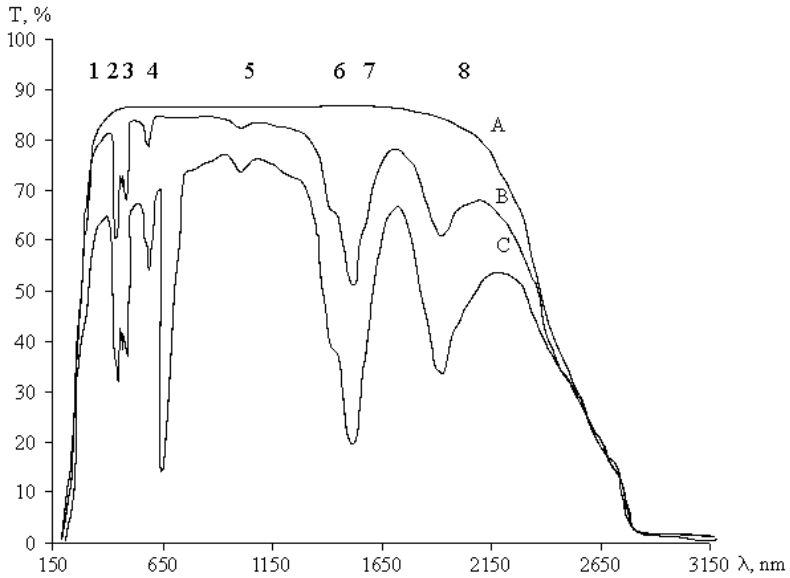

Fig. 1. The transmission spectra of $4SrO{\bullet}7B_2O_3:Pr^{3+}$ glasses: curve A – the glass sample $4SrO{\bullet}7B_2O_3$, curve B – the glass sample $4SrO{\bullet}7B_2O_3:Pr^{3+}$ ($C_1Pr^{3+} = 1.7\times10^{20}$ cm^{-3}), curve C – the glass sample $4SrO{\bullet}7B_2O_3 : Pr^{3+}$ ($N_2Pr^{3+} = 3.5\times10^{20}$ cm^{-3}).

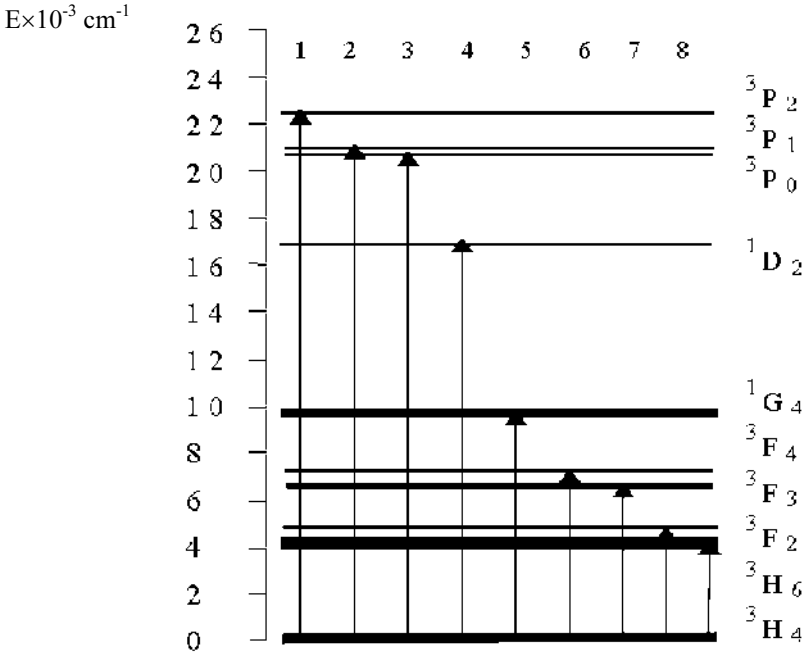

Fig. 2. Energy diagram of Pr^{3+} ion.

ble. The melt was mixed by platinum stirrer, activated by the doping oxides, and then formed and homogenized during 3 hours. After the homogenization, the melt was subjected to ceramic mould and glassed. The sample has been annealed during 4 hour at the temperatures from 800° C to 600° C to decrease the temperature strain. Then the ingot has been processed mechanically in order to obtain the polished samples.

