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FORMATION AND OPTICAL PROPERTIES OF SILVER NANOPARTICLES IN $\text{Li}_2\text{B}_4\text{O}_7\text{-Gd}_2\text{O}_3\text{-Ag}_2\text{O}$ BORATE GLASS

PACS 81.07.-b

The formation of metallic (silver) nanoparticles (AgNPs) in the near-surface layer of $97.0\text{Li}_2\text{B}_4\text{O}_7\text{-}1.0\text{Gd}_2\text{O}_3\text{-}2.0\text{Ag}_2\text{O}$ ($\text{Li}_2\text{B}_4\text{O}_7\text{:Gd,Ag}$) glass at the annealing in vacuum or in air has been reported. The “bottom-up” mechanism of nanoparticle formation is suggested. A conclusion is drawn that the annealing in vacuum does not necessarily require the presence of reducing ions, whereas the formation of nanoparticles at the annealing in air is impossible without reducing agents. Structural defects play a crucial role in the AgNPs nucleation process. The intense plasmon absorption bands peaked at 400.4, 564.2, and 413.7 nm are observed in the absorption spectra of glasses enriched with AgNPs. The average radius of nanoparticles is calculated from the half-width of plasmon bands and falls within the interval of 1.0–1.5 nm. The nonlinear refractive index n_2 related to plasmons in AgNPs is calculated from the normalized transmission and absorption spectra, is positive, and increases approximately 2–4 times as compared to that of $\text{Li}_2\text{B}_4\text{O}_7\text{:Gd,Ag}$ matrix.

Key words: borate glass, metallic Ag nanoparticles, plasmon resonance, nonlinear refractive index.

1. Introduction

Composite materials consisting of metallic nanoparticles (MNPs) in dielectric media have been intensively studied in the last years. The theoretical aspect of such researches is predetermined by a substantial influence of MNPs on the linear and nonlinear susceptibilities of the matrix [1–3], radiative recombination processes [4], and huge surface-enhanced Raman scattering (SERS) [5, 6]. The mechanism of those influences is mainly associated with local fields that are formed in a system of nanoparticles with a fractal structure [7]. The practical interest in dielectric ma-

terials with MNPs is related to the prospects of the creation of optical switches on their basis with an ultra-short response time and optical limiters of a laser beam intensity, to a possibility to synchronize laser modes, and so on [8–11].

Nanoparticles of noble metals in various matrices are studied most intensively, which is associated with their specific chemical properties [12]. Nowadays, the most attention is attracted to Ag nanoparticles (AgNPs) both in bulk [13] and on the surface of glasses, in particular, silicate ones [14]. The main technique of MNPs formation in glasses includes the decay of a supersaturated solid solution of a neutral noble metal in the matrix. The key stage of this method is the process of metal reduction to the neutral state in the glass matrix. For this purpose, the

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thermal treatment in a reducing atmosphere with the additional doping by the so-called ions-reducers [15] is applied, as a rule.

Borate glasses of the system $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ – in particular, $\text{Li}_2\text{B}_4\text{O}_7$ [16] – based on boric anhydride B_2O_3 can be promising for the formation of AgNPs. Since the both stable coordinations of the oxygen environment, triangular BO_3 and tetrahedral BO_4 , of boric anhydride B_2O_3 tend to the polycondensation, its compounds are very well suitable for the glass manufacture [17]. The so-called boric anomaly in the system $\text{B}_2\text{O}_3-\text{Li}_2\text{O}$, which falls just within the interval of the $\text{Li}_2\text{B}_4\text{O}_7$ compound with the maximum ratio $\text{BO}_3:\text{BO}_4 = 1:1$, is responsible for a number of specific properties of this compound, which allows the latter to be used in the form of both single crystals [18, 19] and glass [20]. Structurally, borate glass consists of boron-oxygen groups (tetraborate, triborate, and so forth) connected by bridge oxygen atoms similarly to what takes place in crystalline borates. However, contrary to the latter possessing the long-range order, borate glasses consist of semioordered microdomains of boroxol groups. Such a disordering in the borate glass structure gives rise to an increase of the average B–O distance in both stable oxygen coordinations of boron: triangular, BO_3 , and tetrahedral, BO_4 [21]. At the same time, as was found in works [22, 23], boroxol groups make the borate glass structure some more open in a vicinity of the vitrification temperature T_g . Hence, $\text{Li}_2\text{B}_4\text{O}_7$ glass with $T_g = 713$ K [24] is a well-suitable material for the experiments on the AgNPs formation. It is the more so, because this glass has no such strict restrictions with respect to the doping Ag impurity concentration in the glass structure, as the single crystal has [25]. Taking into account that borate compounds demonstrate considerable nonlinear optical properties resulting from the high values of nonlinear susceptibilities of boron-oxygen complexes [26, 27], which can be controlled with the use of MNPs, borate glasses can be potentially very promising for photonics [28].

Our previous researches showed that AgNPs can be formed on the surface of $\text{Li}_2\text{B}_4\text{O}_7:\text{A}$ glass annealed in a reducing atmosphere without any reducing admixtures [16, 29]. At the same time, the authors of work [30] analyzed the influence of reducing Eu ions on the formation of MNPs in the sodium borate glass $65\text{B}_2\text{O}_3-27\text{Na}_2\text{O}-8\text{Al}_2\text{O}_3-0.5\text{Ag}_2\text{O}-x\text{Eu}_2\text{O}_3$. This work deals with the formation and the study of op-

tical properties of $97.0\text{Li}_2\text{B}_4\text{O}_7-1.0\text{Gd}_2\text{O}_3-2.0\text{Ag}_2\text{O}$ (hereafter, $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$) glasses obtained by the thermal treatment of AgNPs in vacuum and in air, as well as with the revealing of plasmon resonance bands in them.

