Enhancement of the RE^{3+} Luminescence in the RE-Ag Co-doped Tetraborate Glasses

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Abstract—**The Ag-doped Li$_2$B$_4$O$_7$ and LiKB$_4$O$_7$ tetraborate glasses of high optical quality as well as Li$_2$B$_4$O$_7$ glasses co-doped with rare earth (RE = Gd, Eu) and Ag were detailed studied by conventional electron paramagnetic resonance (EPR) and optical spectroscopy. Possible types of the Ag and RE paramagnetic and luminescence centers, their electronic and local structure in the Ag-doped and RE-Ag co-doped borate glasses were proposed based on the published data. The EPR and optical (absorption, emission, and luminescence excitation) spectra as well as luminescence decay kinetics of the Ag$^+$, Gd^{3+}, Eu^{3+} centers in the Li$_2$B$_4$O$_7$:Ag, LiKB$_4$O$_7$:Ag, Li$_2$B$_4$O$_7$:Gd,Ag, and Li$_2$B$_4$O$_7$:Eu,Ag glasses were detailed investigated and analyzed. Significant enhancement of the Gd^{3+} and Eu^{3+} luminescence intensity in the Li$_2$B$_4$O$_7$:RE,Ag glasses is explained by excitation energy transfer from Ag$^+$ ions and Ag metallic nanoparticles to the RE^{3+} centers.**

Index Term —**borate glasses; Ag impurity; SPR; Gd^{3+} ions; Eu^{3+} ions; EPR; luminescence; Ag nanoparticles; energy transfer.**

I. INTRODUCTION

The study of influence of the transitional metals' ions and metallic nanoparticles (or nanoclusters) on enhancement of the rare-earth (RE) photoluminescence (PL) including Gd^{3+}, Eu^{3+}, and other RE^{3+} ions represents a relatively novel and very interesting scientific and practical problem. Improving of PL intensity of several RE^{3+} ions (Er^{3+}, Eu^{3+}, Dy^{3+}, Sm^{3+}, Tb^{3+}, and Gd^{3+}) in different glasses, co-doped with silver due to processes of excitation energy transfer from Ag$^+$ ions to the RE^{3+} ions were investigated in [1–5]. In particular, recently was obtained intense narrow-band UVB emission (λ_{em} = 311 nm) of the Gd^{3+} ions ($^6P_J \rightarrow {}^8S_{7/2}$ transition) caused by resonant excitation energy transfer from Ag$^+$ to Gd^{3+} ions in the Gd-Ag co-doped phosphate [4] and lithium tetraborate (Li$_2$B$_4$O$_7$) [5] glasses. During last decades also intensively investigated the enhancement of the Eu^{3+} red emission in the Eu-Ag co-doped glasses, including borate glasses due to the local-field surface plasmon resonance (SPR) effect caused by the metallic silver nanoparticles [6–9]. Therefore, further investigations are necessary for enhancement of intensity of the RE^{3+} luminescence in dielectric hosts (crystals and glasses) via co-doping by transitional metals' ions and/or introducing nanoparticles of noble metals (Ag, Au), which reveal intense SPR absorption band in the visible spectral range.
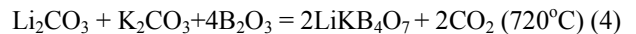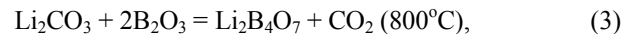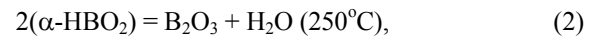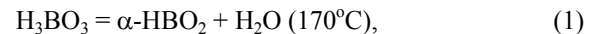
In this paper are described enhancement of the Gd^{3+} emission by resonant excitation energy transfer from Ag$^+$ to the Gd^{3+} luminescence centers and enhancement of the Eu^{3+} emission by excitation energy transfer from the Ag$^+$ centers and metallic Ag nanoparticles, which reveals SPR effect, to the Eu^{3+} centers.

