

Synthesis and optical spectroscopy of the Eu- and Pr-doped glasses with SrO–2B₂O₃ composition

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A series of Eu- and Pr-doped glasses with SrO–2B₂O₃ (or SrB₄O₇) composition were obtained and their spectroscopic properties were investigated. The SrB₄O₇ polycrystalline compounds were synthesised at $T = 1300$ K using high purity strontium carbonate (SrCO₃) and boric acid (H₃BO₃). The Eu and Pr impurities were added to SrB₄O₇ compounds as Eu₂O₃ (amount: 0.167 at.%) and Pr₂O₃ (amounts: 0.05 and 0.25 at.%) oxides. The glass samples of high chemical purity and optical quality were obtained from corresponding polycrystalline compounds in the air atmosphere in platinum crucibles according to standard glass technology. Optical absorption, luminescence excitation and emission spectra of the Eu- and Pr-doped glasses with SrO–2B₂O₃ composition were investigated in the spectral range 300–800 nm at temperatures of 293 and 85 K. On the basis of optical spectra obtained and electron paramagnetic resonance (EPR) data analysis it is shown that Eu and Pr impurities are incorporated into the SrO–2B₂O₃ glass network as Eu³⁺ ($4f^6$, 7F_0) and Pr³⁺ ($4f^2$, 3H_4) ions, exclusively. All the observed transitions of the Eu³⁺ and Pr³⁺ centres in absorption and luminescence spectra were identified. The luminescence kinetics of Eu³⁺ and Pr³⁺ centres were investigated and analysed. The decay constants for main emission transitions in all samples investigated were obtained at room temperature. Peculiarities of incorporating the Eu³⁺ and Pr³⁺ activator ions in the glass with SrO–2B₂O₃ composition and their optical spectra are discussed in comparison with rare-earth doped polycrystalline compounds and single crystals with the same (SrB₄O₇) composition and other borate glasses.

Keywords: borate glasses and crystals, Eu³⁺ centre, Pr³⁺ centre, optical absorption, luminescence, decay kinetics, local structure.

1. Introduction

The strontium tetraborate crystalline compounds (SrB_4O_7) are perspective nonlinear optical and luminescent materials due to their excellent mechanical and optical properties, such as high hardness, non-hygroscopy, high SHG (second harmonic generation) coefficient, high transparency in a wide spectral range (135–3200 nm) and high optical damage threshold [1–3]. The polycrystalline SrB_4O_7 compounds can be obtained by solid state reaction synthesis and corresponding single crystals of high optical quality can be obtained using Kyropoulos and Czochralski methods [1, 2]. Practically, all borate compounds, including tetraborates, can be obtained in both crystalline and glassy forms. From technological point of view the glassy (or vitreous) compounds are more perspective in comparison with corresponding single crystals, because glass synthesis technology is relatively cheap. But spectroscopic studies of the electron and local structure of luminescence centres in oxide glasses are more complicated and require adequate spectroscopic and structural data for their crystalline analogies [4, 5].

During the last decade intensive luminescence investigations of the rare-earth doped crystalline strontium tetraborates, obtained by solid-state synthesis, Czochralski, and Kyropoulos methods have been carried out [6–18]. The results prove the materials under study to be perspective for use as commercial phosphors. In particular, optical and luminescence properties of the Eu- and Pr-doped SrB_4O_7 crystalline compounds were investigated in [6–14] and [15], respectively. Nonlinear optical properties of the SrB_4O_7 single crystals were investigated in [14, 19, 20]. The SrB_4O_7 crystalline and glassy compounds also exhibit thermoluminescence (TL) and were investigated by different authors [21–24] as perspective materials for solid state dosimetry.

For the first time the crystal structure of SrB_4O_7 was reported in [25] and described in detail in [26]. The SrB_4O_7 crystals belong to the rhombic system (space group $Pnm2_1$) and their lattice is formed by fourfold-coordinated boron–oxygen complexes (tetrahedrons) [25, 26]. The Sr atoms are stabilising in the SrB_4O_7 crystal lattice in sites with coordination number to oxygen $N = 9$. The presence of BO_4 tetrahedrons only in the SrB_4O_7 lattice (while in other borate compounds, for example, in the $\text{Li}_2\text{B}_4\text{O}_7$ crystal, the polyanions are formed by both boron–oxygen tetrahedrons and boron–oxygen triangles [27]) provides the stabilisation of rare-earth ions, *e.g.*, Eu, Sm, Yb, Pr, *etc.*, in divalent state even if the compound is synthesised in the air [6, 7, 9–14]. This allows obtaining broad emission and luminescence excitation bands of divalent ions caused by interconfiguration $f-d$ transitions in the UV–VIS spectral region. It is generally acknowledged that rare-earth ions are incorporated in divalent state into the lattice of oxide compounds synthesised in the vacuum or in the inert atmosphere. From the analysis of reference data [6–18] we can conclude that the rare-earth doping of SrB_4O_7 crystals obtained in the air leads to incorporation of rare-earth ions into their lattice, generally, in a divalent state. Only several papers [8–12] report luminescence properties of the Eu^{3+} ions in $\text{SrB}_4\text{O}_7:\text{Eu}$ crystalline