2. Experimental Technique

While fabricating $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass, lithium carbonate Li_2CO_3 , boric acid H_3BO_3 , gadolinium oxide Gd_2O_3 , and silver nitrate AgNO_3 of high purity were used. The mixture of chemical reagents corresponding to the stoichiometric composition of $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ was placed in a ceramic crucible. Within the method of multistage temperature synthesis following the chemical reaction



$\text{Li}_2\text{B}_4\text{O}_7$ powder with $T_{\text{melt}} = 1198$ K was obtained. Then 2 wt.% AgNO_3 and 1 wt.% Gd_2O_3 were added. Glass was fabricated by melting the powder in an Al_2O_3 crucible at a temperature of 1270 K in the air environment. The melt was homogenized for 0.5 h. First, it was quickly cooled down to a temperature of about 670 K and then freely cooled down to room temperature. Plates about $10 \times 7 \times 1$ mm³ in dimension were cut out from the obtained glass, and their surfaces were ground and polished.

In order to form AgNPs, the specimens were annealed at a temperature of 710 ± 5 K for 1–2 h in the air environment or in vacuum ($<10^{-4}$ mm Hg with a titanic getter).

The transmission spectra were measured on an installation created on the basis of an MDP-23 monochromator and a personal computer. An incandescent halogen lamp was used as a light source. A photoelectron multiplier FEP-79 operating in the quantum counting mode played the role of a detector, which provided the linearity of signal registration in the range of 10^2-10^6 .

In order to study the nonlinear optical properties, the traditional single-beam Z-scan technique was applied [31, 32]. The measurements were carried out at room temperature with the help of the second-harmonic radiation by a continuous-wave diode-pumped neodymium laser with a wavelength of 532 nm. The output power of the laser beam amounted to 45 mW. The parameters of the focused laser beam

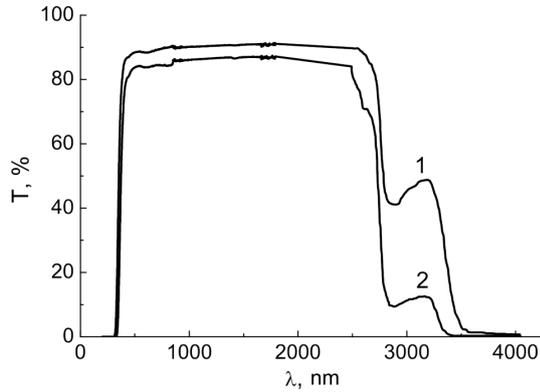


Fig. 1. Spectral intervals of glass transparency for $\text{Li}_2\text{B}_4\text{O}_7$ (1) and $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ (2)

satisfied the basic requirements of the Z -scan experiment: $2\omega_0 = 22.3 \mu\text{m}$ (ω_0 is the Gaussian beam radius at the focus), the diffraction length in the Rayleigh range $b = \frac{n\pi\omega_0}{\lambda} = 1.197 \text{ mm}$, and the laser beam power density at the focus $I_0 = 1.04 \times 10^4 \text{ W/cm}^2$.

The Z -scan experiment allows one to calculate the nonlinear refractive index n_2 in the known expression for the total refractive index

$$n = n_0 + n_2|E|^2, \quad (1)$$

where n_0 is the linear refractive index, and E is the strength amplitude of the electromagnetic field created by the laser radiation. The nonlinear refractive index n_2 was calculated from normalized Z -scan spectra according to the formula [32]

$$n_2 = \frac{\Delta\Phi_0}{kL_{\text{eff}}I_0}, \quad (2)$$

where $\Delta\Phi_0$ is the nonlinear phase distortion, $k = \frac{2\pi}{\lambda}$ is the wave vector, I_0 is the maximum of laser radiation intensity at the focus,

$$L_{\text{eff}} = \frac{1 - e^{-\alpha L}}{\alpha} \quad (3)$$

is the effective specimen thickness, α is the linear absorption coefficient at a wavelength of 532 nm, and L is the specimen thickness.

The nonlinear phase distortion $\Delta\Phi_0$ is empirically connected with the variation of the normalized transmittance $\Delta T_Z = T_{+Z} - T_{-Z}$ obtained from the experimental Z -scan spectrum,

$$|\Delta\Phi_0| \cong \frac{\Delta T_{pv}}{0.406(1 - S)^{0.27}}, \quad (4)$$

where S is the diaphragm transmittance in the absence of a specimen; and ΔT_Z the difference between the values of transmittance, T , maxima at positive, T_{+Z} , and negative, T_{-Z} , Z -coordinates. In our experiment with a closed diaphragm, $S = 0.07$ times the light intensity incident on the diaphragm.

3. Experimental Results

Before proceeding to the thermal treatment of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses to form AgNPs in them, it was worth studying the optical properties of the glass matrix itself and determining the doping-induced variations in the optical properties of $\text{Li}_2\text{B}_4\text{O}_7$ glasses. Therefore, we registered and analyzed the absorption spectra of the following as-fabricated glasses, i.e. without any additional thermal treatment: pure $\text{Li}_2\text{B}_4\text{O}_7$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$.

