Peculiarities of Ag metallic nanoparticles formation in alkaline and alkaline-earth tetraborate glasses


O.Vlokh Institute of Physical Optics, 23 Dragomanov Str., 79005 Lviv, Ukraine
*I.Franko National University, 8 Kyrylo and Methodiy Str., 79005 Lviv, Ukraine

Received December 11, 2014

Investigations of alkaline Li₂B₄O₇:Ag and alkaline-earth CaB₂O₄:Ag tetraborate glasses with Ag nanoparticles (Ag NPs) formed by thermal treatment in vacuum have been performed. It is ascertained that in volumes of both glasses a small number of Ag NPs is formed, whereas their main mass is concentrated near the samples surface. It is obtained from the plasmon resonance results that, under the same annealing conditions, concentration of the Ag NPs in the near-surface layer of CaB₂O₄:Ag glass is appreciably smaller than in the near-surface layer of Li₂B₄O₇:Ag glass. This peculiarity is explained by difference between contributions of alkaline Li⁺ and alkaline-earth Ca²⁺ ions to processes of the Ag NPs formation in respective tetraborate glasses.

Keywords: borate glasses, nonlinear refractive index, Ag nanoparticles, plasmon resonance.

Проведені ісследования щелочного Li₂B₄O₇:Ag и щелочноzemельного CaB₂O₄:Ag тетраборатних стекол з сформованими термічним обробленням в вакуумі наночастинцями Ag (НЧ Ag). Установлено, що в об’ємах обох стекол формується небільше кількість НЧ Ag, ніж у основі їх маси концентрується у поверхні образця. По результатам ісследовання плазмонного резонанса установлено, що при однакових умовах збільшує концентрація НЧ Ag в примітивному структурному слоє CaB₂O₄:Ag стекла ощутимо менша, ніж в примітивному структурному слоє Li₂B₄O₇:Ag стекла. Ця особливість обумовлена різницію складів щелочного Li⁺ і щелочноzemельного Ca²⁺ іонів в процесі формування НЧ Ag в відповідному тетраборатному склі.

Особливості формування металічних наночастинок Ag в лужних і лужноzemельних тетраборатних стеклах. Р.М.Дутха, В.Т.Адамів, Я.В.Бурак, Р.В.Гамерник, І.М.Теслюк.

Проведено дослідження лужного Li₂B₄O₇:Ag і лужноzemельного CaB₂O₄:Ag тетраборатних стекол із сформованими термічною обробкою у вакуумі наночастинами Ag (НЧ Ag). Встановлено, що в об’ємах обох стекол формується невелика кількість НЧ Ag, тоді як основна їх маса концентрується біля поверхонь араклів. За результатами досліджень плазмонного резонансу встановлено, що за однакових умов відповідно концентрація НЧ Ag у примітивному шарі CaB₂O₄:Ag скла є відчутно меншою, ніж у примітивному шарі Li₂B₄O₇:Ag скла. Ця особливість пояснюється різницює вкладів лужного Li⁺ і лужноzemельного Ca²⁺ йонів у процесі формування НЧ Ag у відповідному тетраборатному склі.
1. Introduction

Nanocomposite materials, whose basis is consisted of metallic nanoparticles (MNPs) of noble metals (Au, Ag, Pt) in dielectric media, are the object of significant attention in recent years. This is caused by large influence of the MNPs on linear and nonlinear susceptibilities of dielectric matrix [1–3], radiative recombination [4] and giant surface enhanced Raman scattering (SERS) [5, 6]. Prospects for development of optical switches with ultra-short time response, limiters of optical laser beam intensity for synchronization of the laser modes [7–10], chemical and biochemical sensors caused dominantly by plasmon resonances [11] on the basis of such nanocomposite materials stimulate investigations in this domain of nanotechnologies.