compounds, obtained in the air. The mechanism of incorporation of divalent rare-earth ions into the strontium borate polycrystalline compounds (SrB_4O_7 , $\text{SrB}_6\text{O}_{10}$, *etc.*), obtained by solid-state synthesis in the air was discussed in [28–30]. Luminescence properties of the Pr-doped SrB_4O_7 crystalline compounds were investigated in [15]. In this paper, it is shown that the Pr impurities are incorporated into the SrB_4O_7 lattice as Pr^{2+} ions. Emission lines at 216, 237, 225, 253, 271, 340, 396, and 400 nm in [15] were assigned to the Pr^{2+} transitions from $^1\text{S}_0$ state to $^3\text{H}_4$, $^3\text{H}_6$, $^3\text{F}_2$, $^3\text{F}_4$, $^1\text{G}_4$, $^1\text{D}_2$, $^1\text{I}_6$, and $^3\text{P}_{2,1,0}$ states, respectively.

For the first time the results of optical and EPR investigations of Eu- and Pr-doped glasses with $\text{SrO}-2\text{B}_2\text{O}_3$ (or SrB_4O_7) composition were reported by us in [31]. But up to now, optical spectra and peculiarities of incorporation of Eu and Pr impurities in the glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition have not been systematically investigated nor published. This work presents synthesis peculiarities and systematic investigations of optical and luminescence properties of the $\text{SrO}-2\text{B}_2\text{O}_3$ glasses doped with Eu and Pr. Local symmetry and structure of the luminescence centres are discussed. The results are compared to the ones obtained for corresponding crystalline compounds.

2. Experimental details

2.1. Synthesis and characterisation of the SrB_4O_7 polycrystalline compounds and glasses

The SrB_4O_7 polycrystalline compounds were obtained by solid state reaction synthesis at $T = 700-900\text{ }^\circ\text{C}$ in the air, using a resistance furnace. The high purity strontium carbonate (SrCO_3) and boric acid (H_3BO_3) in the proportion corresponding to SrB_4O_7 composition were used as starting materials. For the purpose of compensating evaporation during the solid state reaction an extra charge of H_3BO_3 in amount of 2 mol% was added. The Eu and Pr impurities were added to the starting composition as Eu_2O_3 (amount: 0.167 at.%) and Pr_2O_3 (amounts: 0.05 and 0.25 at.%) compounds. All chemicals used for sample synthesis are characterised by special purity (99.5 wt%) and were purchased in *Krasnyj khimik* (Saint-Petersburg, Russia). The synthesis process of SrB_4O_7 polycrystalline compounds included the following technological operations: mixing of the starting materials, slow heating (2–3 h) to 200–250 $^\circ\text{C}$, heating (3–4 h) up to 850–900 $^\circ\text{C}$, keeping at this temperature for 2–3 h and cooling together with the furnace. Chemical composition of the compounds obtained was controlled by the X-ray phase analysis.

The Eu- and Pr-doped glasses with $\text{SrO}-2\text{B}_2\text{O}_3$ composition of high chemical purity and optical quality were obtained in the air atmosphere by melting the pre-synthesised $\text{SrB}_4\text{O}_7\text{:Eu}$ and $\text{SrB}_4\text{O}_7\text{:Pr}$ compounds in platinum crucibles according to technology developed by the authors. Synthesised polycrystalline compounds were heated up to melting temperature 1030–1050 $^\circ\text{C}$, mixed by platinum stirrer and held (2 h) at melting temperature to achieve the complete homogenisation and remove any gas bubbles and other centres of crystallisation, then poured into a corundum cylindrical form (20 mm in diameter, 20 mm in length) and fast cooled.

Finally, glasses were annealed at 400 °C during 3–4 h. The obtained glasses were almost uncoloured and characterised by high optical quality and chemical purity. Samples for optical measurements were cut and polished to obtain an approximate size of $5 \times 4 \times 2 \text{ mm}^3$.

2.2. Experimental methods and equipment

The optical absorption spectra of the Eu- and Pr-doped glasses were registered at room temperature on a Specord M-40 (Carl Zeiss Jena) spectrophotometer.

The EPR spectra of non-controlled and rare-earth paramagnetic impurities in the glasses obtained were registered at room and liquid helium temperatures using modernised commercial X-band spectrometer of SE/X-2544 type (RADIOPAN, Poznań, Poland), operating in the high-frequency (100 kHz) modulation mode of magnetic field.