The transparency interval of undoped glass $\text{Li}_2\text{B}_4\text{O}_7$ extends from 350 to 3500 nm (i.e. from 3.54 to 0.35 eV) (Fig. 1, spectrum 1). One can see that no additional pronounced absorption bands are observed on the short-wave spectral side. At the same time, an intense absorption band with a maximum at 2.8–2.9 μm (about 0.43 eV) is distinguished in the long-wave section of the spectrum. The position of this absorption band is determined by the $\text{Li}_2\text{B}_4\text{O}_7$ glass matrix, because the Gd and Ag admixtures do not affect it. However, the intensity of this band appreciably depends on admixtures. In particular, the Ag admixture brings about a drastic growth of its intensity (Fig. 1, spectrum 2). At the same time, the additional researches of absorption in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses in an interval of 2.5–3.5 μm showed that the intensity of absorption by the glass with the single Gd impurity or Gd together with Ag ($\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass) occupies an intermediate position between those for undoped $\text{Li}_2\text{B}_4\text{O}_7$ glass and $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass.

In Fig. 2, the absorption spectra of unannealed glasses – undoped $\text{Li}_2\text{B}_4\text{O}_7$ (a), $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ (b), $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ (c), and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ (d) – in the spectral range 360–720 nm (≈ 3.4 –1.7 eV), where AgNPs plasmon resonance bands [33] should manifest themselves, are exhibited. As one can see, the main differences between the absorption spectra of all four glasses are observed in a spectral range of 2.8–3.3 eV (443–376 nm).

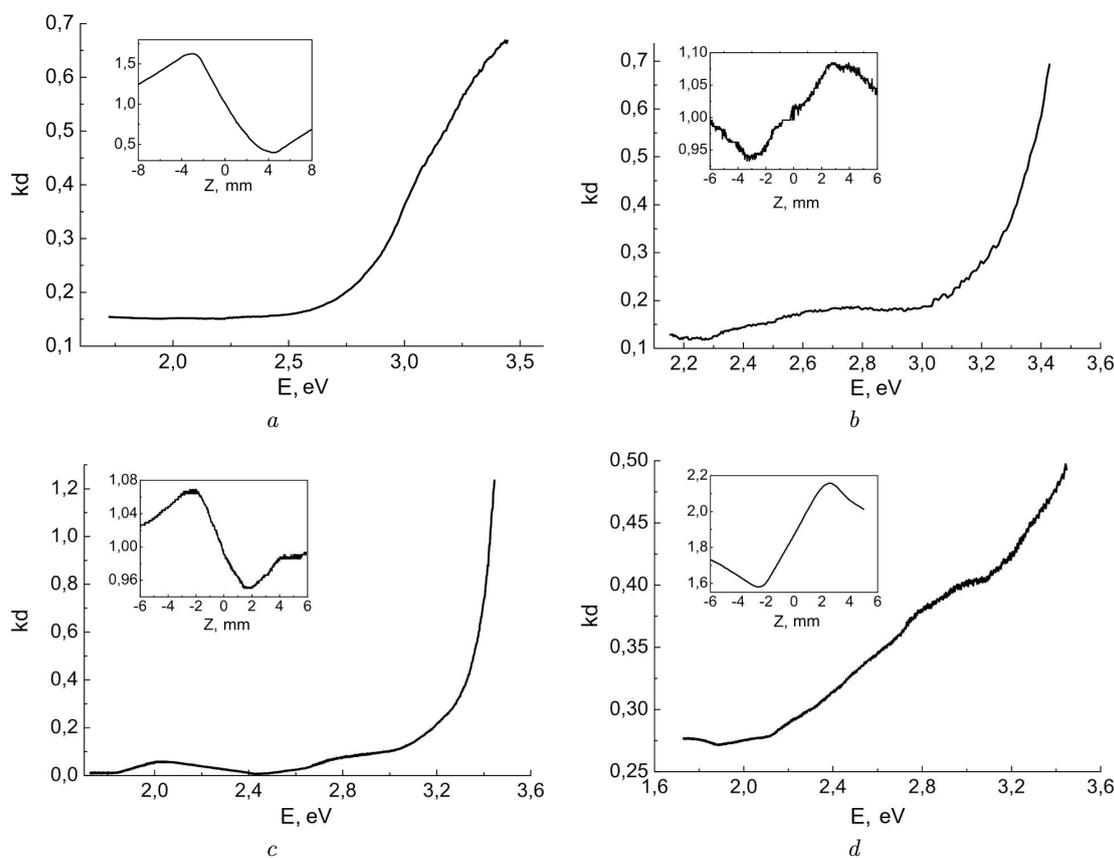


Fig. 2. Absorption spectra of unannealed glasses $\text{Li}_2\text{B}_4\text{O}_7$ (a), $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ (b), $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ (c), and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ (d). The spectra of normalized transmittance obtained from the experimental Z -scan spectra of the corresponding specimens are shown in the insets

In order to estimate the nonlinear properties of unannealed glasses in all four variants, they were used to record spectra in the Z -scan mode at a wavelength of 532 nm, and the corresponding spectra of normalized transmittance were plotted (see insets in Fig. 2). Those spectra demonstrate that the quantity $\Delta T_Z = T_{+Z} - T_{-Z}$ has negative values for undoped $\text{Li}_2\text{B}_4\text{O}_7$ glass (Fig. 2, a) and $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass (Fig. 2, c), whereas it is positive for $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ (Fig. 2, b) and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ (Fig. 2, d) glasses.