II. EXPERIMENTAL DETAILS

A. Technology of the Tetraborate, Doped with Ag and RE-Ag

A series of tetraborate borate glasses with Li$_2$B$_4$O$_7$:Ag, LiKB$_4$O$_7$:Ag, and Li$_2$B$_4$O$_7$:RE,Ag (RE = Gd, Eu) chemical compositions were produced in the Vlokh Institute of Physical Optics (Lviv, Ukraine) from corresponding polycrystalline compounds, obtained by solid-state synthesis. For solid-state synthesis of the LiKB$_4$O$_7$ and Li$_2$B$_4$O$_7$ compounds were used corresponding carbonates (Li$_2$CO$_3$ and K$_2$CO$_3$) and boric acid (H$_3$BO$_3$) of high chemical purity (99.999 %, Aldrich). The Ag impurity was introduced into the raw materials as AgNO$_3$ salt or as highly-dispersed metallic silver in amount 2.0 mol.%. The RE impurities were added to the raw materials as RE$_2$O$_3$ of chemical purity (99.99 %) in amounts 0.5 and 1.0 mol.%.

The solid-state synthesis of the Li$_2$B$_4$O$_7$ and LiKB$_4$O$_7$ polycrystalline compounds was carried out using multi-step heating chemical reactions, which can be described by the following equations:

$$H_3BO_3 = \alpha\text{-}HBO_2 + H_2O \ (170^oC), \qquad (1)$$

$$2(\alpha\text{-}HBO_2) = B_2O_3 + H_2O \ (250^oC), \qquad (2)$$

$$Li_2CO_3 + 2B_2O_3 = Li_2B_4O_7 + CO_2 \ (800^oC), \qquad (3)$$

$$Li_2CO_3 + K_2CO_3 + 4B_2O_3 = 2LiKB_4O_7 + 2CO_2 \ (720^oC) \ (4)$$

Large samples of the Ag-doped and RE-Ag co-doped borate glasses of high optical quality were obtained by fast cooling of the molten polycrystalline compounds using high-temperature glass synthesis under technological conditions, described in [5,9]. Particularly, studied tetraborate glasses were obtained by fast cooling of the corresponding melts, heated more than 100 K higher that their melting temperature (T_{melt} = 1190 and 1080 K for Li$_2$B$_4$O$_7$ and LiKB$_4$O$_7$ compounds, respectively) for excluding the non-controlled crystallization processes.

B. Experimental Methods and Equipment

The obtained Ag-doped and RE-Ag co-doped tetraborate glasses were investigated using conventional EPR and optical spectroscopy methods. The impurity paramagnetic ions (Gd^{3+}, Ag^{2+}, Ag^0) as well as Fe^{3+} ions of non-controlled iron impurity in the obtained glasses were registered by EPR technique using modernized X-band radiospectrometers of the SE/X-2013 and SE/X-2544 types (RADIOPAN, Poznań, Poland), operating in the high-frequency (100 kHz) modulation mode of magnetic field at room temperature (RT). The microwave frequency was measured with usage the Hewlett Packard microwave frequency counter of the 5350 B type as well as DPPH free radical g-marker ($g = 2.0036 \pm 0.0001$). Positions of resonance lines were measured by digital NMR magnetometers.

Optical absorption spectra of the Ag-doped and RE-Ag co-doped tetraborate glasses were recorded using a Varian (model 5E UV–VIS–NIR) and a Shimadzu (model UV-2600) spectrophotometers. The photoluminescence emission and excitation spectra as well as emission decay curves were recorded with usage a HORIBA Yvon spectrofluorimeter (model FluoroMax-4). The external quantum yield (QY) was measured using Hamamatsu Quantaurus-QY Absolute PL quantum yield spectrometer (model C11347) in the Institute of Experimental Physics, University of Gdańsk (Poland).

III. RESULTS AND DISCUSSIONS

A. Spectroscopy of the Ag-Doped Tetraborate Glasses

In Fig. 1 are presented EPR spectra of the un-annealed $Li_2B_4O_7$:Ag glasses, where the Ag impurity was introduced in the raw materials as $AgNO_3$ and highly-dispersed metallic silver nanoparticles (size ~ 100 nm) in amount 2.0 mol.%.
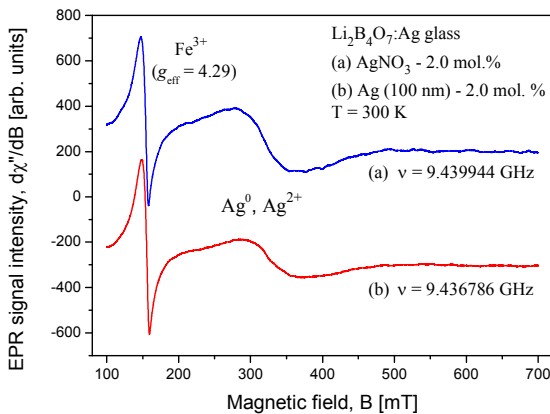

Figure 1. The X-band EPR spectra of un-annealed $Li_2B_4O_7$:Ag glasses at RT.