Photoluminescence (excitation and emission) spectra were obtained at temperatures of 300 and 85 K upon frontal excitation and observation of the sample emission using equipment built in the Condensed Matter Spectroscopy Division (Institute of Experimental Physics, Gdańsk University, Poland). The emission spectra were corrected for spectral sensitivity of the equipment. A Hanovia xenon lamp (power: 1000 W) was used as excitation source. The wavelengths required for excitation and observation were selected using an SPM-2 prismatic monochromator (Carl Zeiss Jena) with stepping motors driven by a computer and photomultipliers used in the detection circuit and working in analog or photon counter regime. In the latter case, they sent data to computer *via* a digital boxcar system. A Hamamatsu R 928 photomultiplier was used as a detector.

The luminescence decays were measured using equipment described in detail in [32]. As excitation source the EKSPLA (Vilnius, Lithuania) laser system was used, which consisted of Nd:YAG pulsed laser (model PL 2143A/SS) and parametric optical generator (model PG 401/SH). The detection part consisted of the 2501S spectrograph (Bruker Optics, USA) and the C4334-01 streak camera (Hamamatsu, Japan).

3. Results and discussion

3.1. The Eu^{3+} centres in glasses with $\text{SrO}-2\text{B}_2\text{O}_3$ composition

The Eu impurity in the oxide compounds can be revealed as Eu^{3+} ($4f^6$, 7F_0) and Eu^{2+} ($4f^7$, $^8S_{7/2}$) ions with characteristic optical absorption and luminescence spectra. The Eu^{2+} paramagnetic ions can also be registered by EPR technique. In the Eu-doped glasses with $\text{SrO}-2\text{B}_2\text{O}_3$ composition the Eu^{2+} EPR spectrum was not observed either at room or liquid nitrogen temperatures. Thus, the Eu impurity is incorporated into the $\text{SrO}-2\text{B}_2\text{O}_3$ glass network as Eu^{3+} ions.

In all $\text{SrO}-2\text{B}_2\text{O}_3$ glass samples doped with Eu there were observed optical absorption and luminescence spectra, characteristic of Eu^{3+} ions, caused by $f-f$ transitions. The optical absorption spectrum of the Eu-doped $\text{SrO}-2\text{B}_2\text{O}_3$ glass registered in the spectral range 230–800 nm at room temperature consists of several

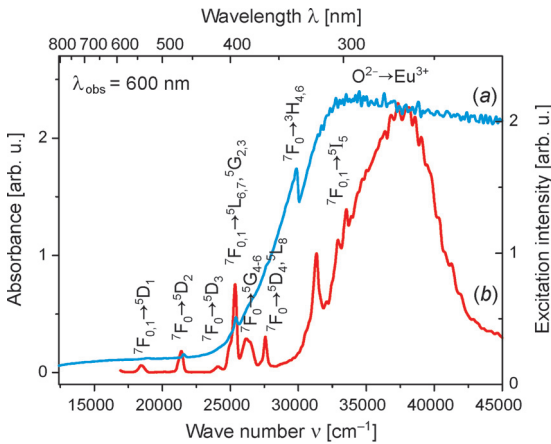


Fig. 1. Optical absorption (a) and luminescence excitation (b) spectra of the Eu-doped (Eu_2O_3 content: 0.167 at.%) glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition, registered at room temperature.

characteristic weak absorption bands (Fig. 1, spectrum a). In accordance with the Eu^{3+} energy level diagram all observed absorption bands were assigned to the following transitions and groups of transitions: ${}^7F_{0,1} \rightarrow {}^5I_5$, ${}^7F_0 \rightarrow {}^3H_{4,6}$, ${}^7F_0 \rightarrow {}^5D_4$, 5L_8 , ${}^7F_0 \rightarrow {}^5G_{4-6}$, ${}^7F_{0,1} \rightarrow {}^5L_{6,7}$, ${}^5G_{2,3}$, ${}^7F_0 \rightarrow {}^5D_3$, ${}^7F_0 \rightarrow {}^5D_2$, ${}^7F_{0,1} \rightarrow {}^5D_1$, ${}^7F_{0,1} \rightarrow {}^5D_0$ (Fig. 1, spectrum a). The intense broad absorption band with pronounced maximum near 300 nm was assigned to the $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ charge transfer band (Fig. 1, spectrum a). One can notice that some absorption bands are only weakly revealed in the absorption spectrum (Fig. 1, spectrum a), but are easily observed in the luminescence excitation spectrum (Fig. 1, spectrum b). The luminescence excitation bands show good correlation with corresponding absorption bands (Fig. 1, spectra a and b). In the optical absorption spectrum of Eu-doped $\text{SrO}-2\text{B}_2\text{O}_3$ glasses, no bands related to Eu^{2+} ions were observed, which confirms incorporation of Eu impurity into the glass as Eu^{3+} ions, exclusively.