After the thermal treatment, the absorption spectrum of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass looks absolutely different. Figure 3, a demonstrates the absorption spectrum (the extinction difference before and after the annealing) of a specimen of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass after its annealing at a temperature of 710 ± 5 K for 1 h in vacuum ($<10^{-4}$ mm Hg with a titanitic getter). Similarly to what was observed earlier for $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$

glass annealed in vacuum [29], the recorded spectrum reveals a very wide nonelementary absorption band associated with the plasmon resonance at AgNPs. This spectrum can be easily resolved at least into two components with maxima at 3.1 and 2.2 eV (400.4 and 564.2 nm, respectively). The normalized transmittance spectrum (Fig. 3, b) demonstrates that the difference $\Delta T_Z = T_{+Z} - T_{-Z}$ is positive for $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass with AgNPs annealed in vacuum.

However, unlike the annealing of $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass in air [29], which did not lead to appreciable modifications in its absorption spectrum, the annealing of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass in air at a temperature of 710 ± 5 K for 1 h resulted in the appearance of an intensive absorption band with a very pronounced maximum at about 3.0 eV (413.7 nm) (Fig. 4, a), which is associated with the plasmon resonance at

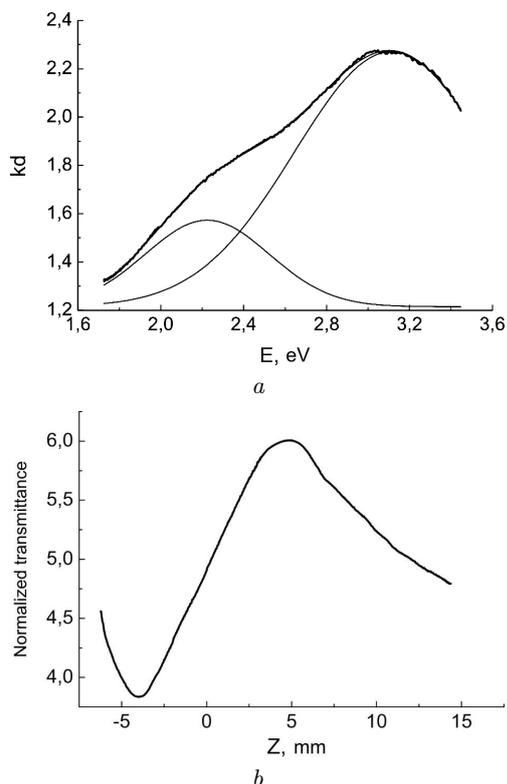


Fig. 3. Differential absorption spectrum and its resolution into components (a) and the spectrum of normalized transmittance from the experimental Z -scan spectrum (b) for the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass annealed in vacuum

AgNPs. The resolution of this spectrum into Gaussians allowed us to single out a weak band at about 2.3 eV (539.6 nm). The normalized transmittance spectrum (Fig. 4, b) showed that $\Delta T_Z = T_{+Z} - T_{-Z}$ is also positive in this case ($\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass with AgNPs annealed in air).

It is worth noting that the surfaces of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens annealed in vacuum or in air differed even by their appearance: the specimen annealed in vacuum was darkish with a nonglare surface, whereas that annealed in air had a glare surface of a yellowish tint. Basing on this fact, the conclusion was drawn that AgNPs in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass annealed in vacuum is mainly located on the surface, whereas the surface of the specimen annealed in air is almost free of AgNPs. To be convinced of that, the surfaces of the specimens were accurately wiped at first. It turned out that a dark deposit could be easily removed from the surface of the specimen annealed in vacuum, whereas the specimen annealed in air re-

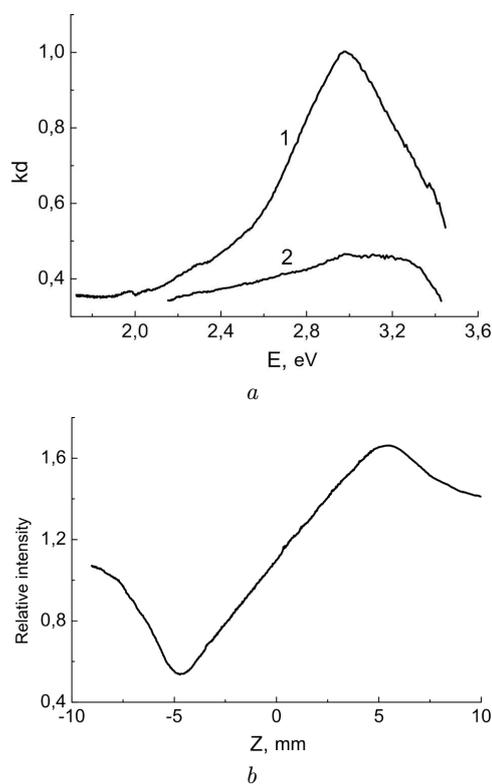


Fig. 4. Differential absorption spectra (1) before and (2) after the removal of the interface layer (a) and the normalized transmittance spectrum (b) for the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimen annealed in air

mained invariant. In order to be convinced of that AgNPs are arranged over the whole volume of the specimen annealed in air, layers about $1 \mu\text{m}$ in thickness were ground off from both its surfaces, and the surfaces were polished again. In the new absorption spectrum (Fig. 4, a, curve 2) registered after the removal of a $2\text{-}\mu\text{m}$ layer from the specimen surfaces, the intensity of the absorption band with the maximum at about 3.0 eV connected with AgNPs becomes very weak. The increase of the ground-off layer thickness practically did not change the absorption spectrum. Hence, we may suppose that this residual absorption band (Fig. 4, a, curve 2) is associated with the plasmon resonance at AgNPs located in the bulk of the glass matrix.

