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Nonlinear optical properties of silver nanoparticles prepared in Ag doped borate glasses

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ABSTRACT

Nonlinear properties of $Li_2B_4O_7$:Ag borate glasses with "$Li_2B_4O_7$:Ag nanoparticles" interface region formed by thermal treatment in hydrogen atmosphere and in vacuum are investigated. From the results of plasmon absorption and normalized transmission measurements in *Z*-scan regime it was ascertained that "$Li_2B_4O_7$:AgNPs" interface region changes the character of nonlinear refraction of $Li_2B_4O_7$:Ag glass from negative to positive, and, due to plasmon resonance, increases significantly its nonlinear properties. In particular, the observed growth of nonlinear refractive index n_2 is more than four orders of magnitude.

1. Introduction

In recent years nanocomposite materials comprising metallic nanoparticles (NPs) in dielectric media have been investigated intensively. Increased interest in such investigations is caused by significant influence of metallic NPs on linear and nonlinear susceptibilities of the host matrix [1–3], radiation recombination processes [4], and giant surface enhanced Raman scattering (SERS) [5,6]. Mechanism of such influences is generally related to local fields, which are formed in the system of NPs with fractal structure [7]. Practical interest in dielectric materials with metallic NPs is connected with the perspective for the development of optical switches with ultra-short time response, limiters of optical laser beam intensity for synchronization of the laser modes, etc. [8–11].

Borate glasses of Li_2O–B_2O_3 system, in particular $Li_2B_4O_7$ [12], based on boric anhydride B_2O_3 are promising for metallic Ag NPs formation. Boric glass consists structurally of boron–oxygen groups (tetraborate, triborate, etc.), which are connected by the oxygen bridge atoms (similarly to crystalline borates). However, unlike crystalline borates, where one observes long-range order, the borate glasses consist of intermediate-range ordered micro-domains of boroxol group, which are located in intermediate range. Such structural disordering in borate glasses leads to some increasing of the average B–O distance in both stable oxygen coordinations of boron: triangular—BO_3 and tetrahedral—BO_4 [13]. And, as it was confirmed by Youngman et al. [14,15], near the glass-transition temperature the boroxol rings breakup leads to more open structure in borate glasses. Therefore, $Li_2B_4O_7$ glass with the glass-transition temperature 713 K [16] is an interesting host material for experiments with metallic Ag NPs formation. And since the borates glasses themselves exhibit nonlinear optical properties [17], which are defined by high values of nonlinear susceptibility for boron–oxygen complexes [18], the possibility for further tailoring with the help of metallic NPs gives these glasses a large potential for photonics [19].

Presented work is devoted to the investigation of nonlinear optical properties of near-surface silver nanoparticles layer, formed by thermal treatment of Ag doped $Li_2B_4O_7$:Ag borate glass.

2. Experimental procedure

For the preparation of $Li_2B_4O_7$:Ag glass highly pure lithium carbonate Li_2CO_3, boric acid H_3BO_3 and silver nitrate $AgNO_3$ were taken. Mixture of initial chemicals, prepared by stoichiometric $Li_2O \cdot 2B_2O_3$ composition, has been placed into ceramic crucible and $Li_2B_4O_7$ powder with $T_{melt}=1198$ K has been obtained by the method of multi-graded temperature synthesis after the following chemical reaction:

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

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1 wt% $AgNO_3$ has been added to this powder. The glass has been prepared by melting technique in Al_2O_3 crucible in air at 1270 K. The melt has been homogenized during 0.5 h and cooled during 1 h down to the temperature of 673 K, followed by inertial cooling down to the room temperature. Plates with dimensions of $\sim 10 \times 7 \times 1$ mm^3 have been cut from the obtained glass and their surfaces have been grinded and polished.

For the formation of a near-surface layer from Ag NPs the samples have been annealed at temperature 710 ± 5 K during 4 h in H_2 atmosphere (gas pressure 700 mmHg) and in vacuum ($< 10^{-4}$ Torr with titanium getter). For the purpose of comparison, one sample was annealed at ambient pressure.

Transmission spectra were measured using the set-up, which included MDR-23 monochromator and a personal computer. Halogen incandescent lamp was used as a light source, and PMT-79 photomultiplier was exploited as a detector in the single photon regime, ensuring linearity of the signal registration in the range 10^2–10^6 photons per second.

Traditional single-beam *Z*-scan method, developed by Sheik-Bahae [20,21], was used for the investigations of nonlinear optical properties of $Li_2B_4O_7$:Ag glass with formed Ag NPs. Measurements were performed at room temperature. Second harmonic radiation from continuous neodymium laser with diode pumping, which works 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 the principal demands of a *Z*-scan experiment: $2\omega_0 = 22.3$ μm (ω_0—radius of Gauss beam in focus); $b = n\pi\omega_0/\lambda = 1.197$ mm (b—diffraction length in Rayleigh range), laser beam power density in focus $I_0 = 1.04 \times 10^4$ W/cm^2.