The luminescence spectra of Eu^{3+} centres (Fig. 2) were registered at temperatures of 293 and 85 K under excitation with $\lambda_{\text{exc}} = 395$ nm that corresponds to the ${}^7F_{0,1} \rightarrow {}^5L_{6,7}$, ${}^5G_{2,3}$ band in absorption and luminescence excitation spectra (Fig. 1, spectra a and b). In the luminescence spectrum at $T = 293$ K five emission bands, characteristic of Eu^{3+} ions, in the spectral range 570–730 nm are observed. These bands belong to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions and are identified in Fig. 2. The absence of emission from higher 5D_J levels can be related to multiphonon or cross-relaxation processes, caused by a relatively high concentration of Eu^{3+} centres in the glass network.

The linewidth and resolution of the Eu^{3+} absorption and luminescence bands (Figs. 1 and 2) remained practically unchanged as the temperature decreased to 85 K. This is an evidence of the inhomogeneous broadening of spectral lines, caused by disorder of the local environment around Eu^{3+} centres. The luminescence excitation and emission spectra of Eu^{3+} ions in the SrB_4O_7 powdered polycrystals (Figs. 3a

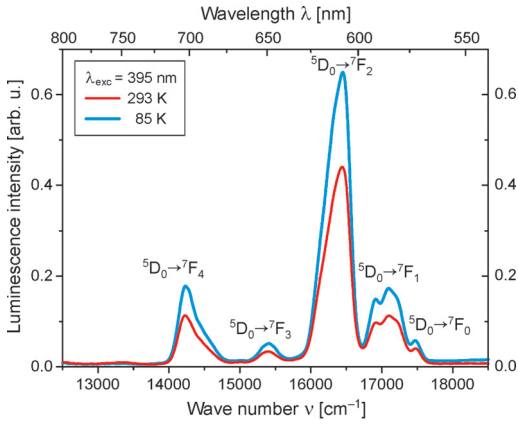
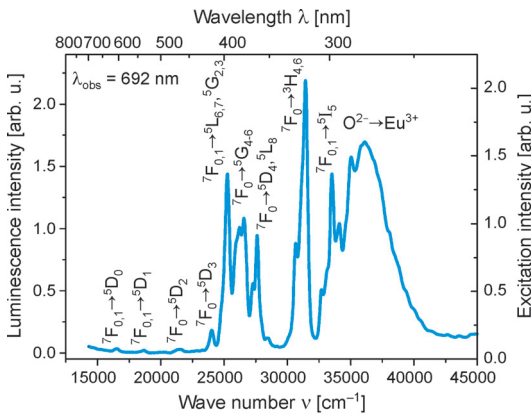
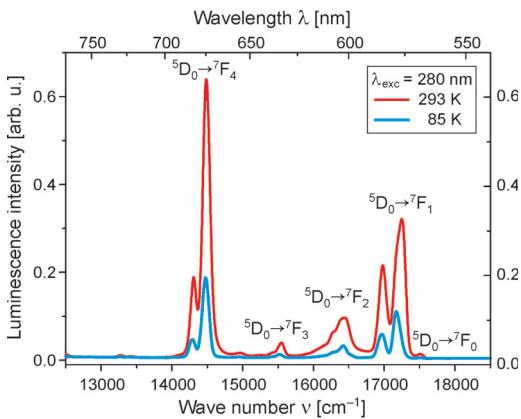


Fig. 2. Luminescence spectra of Eu^{3+} centres in the Eu-doped (Eu_2O_3 content: 0.167 at.%) glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition, registered under excitation with $\lambda_{\text{exc}} = 395$ nm at temperatures of 293 and 85 K.



a



b

Fig. 3. The luminescence excitation ($T = 293$ K, $\lambda_{\text{obs}} = 692$ nm) (a) and emission ($T = 293$ K and $T = 85$ K, $\lambda_{\text{exc}} = 280$ nm) (b) spectra of the Eu^{3+} centres in the $\text{SrB}_4\text{O}_7:\text{Eu}$ (Eu_2O_3 content: 0.167 at.%) polycrystalline powder.

and **3b**, respectively) are characterised by narrower and better resolved bands in comparison with the corresponding spectra in the glasses with SrO–2B₂O₃ composition, registered under the same experimental conditions (Figs. 1 and 2). The number and relative intensities of the Eu³⁺ emission lines (⁵D₀ → ⁷F_J transitions) are defined by the number of crystallographically non-equivalent centres and their local symmetry in the crystal lattice or glass network [33]. Because of the fact that the most intense emission band of the Eu³⁺ luminescence spectra in the SrO–2B₂O₃ glass corresponds to the ⁵D₀ → ⁷F₂ structurally-sensitive electric dipole transition (Fig. 2), one can suppose that the Eu³⁺ centres occupy structural sites without inversion symmetry (non-centrosymmetric sites) [33]. In the luminescence spectra of SrB₄O₇:Eu³⁺ polycrystalline compounds the Eu³⁺ centres are localised in the sites with inversion symmetry (centrosymmetric sites), because the most intense bands correspond to the ⁵D₀ → ⁷F₄ electric and ⁵D₀ → ⁷F₁ magnetic dipole transitions (Fig. 3b). Based on the results obtained and the SrB₄O₇ crystal structure analysis we can suppose that the Eu³⁺ ions occupy Sr²⁺ sites in the crystal and glass with the same composition. In the real glass network the coordination number to oxygen (*N*) is smaller than that in the corresponding real crystal one (for ideal SrB₄O₇ crystal *N* = 9) [26, 27], because it is characteristic of the glass structure in which the number of oxygen vacancies is larger. Based on this result, we can explain the localisation of Eu³⁺ ions in the centrosymmetric Sr-sites of the SrB₄O₇ crystal lattice and non-centrosymmetric Sr-sites in the corresponding glass network.