4. Discussion of Results

In our previous researches on $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glasses annealed in a reducing atmosphere [16, 29], it was found that AgNPs formed at the annealing are mainly

accumulated on the surface, whence they can be mechanically removed rather easily. Similar results were obtained for the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens annealed in vacuum. However, if the specimens of this glass are annealed in air, the situation is absolutely different. It turned out that AgNPs are practically absent from the surface of those specimens. Instead, they are completely concentrated in a thin near-surface layer, which we called the interface layer. They cannot be removed using a simple mechanical rubbing of the surface: a certain interface layer has to be ground off for this purpose.

There are a number of important issues that naturally arise while analyzing the results obtained: 1) the mechanism of AgNPs formation, 2) the size of formed AgNPs and the thicknesses of the active interface layer containing AgNPs, 3) the influence of the interface layer with AgNPs on the nonlinear properties, in particular, on the nonlinear refractive index n_2 of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses with AgNPs.

4.1. Mechanism of AgNPs formation

The results of our researches dealing, in particular, with the mechanical grinding of specimen surfaces allowed us to draw the following conclusions: 1) the majority of AgNPs formed at the annealing of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses in vacuum are located on the specimen surface, and other AgNPs occupy a thin near-surface layer; 2) almost all AgNPs formed at the annealing of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses in air are accumulated in a thin near-surface layer. Hence, we may declare about the formation of the so-called thin interface region with AgNPs on the surface of a glass specimen.

AgNPs are formed on the surface of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens annealed in vacuum mainly owing to the reduction of silver ions near the surface following the process that can be written down in the form $\text{Ag}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 \uparrow + 2\text{Ag}^0$, as was observed for $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glasses [29]. This process becomes possible at elevated temperatures owing to the escape of oxygen atoms from the surface of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimen into vacuum, where they are absorbed by a getter. As a result of this process, the concentration of Ag^+ ions near the surface decreases, and they diffuse from the bulk to the surface of the specimen.

If $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses are annealed in air, the interface region with AgNPs is formed in accordance

with an absolutely different scenario, because the oxygen available in air prevent oxygen atoms from escaping from the specimen surface into vacuum, where they are absorbed by a getter. Therefore, in this case, there must be a mechanism which allows the reduction of Ag^+ to the neutral state Ag^0 in the glass bulk. Gadolinium can evidently play such role of a reducing agent. The basic valency of gadolinium equals +3. Since we add Gd_2O_3 to glass, Gd^{3+} must prevail in it. However, Gd was found to form unstable derivative peroxide compounds, in which it has the valencies 4 (Gd^{4+}) and 5 (Gd^{5+}), e.g., $\text{Gd}_2\text{O}_4 \times 2\text{H}_2\text{O}$ and $\text{Gd}_2\text{O}_5 \times 2\text{H}_2\text{O}$ [34]. In other words, gadolinium can change its valency under certain conditions. Probably, such conditions may be realized in the structure of our glass $97.0\text{Li}_2\text{B}_4\text{O}_7-1.0\text{Gd}_2\text{O}_3-2.0\text{Ag}_2\text{O}$, and Gd^{3+} ions play the role of a reducing agent in this case. This reduction process at elevated temperatures can be presented as follows:



Neutral Ag^0 atoms, which can migrate over the frame structure of borate glass rather easily, are able to unite into clusters serving as nuclei in the following formation of AgNPs. Most probably, such nuclei can be formed near the structural defects of the glass matrix. It is clear that there are much fewer structural defects in the glass bulk than near the glass surface, because, in the course of glass specimen manufacture, a mechanical treatment (cutting, grinding, or polishing) is applied, which results in the emergence of a well-developed system of defects on the specimen surface. Therefore, the number of AgNPs nuclei at the surface defects prevails. Just this conclusion is confirmed by the results of our researches concerning the plasmon spectra registered for a glass specimen annealed in air (Fig. 4, *a*, spectrum 1) and the same specimen but with both surfaces grounded to remove the interface layers (Fig. 4, *a*, spectrum 2). Since the plasmon band intensity undoubtedly depends on the AgNPs concentration, Fig. 4, *a* unambiguously testifies to a huge difference between the AgNPs concentrations in the near-surface layer and in the bulk of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimen annealed in air.

Hence, the registered fact that an interface layer is formed in the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens dur-

ing their annealing in air can be explained as follows. A small number of neutral Ag^0 atoms formed in the specimen bulk owing to the reduction, in which gadolinium ions participate, succeed in the uniting into clusters at bulk defects. At the same time, the majority of neutral Ag^0 atoms migrate to the surface, where this process runs much more intensively. Here, the formation of AgNPs occurs by adding single Ag^0 atoms to the nucleus. Therefore, the proposed mechanism of AgNPs growth in the near-surface layer of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass during its annealing in air belongs to the “bottom-up” class. On the other hand, if the specimen is annealed in vacuum, the process of formation of neutral Ag^0 atoms on the surface substantially dominates over the reduction with the participation of gadolinium ions in bulk. As a result, the processes of AgNPs nucleation and formation run more intensively on the specimen surface.