The main attention among abovementioned noble materials is paid to silver (Ag) in process of the MNPs formation in different glass matrices, for example [12–14]. Doping of glasses by Ag⁺ ions with their next reducing to neutral Ag⁰ condition in the glass matrix by means of thermal treatment in reducing atmosphere [12] is the main method of Ag NPs formation.

Borate glasses, the basis of which is boron anhydride B₂O₃ with its tendency to polycondensation [15], can be prospective for Ag NPs formation. The borate glasses structurally consist of boroxole groups which are joined by the bridge oxygen atoms that makes their structure enough open. These boroxole groups make the borate glass structure more open near the glass transition temperature T_g [16, 17] that simplifies the process of Ag NPs formation.

An important advantage of borate compounds as the glass matrix for Ag NPs formation, is their proper nonlinear optical properties which are defined by high values of nonlinear susceptibilities of boroxole complexes [18, 19]. And plasmon resonance on Ag NPs in borate glasses can influence essentially on their nonlinear properties that makes them potentially very prospective for photonics [20].

Ag NPs formation on surface of Li₂B₄O₇:Ag glass from Li₂O–B₂O₃ system by annealing in reducing atmosphere without application of reducing admixtures was successful and permitted to observe powerful surface plasmon resonance [21, 22]. But, since presence of Li in Li₂B₄O₇ glass makes it somewhat sensitive to moisture. Therefore it is necessary to pay attention to another borate glasses, in particular, tetraborate CaB₂O₇ glass from CaO–B₂O₃ system [23]. The substitution of univalent Li⁺ ions by bivalent Ca²⁺ ones causes their very low hygroscopic nature [24].

This work is devoted to formation of Ag NPs by thermal treatment and comparative investigation of the optical properties, in particular, plasmon resonance bands in alkaline and alkaline-earth tetraborate glasses by giving two representatives of such glasses: alkaline Li₂B₄O₇:Ag glass (98.0 Li₂B₄O₇–2.0 Ag₂O) and alkaline-earth CaB₂O₇:Ag glass (98.0 CaB₂O₇–2.0 Ag₂O).

2. Experimental

For preparation of Li₂B₄O₇:Ag and CaB₂O₇:Ag glasses there were taken highly pure lithium carbonate Li₂CO₃ or calcium carbonate CaCO₃, boric acid H₃BO₃ and silver nitrate AgNO₃. Synthesis of Li₂B₄O₇ or CaB₂O₇ compound firstly was performed:

1) for Li₂B₄O₇ compound synthesis the mixture of initial chemicals prepared by stoichiometric Li₂O–2B₂O₃ composition was placed into ceramic crucible and Li₂B₄O₇ powder with T_melt = 1198 K (congruently) was obtained by the method of multi-graded temperature synthesis according to the following chemical reaction:

\[ \text{Li}_2\text{CO}_3 + 4\text{H}_3\text{BO}_3 \rightarrow \text{Li}_2\text{B}_4\text{O}_7 + \text{CO}_2 \uparrow + 6\text{H}_2\text{O} \uparrow; \]

2) for CaB₂O₇ synthesis the mixture of initial chemicals prepared by stoichiometric CaO–2B₂O₃ composition was placed into ceramic crucible and CaB₂O₇ powder with T_melt = 1260 K (incongruently) was obtained by the method of multi-graded temperature synthesis according to the following chemical reaction:

\[ \text{CaCO}_3 + 4\text{H}_3\text{BO}_3 \rightarrow \text{CaB}_2\text{O}_7 + \text{CO}_2 \uparrow + 6\text{H}_2\text{O} \uparrow. \]

Two mole percent of AgNO₃ was added to these powders. Li₂B₄O₇:Ag glass was prepared by melting technique in Al₂O₃ crucible in air at 1270 K, and CaB₂O₇:Ag glass was prepared at 1320 K. The melts were homogenized during 0.5 h and cooled during one hour down to temperature 673 K followed by inertial cooling down to the room temperature.

