MATERIALS OF THE INTERNATIONAL CONFERENCE
"GLASS: SCIENCE AND PRACTICE 2017"

Radiation Effects and Optical Properties of Aluminoborosilicate Glass Doped with RE Ions

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Received September 5, 2017

Abstract—The relationship between the oxidation-reduction state of rare-earth (RE) elements (Sm, Gd, Eu, Ce, Nd), optical properties and the structural evolution of aluminoborosilicate glasses is studied. The study of the optical characteristics of glass is carried out by measuring optical transmission and analyzing Raman spectra. It is found that the increase in the concentration of monovalent Nd ions leads to the broadening of the optical band of forbidden energies (the band gap E_g), while the larger content of multivalent Sm, Eu, and Ce ions significantly decreases its width. The narrowing of E_g results from the irradiation of glass with a high-energy electron flux (2.5 MeV, a dose of up to 109 Gy). The observed evolution is explained by the coexistence of different charge states and the local environments of RE ions in the studied glass. The presence of different charge states of RE ions causes an increase in the number of color centers, while variations in the local environment of ions change the amount of nonbridging oxygen in the structure.

Keywords: alumina borosilicate glass, RE ions, β-radiation, reduction−oxidation, optical band of forbidden energies

INTRODUCTION

Glass doped with rare-earth (RE) elements plays a key role in many areas of modern life. These materials are well known as fluorescent substances because of their high luminescence efficiency, and therefore they are considered as promising matrices for quantum electronics devices. The synthesis of RE-doped materials for use in lighting technologies has been the subject of intensive research in recent decades. This is due to the need to improve the efficiency of radiating solid-state devices, e.g., light-emitting diodes (W-LED). Some of the RE ions are polyvalent (e.g., Sm^{3+}/Sm^{2+}, Eu^{3+}/Eu^{2+}, Ce^{4+}/Ce^{3+}) and can be represented in a matrix in two charge states as a function of the conditions of the glass melting technology. Glass doped with $Sm^{2+}(Eu^{2+})$ ions are quite attractive matrices as optical materials for data storage in devices with a high memory density, and the properties of glass doped with Ce^{3+} ions are widely used in the LED technology. Thus, the preparation of these glass materials is an important scientific problem, the solution of which opens promising prospects for their practical use.

The valence of RE ions in glass is changed either by the traditional method of synthesis in a reducing atmosphere or by exposure to high-energy radiation (X-ray, fs-laser, γ, or β). There is evidence that the valence transformation can occur in the synthesis of glass in air. It should be noted that conversion is usually accompanied by the formation of defects in the glass, which include electron and hole centers. Since some defect centers are paramagnetic, electron paramagnetic resonance (EPR) method can be used to study their nature [1].

The studies carried out to analyze the effect of the external ionizing radiation on the microstructure of complex aluminoborosilicate (ABS) glass doped with RE elements showed that the glass matrix is a radiation-resistant material [2−4]. The increase in the concentration of doping RE impurities limits both the microstructural modifications and the process of the formation of radiation defects. The evolution is observed for polyvalent RE ions (Sm, Eu, and Ce). It was shown that ABS glass is less subjected to radiational coloration by introducing Gd and Nd ions in comparison with variable valence ions.

Knowledge of the charge state of an RE element in a glass matrix is an important issue both from the fundamental and from the technological points of view.

The study of the conditions for changing the charge state of an RE ion in ABS glass, as well as its consequences for structural modifications, are of great interest.

For this purpose, this work was carried out to study the optical properties of glass doped with RE ions as a function of their nature and concentration, as well as the effect of high-dose β-radiation.