Z-scan experiment permits to calculate the nonlinear refractive index n_2, which enters into known expression for overall refractive coefficient $n = n_0 + n_2|E|^2$, where n_0 is the linear refractive index and E denotes the magnitude of the laser radiation electromagnetic field strength. Calculation of the nonlinear refractive index n_2 from normalized *Z*-scan spectra was performed using the formula [22]:

$$n_2 = \frac{\Delta\Phi_0}{kL_{eff}I_0}, \tag{1}$$

where $\Delta\Phi_0$ is the nonlinear phase deformation; $k = 2\pi/\lambda$—wave vector; I_0—the maximum of the laser radiation intensity in focus; L_{eff}—efficient thickness of sample:

$$L_{eff} = \frac{1 - e^{-\alpha L}}{\alpha}, \tag{2}$$

where α denotes the linear absorption coefficient at 532 nm and L is the thickness of sample.

Nonlinear phase deformation $\Delta\Phi_0$ is connected empirically with the change of the normalized transmission $\Delta T_Z = T_{+Z} - T_{-Z}$ obtained from experimental *Z*-scan spectrum:

$$\left|\Delta\Phi_0\right| \cong \frac{\Delta T_{pv}}{0.406(1-S)^{0.27}}, \tag{3}$$

where S is the transmission of the diaphragm in the absence of the sample, ΔT_Z is the difference between values of transmission maximum T in positive (T_{+z}) and negative (T_{-z}) coordinates Z. In our experiment with closed diaphragm S was equal to 0.07 of the intensity of the incident light.

3. Results and discussion

$Li_2B_4O_7$:Ag borate glasses with formed Ag NPs exhibit very intensive plasmon bands in their absorption spectra. There is a difference in absorption for the glass samples with Ag NPs that have been annealed in hydrogen reducing atmosphere and in vacuum.

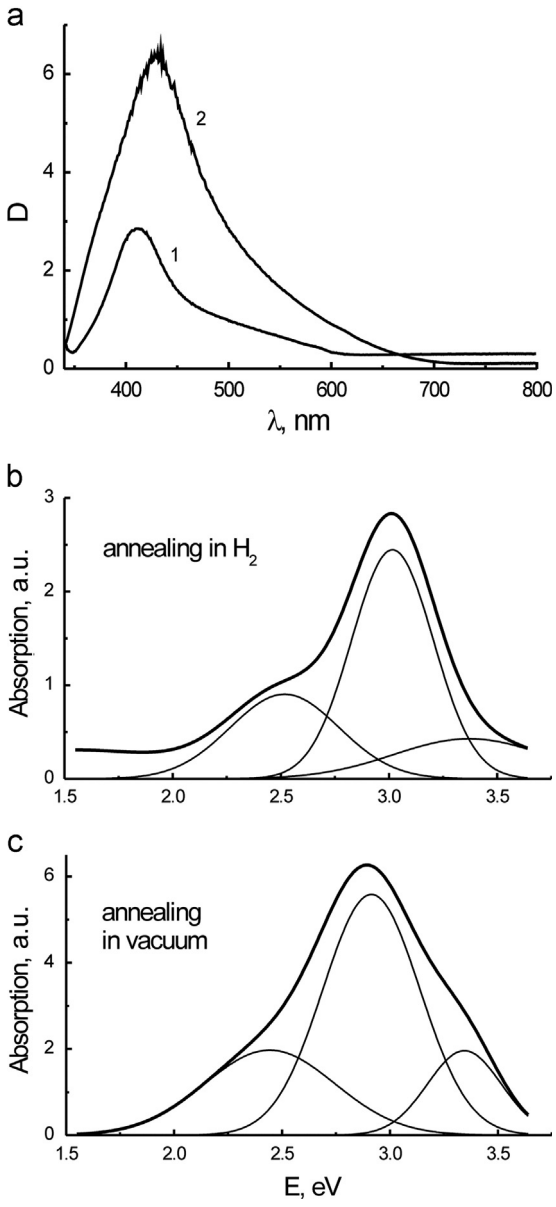

Fig. 1. Difference absorption spectra of $Li_2B_4O_7$:Ag glasses: (a) annealed in hydrogen (curve 1) and vacuum (curve 2); (b), (c) decomposition of given spectra by components.

In Fig. 1 one can see the difference (as compared to not annealed glasses) absorption spectra of $Li_2B_4O_7$:Ag borate glasses, annealed in hydrogen atmosphere (curve 1) and in vacuum (curve 2). One have to mention that the difference absorption spectrum for the sample of $Li_2B_4O_7$:Ag glass annealed at air pressure is the same before and after annealing, therefore it is not shown in Fig. 1.

In spectra of $Li_2B_4O_7$:Ag glass samples annealed in hydrogen atmosphere there appears intensive non-elementary plasmon band with the maximum at nearly 411 nm (3.02 eV, Fig. 1a, curve 1) which is backgrounded by considerable nonselective absorption. Decomposition of this band into components permitted to observe the long-wave component with the maximum at 492 nm (2.52 eV) (Fig. 1b). Weak band observed near long-wave edge of spectrum is connected with the host matrix absorption, which appears after annealing of glasses in hydrogen.

Plasmon resonance spectra of obtained glasses changes significantly after annealing of glasses in vacuum (Fig. 1a, curve 2). First of all, peaks mentioned above shift towards long-wave range to 425 nm and 507 nm (Fig. 1b). Another component with maximum