In all obtained $Li_2B_4O_7$:Ag glasses at RT has been clearly observed characteristic EPR signal with effective g-factor $g_{eff} \cong 4.29$ that belongs to the Fe^{3+} ($3d^5$, $^6S_{5/2}$) ions of non-controlled iron impurity. Broad asymmetric EPR signal with $g_{eff} = 2.05$ was observed at RT in all Ag-doped and RE-Ag co-doped tetraborate glasses. This signal is typical for glasses highly doped with Ag and associated with paramagnetic silver centers and their clusters. Based on the EPR spectroscopy and published data we can suggested that the Ag impurity can be

incorporated into the network of un-annealed $Li_2B_4O_7$ glasses as the Ag^{2+} ($4d^9$), Ag^0 ($4d^{10}s^1$), and possibly Ag_2^+ ($Ag^0 + Ag^+$) paramagnetic centers and their clusters. Observed EPR spectra show that the incorporation of the Ag impurity into $Li_2B_4O_7$ glass is independent of silver form added in the raw materials. Thermal annealing of the $Li_2B_4O_7$:Ag and $LiKB_4O_7$:Ag glasses in vacuum and air at 460°C during 2 hours leads to disappearing the main part of complex EPR signal with $g_{eff} \cong 2.05$, whereas the Fe^{3+} EPR signal practically is unchanged after annealing in vacuum and air.

In un-annealed and annealed in air Ag-doped tetraborate glasses were not reveal SPR band of metallic Ag nanoparticles in optical absorption spectra, whereas in the annealed in vacuum glasses has been observed intense SPR band peaked at 409 nm ($Li_2B_4O_7$:Ag) and 407 nm ($LiKB_4O_7$:Ag) (Fig. 2).
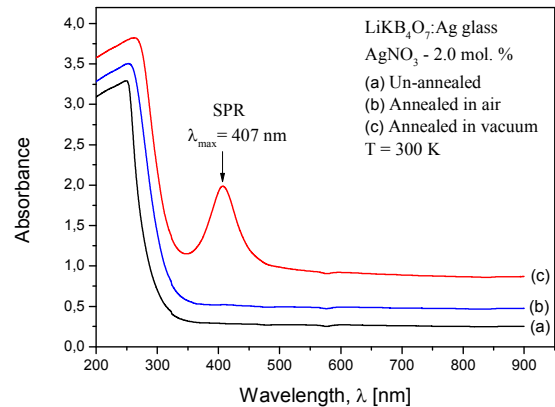

Figure 2. Optical absorption spectra of un-annealed and annealed Ag-doped $LiKB_4O_7$ glasses, recorded at RT.

In the un-annealed and Ag-doped tetraborate glasses at RT were observed typical for Ag^+ ($4d^{10}$) centers luminescence excitation and emission spectra (Fig. 3). The luminescence decay curves are single exponential with lifetimes $\tau \cong 161$ μs (for $Li_2B_4O_7$:Ag glass) and $\tau \cong 119$ μs (for $LiKB_4O_7$:Ag glass).
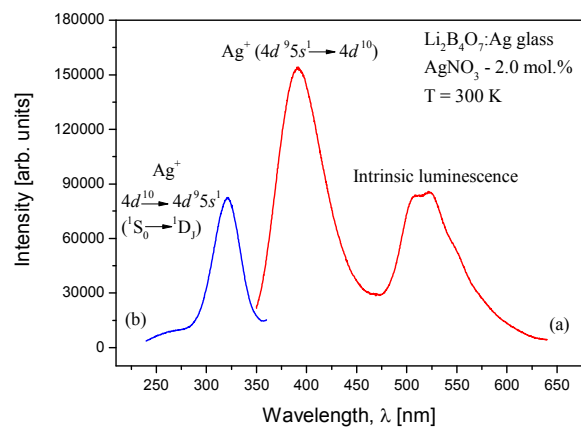

Figure 3. Luminescence spectra of the un-annealed $Li_2B_4O_7$:Ag glass at RT; (a) emission spectrum recorded under excitation with $\lambda_{exc} = 333$ nm ($4d^{10} \rightarrow 4d^9 5s^1$ ($^1S_0 \rightarrow {}^1D_J$) transitions of the Ag^+ ions); (b) luminescence excitation spectrum recorded at $\lambda_{mon} = 384$ nm ($4d^9 5s^1 \rightarrow 4d^{10}$ transition of the Ag^+ ions).