The transmission and luminescence spectra have been investigated under the pumping into the most intensive absorption lines. For the investigation of transmission spectra of $4SrO{\bullet}7B_2O_3:Pr^{3+}$ glass, the spectrophotometers Shimadzu UV3101 PC and DFS–456 have been used. The spectrophotometer DFS–456 with photomultiplier as a photodetector have been

used for the investigation of absorption spectra of $4SrO•7B_2O_3:Eu^{3+}$. The high-brightness light-emitting diode (LED) EP2036-150B (Paralight Corp.) has served as a pump source. The luminescence of $4SrO•7B_2O_3:Pr^{3+}$ has been studied at the room temperature with the spectrophotometer MDR 23 and the Ar^+ laser.

3. Results

3.1 Spectroscopy of $4SrO•7B_2O_3:Pr^{3+}$

The transmission spectra of $4SrO•7B_2O_3:Pr^{3+}$ are presented in Fig. 1. The spectrum of $4SrO•7B_2O_3:Pr^{3+}$ glass sample consists of 8 inhomogeneous non-structured broad absorption bands. All the bands belong to earlier known electronic transitions within Pr^{3+} ions. The energy diagram embracing all the transitions manifesting themselves in the absorption is represented in Fig. 2. Table 1 presents the relevant electronic transitions, together with the wavelengths of the absorbed radiation. The lines $^3H_4 \rightarrow {}^3F_2$ and $^3H_4 \rightarrow {}^3F_{3+4}$ have the largest intensities. The absorption lines $^3H_4 \rightarrow {}^3P_2$, $^3H_4 \rightarrow {}^3P_1$, $^3H_4 \rightarrow {}^3P_0$ are also very intense. The spectral location of the absorption band λ_{max}=482 nm ($^3H_4 \rightarrow {}^3P_0$) fits well the wavelength of Ar^+ laser radiation and so may be used for efficient luminescence pump.

Table 1. Electronic transitions in $4SrO•7B_2O_3$ glass sample doped with Pr^{3+}.

	Wavelength 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	$^3H_4 \rightarrow {}^3H_6$

We have further studied the luminescence in the $4SrO•7B_2O_3:Pr^{3+}$ glass sample pumped with the Ar^+ laser into the absorption line corresponding to the transition $^3P_0 \rightarrow {}^3H_4$ and used MDR 23 as a monochromator. The luminescence spectrum of $4SrO•7B_2O_3:Pr^{3+}$ sample is presented in Fig. 3.

The registered spectrum consists of three non-structured inhomogeneous broad spectral bands. The largest intensity is characteristic of the line located at λ_{max} = 606 nm. The contour of this line has a complex character, with the three

