Nonlinear optical parameters of borate glasses with Ag nanoparticles formed using reducing Gd^{3+} ions

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Abstract. Basing on experimental absorption spectra and Z-scan spectra measured in the closed- and open-aperture regimes, we have calculated the nonlinear optical parameters (the refractive index n_2, the absorption coefficient β, and the third-order susceptibility $\chi^{(3)}$) of borate glasses (BGs) $Li_2B_4O_7$–Gd_2O_3–Ag_2O, CaB_4O_7–Gd_2O_3–Ag_2O and $LiCaBO_3$–Gd_2O_3–Ag_2O that include Ag nanoparticles (NPs). The Ag NPs have been formed by annealing the glasses in the air atmosphere at the temperatures close to the glass-transition ones. We have proven that Gd^{3+} represents an efficiently reducing ion in the BGs. We have also ascertained that the plasmon resonance caused by the presence of Ag NPs increases significantly the nonlinear optical parameters n_2, β and $|\chi^{(3)}|$ of the BGs.

Keywords: borate glasses, Ag nanoparticles, nonlinear refractive index, third-order nonlinear susceptibility, nonlinear absorption coefficient.

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1. Introduction

A wide range of novel techniques have offered unprecedented facilities for producing various structural elements of nanometre sizes, which have caused the appearance of novel scientific branches such as nanophotonics or plasmonics [1–3]. Plasmonics has now become an area of numerous intense investigations [4, 5], because the frequencies of plasmon resonances in isolated nanoparticles (NPs) of some metals, in particular Au and Ag, are located in the visible spectral range. Especial interest is connected with nanocomposites consisting of dielectric materials, or matrices in which metal NPs are formed. Today a significant portion of attention of researchers is paid to formation of Ag NPs in different glass matrices [6–15]. Indeed, the plasmon resonance bands for this metal, which are caused by the Ag NPs, are observed in a very convenient visible spectral range (400–500 nm or so). This facilitates many applications of nanocomposite materials for the optical information storage, ultra-high speed communications, optical limitation of laser radiation, all-optical switching, etc. [9, 16, 17]. The appearance of nonlinear absorption, which can be used when synchronizing laser modes [18], represents another dominant property of the nanocomposite structures mentioned above.

In our previous works [11, 13–15], the Ag NPs in a number of borate glasses (BGs) such as $Li_2B_4O_7$:Ag and CaB_4O_7:Ag have been formed through annealing the latter in vacuum or in reducing hydrogen atmosphere. Note that it has been virtually impossible to form Ag NPs in the $Li_2B_4O_7$:Ag and CaB_4O_7:Ag glasses when the glasses are annealed in the air. Therefore it becomes evident that a presence of so-called 'reducing' ions in the BGs is a necessary condition for forming

the Ag NPs in the air atmosphere. As a consequence, the present work is aimed at studying nonlinear optical parameters of the BGs $Li_2B_4O_7$–Gd_2O_3–Ag_2O, CaB_4O_7–Gd_2O_3–Ag_2O and $LiCaBO_3$–Gd_2O_3–Ag_2O in which the Ag NPs are formed using Gd^{3+} as reducing ions.

2. Experimental techniques

To prepare $Li_2B_4O_7$–Gd_2O_3–Ag_2O ($Li_2B_4O_7$:Gd,Ag), CaB_4O_7–Gd_2O_3–Ag_2O (CaB_4O_7:Gd,Ag) and $LiCaBO_3$–Gd_2O_3–Ag_2O ($LiCaBO_3$:Gd,Ag) glasses, we used high-purity lithium carbonate (Li_2CO_3), calcium carbonate ($CaCO_3$), boric acid (H_3BO_3), gadolinium oxide (Gd_2O_3), and silver nitrate ($AgNO_3$) compounds. As a first step, we prepared $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$ with a multi-staged solid-phase synthesis performed in a ceramic crucible. The following procedures were used:

(1) a $Li_2B_4O_7$ powder with T_{melt} = 1198 K was obtained with the aid of the chemical reaction

$$Li_2CO_3 + 4H_3BO_3 \rightarrow Li_2B_4O_7 + CO_2\uparrow + 6H_2O\uparrow;$$

(2) a CaB_4O_7 powder (T_{melt} = 1260 K) was obtained using the reaction

$$CaCO_3 + 4H_3BO_3 \rightarrow CaB_4O_7 + CO_2\uparrow + 6H_2O\uparrow;$$

(3) a $LiCaBO_3$ powder (T_{melt} = 1050 K) was obtained through

$$Li_2CO_3 + 2CaO + 2H_3BO_3 \rightarrow 2LiCaBO_3 + CO_2\uparrow + 3H_2O\uparrow.$$

0.7 mol % $AgNO_3$ and 1 mol % Gd_2O_3 were added to the $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$ powders thus obtained, and then carefully mixed. The glasses were obtained by melting, in an Al_2O_3 crucible, of the corresponding mixtures. This was done in the air atmosphere at the following temperatures: 1270 K for the case of $Li_2B_4O_7$:Gd,Ag, 1320 K for CaB_4O_7:Gd,Ag, and 1150 K for $LiCaBO_3$:Gd,Ag. The melts were homogenized during 0.5 h and cooled during 1 h down to ~ 670 K, with a further inertial cooling down to the room temperature. Rectangular plates (the lateral sizes ~ 10 × 7 mm^2 and the thickness L ~ 1 mm) were cut for further experiments from the glass boules.

The most optimal regime for forming the Ag NPs in our glass samples was determined empirically. It was revealed to correspond to annealing, during 2 h, in the air atmosphere at the temperatures approximately equal to the temperatures T_g of glass transitions [19]: 710 ± 5 K in $Li_2B_4O_7$:Gd,Ag, 870 ± 5 K in CaB_4O_7:Gd,Ag, and 730 ± 5 K in $LiCaBO_3$:Gd,Ag.

Optical transmission spectra were detected using a setup built on the basis of a monochromator MDR-23 and a personal computer. An incandescent halogen lamp was used as a light source, and a photomultiplier PMT-79 as a receiver. We measured the transmission spectra in order to determine the positions and the intensities of plasmon absorption bands.

Nonlinear properties were studied with a standard single-beam Z-scan method applied in the regimes of closed and open aperture [20, 21]. The measurements were performed at the room temperature. A second-harmonic radiation from a diode-pumped, continuous-wave neodymium laser was used (the wavelength of 532 nm). The output laser beam power was 45 mW. The parameters of the focused laser beam safely satisfied the main demands of Z-scan experiments. The relevant parameters were as follows: the diameter of the Gaussian beam in its focus $2r_0$ = 22.3 μm, the diffraction length in the Rayleigh range $b = n\pi\omega_0/\lambda$ = 1.197 mm (with λ being the wavelength and ω_0 the beam waist), and the laser beam power density in the focus $I_0 = 1.04\times10^4$ W/cm^2.

Issuing from the experimental Z-scan spectra detected in the regime of closed aperture, we calculated the nonlinear refractive index n_2 (see Ref. [21]):

$$n_2 = \frac{\Delta\Phi_0}{kL_{eff}I_0}. \quad (1)$$

Here $|\Delta\Phi_0| \cong \Delta T_Z/0.406(1-S)^{0.27}$ is the nonlinear phase distortion, $\Delta T_Z = (T_{+Z} - T_{-Z})$ the difference between the normalized transmission maxima T at the positive (T_{+Z}) and negative (T_{-Z}) coordinates Z; S the closed-aperture transmission in the absence of a sample (in our experiment it equals to a 0.07 fraction of the incident light intensity as measured on the aperture), $k = 2\pi/\lambda$ the light wave vector, I_0 the focused laser radiation intensity maximum, $L_{eff} = 1 - e^{-\alpha L}/\alpha$ the effective sample thickness, α the linear absorption coefficient at 532 nm, and L the actual sample thickness.