The luminescence decay curves of Eu³⁺ centres for the ⁵D₀ → ⁷F₂ emission transition registered under excitation at λ_{exc} = 280 nm and *T* = 300 K in the narrow and wide (whole) emission band ranges are presented in Figs. 4a and 4b, respectively. Decay curves for glass in the Δλ = 607–627 nm (Fig. 4a) and whole band (Fig. 4b) ranges were described in the framework of a single exponential model with close lifetime values: τ₁ = 1.82 ms and τ₁ = 1.97 ms, respectively. At the same time, decay curves for the polycrystalline compound in the Δλ = 586–596 nm (Fig. 4a) and whole band (Fig. 4b) ranges were satisfactorily fitted with double exponential decay with lifetimes τ₁ = 1.76 ms, τ₂ = 0.48 ms and τ₁ = 2.02 ms, τ₂ = 0.56 ms, respectively. The τ₁ values for glasses and polycrystalline samples are very similar and can be assigned to the same centres, whereas the τ₂ values are considerably (approximately 4 times) lower than those of τ₁. The longer (τ₁) values are characteristic of Eu³⁺ luminescence centres in other oxide glasses and crystals including borate compounds and belong to isolated Eu³⁺ centres in glassy and polycrystalline samples. Because the observed optical spectra show only one type of Eu³⁺ centres in the SrB₄O₇:Eu glass network, according to [34, 35] we can suppose that the centres with shorter lifetime values belong to the Eu³⁺–Eu³⁺ exchange-coupled pairs or small exchange-coupled Eu³⁺ clusters.

The results presented above correlate with spectroscopic data for SrB₄O₇ crystalline compounds [8–12] and other Eu-doped borates obtained in the air, in particular for glasses with 4SrO–7B₂O₃ (or Sr₄B₁₄O₂₅) composition [36]. On the other hand, in [6, 7, 13–18] it was shown that the europium impurity can be stabilised in

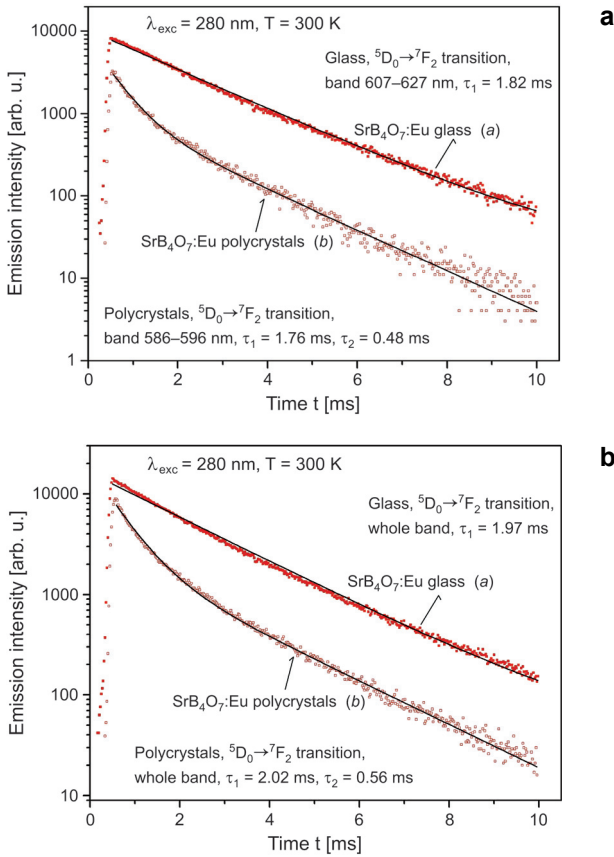


Fig. 4. Luminescence decay curves of the Eu^{3+} centres for ${}^5D_0 \rightarrow {}^7F_2$ emission transition in the narrow (a) and whole (b) bands, registered in the $\text{SrB}_4\text{O}_7:\text{Eu}$ glass (curves a) and corresponding polycrystalline powder (curves b) under excitation with $\lambda_{\text{exc}} = 280 \text{ nm}$ at $T = 300 \text{ K}$. Solid lines – results of fitting.