B. Enhancement of the Gd^{3+} PL in $Li_2B_4O_7$:Gd,Ag Glasses

In all Gd-doped tetraborate glasses at RT was observed EPR U-spectrum of the Gd^{3+} ($^8S_{7/2}$, $4f^7$) paramagnetic ions that is typical for all Gd-doped glasses and practically independent of the basic glass composition.

In the Gd-doped $Li_2B_4O_7$ and CaB_4O_7 glasses at RT besides complex broad emission band of intrinsic luminescence, described in [10], is observed weak narrow UV emission band peaked at 311 nm under excitation with 273 nm and 252 nm (Fig. 4). The emission band peaked at 311 nm is extremely efficient at excitation with 273 nm. Emission band peaked at 311 nm was assigned to the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ intraconfiguration $4f - 4f$ transition of the Gd^{3+} ions. Co-doping of the $Li_2B_4O_7$:Gd glass by Ag leads to significant (~100 times) increasing of intensity of the Gd^{3+} emission band at 311 nm (Fig. 4).
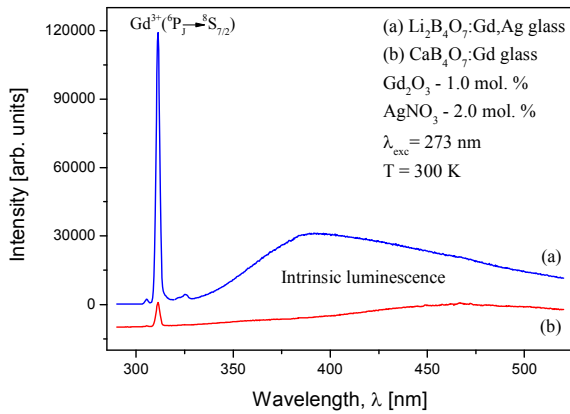

Figure 4. Emission spectra of the $Li_2B_4O_7$:Gd,Ag and CaB_4O_7:Gd glasses, recorded at RT under excitation with λ_{exc} = 273 nm ($^8S_{7/2} \rightarrow {}^6I_J$ transition).

In the luminescence excitation spectra of the Gd-doped and Gd-Ag co-doped tetraborate glasses are well observed three characteristic group of bands, which correspond to the characteristic Gd^{3+} transitions: $^8S_{7/2} \rightarrow {}^6P_J$, ^6I_J, and ^6D_J (Fig. 5).
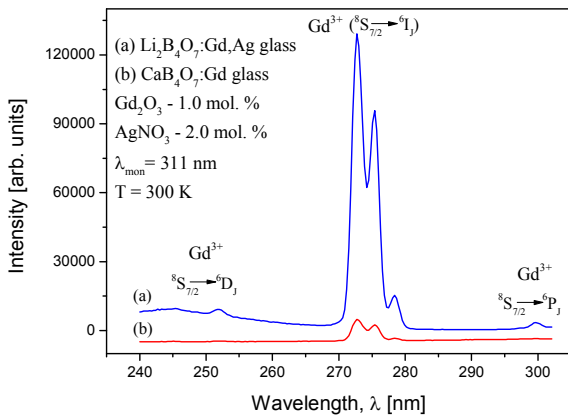

Figure 5. Luminescence excitation spectra of the $Li_2B_4O_7$:Gd,Ag and CaB_4O_7:Gd glasses, recorded at RT and λ_{mon} = 311 nm ($^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition).

Luminescence kinetics of the Gd^{3+} emission band peaked at 311 nm in the $Li_2B_4O_7$:Gd,Ag and CaB_4O_7:Gd,Ag glasses are satisfactory described by single exponential decay with lifetimes ~ 4.1 ms and ~ 4.2 ms, respectively (see Fig. 6).
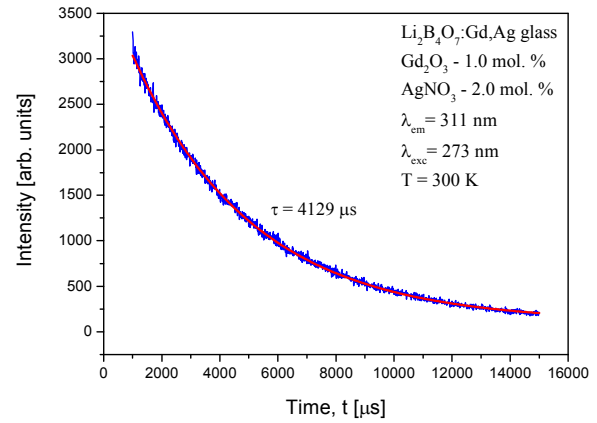

Figure 6. Luminescence decay curve of the Gd^{3+} centers ($^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition, λ_{em} = 311 nm) in the $Li_2B_4O_7$:Gd,Ag glass, recorded at RT under excitation with λ_{exc} = 273 nm ($^8S_{7/2} \rightarrow {}^6I_J$ transitions).