Using the Z-scan spectra measured in the regime of open aperture, we calculated the nonlinear absorption coefficient β as [22]

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}, \quad (2)$$

where $\Delta T = 1 - T_\upsilon$ and T_υ is the minimal normalized transmission at $Z = 0$ in the Z-scan scheme with the open aperture.

When the nonlinear refraction and the nonlinear absorption are simultaneously present in a material, its third-order nonlinear susceptibility can be represented as a complex quantity [23]:

$$\chi^{(3)} = \mathrm{Re}\chi^{(3)} + i\ \mathrm{Im}\chi^{(3)}, \quad (3)$$

where the real part of $\chi^{(3)}$ is associated with the nonlinear refractive index n_2 via the relation [24]

$$\mathrm{Re}\,\chi^{(3)} = \frac{n_0}{3\pi} n_2, [esu], \quad (4)$$

while its imaginary part is defined by the nonlinear absorption coefficient β [25],

$$\mathrm{Im}\,\chi^{(3)} = \frac{n_0 \varepsilon_0 c^2}{\omega} \beta, [esu]. \quad (5)$$

Here ω denotes the frequency of laser radiation and ε_0 the dielectric constant. As a result, the absolute value of the third-order nonlinear susceptibility $|\chi^{(3)}|$ can be calculated as

$$|\chi^{(3)}| = [(\mathrm{Re}\chi^{(3)})^2 + (\mathrm{Im}\chi^{(3)})^2]^{1/2}. \quad (6)$$

3. Experimental results and discussion

It is known that the plasmon absorption in the Ag NPs is caused by oscillatory motion of free electrons in a limited volume of a metal Ag NP, which is excited by the electromagnetic field of light wave. This takes place because the Ag NPs in the glass matrix do not contact with each other, and the electrons can move only inside a NP in such a way that the negative charge is accumulated near one surface, and the positive near the opposite one, thus creating electric dipole. When the frequency of the electric component of the light wave approaches the natural frequency of such an electric dipole, resonance processes appear accompanied by absorption of electromagnetic energy. The frequency, at which the light absorption maximum is observed, is termed as a plasmon frequency [18]. As a result, the very appearance of the additional absorption bands in the BGs after their relevant annealing can serve as a first proof that the Ag NPs have been formed in the glasses.

The plasmon absorption bands are readily observed in the optical spectra of the $Li_2B_4O_7$:Gd,Ag, CaB_4O_7:Gd,Ag and $LiCaBO_3$:Gd,Ag glasses after they have been thermally treated in the air atmosphere. To be more demonstrative, we present in Fig. 1 the 'difference' absorption spectra for the samples of all our glasses. These curves are differences between the optical extinctions recorded after annealing in the air and before the annealing. As seen from

Fig. 1, the shapes of the plasmon bands for all the glasses are very similar, with only small differences among the positions of their maxima (see Table 1).

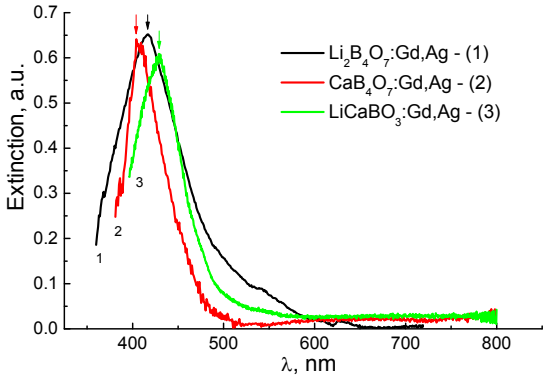

Fig. 1. Difference extinction spectra for $Li_2B_4O_7$:Gd,Ag (1), CaB_4O_7:Gd,Ag (2) and $LiCaBO_3$:Gd,Ag (3) glasses annealed in the air.