the SrB_4O_7 crystalline compounds in divalent (Eu^{2+}) state during synthesis in the air atmosphere. In [13], authors reported on the preparation of a system containing $(\text{RE})^{2+}$ ions ($\text{RE} = \text{Sm}, \text{Eu}$) in the SrB_4O_7 crystalline matrix by ceramic, Pechini, and combustion methods using reduction of $(\text{RE})^{3+}$ to $(\text{RE})^{2+}$ ions in the air. The emission spectra of the $\text{SrB}_4\text{O}_7:\text{Eu}^{2+}$ system prepared by combustion and Pechini methods are characterised by a broadband assigned to the $4f^6 5d-4f^7$ interconfiguration transition. The $\text{SrB}_4\text{O}_7:\text{RE}$ compounds prepared by combustion method present emission bands from $(\text{RE})^{3+}$ ions as intense as that arising from $(\text{RE})^{2+}$, suggesting that the preparation route is not efficient for $(\text{RE})^{3+} \rightarrow (\text{RE})^{2+}$ reduction [13].

3.2. The Pr^{3+} centres in glasses with $\text{SrO}-2\text{B}_2\text{O}_3$ composition

The Pr impurity in the oxide compounds can be revealed as Pr^{3+} ($4f^2, {}^3H_4$) and Pr^{2+} ($4f^3, {}^4I_{9/2}$) ions with characteristic optical absorption and luminescence spectra. The paramagnetic Pr^{2+} ions can be registered also by EPR technique. In the Pr -doped

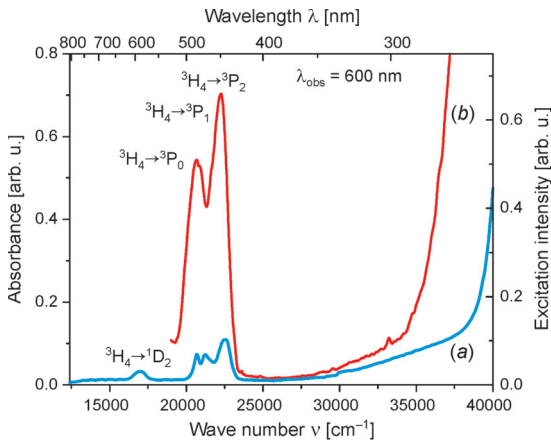


Fig. 5. Optical absorption (curve *a*) and luminescence excitation (curve *b*) spectra of the Pr-doped (Pr_2O_3 content: 0.25 at.%) glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition, registered at room temperature.

glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition the Pr^{2+} EPR spectrum was not observed even at liquid helium temperatures. Thus, the praseodymium impurity is incorporated into the $\text{SrO}-2\text{B}_2\text{O}_3$ glass network as Pr^{3+} ions, exclusively.

The optical absorption spectrum of the Pr-doped glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition in the spectral range 250–800 nm at room temperature consists of four characteristic absorption bands. According to rare-earth energy level diagram the observed bands were assigned to appropriate $f-f$ electronic transitions of the Pr^{3+} ions from the $^3\text{H}_4$ ground state to the $^1\text{D}_2$, $^3\text{P}_0$, $^3\text{P}_1$, $^3\text{P}_2$ excited states (Fig. 5, spectrum *a*).

In the luminescence excitation spectrum of the $\text{SrO}-2\text{B}_2\text{O}_3$ glass doped with Pr (Pr_2O_3 content: 0.25 at.%) one can observe three resolved bands in the spectral range 550–280 nm, which correspond to the $^3\text{H}_4 \rightarrow ^3\text{P}_0$, $^3\text{H}_4 \rightarrow ^3\text{P}_1$, $^3\text{H}_4 \rightarrow ^3\text{P}_2$ transitions (Fig. 5, spectrum *b*). The Pr^{3+} luminescence excitation bands show good correlation with corresponding absorption bands (Fig. 5, spectra *a* and *b*). It should be noted that the resolution of Pr^{3+} optical absorption and luminescence excitation bands in the glass containing 0.25 at.% of Pr_2O_3 is lower than that in the glass containing 0.05 at.% of Pr_2O_3 . This is related to homogeneous broadening of spectral lines, which depends on centres concentration and temperature.

The luminescence spectrum of Pr^{3+} centres (Fig. 6) was registered at temperatures of 293 and 85 K under excitation with $\lambda_{\text{exc}} = 450$ nm that corresponds to the $^3\text{H}_4 \rightarrow ^3\text{P}_1$ transition in the absorption and luminescence excitation spectra (Fig. 5, spectra *a* and *b*). In the Pr^{3+} luminescence spectrum at temperatures of 293 and 85 K there were observed an intense broad complex emission band, peaking near 600 nm, which corresponds to the $^3\text{P}_0 \rightarrow ^3\text{F}_2$, $^3\text{H}_6$ and $^3\text{P}_0 \rightarrow ^3\text{H}_4$ transitions, and weak emission bands, peaking near 450, 690, and 800 nm, which corresponds to the $^3\text{P}_0 \rightarrow ^3\text{H}_4$, $^3\text{P}_0 \rightarrow ^3\text{F}_3$, $^3\text{P}_0 \rightarrow ^3\text{F}_4$ transitions (Fig. 6). The luminescence spectra of the $\text{SrO}-2\text{B}_2\text{O}_3$ glasses which contained 0.05 and 0.25 at.% of Pr_2O_3 are similar and characterised by