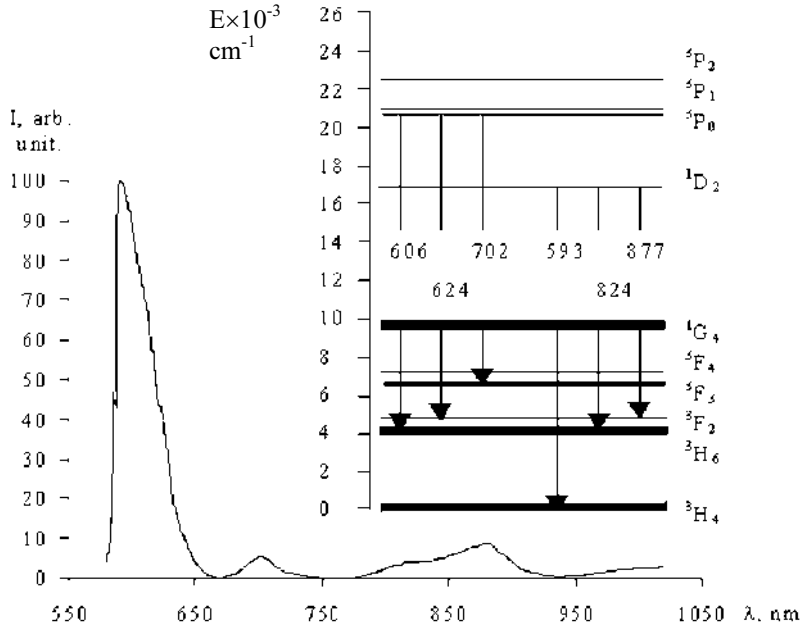

Fig. 3. Luminescence spectrum of $4SrO • 7B_2O_3:Pr^{3+}$ glass sample.

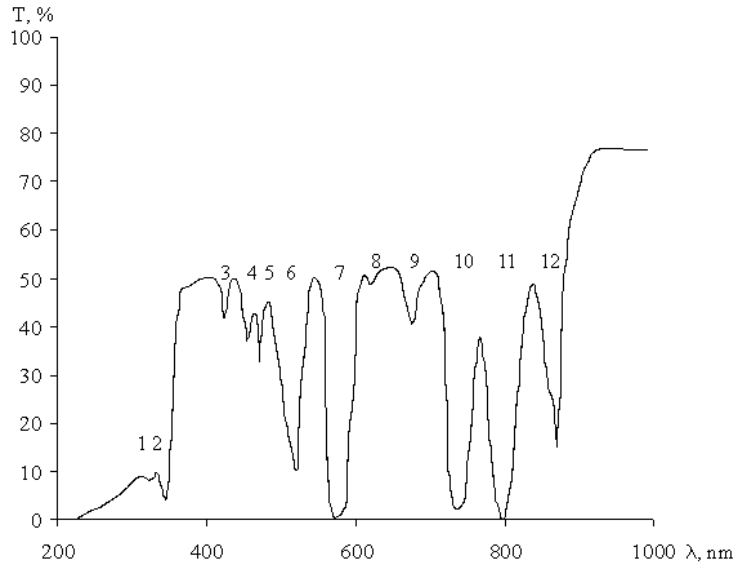

Fig. 4. Transmission spectrum of $4SrO \cdot 7B_2O_3:Nd^{3+}$ glass in the range of 200 ~1000 nm.

Fig. 5. Transmission spectrum of $4SrO \cdot 7B_2O_3:Nd^{3+}$ in the range of 900~2700 nm.

extremum points. This could be explained by overlapping of the three luminescence lines corresponding to the transitions $^1D_2 \rightarrow {}^3H_4$ (λ_{max}= 595 nm), $^3P_0 \rightarrow {}^3H_6$ (λ_{max}= 606 nm) and $^3P_0 \rightarrow {}^3F_2$ (λ_{max}= 624 nm). Another less intensive transitions $^3P_0 \rightarrow {}^3F_3$ (λ= 702 nm), $^1D_2 \rightarrow {}^3H_6$ (λ= 824 nm) and $^1D_2 \rightarrow {}^3F_2$ (λ= 877 nm) have been additionally detected.