Increasing of emission band intensity in the $Li_2B_4O_7$:Gd,Ag glasses is explained by energy transfer from Ag^+ to Gd^{3+} centers under excitation with 273 nm that is resonant for the $4d^{10} \rightarrow 4d^9 5s^1$ and $^8S_{7/2} \rightarrow {}^6I_J$ ($^6P_{7/2}$ level) transitions of Ag^+ and Gd^{3+}, respectively. Proposed mechanism of the resonant energy transfer in $Li_2B_4O_7$:Gd,Ag glass is presented in Fig. 7.
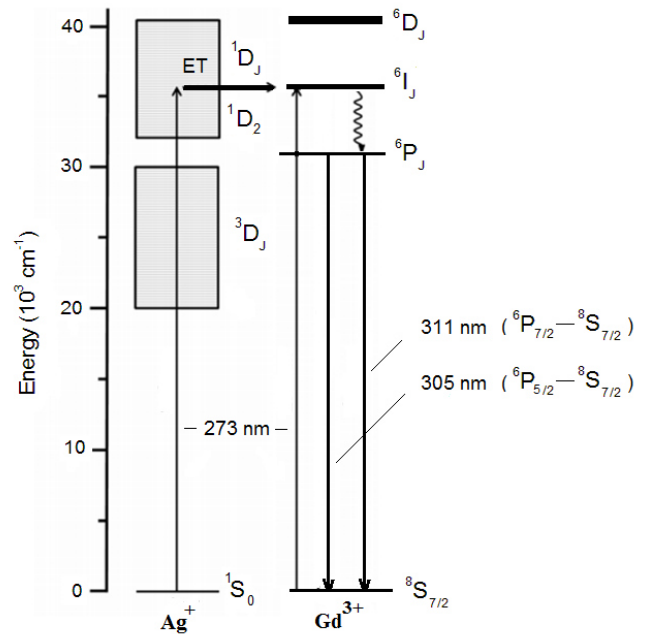

Figure 7. Partial energy levels diagram of the Ag^+ and Gd^{3+} centers in the $Li_2B_4O_7$:Gd,Ag glass showing excitation, resonant excitation energy transfer (ET), emission, and non-radiative relaxation transitions.

C. Enhancement of the Eu^{3+} PL in $Li_2B_4O_7$:Eu,Ag Glasses

In all Eu-doped and Eu-Gd co-doped tetraborate glasses at RT was not observed Eu^{2+} ($^8S_{7/2}$, $4f^7$) EPR spectrum and un-annealed and annealed in air $Li_2B_4O_7$:Eu,Ag glasses shows

only EPR signal of the Fe^{3+} non-controlled impurity. Optical absorption spectrum of the un-annealed $Li_2B_4O_7$:Eu,Ag glass shows characteristic $4f – 4f$ bands of the Eu^{3+} ions, whereas the annealed in air $Li_2B_4O_7$:Eu,Ag glass shows additional broad band in the $400 – 430$ nm range with maximum about 417 nm that is attributed to the SPR of Ag nanoparticles. The PL emission spectra of $Li_2B_4O_7$:Eu,Ag glass reveal characteristic Eu^{3+} $4f – 4f$ bands corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J = 0 – 6$) transitions, complex band of intrinsic luminescence [10] and Ag^+ broad band ($4d^9 5s^1 \rightarrow 4d^{10}$ transition) (Fig. 8).
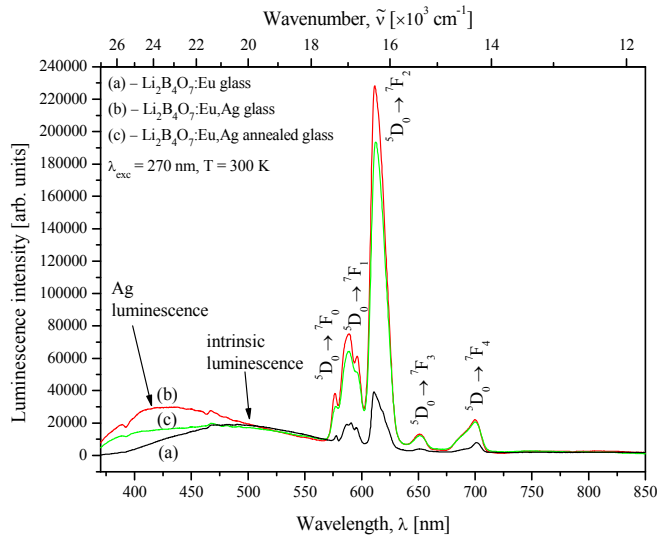