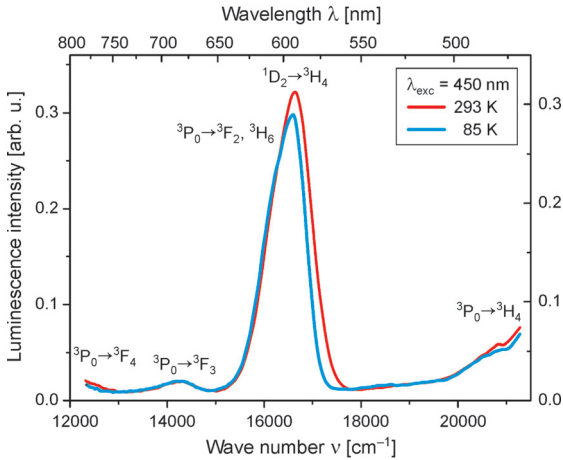


Fig. 6. The luminescence spectrum of the Pr^{3+} centres in the Pr-doped (Pr_2O_3 content: 0.25 at.%) glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition, registered under excitation with $\lambda_{\text{exc}} = 450$ nm at temperatures of 293 and 85 K.

practically the same resolution at temperatures of 293 and 85 K. The linewidth and resolution of the Pr^{3+} absorption, luminescence excitation and emission bands in the glass samples with the same Pr^{3+} content practically did not change with temperature decreasing to 85 K, which is an evidence of the inhomogeneous broadening of spectral lines, caused by disorder of the local structure of Pr^{3+} centres.

The results of investigation of luminescence kinetics for Pr^{3+} centres in the $\text{SrO}-2\text{B}_2\text{O}_3$ glass containing 0.05 and 0.25 at.% of Pr_2O_3 are presented in Fig. 7. Luminescence kinetics of the Pr^{3+} centres for the whole emission band corresponding to the ${}^1D_2 \rightarrow {}^3H_4$ transition is satisfactorily described by a two-exponential model with decay constants $\tau_1 = 32.92 \mu\text{s}$ and $\tau_2 = 16.2 \mu\text{s}$ for glass containing 0.05 at.% of

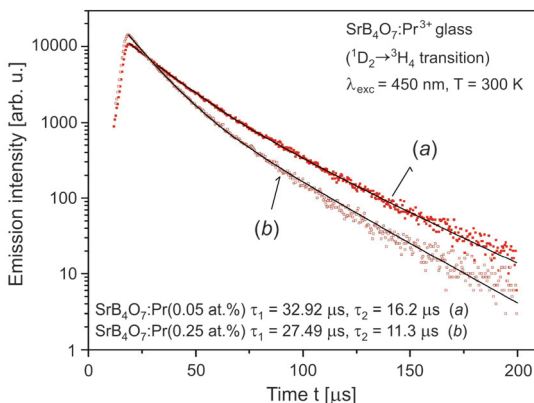


Fig. 7. Luminescence decay curves of the Pr^{3+} centres for ${}^1D_2 \rightarrow {}^3H_4$ transition ($\lambda_{\text{max}} = 599$ nm), registered under excitation with $\lambda_{\text{exc}} = 450$ nm at $T = 300$ K in the SrB_4O_7 glasses containing 0.05 at.% (curve a) and 0.25 at.% (curve b) of Pr_2O_3 . Solid lines – results of fitting.

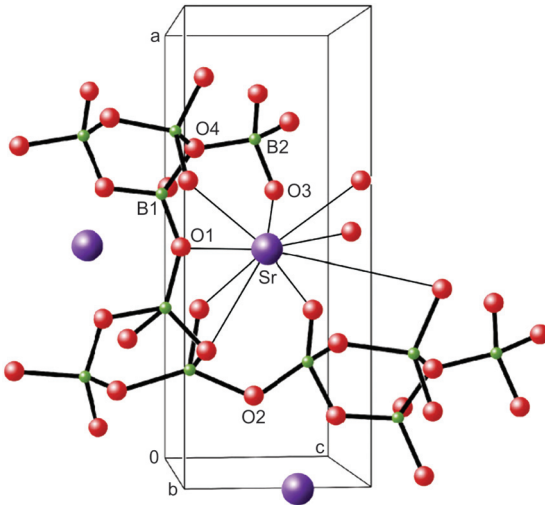


Fig. 8. A fragment of SrB_4O_7 single crystal ideal structure. A unit cell is shown by lines. The B1 and B2 atoms have coordination numbers to oxygen $N = 3$ and $N = 4$, respectively. The Sr atoms stabilising in the framework have coordination number to oxygen $N = 9$.