4.2. Calculation of AgNPs radii

The fact that the plasmon absorption bands for the annealed specimens of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass can be definitely resolved into two components testifies to an uncertainty concerning AgNPs formed in them, because it is known [12] that the spherical AgNPs with the same radius have a single band of the plasmon resonance, which shifts toward the long-wave region as the particle radius increases. However, some authors [14] consider that the spectral position and the shape of the plasmon band given by AgNPs can be modified by other factors as well, in particular, by a deviation of the AgNPs shape from the sphere, multipole effects (in the case where the particle radius $R > 20$ nm), and the electromagnetic interaction between nanoparticles (when the distance between particles is less than 10 nm). In our case, two plasmon absorption bands most probably testify that there are AgNPs with two different radii.

Table 1. AgNPs radii calculated from the plasmon band half-widths of annealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass

Annealing atmosphere	ε_{\max} , eV	$\Delta\varepsilon$, eV	$\Delta\omega$, 10^{15}s^{-1}	R , nm
Vacuum	band 1	3.1	1.0	0.9
	band 2	2.2	0.65	1.5
Air		3.0	0.65	1.4

The half-width of the plasmon absorption band can be used to estimate the AgNPs radius R [35],

$$R = \frac{V_F}{\Delta\omega}, \quad (5)$$

where V_F is the Fermi velocity, and $\Delta\omega$ the half-width of the plasmon absorption band. In metallic Ag, the Fermi velocity $V_F = 1.39 \times 10^6$ m/s [36]. The radii R of AgNPs calculated for our $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses annealed in vacuum and in air are quoted in Table 1.

One can see that AgNPs in our borate glass are characterized by rather small dimensions, provided of course that the method applied by us to calculate the AgNPs radii is correct. The radii calculated by us on the basis of the plasmon band half-width well correlate with radii of 2.8–6.0 nm obtained for AgNPs in various glasses by other authors [30, 37, 38]. However, our previous AFM researches of AgNPs formed by annealing in the reducing atmosphere of H_2 [16] or in vacuum [29] on the surface of $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass showed that the value of R falls within the limits from 7 to 25 nm, with a maximum near 15 nm. Such a spread in the dimensions of AgNPs obtained using different methods in $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses can be explained by the fact that different techniques of radius determination may give rise to nonidentical results. In particular, the AFM method did not allow us to reveal AgNPs smaller than 7 nm in dimension.

4.3. Nonlinear properties of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass with AgNPs

Since the dimensions of AgNPs are much smaller than the laser radiation wavelength, $\text{Li}_2\text{B}_4\text{O}_7$ glass with AgNPs can be considered as a homogeneous composite material, which can be described by some effective parameters. In the framework of the standard two-level scheme for this medium, the expression for the nonlinear refractive index n_2 in relation (1) looks like [39]

$$n_2(\omega_i) = -2\pi N \frac{|\mu_{i0}|^4}{n_0 \hbar (\omega_{i0} - \omega)^3}, \quad (6)$$

where N is the concentration of active centers of the nonlinear excitation, the subscript i denotes the one- or two-photon excitation process, and μ_{i0} is the dipole

moment of the transition at a frequency ω_{i0} . The parameters ω_{i0} and ω describe the frequencies of the laser radiation and oscillators that form the nonlinear response, respectively.

From relation (6), one can see that the sign of the nonlinear index n_2 does not depend on N and μ_{i0} , being determined only by the sign of the quantity $\Delta = \omega_{i0} - \omega$, which describes a deviation of the oscillator frequency from the resonance one. Since the real part of the complex third-order susceptibility $\chi^{(3)}$ is linearly proportional to n_2 [39], the relation that determines the nonlinearity sign for the composite medium looks like

$$\text{Re } \chi^{(3)} \sim (\omega_{i0} - \omega). \quad (7)$$

In our case, the frequency of the laser radiation used in this work amounted to $\omega_{i0} = 18796 \text{ cm}^{-1}$ or 2.33 eV ($\lambda = 532 \text{ nm}$). Therefore, the oscillators with frequencies $\omega < \omega_{i0}$ have to take part in the formation of negative n_2 -values for unannealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ and undoped $\text{Li}_2\text{B}_4\text{O}_7$ glasses (Figs. 2, *a* and *c*). One can see that there exists an intense wide absorption band with a maximum at about $2.8 \mu\text{m}$ in the range of about 4000 cm^{-1} ($2.5\text{--}3.0 \mu\text{m}$) in the transmission spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ and undoped $\text{Li}_2\text{B}_4\text{O}_7$ glasses (Fig. 1). Therefore, it is quite reasonable to suppose that just the oscillators responsible for the absorption of our glasses in this spectral range are also responsible for the negative nonlinear response. This hypothesis makes it possible to explain the registered fact that the Gd admixture in unannealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses brings about a certain reduction in the intensity of the band at $2.8 \mu\text{m}$.

After the annealing in vacuum or in air, AgNPs are formed in bulk and near the surface of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens. As is seen from Fig. 3, the maxima of the components of surface plasmon resonance bands for glasses with AgNPs annealed in vacuum are located on the different sides from the laser working frequency ω_{i0} : one band at 400.4 nm (3.1 eV), i.e. at the frequency $\omega > \omega_{i0}$, and the other band at 564.2 nm (2.2 eV), i.e. at the frequency $\omega < \omega_{i0}$. From expression (7), one can see that the plasmon bands with $\omega > \omega_{i0}$ should make a positive contribution to the value of nonlinear refractive index n_2 , whereas the bands with $\omega < \omega_{i0}$ a negative one. This means that, in our glasses annealed in

vacuum, the plasmon band at 400.4 nm inserts a positive contribution to n_2 , whereas the plasmon band at 564.2 nm a negative one. Hence, the final magnitude and the sign of the nonlinear refractive index n_2 induced by AgNPs in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass annealed in vacuum are determined by the ratio between those contributions.