EXPERIMENTAL

Various ABS glass compositions were prepared by mixing the appropriate quantities of the following analytical reagents in SiO_2, Al_2O_3, H_3BO_3, Na_2CO_3, ZrO_2, and P_2O_3. The concentration of RE oxides (Sm_2O_3, Gd_2O_3, Eu_2O_3, CeO_2, Nd_2O_3) was 0.5–5 wt %. The synthesis is detailed in [2–4]. The mixture was heated at 750°C for 10 h in air and melted at 1500°C for 2 h, then quenched on a copper plate. Before cutting, annealing at 500°C for 1–2 h was necessary to remove the internal stress. Samples were polished on a hand grinding wheel with a silicon carbide abrasive having the average grain size of 10 μm (1000 grain) to achieve the average thickness of 0.56 ± 0.05 mm. The glass was irradiated by electrons with an energy of 2.5 MeV (14 μA) generated by a Van de Graaff accelerator (LSI, Ecole Polytechnique, Palaiseau, France). The temperature of the sample during irradiation was maintained at about 50°C with the help of cooling the sample holder with water. The used thickness (0.56 ± 0.05 nm) makes it possibe to obtain uniform irradiation on the entire glass volume. The irradiation dose was 4×10^9 Gy. The optical transmission spectra were measured on an Agilent Varian Cary 5000 spectrophotometer in 1 nm steps in the range of 200 to 1500 nm. Raman spectra were taken on a Labram HR microspectrometer using the radiation of an Ar^+ laser (λ = 514.5 nm). The measurements were carried out using an Olympus lens (magnif. 50) with the laser radiation power of about 20 mW to avoid significantly heating the samples.

RESULTS

Figure 1 shows the transmission spectra of ABS glass as a function of the RE dopants before β-irradiation. We note that the transmission spectra shift towards lower wavelengths for glass doped with Gd, Nd, and Sm ions compared to the undoped sample, which demonstrates an increase in the energy of the band gap. The values of the energy of the band gap for all samples were estimated from the following equation [5–7]:

$$\alpha(h\nu) \propto (h\nu - E_g)^n, \tag{1}$$

where α is the the optical absorption coefficient calculated using the relation $\alpha(\nu) = A/d$ (A is absorption and d is the sample thickness), $h\nu$ is the photon energy, and E_g is the band gap energy. Parameter n

depends on the characteristic of the band gap: $n = 1/2$ for the direct allowed transition, $n = 3/2$ for the direct forbidden transition, $n = 2$ for the indirect allowed transition, and $n = 3$ for the indirect forbidden transition. The values of the width of the optical band gap of ABS glass doped with the RE ions are obtained by plotting the dependence $(\alpha h\nu)^{1/n}$ versus $h\nu$ in the high-energy region with the subsequent extrapolation of the linear region of the plots $(\alpha h\nu)^{1/n} = 0$. The analysis of our data showed that the plots $(\alpha h\nu)^{1/n}$ give a linear relationship, which corresponds to (1) at $n = 1/2$. This indicates that the allowed direct transition is responsible for interband transitions in all the studied glass. The dependence of $(\alpha h\nu)^2$ versus the photon energy for all the samples studied before and after irradiation is presented in Figs. 2a and 2b and the experimental values of the direct band gap are given in Tables 1 and 2. The theoretical value of the optical band gap (E_{th}) can be calculated using the boundary wavelength values ($\lambda_{cut-off}$)

$$E = hc/\lambda, \tag{2}$$

where h is Planck's constant, c is the speed of light, and λ is the boundary wavelength, respectively. The calculated values for some values of the optical band of forbidden energies E_g, as well as $\lambda_{cut-off}$ and E_{th} for the samples, are presented for comparison in Table 3. It was taken into account that the behavior of the optical absorption coefficient near the fundamental absorption band obeys the Urbach rule [8, 9]

$$\alpha = \alpha_0 \exp(h\nu/E_U), \tag{3}$$

where α_0 is a constant and E_U is the Urbach energy [8]. E_U corresponds to the optical transitions between localized tail states adjacent to the valence band and extended states in the conduction band above the mobility edge [10]. It was found from the analysis of the behavior of the absorption coefficient near the fundamental absorption band that the Urbach energy values for the nonirradiated and irradiated ABS glass are 0.62 eV in each case.

The width of the direct band gap of the ABS glass as a function of the RE ion is shown in Figs. 3a and 3b. In the presence of Gd, Nd, and Sm ions, the values of the energy of the band gap increase in comparison with the undoped ABS glass, being 5.34, 6.0, and 5.56 eV for the nonirradiated samples, respectively. The trend persists also after the β-irradiation (4×10^9 Gy). The estimated Urbach energy values revealed different evolutions for the mono- and polyvalent RE elements. The E_U values obtained for Sm, Eu, and Ce-doped glass increase with an increasing RE ion concentration. The increase in the Nd_2O_3 content from 0.5 to 5 wt % leads to a decrease in the E_U values from 0.67 to 0.20 eV. With an increase in the gadolinium concentration from 1 to 5 wt %, this value reaches 0.6 and 0.53 eV, respectively.

