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AMORPHOUS, VITREOUS, AND ORGANIC SEMICONDUCTORS

Aluminoborosilicate Glasses Codoped with Rare-Earth Elements as Radiation-Protective Covers for Solar Cells

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Abstract—The radiation hardness of aluminoborosilicate glasses codoped with rare-earth ions of Sm, Gd or Sm, Eu in various ratios is studied. The effect of codoping and β irradiation at a dose of 10^9 Gr on the optical transmission and electron paramagnetic resonance spectra is examined. It is found that the introduction of Sm and Gd codopants in a 1 : 1 ratio reduces the number of radiation defects and raises the transmission of irradiated glasses in the visible spectral range.

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1. INTRODUCTION

The development of practical solar cells was initiated at Bell Laboratories in the early 1950s [1]. Since that time these devices have been used to solve both space-related and terrestrial problems. The functioning of modern spacecraft requires significant energy resources which are replenished specifically by photovoltaic converters, solar cells.

Ionizing radiation of various kinds is among the main factors that affect the operation of solar cells in spacecraft and is responsible for the degradation of their parameters. Solar cells are commonly protected from the effects of radiation in outer space by protective covers designed for the absorption of ionizing radiation. Such covers should have, in addition to a high absorption efficiency of ionizing radiation, high radiation-optical stability to preclude a decrease in their transparency, leading to the degradation of solar-cell arrays.

Glass plates fabricated from multicomponent silicate glass serve as the main protective covers. Exposure to ionizing radiation may lead to coloration of protective covers of this kind, which is due to the formation of defects that give rise to absorption in the visible spectral range. The appearance of color centers in the cover material leads to a decrease in its transmission and, consequently, to optical degradation of the solar cell [2, 3]. To preclude the formation of centers of this kind, so-called protectors are introduced into protective covers. These protectors are elements with active donor-acceptor properties exhibited by polyvalent ions (antimony, bismuth, cerium, tin, iron). It has been shown that the introduction of cerium (Ce) ions into a borosilicate glass and the presence of two charge states of cerium (Ce^{3+}, Ce^{4+}) in the matrix in a certain ratio not only provide radiation-optical stability, but also block out harmful UV radiation [2-4]. It is known that $[Ce^{3+}]/[Ce^{4+}]$ equilibrium is affected by such factors as the CeO_2 concentration in the glass and the technological parameters of glass melting: the redox conditions and melting duration [5]. Therefore, the problem of the $[Ce^{3+}]/[Ce^{4+}]$ ratio is solved separately for each particular case with consideration for the following factors: composition of the glass; cerium concentration introduced into the glass; type, dose rate, and dose of ionizing radiation; and spectral range of application. This makes the use of cerium as a protector rather complicated.

Our recent studies carried out in order to analyze the influence exerted by ionizing radiation on the microstructure of a multicomponent aluminoborosilicate glass doped with rare-earth elements (REEs) have shown that this glass matrix is a radiation-hard material: raising the concentration of REE dopants restricts both microstructural modifications and the process of the formation of radiation defects [6-8]. The observed evolution is manifested with a higher efficiency for polyvalent REEs (Sm, Eu, and Ce). At the same time, it is known that aluminoborosilicate glasses are less subject to radiation coloration upon the introduction of Gd and Nd ions, compared with the introduction of variable-valence REE ions. Therefore, it is of interest to determine the influence exerted by the presence of two types of REE dopants on the structure and optical characteristics of the aluminoborosilicate matrix.

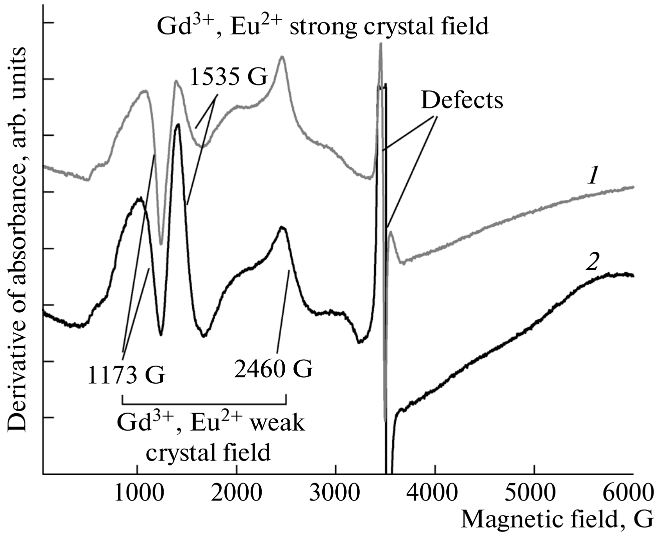

Fig. 1. EPR spectra of aluminoborosilicate glass codoped with (*1*) Sm, Gd and (*2*) Sm, Eu at a codopant ratio of 1 : 3 upon irradiation with a dose of 10^9 Gy.