For the specimen annealed in air, the band at 413.7 nm (3.0 eV), i.e. with the frequency $\omega > \omega_{i0}$, dominates. Accordingly, it makes a substantial positive contribution to the value of nonlinear refractive index n_2 . The very weak band at 539.6 nm (2.3 eV), which was mentioned above and whose frequency slightly exceeds ω_{i0} , probably gives no appreciable negative contribution to n_2 . This circumstance can be registered experimentally.

The contribution of the nonlinear refractive index n_2 to the total refractive index n described by expression (1) can be calculated for $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses annealed in vacuum and in air with the use of the normalized transmittance spectra obtained from the experimental Z-scan spectra (Figs. 3, *b* and 4, *b*), as well as relations (2)–(4). Despite that the plasmon absorption bands were absent (Fig. 2), we calculated the n_2 -values for undoped $\text{Li}_2\text{B}_4\text{O}_7$ and doped $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses without AgNPs in order to estimate the contribution given by the matrix to the index n_2 of annealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses with AgNPs. Since the impurity distribution over the specimens of unannealed glasses without AgNPs can be considered as uniform, and the contribution to n_2 is determined by the nonlinear properties of the whole matrix, the total thickness of the specimens was taken into account, while calculating L_{eff} and, accordingly, n_2 . The corresponding results are presented in the summarizing Table 2. One can see that undoped $\text{Li}_2\text{B}_4\text{O}_7$ glass and $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass doped with silver and annealed have negative n_2 -values from -1.44×10^{-9} to -3.8×10^{-9} , whereas doped $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$ and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses have positive n_2 -values of 1.15×10^{-9} and 1.49×10^{-8} , respectively. Hence, the glass matrix itself without AgNPs, irrespectively of whether it is doped or not, makes a contribution of about 10^{-9} – 10^{-8} to the nonlinear refractive index n_2 .

In order to calculate the nonlinear refractive index n_2 for the specimens of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass with AgNPs formed at the annealing, it is necessary to

Table 2. Nonlinear refractive index n_2 calculated from normalized transmittance spectra

Specimens	L , cm	α , cm^{-1}	L_{eff} , cm	$\Delta\Phi_0$	ΔT_Z	n_2 , cm/W
$\text{Li}_2\text{B}_4\text{O}_7$	0.11	0.68	2.42	-4.282	-1.70	-1.4×10^{-9}
$\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$	0.2	1.525	0.175	0.369	0.147	1.2×10^{-9}
$\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$	0.12	0.4	0.48	-2.26	-0.90	-3.8×10^{-9}
$\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ unannealed	0.074	4.12	0.0648	1.445	0.575	1.5×10^{-8}
$\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ annealed in vacuum	0.074	15.11	$2^*L_1 = 2.0 \times 10^{-4}$	1.173	0.467	3.2×10^{-6}
			$2^*L_2 = 1.0 \times 10^{-5}$	1.173	0.467	6.4×10^{-5}
$\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ annealed in air	0.074	2.79	$2^*L_1 = 2.0 \times 10^{-4}$	2.81	1.118	7.6×10^{-6}
			$2^*L_2 = 1.0 \times 10^{-5}$	2.81	1.118	1.1×10^{-4}

Note. 2^*L_i stands for the total thickness of two surfaces of active (interface) layers with AgNPs (L_{eff}) for each of the annealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens.

estimate the thickness of the active (interface) layer filled with those nanoparticles. In our previous work [29] on the formation of AgNPs in $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$ glass by the annealing, it was unambiguously established that AgNPs are formed in the near-surface layer. The existence of such active layers was also reported in other works. For instance, the authors of work [40] informed that the annealing of alkaline-silicate glass with admixtures, into which Ag^+ ions were introduced to a depth down to $20 \mu\text{m}$, using the ion exchange technique, in a wet atmosphere gave rise to the formation of an active layer $1 \mu\text{m}$ in thickness with AgNPs. The authors of work [38] informed about a layer of AgNPs with a thickness of 200–300 nm hidden at a depth of 100 nm below the specimen surface; the layer was also formed by the ionic exchange in industrial soda glass. In work [37], the thickness of an active layer with AgNPs obtained by the annealing of sodium-lead-germanate glass doped with AgNO_3 was estimated to equal only 50 nm. Such divergences of the thicknesses for the active layers with AgNPs in various glasses can be explained by the formation of the so-called Liesegang-like layers with AgNPs, the thickness of which does not exceed 100 nm. The existence of such layers was experimentally revealed [41] and theoretically substantiated [42].