For formation of the near-surface layer from Ag NPs the sample Li₂B₄O₇:Ag was annealed at temperature 710 ± 5 K (the glass transition temperature for Li₂B₄O₇ glass T_g = 713 K [25]) and the sample CaB₂O₇...
glass was annealed at temperature ~870 K (the glass transition temperature for CaB$_2$O$_7$ glass $T_g = 883$ K [25]) during 2 h in vacuum (~10$^{-4}$ Torr with titanium getter) or in air atmosphere.

Plates with dimensions of ~10×7×1 mm$^3$ were cut from obtained glasses, and their surfaces were grinded and polished. Transmission spectra were measured using set-up, which included MDR-23 monochromator and personal computer. Halogen incandescent lamp was used as a light source, and PMT-79 photomultiplier was exploited as detector in the single-photon regime ensuring linearity of the signal registration in the range of 10$^2$–10$^6$ photons per second. Traditional single-beam Z-scan method developed by Sheik-Bahae et al. [26, 27] was used for investigations of the nonlinear optical properties of Li$_2$B$_4$O$_7$:Ag and CaB$_2$O$_4$:Ag glasses with formed Ag NPs. Measurements were performed at the room temperature. Second harmonic radiation from continuous neodymium laser with diode pumping, operating on wavelength 532 nm, was used. Output power of the laser beam was 45 mW. Parameters of the focused laser beam were in agreement with principal demands of Z-scan experiment: $2\omega_0 = 22.3$ μm ($\omega_0$ — radius of the Gauss beam in focus); $b = \pi \omega_0 \lambda / 1.197$ mm ($b$ — diffraction length in the Rayleigh range), laser beam power density in focus $I_0 = 1.04 \times 10^4$ W/cm$^2$.

### 3. Results and discussion

The main parameters of undoped Li$_2$B$_4$O$_7$ and CaB$_2$O$_4$ glass matrices were determined, in particular, density $d$ (hydrostatic method), thermal expansion coefficient $\alpha$ (dilatometry method), microhardness $H$ (the Whisker method). These parameters at the same time the type of boroxole group, number of boroxole groups in cm$^3$ $N_{bg}$ and nonlinear refractive index $n_2$ are presented in Table 1. As it is seen from Table 1, substitution of univalent Li$^+$ ions by bivalent Ca$^{2+}$ ones changes significantly the main parameters of the tetraborate glass. Significantly larger density $d$ of CaB$_2$O$_4$ glass in comparison with Li$_2$B$_4$O$_7$ glass can be easy explained by significantly larger atomic mass of Ca (~40) than mass of two Li atoms (~14). And differences in coefficients $\alpha$ and microhardnesses $H$ are defined by differences in electron bonds in structure of Li$_2$B$_4$O$_7$ and CaB$_2$O$_4$ glasses.

As it is seen from Table 1, the crystal structure of Li$_2$B$_4$O$_7$ and CaB$_2$O$_4$ compounds consists of very similar boroxole groups. So, Li$_2$B$_4$O$_7$ structure is formed only from tetraborate (2BO$_3$ + 2BO$_4$) boroxole groups, which refer to anion $[\text{B}_4\text{O}_6]^2$ [28, 29], and the structure of CaB$_2$O$_4$ is formed from somewhat more complex boroxole groups (4BO$_3$ + 4BO$_4$): one tetraborate (3BO$_3$ + 2BO$_4$) and one triborate (2BO$_3$ + BO$_4$) boroxole group attached to it by additional tetrahedron BO$_4$ that form together anion $[\text{B}_8\text{O}_{14}]^{10}$ [30]. And since in publication [31] it was ascertained that dominant boroxole structural elements of corresponding tetraborate crystal are clearly observed in the glass structure, then one can make a conclusion that significant differences in values $\alpha$ and $H$ in Li$_2$B$_4$O$_7$ and CaB$_2$O$_4$ glasses are caused by differences in Li–O and Ca–O bonds in their structure. This conclusion is confirmed by the authors of recent publication [24], who investigated the changes of CaB$_2$O$_4$ glass properties under particular substitution of Ca by Li (90 CaB$_2$O$_4$–10Li$_2$O) and explained the effect of Li$^+$ on characteristic of CaB$_2$O$_4$ glass in terms of the Li–O bonding interaction, since the monovalent Li$^+$ ions produce the lower cross-linking efficiency when compared to the bivalent Ca$^{2+}$ ion.