3.2. Spectroscopy of $4SrO \cdot 7B_2O_3:Nd^{3+}$

In order to study the transmission spectra of $4SrO \cdot 7B_2O_3:Nd^{3+}$ glass sample, the spectrophotometer Shimadzu UV3101-PC has been utilized. The transmission spectra of $4SrO \cdot 7B_2O_3:Nd^{3+}$ in the range of 200~2600 nm are presented in Fig. 4,5. The short-wavelength absorption edge in the $4SrO \cdot 7B_2O_3:Nd^{3+}$ glass sample corresponds to 200 nm. 14 absorption bands, which correspond to the known electronic transitions of Nd^{3+} ions, have been detected. The most intensive ones are $^4I_{9/2} \rightarrow {}^2K_{13/2} + {}^2G_{7/2} + {}^4G_{9/2}$, $^4I_{9/2} \rightarrow {}^2G_{7/2} + {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^4S_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2} + {}^2H_{9/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$. Besides, the absorption line $^4I_{9/2} \rightarrow {}^2K_{13/2} + {}^2G_{7/2} + {}^4G_{9/2}$ is of some interest for laser pumping of luminescence (e.g., with the second harmonics of YAG: Nd^{3+}). It is necessary to note the absence of absorption at the wavelength of the most frequently used Nd^{3+} laser

Table 2. Electronic transitions of Nd^{3+} - ions in $4SrO•7B_2O_3$: Nd^{3+} sample

№	Wavelength λ, nm	Transition	№	Wavelength λ, nm	Transition
1	345	$^4I_{9/2} \rightarrow {}^4D_{1/2} + {}^4D_{3/2} + {}^4D_{5/2}$	8	620	$^4I_{9/2} \rightarrow {}^2H_{11/2}$
2	377	$^4I_{9/2} \rightarrow {}^2P_{3/2}$	9	676	$^4I_{9/2} \rightarrow {}^4F_{9/2}$
3	425	$^4I_{9/2} \rightarrow {}^2P_{1/2} + {}^2D_{5/2}$	10	736	$^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^4S_{3/2}$
4	458	$^4I_{9/2} \rightarrow {}^4G_{9/2} + {}^4G_{11/2}$	11	794	$^4I_{9/2} \rightarrow {}^4F_{5/2} + {}^2H_{9/2}$
5	471	$^4I_{9/2} \rightarrow {}^2K_{15/2} + {}^2D_{3/2}$	12	871	$^4I_{9/2} \rightarrow {}^4F_{3/2}$
6	520	$^4I_{9/2} \rightarrow {}^2K_{13/2} + {}^2G_{7/2} + {}^4G_{9/2}$	13	1554	$^4I_{9/2} \rightarrow {}^4I_{15/2}$
7	574	$^4I_{9/2} \rightarrow {}^2G_{7/2} + {}^4G_{5/2}$	14	2408	$^4I_{9/2} \rightarrow {}^4I_{13/2}$

channel $^4F_{5/2} \rightarrow {}^4I_{11/2}$ (λ = 1064 nm). It is a favourable difference of $4SrO•7B_2O_3:Nd^{3+}$ from the neodymium-doped silicate laser glasses. The energy diagram involving all the detected electronic transitions is presented in Fig. 6. Table 2 gives the appropriate electronic transitions and the maximum wavelengths of the absorbed radiation.

3.3. Spectroscopy of $4SrO • 7B_2O_3:Eu^{3+}$

The transmission spectra of $4SrO•7B_2O_3:Eu^{3+}$ glass sample have been studied with the DFS 456 spectrophotometer in the spectral range 300 - 1100 nm. The relevant results are represented in Fig. 7.

Three absorption lines $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_0$ corresponding to the known electronic transitions of Eu^{3+} ions have been detected. The absorption band $^7F_0 \rightarrow {}^5D_0$ is less intense, though it matches fairly well the second harmonics of YAG : Nd^{3+} radiation and may be therefore used for the efficient pumping of $4SrO•7B_2O_3:Eu^{3+}$ luminescence. The luminescence spectra of $4SrO•7B_2O_3:Eu^{3+}$ glass sample have been measured with the DFS-456 spectrophotometer. The high-brightness EP2036-150B (Paralight Corp.) LED, whose radiation matches well the absorption line $^7F_0 \rightarrow {}^5D_0$ (λ_{max}=485 nm), has been used as a pumping source. The