Taken into account that grinding off a $1\text{-}\mu\text{m}$ layer from each surface of the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ specimen annealed in air gives rise to a complete removal of the active layer. With regard for the results obtained by other authors, which were mentioned above, we calculated the nonlinear refractive index n_2 for two thicknesses of the interface layer with

AgNPs: $^*L_1 = 1.0 \mu\text{m}$ and 50 nm. The results of those calculations together with the calculated n_2 -values for unannealed undoped $\text{Li}_2\text{B}_4\text{O}_7$ glass and unannealed doped $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd}$, $\text{Li}_2\text{B}_4\text{O}_7:\text{Ag}$, and $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses are quoted in Table 2. It is practically impossible to separate the absorption in the most active layers and the absorption by the matrix at the working laser wavelength 532 nm. Therefore, the L_{eff} values calculated for the selected values of the thicknesses of the interface layer with AgNPs 2^*L_1 are not quite correct. However, by the order of magnitude, the obtained n_2 -values, which are related to the existence of active layers with AgNPs, can be regarded as rather reliable.

Hence, as is seen from Table 2, the nonlinear properties of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens after their annealing in vacuum or on air, which results in the formation of the interface layer “ $\text{Li}_2\text{B}_4\text{O}_7:\text{AgNPs}$ ”, change appreciably. In particular, the nonlinear refractive index n_2 remains positive, as it was in the unannealed $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ specimen, but its value grows at least by 2 to 4 orders of magnitude. Hence, a conclusion can be drawn that the plasmon resonance in thin near-surface interface layers “ $\text{Li}_2\text{B}_4\text{O}_7:\text{AgNPs}$ ” formed on the surface of borate $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass by the annealing in vacuum or in air considerably enhances the nonlinear properties.

5. Conclusions

By melting a preliminarily synthesized compound $\text{Li}_2\text{B}_4\text{O}_7$ with Gd_2O_3 and AgNO_3 admixtures in an Al_2O_3 crucible at a temperature of 1270 K

in air, glass with the composition $97.0\text{Li}_2\text{B}_4\text{O}_7-1.0\text{Gd}_2\text{O}_3-2.0\text{Ag}_2\text{O}$ (briefly, $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$) was fabricated. By annealing it at a temperature of $710 \pm \pm 5$ K for 1 h in air or in vacuum ($<10^{-4}$ mm Hg with a titanic getter), AgNPs were formed in the glass specimens.

A model was proposed that the formation of AgNPs in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses is governed by the “bottom-up” mechanism realized in two variants. At the annealing in vacuum, the “bottom-up” migration process mainly engages Ag^+ ions. The generation process of neutral Ag^0 atoms occurs owing to the escape of oxygen atoms into vacuum. In this case, the nucleation and the formation of AgNPs take place on the specimen surface. At the annealing in air, neutral Ag^0 atoms are formed in the glass bulk owing to the valency variation of Gd^{3+} ions, which play the role of a reducing agent; afterward, neutral silver atoms migrate to the surface. In this case, the nucleation and the formation of AgNPs take place in the near-surface layer, so that an interface layer with AgNPs emerges.

The results obtained allow us to draw a conclusion that the former variant of the AgNPs formation in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses at the annealing in vacuum is much more intense and does not require the existence of a reducing process, in contrast to the latter variant with the annealing in air. The crucial role in the nucleation of AgNPs in $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glasses at elevated temperatures is played by structural defects and, especially, their concentration.

In the absorption spectra of $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ glass specimens annealed in vacuum and in air (the extinction difference before and after the annealing), the intense plasmon absorption bands with maxima and 400.4 and 564.2 nm (annealing in vacuum), and 413.7 nm (annealing in air) were observed. The calculations based on the plasmon band half-width showed that the radii of AgNPs formed on the surface and in the near-surface layer fall within the limits of 1.0–1.5 nm.

Using the spectra of the normalized transmittance and the absorption spectra, the contribution of the nonlinear refractive index n_2 to the total refractive index n was calculated. The nonlinear refractive index n_2 associated with plasmons at AgNPs was found to be positive and grows at least by 2 to 4 orders of magnitude in comparison with that for the $\text{Li}_2\text{B}_4\text{O}_7:\text{Gd,Ag}$ matrix free of nanoparticles.

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Received 18.06.14.

Translated from Ukrainian by O.I. Voitenko

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ФОРМУВАННЯ І ОПТИЧНІ
ВЛАСТИВОСТІ МЕТАЛІЧНИХ НАНОЧАСТИНОК Ag
В БОРАТНОМУ СКЛІ Li₂B₄O₇-Gd₂O₃-Ag₂O

Резюме

Повідомляється про формування металічних наночастинок Ag (МНЧ Ag) в приповерхневому шарі скла 97,0Li₂B₄O₇-1,0Gd₂O₃-2,0Ag₂O (Li₂B₄O₇:Gd,Ag) відпалом в атмосфері повітря чи вакуумі. Запропоновано механізм формування МНЧ Ag методом “знизу–вгору”. Зроблено висновок про те, що відпал у вакуумі не вимагає наявності відновлюючих йонів, тоді як формування МНЧ Ag в цьому склі відпалом в атмосфері повітря неможливе без них. Визначальну роль в утворенні зародків МНЧ Ag відіграють структурні дефекти. В спектрах поглинання в зразках скла з МНЧ Ag виявлені інтенсивні плазмонні смуги поглинання з максимумами 400,4 і 564,2 нм та 413,7 нм, відповідно. Розрахунок за півшириною плазмонних смуг показав, що радіуси МНЧ Ag знаходяться в межах 1,0–1,5 нм. Із спектрів нормалізованого пропускання і спектрів поглинання розраховано, що нелінійний показник заломлення n_2 , пов'язаний з плазмонами в МНЧ Ag, є додатним і зростає на 2–4 порядки, в порівнянні з матрицею Li₂B₄O₇:Gd,Ag.