It is interesting to note the different behavior of the band gap with the concentration of RE ions. The
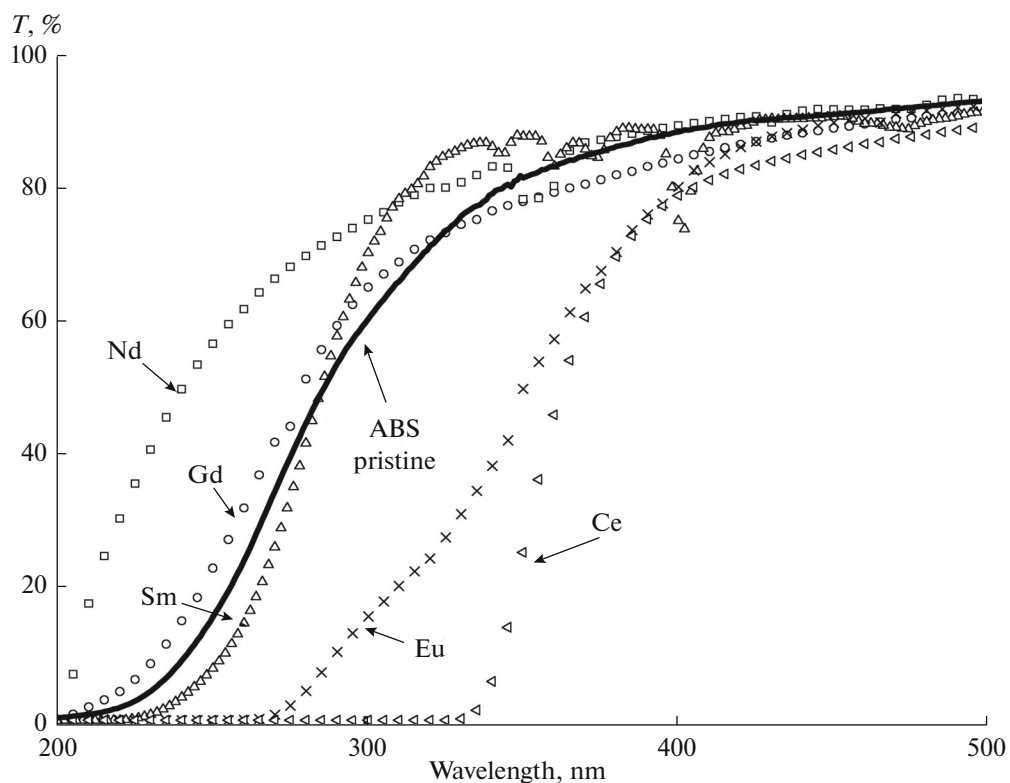
Fig. 1. Transmission spectra of undoped and doped ABS glass (thickness of samples of 0.56 ± 0.05 mm).
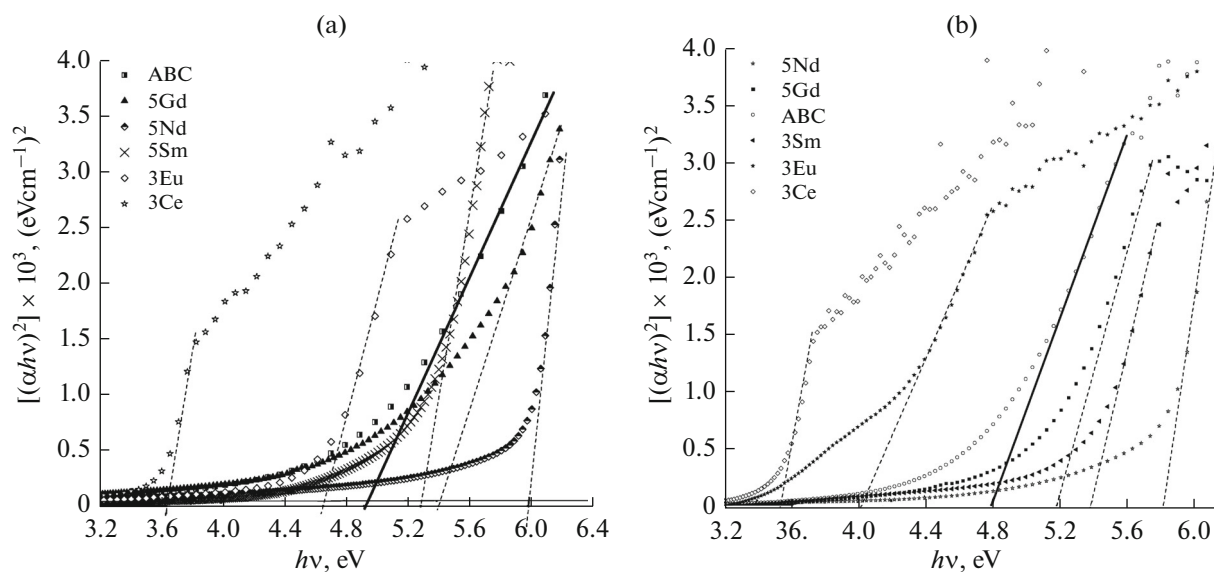