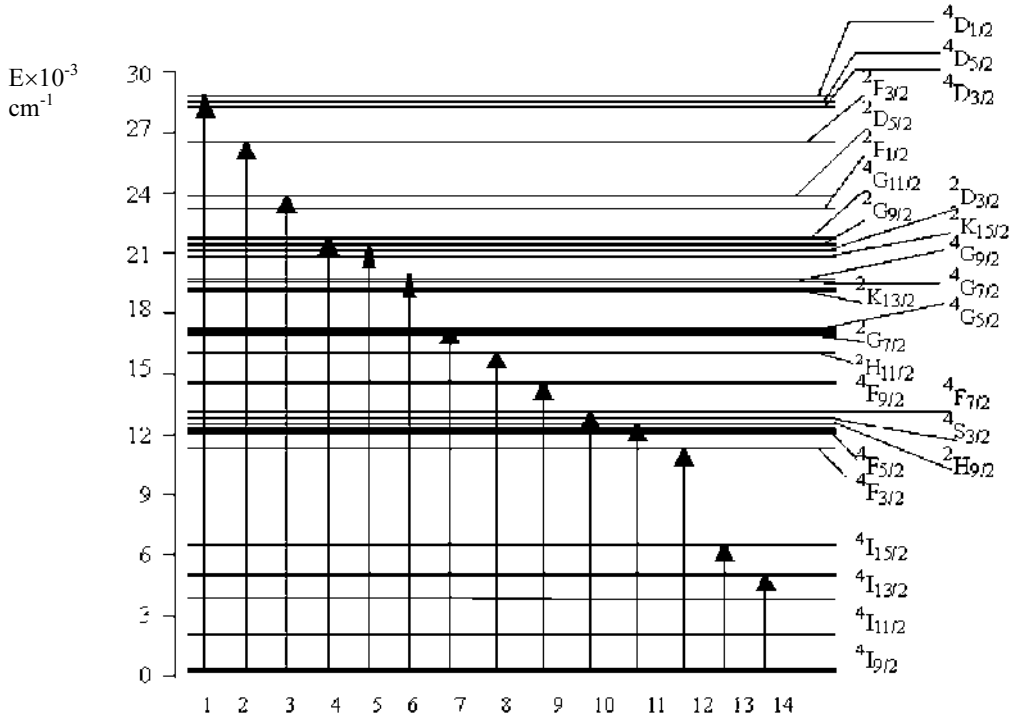

Fig. 6. Energy diagram of Nd^{3+} ions in $4SrO•7B_2O_3$ glass matrix.

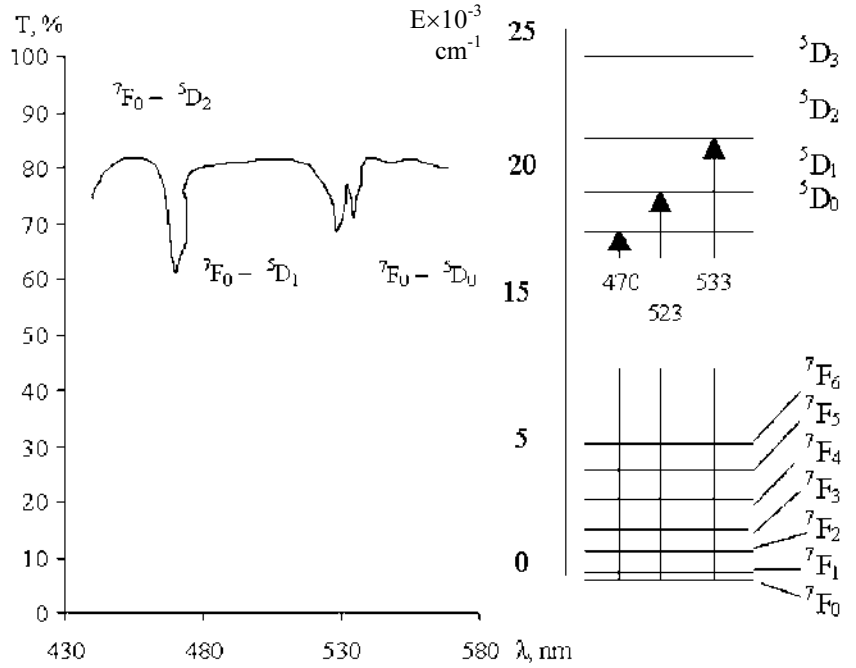

Fig. 7. Transmission spectrum of $4SrO•7B_2O_3:Eu^{3+}$ in the spectral range of 430~570 nm and energy diagram of Eu^{3+} ions with the electronic transitions revealed in the transmission.