Appearance of corresponding characteristic plasmon bands in the absorption spectra is the most cogent argument for presence of MNP’s in the glass matrices. And for Ag NPs these bands are in the range of 360–500 nm [32]. In Fig. 1 and 2 one can observe transmission spectra of our Li$_2$B$_4$O$_7$:Ag and CaB$_2$O$_4$:Ag glasses before and after annealing in vacuum. Comparative analysis of these spectra shows that after annealing of our glasses samples in vacuum there appear the sharply defined absorption plasmon bands in transmission.

<table>
<thead>
<tr>
<th>$d$, g/cm$^3$</th>
<th>$\alpha$, K$^{-1}$</th>
<th>$H$, N/mm$^2$</th>
<th>Boroxole group</th>
<th>$N_{bg}$, cm$^{-3}$</th>
<th>$n_2$, cm$^2$/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$B$_4$O$_7$</td>
<td>2.2</td>
<td>6.9×10$^{-6}$</td>
<td>5164.6</td>
<td>2BO$_3$ + 2BO$_4$</td>
<td>8.1×10$^{-11}$</td>
</tr>
<tr>
<td>CaB$_2$O$_4$</td>
<td>2.5</td>
<td>3.6×10$^{-6}$</td>
<td>8369.2</td>
<td>4BO$_3$ + 4BO$_4$</td>
<td>7.6×10$^{-11}$</td>
</tr>
</tbody>
</table>
spectra with maximums near 400–420 nm (Fig. 1, curve 2 and Fig. 2, curve 2), indicative of Ag NPs existence in these samples. The plasmon absorption band in Li$_2$B$_4$O$_7$:Ag glass (Fig. 1, curve 2) is especially intensive and wide after annealing in vacuum, while in the CaB$_4$O$_7$:Ag glass sample the plasmon band stands out very sharply, but has considerably smaller intensity. From this one can make concrete conclusion that number of Ag NPs in Li$_2$B$_4$O$_7$:Ag glass formed by annealing in vacuum under the same conditions is considerably larger than in CaB$_4$O$_7$:Ag glass.

Estimation of Ag NPs radii in the annealed Li$_2$B$_4$O$_7$:Ag and CaB$_4$O$_7$:Ag glasses can be made from relationship $R = V_F/\Delta \omega_{1/2}$, where $V_F = 1.39 \times 10^6$ m/s — velocity of the Fermi electrons in silver, and $\Delta \omega_{1/2}$ — band half-width according to the Mie theory approximation [33]. The results of calculations for $R$ are given in Table 2.

In Fig. 3 Z-scan spectra are presented for Li$_2$B$_4$O$_7$:Ag and CaB$_4$O$_7$:Ag glasses annealed in vacuum. The Z-scan experiment permits to calculate the nonlinear refractive index $n_2$, which enters into known expression for the total refractive coefficient $n = n_0 + n_2 |E|^2$, where $n_0$ — linear refractive index, and $E$ denotes magnitude of electromagnetic field strength of the laser radiation. Calculation of the nonlinear refractive index $n_2$ from normalized Z-scan spectra was performed using formula $n_2 = \Delta \Phi_0/kL_{eff}$, where $\Delta \Phi_0$ is nonlinear phase shift, $k$ is wave number, and $L_{eff}$ denotes effective length of the sample [33], and the results of calculations are shown in Table 2. Values $n_2$ for undoped Li$_2$B$_4$O$_7$ and CaB$_4$O$_7$ glasses, obtained analogously from their Z-scan spectra, are given in Table 1 and indicate about the presence of intrinsic nonlinear properties in these glasses, caused by nonlinear susceptibilities of their boroxole complexes [18, 19]. As it is seen from Tables 1 and 2, the nonlinear refractive index $n_2$ of undoped Li$_2$B$_4$O$_7$ and CaB$_4$O$_7$ and doped unannealed Li$_2$B$_4$O$_7$:Ag and CaB$_4$O$_7$:Ag glasses are negative, but have somewhat different absolute values. After annealing, which leads to formation of Ag NPs, the nonlinear properties of the both glasses change cardinaly — the nonlinear refractive index $n_2$ becomes positive and larger for some orders of magnitude (Table 2).