Fig. 2. Dependence of $(\alpha h\nu)^2$ on photon energy for nonirradiated (a) and irradiated (b) ABS glass doped with RE ions.

energy value does not change for Gd-doped glass with an increase in the concentration of Gd ions (to 5 wt %). The increase in the concentration of Nd ions leads to an increase in the energy of the band gap in the Nd-doped ABS glass. There are no changes in the value of the band gap of the ABS glass doped with Sm, Eu ions

with the increase in their concentration up to 3 wt %. These data are reflected in Table 1. After irradiation, there was no change in the gap in the band gap region for ABS glass doped with Gd ions. For all the other dopant impurities, the band of forbidden energies tends to decrease upon irradiation (see Table 2). The

Table 1. Width of optical (E_g) nonirradiated ABS glass as function of concentration of RE-doping ions

Re_2O_3, wt %	E_g, eV			
	Gd_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3
0.5	–	5.79	5.50	4.67
1	5.40	5.85	5.49	4.69
2	5.41	–	–	–
3	5.39	5.91	5.50	4.66
5	5.41	6.00	5.30	4.39

Table 2. Width of optical zone (E_g) of irradiated ABS glass as function of concentration of RE-doping ions

| Re_2O_3, wt %	E_g, eV			
	Gd_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3
0.5	–	5.76	5.40	4.47
1	5.39	5.83	5.39	4.39
2	5.41	–	–	–
3	5.39	5.89	5.20	4.03
5	5.40	5.85	5.11	3.89

Table 3. Boundary wavelength, experimental and theoretical width of optical band gap of ABS glass (numbers in front of symbols of RE elements mean their concentration in glass)

Samples	E_g, eV		E_{th}, eV			
	Pristine	10^9 Gy	Pristine		10^9 Gy	
			$\lambda_{cut-off}$, nm		$\lambda_{cut-off}$, nm	
BS	5.03	4.80	262.7	4.72	285.29	4.34
5Gd	5.41	5.40	241.0	5.15	251.00	4.94
5Nd	6.00	5.85	205.0	6.05	218.00	5.69
3Sm	5.50	5.20	226.0	5.49	236.00	5.26
3Eu	4.66	4.03	279.0	4.45	330.00	3.76
3Ce	3.63	3.52	346.0	3.59	358.00	3.47

Raman spectra of undoped and RE-doped ABS glass before and after irradiation are discussed in detail in [11]. The Raman spectra for the glass under study were measured in the range of 200 to 1600 cm^{-1} (Fig. 4a). The main features of the presented spectra are the complex inhomogeneous band located at the frequency of 900 to 1200 cm^{-1} and the wide band fixed at about 1450 cm^{-1}. This band is ascribed to the vibrational coupling mode B—O [12]. It is known [13] that in the glass of such composition, according to the experimental data of nuclear magnetic resonance, boron ions are found in the environment of three or four oxygen species. It is seen in Fig. 4a that the posi-