luminescence spectrum of $4SrO•7B_2O_3:Pr^{3+}$ glass sample is presented in Fig. 8.

Five inhomogeneous non-structured broad absorption bands have been obtained: $^5D_0 \rightarrow {}^7F_0$ (λ_{max}= 586 nm), $^5D_0 \rightarrow {}^7F_1$ (λ_{max}= 600 nm), $^5D_0 \rightarrow {}^7F_2$ (λ_{max}= 620 nm), $^5D_0 \rightarrow {}^7F_3$ (λ_{max}= 658 nm) and $^5D_0 \rightarrow {}^7F_4$ (λ_{max}= 705 nm).

Conclusion

The paper has been devoted to studies of the spectroscopy properties of $4SrO•7B_2O_3:RE^{3+}$ (RE = Eu^{3+}, Pr^{3+}, Nd^{3+}) glasses. The absorption and luminescence spectra have been investigated, using the pumping into the most intensive absorption lines.

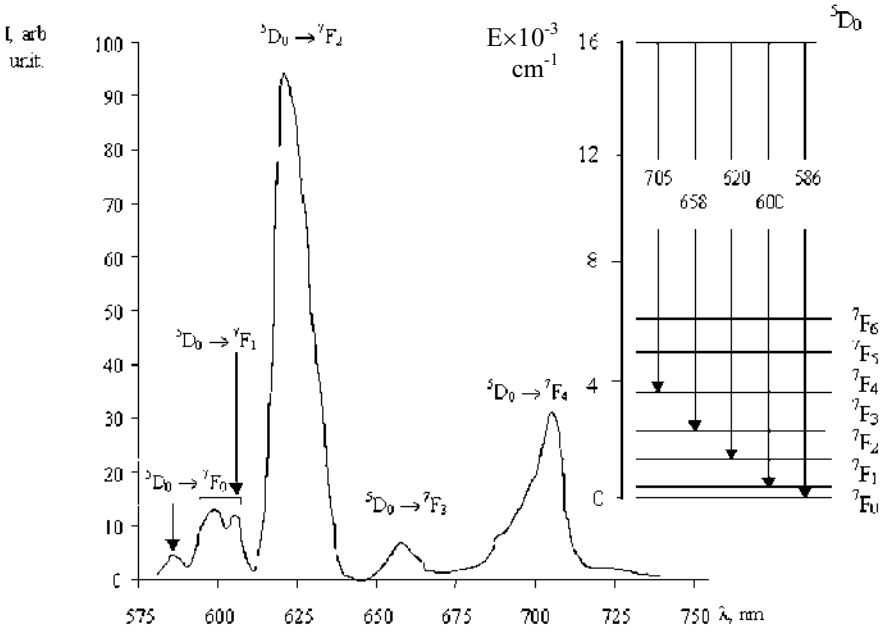

Fig. 8. Luminescence spectrum of $4SrO•7B_2O_3:Eu^{3+}$ glass sample.