Figure 8. The luminescence emission spectra of the $Li_2B_4O_7$:Eu (a), $Li_2B_4O_7$:Eu,Ag (b), and annealed $Li_2B_4O_7$:Eu,Ag (c) glasses, recorded at RT under λ_{exc} = 270 nm.

The average exponential lifetimes, obtained by linear regression of the linear part of the semi-logarithmic plots, equal: 2.18, 2.23, and 2.20 ms for $Li_2B_4O_7$:Eu, $Li_2B_4O_7$:Eu,Ag, and annealed in air $Li_2B_4O_7$:Eu,Ag glasses, respectively.

In Fig. 9 are presented dependencies of the external QY on the wavelength of excitation light for the $Li_2B_4O_7$:Eu, $Li_2B_4O_7$:Eu,Ag, and annealed in air $Li_2B_4O_7$:Eu,Ag glasses.
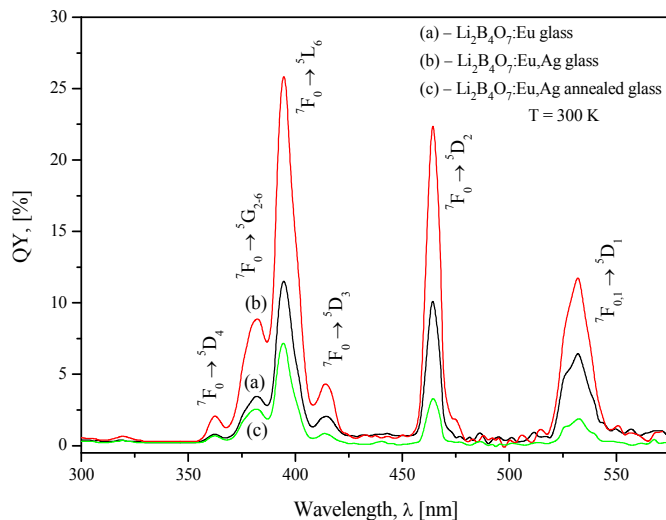

Figure 9. The dependence of external quantum yield of Eu^{3+} luminescence with wavelength of excitation light in the $Li_2B_4O_7$:Eu (a), $Li_2B_4O_7$:Eu,Ag (b) and annealed $Li_2B_4O_7$:Eu,Ag (c) glasses.

The following external QY values for Eu^{3+} luminescence were obtained upon excitation at 393 nm: 11.7 %, 26.1 %, and 7.4 % for the $Li_2B_4O_7$:Eu, $Li_2B_4O_7$:Eu,Ag, and annealed $Li_2B_4O_7$:Eu,Ag glasses, respectively. Absolute quantum yield of the $Li_2B_4O_7$:Eu,Ag glass significantly increase to 26.1 % in comparison with $Li_2B_4O_7$:Eu glass (QY = 11.7 %). Obtained QY of the Eu^{3+} luminescence in the $Li_2B_4O_7$:Eu,Ag glass is close to QY of well-known commercial phosphor Y_2O_3:Eu^{3+} (QY = 29.5 %). According to [9] the enhancement of Eu^{3+} photoluminescence is attributed to excitation energy transfer from Ag^+ ions and small molecule-like non-plasmonic Ag aggregates to the Eu^{3+} ions as the major factor, and local field effects induced by SPR of the Ag nanoparticles.

IV. CONCLUSIONS

Obtained results clearly show that the Gd-Ag co-doped tetraborate glasses are promising materials for effective sources of UVB radiation including therapy lamps and solid-state UV lasers with working wavelength 311 nm ($^6P_{7/2} \rightarrow {}^8S_{7/2}$ channel).

High external quantum yield of the $Li_2B_4O_7$:Eu,Ag glass clearly shows that the Eu-Ag co-doped borate glasses belong to very perspective luminescent materials of red spectral range.

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