It is necessary to pay some attention to a 'tail' occurring in the region of 500–550 nm for the $Li_2B_4O_7$:Gd,Ag glass. It can indicate that an additional, very weak absorption band appears here. A presence of this absorption band (or bands) causes some coloration of our annealed glasses. More precisely, these samples reveal an intense enough yellow colour.

Table 1. Positions λ_{max} of plasmon absorption bands detected in our BGs.

Glass	$Li_2B_4O_7$:Gd,Ag	CaB_4O_7:Gd,Ag	$LiCaBO_3$:Gd,Ag
λ_{max}, nm	416.5	406.0	432.0

There is a possibility to estimate the radiuses R of the Ag NPs typical for the glasses $Li_2B_4O_7$:Gd,Ag, CaB_4O_7:Gd,Ag and $LiCaBO_3$:Gd,Ag annealed in the air. This can be done using the suggestion of Ref. [26]: $R = V_F/\Delta\omega$, where $V_F = 1.39\times10^6$ m/s implies the Fermi velocity in the metallic Ag (see Ref. [27]) and $\Delta\omega$ the halfwidth of the plasmon absorption that can be evaluated from Fig. 1. The diameter of Ag NPs calculated in this manner for our BGs annealed in the air falls into the region 3.0–6.0 nm.

Fig. 2 displays the Z-scan spectra detected in the regimes of open and closed aperture. First of all, one can notice that the difference between the normalized transmittance maxima $\Delta T_Z = (T_{+Z} - T_{-Z})$ remains positive for all of our glasses, which include Ag NPs and are formed by annealing in the air. Hence, both the nonlinear refractive index n_2 and the nonlinear absorption coefficient β have the positive signs.

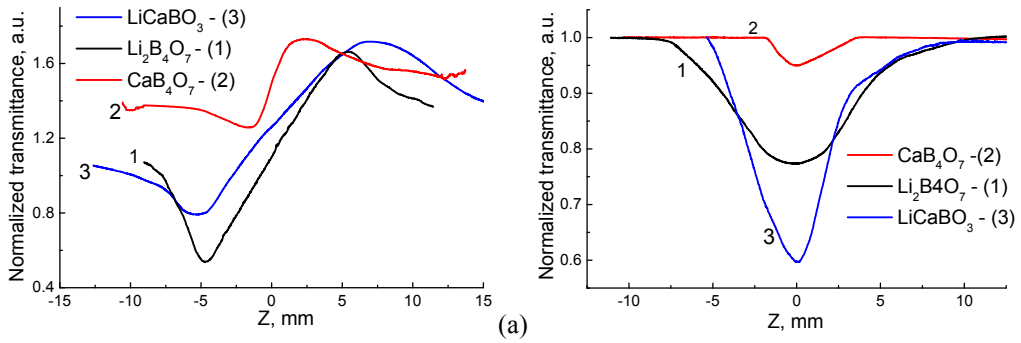

Fig. 2. Z-scan spectra measured under the conditions of closed (a) and open (b) aperture for the $Li_2B_4O_7$:Gd,Ag (1), CaB_4O_7:Gd,Ag (2) and $LiCaBO_3$:Gd,Ag (3) glasses annealed in the air atmosphere.

The values of the nonlinear parameters n_2, β and $|\chi^{(3)}|$ calculated basing on our experimental results (see Fig. 1 and Fig. 2) and Eqs. (1), (2) and (6) are listed in Table 2. The nonlinear parameters calculated by us for the non-annealed samples of our glasses are also presented in Table 2. A comparison for the non-annealed and annealed glasses is necessary because, as known from Refs. [27, 28], the BGs manifest some intrinsic nonlinear properties. They are caused by high enough nonlinear susceptibilities of boron-oxygen complexes present in the glass structure. Moreover, a small (and uncontrollable) number of Ag NPs, which could be formed during inertial cooling of our glass boules from 670 K down to the room temperature, can also be a probable source of 'residual' nonlinear properties of the non-annealed samples.