tion and intensity of this band vary depending on the concentration of the RE ion. It can be concluded that the introduction of RE ions into the ABS glass matrix leads to changes in the local environment of the boron ions. The band located at characteristic frequencies of 900 to 1200 cm^{-1}, as a rule, is associated with the stretching vibrations of the symmetric Si—O bond described by the parameter Qn (where Q = $SiOn$, n is the number of bridging oxygens) [14]. It is seen in Fig. 4a that this band is inhomogeneous. This is due to the effect of Si—On complexes, where silicon is bound to a different number of bridging oxygen. The decomposition of this band and the separation and justification of the individual contributions of the Si—On vibrations (where $n = 1–4$) is based on numerous experimental data on the Raman spectra of alkaline-earth, alkali-silicate, and aluminosilicate compositions and melts [15–17]. The small band between 900 and 920 cm^{-1} can be attributed to the vibrational stretching mode of the Si—O bond with three non-bridging oxygen atoms (Q1) or may arise due to oscillations in the stretching of the BO—Si bonds (925 cm^{-1}) [18]. The band between 950 and 980 cm^{-1} can be attributed to the vibrational stretching mode of the Si—O bond in the structural unit with two nonbridging oxygen atoms (Q2). The band located in the center between 1050 and 1100 cm^{-1} is attributed to the vibrational stretching mode of Si—O in the structural unit with one nonbridging oxygen (Q3). The high-frequency band between 1120 and 1190 cm^{-1} is due to the presence of fully polymerized structural units (Q4) [19, 20]. Taking into account the published data, we decomposed the obtained Raman spectra of RE-doped ABS glass using four Gaussian bands centered at 910 cm^{-1} (Q1), 960 cm^{-1} (Q2), 1060 cm^{-1} (Q3), and 1150 cm^{-1} (Q4). Figure 4b shows the change of the ratio (Q4 + Q3)/(Q2 + Q1), with the help of which it is possible to analyze the modifications of the local environment of silicon with the introduction of RE ions into the structure of the ABS glass, i.e., the change in the umber of bridging oxygens, and, thereby, evaluate the degree of polymerization of the silicate network. According to these results, the polymerization of the silicate network increases with the increase in the amount of Gd_2O_3 and decreases with an increase in the content of CeO_2. The structural evolution for glass doped with Gd and Ce ions, observed in the analysis of the decomposition results of the Raman spectra, is obvious and is in agreement with the data on the optical band gap. The situation with samples doped with Nd ions is difficult to interpret (Fig. 4b). It should be noted that the position for component Q4 considered during the decomposition into separate Gaussian components does not coincide with the declared value and is shifted to a lower wave number.
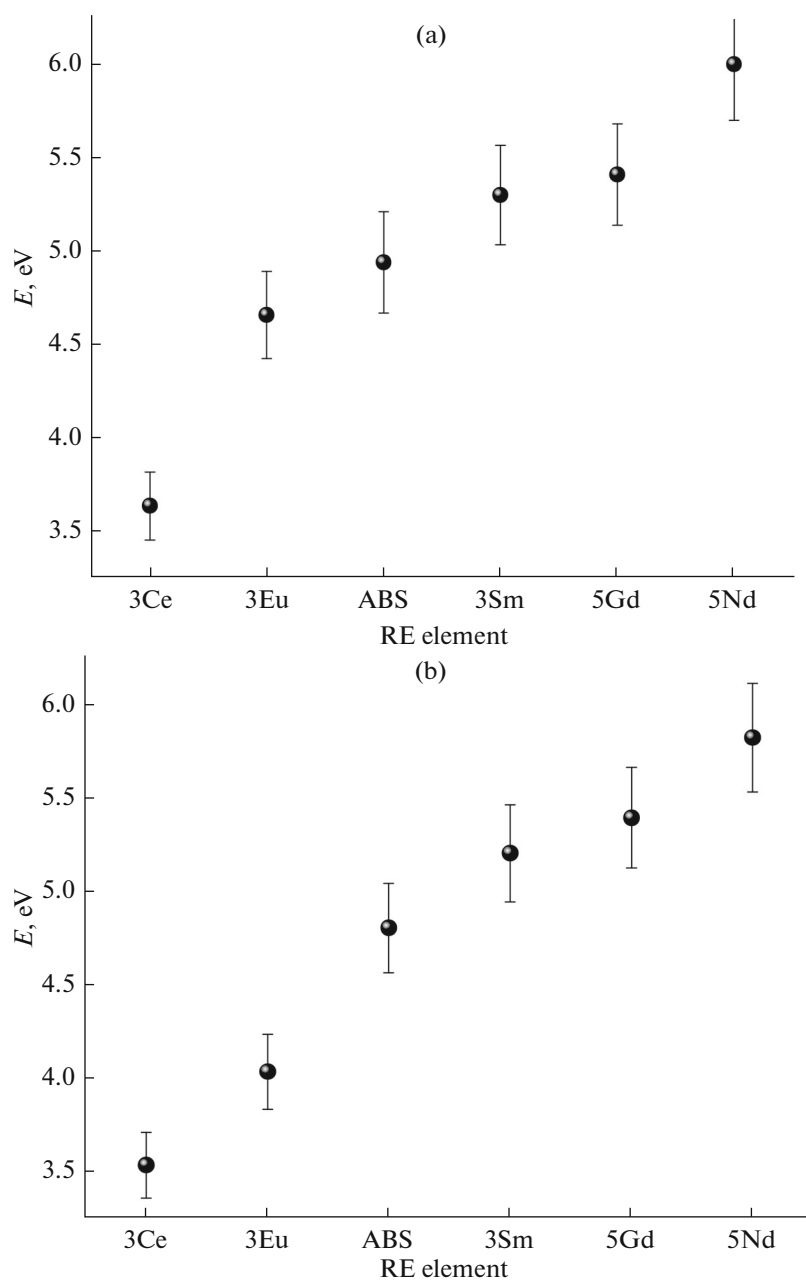
Fig. 3. Experimental value of band of forbidden energies as function of RE ion: for nonirradiated (a) and irradiated (b) ABS glass (figures before symbols of RE elements mean their concentration in glass).