The transmission spectrum of $4SrO•7B_2O_3:Pr^{3+}$ consists of 8 inhomogeneous non-structured broad absorption bands. The lines $^3H_4 \rightarrow {}^3F_2$ and $^3H_4 \rightarrow {}^3F_{3+4}$ are of the highest intensity. The band λ_{max}=482 nm ($^3H_4 \rightarrow {}^3P_0$) matches well the Ar^+ laser radiation and it has been used for the luminescence pump. The luminescence spectrum of $4SrO•7B_2O_3:Pr^{3+}$ consists of three non-structured inhomogeneous broad spectral bands: $^1D_2 \rightarrow {}^3H_4$ (λ_{max} = 595 nm), $^3P_0 \rightarrow {}^3H_6$ (λ= 606 nm), $^3P_0 \rightarrow {}^3F_2$ (λ= 624 nm), $^3P_0 \rightarrow {}^3F_3$ (λ = 702 nm), $^1D_2 \rightarrow {}^3H_6$ (λ = 824 nm) and $^1D_2 \rightarrow {}^3F_2$ (λ = 877 nm). The most intensive line correspond to λ = 606 nm.

The transmission spectrum of $4SrO•7B_2O_3:Nd^{3+}$ in the spectral range of 200 – 2600 nm has been investigated. 14 absorption bands of Nd^{3+} ions have been detected. The most intensive are $^4I_{9/2} \rightarrow {}^2K_{13/2} + {}^2G_{7/2} + {}^4G_{9/2}$, $^4I_{9/2} \rightarrow {}^2G_{7/2} + {}^4G_{5/2}$, $^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^4S_{3/2}$, $^4I_{9/2} \rightarrow {}^4F_{5/2} + {}^2H_{9/2}$ and $^4I_{9/2} \rightarrow {}^4F_{3/2}$. The absorption line $^4I_{9/2} \rightarrow {}^2K_{13/2} + {}^2G_{7/2} + {}^4G_{9/2}$ almost coincides with the YAG: Nd^{3+} second harmonics.

The transmission spectrum of $4SrO•7B_2O_3:Eu^{3+}$ glass sample has been studied in the spectral range of 300 – 1100 nm. Three absorption lines $^7F_0 \rightarrow {}^5D_2$, $^7F_0 \rightarrow {}^5D_1$ and $^7F_0 \rightarrow {}^5D_0$, which correspond to the known electronic transitions in Eu^{3+} ions, have been observed. The absorption band $^7F_0 \rightarrow {}^5D_0$ matches the second harmonics of the YAG:Nd^{3+} radiation. The luminescence spectrum of $4SrO•7B_2O_3:Eu^{3+}$ glass sample has been investigated with LED pumping. Five inhomogeneous non-structured broad absorption bands $^5D_0 \rightarrow {}^7F_0$ (λ_{max}= 586 nm), $^5D_0 \rightarrow {}^7F_1$ (λ_{max}= = 600 nm), $^5D_0 \rightarrow {}^7F_2$ (λ_{max}= 620 nm), $^5D_0 \rightarrow {}^7F_3$ (λ_{max}= 658 nm) and $^5D_0 \rightarrow {}^7F_4$ (λ_{max}= 705 nm) have been obtained.

References

1. Snitzer E. Phys. Rev. Lett. **7** (1961), 444.
2. A.A. Mak, D.S. Prileshaev, V.A. Serebrjakov. Opt. Spect. **33** (1972) 689. (in Russiam).
3. N.B. Brachkovskaja, A.A. Grubin, S.G. Lunter. Quant. Electron **3** (1976) 998.(in Russiam).
4. M. Naftaly et al. J. Lumin. **91** (2000) 133.
5. C.J.da Silva, M.T. de Araujo, E.A.Gouveia, Appl. Phys. B **70** (2000) 185.
6. L.A. Maks, L.N Soms, V.A. Fromsel. Lasers on the Base of Neodymium Glass, Nauka, 1990 (In Russian).
7. D.P. Kudrjavtcev, Yu.S. Oseledchik, A.L. Prosvirnin, N.V.Svitanko Ukr. J. Phys. Opt., **2** (2002) 155.
8. D.P. Kudrjavtcev, Yu.S. Oseledchik, A.L. Prosvirnin, N.V.Svitanko Ukr. J. Phys. **48** (2003) 11.(In Russian)