Pr_2O_3 and $\tau_1 = 27.49 \mu\text{s}$ and $\tau_2 = 11.3 \mu\text{s}$ for glass containing 0.25 at.% of Pr_2O_3 . According to [34, 35] and the data analysis we can suppose that longer lifetimes correspond to isolated Pr^{3+} centres and shorter lifetimes correspond to the $\text{Pr}^{3+}-\text{Pr}^{3+}$ pair centres in the SrB_4O_7 glass network.

The results obtained do not correlate with the results published in [15], where the incorporation of Pr impurity ions in divalent state into the SrB_4O_7 crystal lattice is described. On the other hand, the results of optical spectroscopy of $\text{SrO}-2\text{B}_2\text{O}_3$ glasses doped with Pr show good correlation with the optical spectroscopy of the Pr-doped glass and crystal with $4\text{SrO}-7\text{B}_2\text{O}_3$ (or $\text{Sr}_4\text{B}_{14}\text{O}_{25}$) composition that shows the presence of Pr^{3+} luminescence centres exclusively in the glass network [36] and crystal lattice [37, 38].

Based on structural [25–27] and optical spectroscopy data for Eu^{3+} in the SrB_4O_7 crystal [8–12] and $\text{SrO}-2\text{B}_2\text{O}_3$ glass (see Section 3.1) as well as for Pr^{3+} in the $\text{Sr}_4\text{B}_{14}\text{O}_{25}$ crystal [37, 38] and $4\text{SrO}-7\text{B}_2\text{O}_3$ glass [36] we confirm incorporation of trivalent rare-earth ions (Eu^{3+} , Pr^{3+} , etc.) into the Sr-sites (Fig. 8) with coordination number to oxygen $N = 8$ for real crystalline and $N = 7$ for real glassy compounds.

4. Conclusions

The Eu- and Pr-doped borate glasses of high optical quality and chemical purity with the $\text{SrO}-2\text{B}_2\text{O}_3$ basic composition were synthesised in the air according to technology conditions, developed by the authors. On the basis of optical absorption and luminescence spectra analysis it was shown that the Eu and Pr impurities are incorporated into the $\text{SrO}-2\text{B}_2\text{O}_3$ glass network in trivalent state, exclusively and form

the Eu^{3+} ($4f^6$, 7F_0) and Pr^{3+} ($4f^2$, 3H_4) luminescence centres. All transitions of the Eu^{3+} and Pr^{3+} centres, observed in the UV–VIS optical spectra are identified. Peculiarities of absorption and luminescence spectra as well as luminescence kinetics of the Eu^{3+} and Pr^{3+} centres in the glass with $\text{SrO}-2\text{B}_2\text{O}_3$ composition were analysed in comparison with their crystalline analogs and other borate glasses. In particular, it was shown that the Eu^{3+} and Pr^{3+} optical absorption and luminescence spectra in the SrB_4O_7 and $\text{Sr}_4\text{B}_{14}\text{O}_{25}$ crystalline and glassy compounds are very similar, which is an evidence of the same local structure for rare-earth luminescence centres in strontium borate glasses with different compositions and their crystalline analogs. Luminescence kinetics of the $\text{SrB}_4\text{O}_7:\text{Eu}$ compounds shows only isolated Eu^{3+} centres in the glass network, whereas it is the Eu^{3+} isolated and $\text{Eu}^{3+}-\text{Eu}^{3+}$ pair centres that are characteristic of SrB_4O_7 crystal lattice. Luminescence kinetics of the $\text{SrB}_4\text{O}_7:\text{Pr}$ glass with 0.05 and 0.25 at.% Pr_2O_3 content shows the presence of the Pr^{3+} isolated and $\text{Pr}^{3+}-\text{Pr}^{3+}$ pair centres in the glass network.

On the basis of reference data and analysis of the results it was confirmed that the Eu^{3+} , Pr^{3+} and other trivalent rare-earth ions in the structure of SrB_4O_7 compounds are localised in one type of structural positions according to $\text{RE}^{3+} \rightarrow \text{Sr}^{2+}$ heterovalent substitution with coordination number to oxygen $N = 8$ for SrB_4O_7 real crystal and $N = 7$ for real glass with the same composition. The multisite character of the Eu^{3+} and Pr^{3+} luminescence in the strontium borate glasses can be explained by compositional (or substitutional) disorder and continual disturbance of short-range order that leads to statistical distribution of local crystal field parameters for luminescence centres and is revealed in the inhomogeneous broadening of spectral lines.

Acknowledgements – This work was supported by the Ministry of Education and Science of Ukraine (scientific research project No. 0109U001063) and University of Zielona Góra (Poland).

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*Received November 12, 2009
in revised form December 30, 2009*