DISCUSSION OF RESULTS

It is possible to conclude from the analysis of the transmission spectra (Fig. 1) and the results of the measurement of the band gap (Fig. 2) about the effect of the doping impurity of RE ions on the optical characteristics of the ABS glass. The decrease in the band gap in the undoped ABS glass upon irradiation can be explained as follows. The presence of modifier ions (e.g., sodium) in the glass matrix strongly affects the width of the band gap and shifts the edge of the absorption band to low wavelengths. In glass with a low content of calcium aluminosilicates, this phenomenon can be explained by the rupture of chemical bonds and the appearance in the structure of a large number of nonbridging oxides (NBOs) mainly associated with Al or Si atoms [21, 22]. At the same time, the study of the effects of irradiation in aluminoborosilicate glass, carried out using spectroscopic methods (Raman spectroscopy, EPR and NMR) [1.11], indicates an increase in the degree of polymerization of the ABS glass structure caused by the migration of the sodium ions, and the concomitant formation of
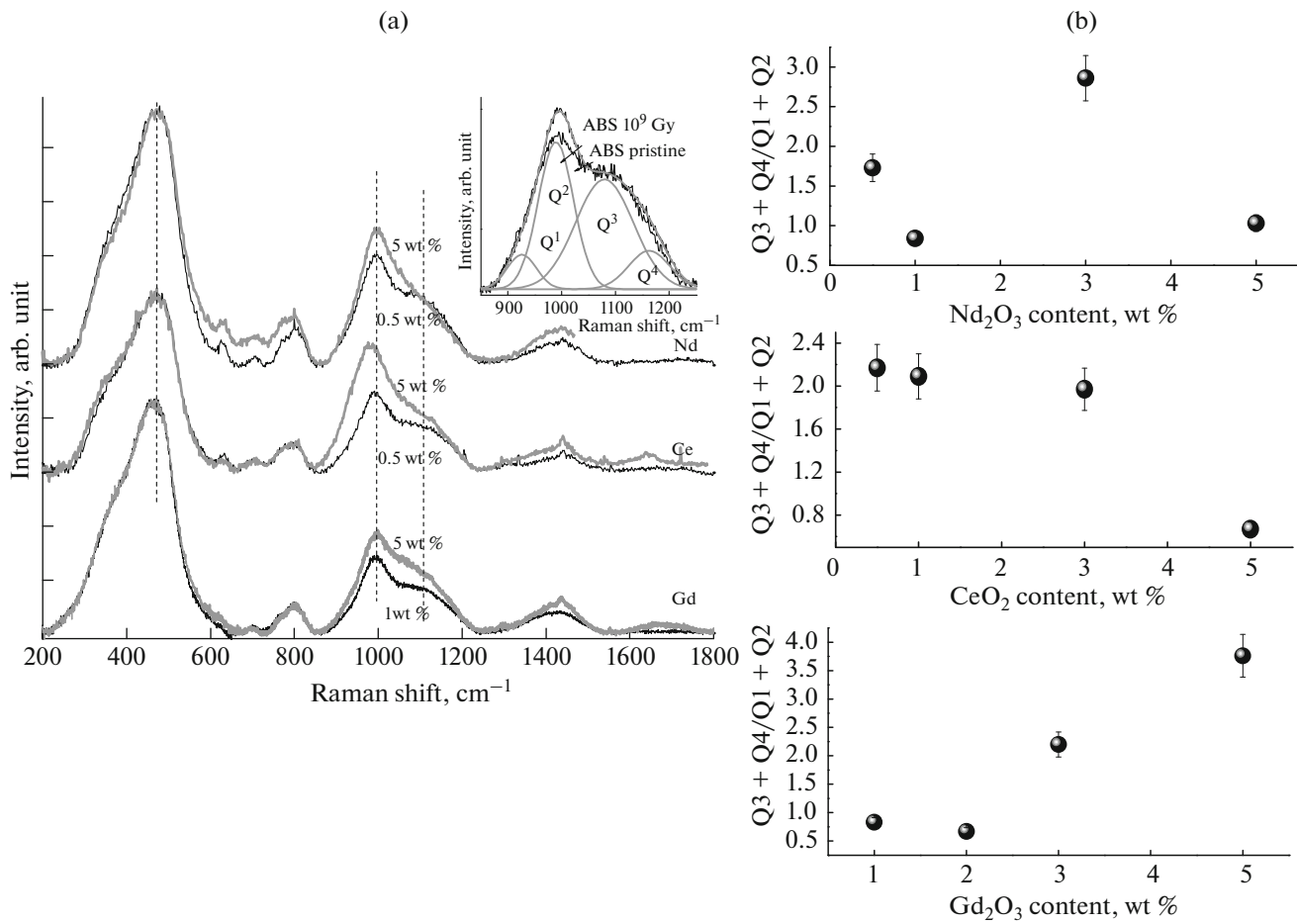
Fig. 4. Raman spectra of ABS glass doped with RE ions (a); change in ratio of Q_n groups with concenration of RE ions (b).