Distribution of the Ag NPs in Li$_2$B$_4$O$_7$:Ag and CaB$_4$O$_7$:Ag glass samples annealed in vacuum is an important question. The atomic-force microscope investigations of the Li$_2$B$_4$O$_7$:Ag glasses surface topology allowed to make a conclusion that the Ag NPs formed by annealing of Li$_2$B$_4$O$_7$:Ag glasses

![Fig. 1](image1.png)  
Fig. 1. Transmission spectra of Li$_2$B$_4$O$_7$:Ag glass: 1) without annealing or annealed in air; 2) annealed in vacuum.

![Fig. 2](image2.png)  
Fig. 2. Transmission spectra of CaB$_4$O$_7$:Ag glass: 1) without annealing; 2) annealed in vacuum.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$R$, nm</th>
<th>$n_2$, cm$^2$/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$B$_4$O$_7$:Ag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>without annealing</td>
<td>1.5</td>
<td>$5.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>annealed in vacuum</td>
<td>1.2</td>
<td>$9.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>CaB$_4$O$_7$:Ag</td>
<td></td>
<td></td>
</tr>
<tr>
<td>without annealing</td>
<td>0.5</td>
<td>$-3.8 \times 10^{-9}$</td>
</tr>
<tr>
<td>annealed in vacuum</td>
<td>1.2</td>
<td>$9.6 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

Note: calculations for $n_2$ were performed for thickness of active layer with Ag NPs $2 \times L_1 = L_{eff} = 3.6 \times 10^{-4}$ cm.
in hydrogen and in vacuum are concentrated in a thin near-surface layer, so-called "Li₂B₂O₇:Ag + Ag NPs" interface layer, which is observed in the transmission spectra as intensive plasmon absorption bands [21, 22]. To receive an evidence that after annealing of our Li₂B₂O₇:Ag and CaB₄O₇:Ag glasses in vacuum the Ag NPs are also concentrated near the samples surface after recording of the transmission spectra (Fig. 1, curve 2 and Fig. 2, curve 2) the layers with thickness of 2 μm were mechanically deleted (ground) from the both their surfaces for guaranteed delivery from "Li₂B₂O₇:Ag + Ag NPs" interface layer. Obtained transmission spectra of the Li₂B₂O₇:Ag and CaB₄O₇:Ag glass samples after deleting of "Li₂B₂O₇:Ag + Ag NPs" interface layer coincided completely with the transmission spectra of these samples recorded before annealing (Fig. 1, curve 1 and Fig. 2, curve 1).