Table 2. Nonlinear optical parameters of our BGs containing Ag NPs.

Glass	L, cm	n_2, 10^{-10} cm^2/W	β, 10^{-5} cm/W	$\lvert\chi^{(3)}\rvert$, 10^{-11} esu
$LiCaBO_3$:Gd,Ag (not annealed)	0.130	1.2	2.0	1.9
$LiCaBO_3$:Gd,Ag (annealed in the air)	0.130	1.8	98	2.1
$Li_2B_4O_7$:Gd,Ag (not annealed)	0.074	2.3	54	3.6
$Li_2B_4O_7$:Gd,Ag (annealed in the air)	0.074	150	92	240
CaB_4O_7:Gd,Ag (not annealed)	0.090	–6.0	13	9.5
CaB_4O_7:Gd,Ag (annealed in the air)	0.090	60	31	95

As seen from Table 2, all of the nonlinear parameters n_2, β and $|\chi^{(3)}|$ increase notably whenever the Ag NPs of high enough concentrations appear in the $Li_2B_4O_7$:Gd,Ag, CaB_4O_7:Gd,Ag and $LiCaBO_3$:Gd,Ag glass matrices as a result of annealing of the glass samples in the air. The first column of Table 2 reports the actual thicknesses of the glass samples used in our calculations of L_{eff} (see Eqs. (1) and (2)). Here we have consciously disregarded a possible effect of concentration distribution of the Ag NPs over the sample thickness and have determined instead some integral (i.e., those associated with the total thickness) values of the nonlinear parameters.

On the other hand, this allows making comparative analysis of the parameters for different glass compositions. In particular, one can see that the largest (almost two orders of magnitude) increase in the n_2 and $|\chi^{(3)}|$ parameters is observed for the annealed $Li_2B_4O_7$:Gd,Ag glass. The lowest (only 1.5 times) increase is typical for the annealed $LiCaBO_3$:Gd,Ag glass. It is worthwhile that the CaB_4O_7:Gd,Ag glass demonstrates a unique property: its parameter n_2 changes the sign from negative to positive after the annealing, while its absolute magnitude increases one order of magnitude. The nonlinear parameter β reveals somewhat different behaviour: it increases nearly twice for the annealed glasses $Li_2B_4O_7$:Gd,Ag and CaB_4O_7:Gd,Ag, whereas the corresponding increase for the case of $LiCaBO_3$ glass exceeds one order of magnitude.

There is no doubt that the increase in the nonlinear parameters n_2, β and $|\chi^{(3)}|$ observed in our $Li_2B_4O_7$:Gd,Ag, CaB_4O_7:Gd,Ag and $LiCaBO_3$:Gd,Ag BGs after the annealing in the air atmosphere, as well as the formation of Ag NPs in these glasses, should be linked with the

plasmon resonance in the metal NPs. There is simply no alternative physical explanation for this. In particular, the first studies of silicate glasses including Au, Ag and Cu NPs [10, 12] have revealed a significant increase in the third-order nonlinear susceptibility $\chi^{(3)}$, which is caused by the metal NPs.

If we ignore a negative n_2 sign observed for the particular case of non-annealed CaB_4O_7:Gd,Ag, the conclusion follows that the parameters n_2, β and $|\chi^{(3)}|$ of all the non-annealed glasses do not differ radically. Then the differences in the quantitative increase of those parameters occurring after the Ag NPs are formed can be caused by different concentrations and volume distributions of the NPs, as well as their different sizes and shapes. In its turn, these effects can have the following underlying reasons:

(1) different efficiencies of the processes of reduction of Ag^+ ions to their neutral states Ag^0, which occur with participation of Gd^{3+} ions in different BGs matrices (univalent alkaline metals in $Li_2B_4O_7$, borates of bivalent metals in CaB_4O_7, etc.);