molecular oxygen, which is accompanied by the modification of the oxygen environment of boron from the tetrahedral position to the trigonal one $B^{IV} \rightarrow B^{III}$.

The main radiation defects in ABS glass are the hole defects associated with boron and silicon: BOHC is the hole trapped on the nonbridging oxygen bound to the boron; and HI and HII are the holes trapped on one or two nonbridging oxygens bound to silicon [23]. These defects are paramagnetic and can be easily detected using EPR measurements. RE doping suppresses the changes in the structure of the ABS glass induced by irradiation as a function of the oxidation–reduction ability of the RE ion [2–4]. After irradiation, the glass samples show a brown color (radiationak color centers), and the color of the glass becomes deeper and more intensive in the following sequence: Nd < Gd < Sm = Eu < Ce.

It should be noted that the defects in multicomponent glass are numerous and diverse; thus, the representation of their models is extremely difficult. Moreover, not all the induced optically active defects are paramagnetic or recognizable by the EPR measurements. The increase in the NBOs and the formation of

color centers can reduce the value of the band gap in ABS glass. Taking into account the increase in polymerization in irradiated undoped ABS glass [1, 11], the insignificant red shift of the band gap (from 4.94 to 4.8 eV) can be associated with the formation of radiational color centers. This result is confirmed by the evolution of the Urbach energy values. According to the Mott and Davis model [6], this energy depends on the degree of disorder and defects in the amorphous structure. If the glass has a more polymerized network (which corresponds to a lower NBO content), the Urbach energy is lower. The Urbach energy value for the irradiated ABS glass differs somewhat from the nonirradiated sample (0.618 eV). A change in the value of the band gap is observed in the ABS glass upon doping with various RE ions as can be seen in Fig. 3. It is interesting to note that the width of the zone increases with the introduction of Nd, Gd, and Sm, whereas with the introduction of Eu and Ce ions it decreases. The main reason is that the ions of polyvalent europium (Eu^{2+}) and cerium (Ce^{4+}, Ce^{3+}) have broad absorption bands in the UV region of about 250 and 350 nm, respectively.