Nevertheless, if to look carefully at our transmission spectra recorded before annealing of the Li₂B₂O₇:Ag and CaB₄O₇:Ag glass samples (Fig. 1, curve 1 and Fig. 2, curve 1) one can see the weak but still noticeable plasmon absorption bands in the neighborhood of 400–450 nm. This indicates the presence of some number of the Ag NPs in volumes of our glass samples, which were not additionally annealed after the glass preparation. It is interesting to note that annealing in air under the same conditions (temperature and anneal time) of the newly prepared samples from Li₂B₂O₇:Ag and CaB₄O₇:Ag glasses does not lead to noticeable changes in the absorption spectra, i.e., these practically coincide with the spectra of unannealed samples (as on Fig. 1, curve 1 and Fig. 2, curve 1). This can mean that some number of the Ag NPs is formed in volume of Li₂B₂O₇:Ag and CaB₄O₇:Ag glasses just on the stage of glass formation from corresponding melt in the process of its cooling. And this number of the Ag NPs formed in the volume has time to reach saturation in the process of cooling, because additional annealing does not lead to increasing of their concentration. Almost equal intensities of the plasmon absorption bands of the unannealed Li₂B₂O₇:Ag and CaB₄O₇:Ag glass samples (Fig. 1, curve 1 and Fig. 2, curve 1) permit to state that the Ag NPs concentration in volumes of the both glasses must be almost the same, although there is more free volume in the CaB₄O glass than in the Li₂B₂O₇ glass [34]. This can be easily explained: in the volume, at absence of ions-reducers the process of

Ag⁺ ions reducing practically does not take place, and this small number of Ag NPs in the volume of the glass is formed from the neutral Ag atoms, which, evidently, are available in it from the moment of synthesis.

Therefore, the main difference between the Li₂B₂O₇:Ag and CaB₄O₇:Ag glasses is seen in the mechanism and efficiency of Ag NPs formation in the near surface of the glass samples. Undoubtedly, the process of Ag⁺ ions reducing to neutral Ag⁰ atoms and the Ag NPs formation takes place by the same mechanism on surface of the glass samples, but with different intensity (velocity). This intensity is defined by ratio of velocities for three main processes, which take place in the glasses at annealing temperature (∼713 K for Li₂B₂O₇ and ∼870 K for CaB₄O₇ glasses): 1) velocity of the process O₂⁻ → 2 e⁻ + O⁰ on the glass surface and transition of the neutral oxygen atoms into vacuum, where these are absorbed by getter; 2) intensity of Ag⁺ ions reducing to neutral atoms near the glass surface (Ag⁺ + e⁻ → Ag⁰); 3) velocity of Ag⁺ ions diffusion from the glass volume to surface, because in reducing process the concentration of Ag⁺ ions decreases near the surface, and their delivery to near-surface layer takes place owing to diffusion from the sample volume in direction to the surface.

Let us compare successively the passage of all these three processes in the Li₂B₂O₇:Ag and CaB₄O₇:Ag glasses. Therefore, at preparation of the glass samples there is used mechanical treatment (cutting, grinding and polishing), which leads to appearance of well developed network of defects with damaged, in particular, dangling interatomic bonds on surface of the both
glass samples. If such glass samples are heated in vacuum to temperatures $T^*$, then near such defective places the neutral oxygen atom, which is formed from $O^2-$ (or $O^-$) ion, can easily lose contact and come from surface of borate glass into vacuum, returning excess electrons to the neutral $Li^+$ or $Li^{2+}$ ions in the $Li_2B_4O_7$-$Ag$ glass, and $Ag^+$ or $Ca^{2+}$ in the $CaB_4O_7$-$Ag$ glass, because electron affinity of $O$ atoms is negative. And velocity of this process must not differ essentially for the $Li_2B_4O_7$-$Ag$ and $CaB_4O_7$-$Ag$ glasses, because the basis of their structure is consisted of similar boroxole groups, and $B-O$ bonds are definitive in the borate glasses.