(2) different participations of the univalent (Li^+) and bivalent (Ca^{2+}) ions, which differ essentially in their ionization potentials, in the processes of reduction of Ag^+ to its neutral state Ag^0. Notice that the competition of Li^+ and Ca^{2+} ions in these processes can also be a reason why the annealed glasses $Li_2B_4O_7$:Gd,Ag and CaB_4O_7:Gd,Ag have the same nonlinear properties, while the properties of the annealed $LiCaBO_3$:Gd,Ag glass (with both of the above ions present) are different;

(3) one must not ignore a possible influence of differences in the structural boron-oxygen complexes, which are specific for each compounds. Tetraborate boroxole groups ($2BO_3$+$2BO_4$) that correspond to the anion $[B_4O_9]^{6-}$ are characteristic for $Li_2B_4O_7$, more complex boroxole groups ($4BO_3 + 4BO_4$) + ($2BO_3 + BO_4$), which compose the anion $[B_8O_{14}]^{4-}$, are characteristic for CaB_4O_7, and $(BO_3)_\infty$ chains consisting of the anions $[BO_3]^{3-}$ compose a basis of $LiCaBO_3$.

However, it would be premature to prefer some specific reasoning among the items (1) to (3) to the others, at least at the given stage of studies for the nonlinear properties of the BGs with Ag NPs.

4. Conclusions

Summing up our main results, we have obtained $Li_2B_4O_7$:Gd,Ag, CaB_4O_7:Gd,Ag and $LiCaBO_3$:Gd,Ag glasses by melting preliminary synthesized compounds $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$, and then adding the impurities $AgNO_3$ and Gd_2O_3. After annealing those glasses in the air atmosphere for 2 h at the temperatures approximately equal to the glass-transition temperatures T_g, we have introduced the Ag NPs of significant concentrations into our glass samples. This fact has been evidenced by the intense plasmon absorption bands.

We have proven that addition of the gadolinium oxide Gd_2O_3 to the BGs $Li_2B_4O_7$:Ag, CaB_4O_7:Ag and $LiCaBO_3$:Ag enables producing the Ag NPs in those glasses, using a simple annealing in the air, which demands no special reducing atmospheres. This means that the ions of Gd^{3+} represent efficient enough reducing ions for the case of BGs.

We have shown that the plasmon resonance caused by the Ag NPs enhances the nonlinear optical parameters n_2, β and $|\chi^{(3)}|$ for all of the BGs under test, though to different extents. A number of versions of the explanation of such differences have been suggested, although we are still not in a position to decide in favour of one of these hypotheses. Maybe, several different effects are simultaneously at work, such that one of them dominates in one of our glasses and the other in the other glasses.

The magnitudes of the nonlinear parameters n_2, β and $|\chi^{(3)}|$ calculated by us show that the matrices of the BGs $Li_2B_4O_7$, CaB_4O_7 and $LiCaBO_3$ can be promising for many applications dealing with optical communication systems. As a single example, notice that the authors of Ref. [9] have suggested silicate glasses with Ag NPs for developing optical switches.

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Анотація. *На основі експериментальних спектрів поглинання та спектрів Z-скану в режимах із закритою і відкритою діафрагмою розраховано нелінійно-оптичні параметри (показник заломлення n_2, коефіцієнт поглинання β і сприйнятність третього порядку $\chi^{(3)}$) для боратних стекол $Li_2B_4O_7$–Gd_2O_3–Ag_2O, CaB_4O_7–Gd_2O_3–Ag_2O і $LiCaBO_3$–Gd_2O_3–Ag_2O з наночастинками (НЧ) Ag. НЧ Ag було сформовано шляхом відпалу стекол в атмосфері повітря за температур, близьких до температур склування. Доведено, що йони Gd^{3+} є ефективними йонами-відновлювачами в боратних стеклах. Установлено, що зумовлений НЧ Ag плазмонний резонанс суттєво підвищує нелінійно-оптичні параметри боратних стекол n_2, β і $|\chi^{(3)}|$.*