With the increase in the concentration of Nd_2O_3 or Gd_2O_3, we can observe either the increase or a constant value of the width of the band gap (Table 1). The inclusion of the remaining RE ions (Sm, Eu, Ce) leads to a decrease in the width of the band gap (Table 2). These results are in agreement with the obtained values of the Urbach energy (E_U). Since E_U characterizes both the disorder and structural imperfections (such as network defects) in the network of the amorphous matrix, a decrease in this quantity should correspond to the decrease in the number of NBOs or the number of defects. With an increase in the RE concentration in the case of Nd- and Gd-doped ABS glass, the E_U decreases indicating an increase in the polymerization in the glass network. The Raman spectra were measured to test our hypothesis about the relationship between the NBOs, optical properties, and color centers in ABS glass. The results are presented in Fig. 4a. It can be seen that only two parts of the spectrum exhibit appreciable changes from the inclusion of the RE ion: the complex band near 1000 cm^{-1} (characterized by the parameter Qn) and the wide band at 1450 cm^{-1} attributed to boron in the trigonal oxygen environment in these types of glass. The effect of the concentration of RE ions on the evolution of the parameter Qn is presented in Fig. 4b. It can be seen that the introduction of RE ions into the glass structure is responsible for the evolution of the relationship between the various components composing Qn. The analysis of the relationship $(Q4 + Q3)/(Q2 + Q1)$ for the ABS glass doped with Gd ions showed that the increase in the gadolinium concentration leads to a decrease in the amount of NBOs surrounding the silicon tetrahedron. As the amount of Ce ions increases, the increase in the amount of NBOs is observed, as is evident for Ce-doped glass. The results of studying the Raman spectra confirmed the data obtained from the optical transmission spectra. The decrease in the amount of NBOs leads both to an increase in the band gap of the ABS glass and to the polymerization of the glass matrix. The data on the structural modifications and optical characteristics for glass doped with Nd ions, obtained from the analysis of the transmission spectra and Raman scattering, are apparently not correlated. With an increase in the Nd content, the value of the band gap increases, which means that the production of NBO as color centers is suppressed by neodymium. Apparently, Nd ions can be distributed in the glass in two environments differing in their local symmetry and, in this case, the sodium ions in the structure either neutralize their environment (the position of the charge compensator) or depolymerize it (the position of the modifier). In the borate framework, we should observe the yield of sodium ions needed to compensate the charge of the borate tetrahedral structural unit (B^{IV}). The fraction of four-coordinated boron decreases, which is confirmed by the increase in the intensity of the band at 1450 cm^{-1}, corresponding

to the trigonal position of boron (B^{III}) in the glass matrix. This hypothesis is consistent with the well-known phase separation hypothesis for Ln-doped aluminoborosilicate glass proposed by H. Li [24], according to which an Nd ion is preferentially introduced into a borate environment consisting of two trigonal (B^{III}) and one tetrahedral boron (B^{IV}).

In addition, the procedure for the decomposition into Gaussian components should be carried out more carefully, and, possibly, the contribution of various Qn components and their descriptions should be reviewed. Our previous study of nonirradiated and irradiated ABS glass doped with Gd ions showed that the Gd^{3+} ions can exist in these types of glass in two structural positions having a high and low symmetry of the environment [3]. It was also shown that the number of Gd ions in either environment barely changes with the increase in the number of Gd ions. This result agrees with the obtained values of the optical band gap (Table 1). It is possible that the [11]B, ^{17}O, ^{23}Na, and ^{29}Si MAS-NMR study of the Nd-doped ABS glass, as well as the analysis of the Raman spectra of Sm and Eu-doped ABS glass obtained using the appropriate laser excitation ($\lambda = 473$ nm), making it possible to minimize the effect of the luminescence of Sm (Eu) ions, will help to test this hypothesis by determining the changes in the environments of boron and silicon depending on the content of the RE elements in the glass. Further studies of the absorption and luminescence of both color centers and radiation defects in RE-doped ABS glass are continuing, and the results obtained will be presented.

CONCLUSIONS

The incorporation of RE ions into the ABS glass matrix affects its optical and structural characteristics. The evolution of both optical and structural modifications is associated with the formation of non-bridging oxygens in the glass network, as well as color centers as a function of the nature of the RE element. By increasing the number of Nd (Gd) ions in ABS glass, it is possible to observe a decrease in the number of nonbridging oxygens per silicon tetrahedron in the glass under study, which is confirmed by the estimate of the energy of the band gap and the Raman spectroscopy data. The presence of two charge states of multivalent Eu and Ce ions having absorption in the UV region complicates the consideration of the effect of the processes on the observed change in the energy of the band gap and the structural modifications. The effect of irradiation leads to an increase in the formation of color centers in the following sequence, Nd < Gd < Sm = Eu < Ce and, as a consequence, to the narrowing of the optical band of forbidden energies.

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Translated by L. Mosina