However the processes of $Ag^+$ ions reducing to neutral $Ag^0$ atoms near the surface of the $Li_2B_4O_7$-$Ag$ and $CaB_4O_7$-$Ag$ glasses take place somewhat differently. For the $Li_2B_4O_7$-$Ag$ glass the electrons can be captured by $Li^+$ ($Li^+ + e^- \rightarrow Li^0$) ions, if $Ag^+$ ions are absent near position in which the process $O^2-\rightarrow 2e^-\rightarrow O^-$ took place. The captured electron can easily migrate on the neighbor $Li^+$ ions until it will be met and captured by $Ag^+$ ion. But neutral $Ag^0$ atom will not send so easily the captured electron to neighbor $Li^+$ ion, because ionization potential for $Ag \rightarrow Ag^+ \rightarrow 7.6$ eV, while for $Li \rightarrow Li^+ \rightarrow 5.4$ eV. Another situation takes place for the $CaB_4O_7$-$Ag$ glass: if electron, released by oxygen, is captured by $Ca^{2+}$ ion but not directly by $Ag^+$ ion, then, practically, it will not be delivered, because ionization potential for $Ca^+ \rightarrow Ca^{2+} \rightarrow 11.87$ eV. If take into account that here we observe an accumulation of negative charge on the sample that will slow down the process $O^2-\rightarrow 2e^-\rightarrow O^-$, then the large difference between the velocities of $Ag^+$ ions reducing to neutral atoms near the surface of $Li_2B_4O_7$-$Ag$ and $CaB_4O_7$-$Ag$ glasses becomes understandable, in the $CaB_4O_7$-$Ag$ glass it is significantly smaller.

In regard to the velocity of $Ag^+$ ions diffusion from the glass volume to the surface, where their concentration decreases because of reducing process $Ag^+ + e^- \rightarrow Ag^0$, one can note that $Ag^+$ ions, without doubt, diffuse easier on lithium vacancies ($V_{Li}$) in the structure of the $Li_2B_4O_7$ glass, than on $V_{Ca^{2+}}$ vacancies in the structure of $CaB_4O_7$ glass. Therefore, the velocity of $Ag^+$ ions supply from the glass volume to its surface in the $CaB_4O_7$-$Ag$ glasses by means of diffusion also must be significantly smaller.

The neutral $Ag^0$ atoms near the surface can migrate enough easy on the frame structure of the borate glass that gives them a possibility to unite into clusters-nuclei with the next formation of the Ag NPs on these surface defects, the number of which on/near the surface is significantly larger than in the glass volume. Therefore, at annealing in vacuum, the layers with Ag NPs are formed on the surface and in near-surface regions of the $Li_2B_4O_7$-$Ag$ and $CaB_4O_7$-$Ag$ glass samples. Nevertheless, owing to above described difference between the velocities of the processes, equipped in formation of the Ag NPs, their concentration in the near-surface layers of the $Li_2B_4O_7$-$Ag$ and $CaB_4O_7$-$Ag$ glasses differ significantly. For the $CaB_4O_7$-$Ag$ glass it is significantly lower that is confirmed by intensity of the plasmon absorption bands (Fig. 1, curve 2 and Fig. 2, curve 2).

4. Conclusions

Performed investigations showed that Ag NPs can be formed both in alkaline $Li_2B_4O_7$-$Ag$ and in alkaline-earth $CaB_4O_7$-$Ag$ tetraborate glasses by thermal treatment in vacuum at the glass transition temperature $T^*$. And it was observed that almost equal, but not large, number of the Ag NPs is formed in volumes of the both glasses, whereas the major mass of the Ag NPs with size to $2R = 3.0$ nm is concentrated near the surfaces of the glass samples. On the basis of the plasmon resonance results it was made a conclusion that concentration of the Ag NPs in the near-surface layer of $CaB_4O_7$-$Ag$ glass is significantly smaller than in the near-surface layer of $Li_2B_4O_7$-$Ag$ glass. This peculiarity can be explained by difference between contributions of alkaline $Li^+$ and alkaline-earth $Ca^{2+}$ ions in processes of the Ag NPs formation in corresponding tetraborate glass.

Despite smaller concentration of the Ag NPs in the near-surface layer of $CaB_4O_7$-$Ag$ glass and, respectively, weaker intensity of the plasmon resonance in it, this glass can be very prospective for plasmonics owing to high value of the nonlinear refractive index $n_2$ (Table 2) and total nonhygroscopicity.

References