In this investigation, we present the first results of an integrated study of aluminoborosilicate glass codoped with REEs (REE = Sm, Gd and Sm, Eu), aimed at finding conditions for the synthesis of materials with enhanced radiation-optical stability necessary for their use as protective radiation-optical covers for solar cells.

2. EXPERIMENTAL

Aluminoborosilicate glasses codoped with Sm, Gd or Sm, Eu were prepared by the addition of 1 and 2 wt % ($Sm_2O_3 + Gd_2O_3$) or ($Sm_2O_3 + Eu_2O_3$) in 1 : 3, 1 : 1, and 3 : 1 ratios ($[Sm_2O_3]/[Gd_2O_3]$ or $[Sm_2O_3]/[Eu_2O_3]$) to a charge composed of five oxides (wt %): SiO_2 59.13, Al_2O_3 6.38, B_2O_3 18.24, Na_2O 12.82, and ZrO_2 3.5. The glasses were produced by melting the mixture of powders at 1500°C in air. The irradiation of 0.5-mm-thick samples was performed with 2.5-MeV electrons from a Van de Graaff accelerator.

The optical transmission spectra of the glasses were measured with an Agilent Varian Cary 5000 spectrophotometer on 0.5-mm-thick samples polished on a hand grinding wheel with a silicon-carbide abrasive having an average grain size of 10 μm (1000-grit). The transmission spectra were measured with a step of 1 nm in the range from 200 to 1500 nm, which covers the range of spectral sensitivity of not only silicon solar cells, but also most photovoltaic converters fabricated by other technologies.

The electron paramagnetic resonance (EPR) spectra were obtained at room temperature for the *X*-band (frequency $\nu \approx 9.420$ GHz) with an EMX Bruker spectrometer. The EPR spectra were normalized to a sample weight of 100 g.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Electron Paramagnetic Resonance Spectra

Figure 1 shows the EPR spectra observed for aluminoborosilicate glass codoped with Sm, Gd and Sm, Eu. It should be noted that the spectra have no specific features in the positions of the main bands, compared with the spectra of Gd- or Eu-doped glasses [7, 8]. The observed EPR signal is attributed to Gd^{3+} or Eu^{2+} ions contained in the glass matrix structure under the action of crystal fields of varied strength [9, 10]. For example, the resonances at 1173 and 2460 G are characteristic of Gd^{3+} and Eu^{2+} ions localized in positions subject to the influence of the weak field of the surrounding ligands, whereas the resonance at 1535 G is attributed to the strong influence of the nearest environment. The first position is described by the coordination number $n = 8$ or more: $Gd_{[n > 6]}$, $Eu_{[n > 6]}$. At the same time, Gd^{3+} and Eu^{2+} ions in the second position may have less than six surrounding ligands ($n \le 6$): $Gd_{[n < 6]}$, $Eu_{[n < 6]}$ [9, 10]. This conclusion is in agreement with the statement that rare-earth ions in general, and Gd^{3+} ions in particular [11], determine their own characteristic environment in the glass.

Despite the fact that the positions and shapes of the main bands in the EPR spectra of aluminoborosilicate glass doped with Gd, Eu separately or codoped with Sm, Eu or Sm, Gd are invariable, the dependence of the ratio between the intensities of the EPR bands attributed to various environments of REE ions on the codopant concentration exhibits a behavior different from that of Gd- or Eu-doped glasses [7, 8]. Figure 2 shows the intensity ratio of the EPR signals related to Gd and Eu ions with coordination numbers smaller and larger than six: $I(Gd_{[n < 6]})/I(Gd_{[n > 6]})$, $I(Eu_{[n < 6]})/I(Eu_{[n > 6]})$. It can be seen in Fig. 2 that, with increasing codopant (Gd or Eu) concentration, the intensity ratio of the EPR bands corresponding to the positions of gadolinium and europium ions in a strong ($n < 6$) or weak ($n > 6$) crystal field decreases with increasing [Gd]/[Sm] and [Eu]/[Sm] ratios, with the minimum value reached at a ratio of ~1 : 1. With the [Gd]/[Sm] and [Eu]/[Sm] ratios increasing further, the EPR-band-intensity ratios $I(Gd_{[n < 6]})/I(Gd_{[n > 6]})$, $I(Eu_{[n < 6]})/I(Eu_{[n > 6]})$ again increase (Figs. 2a and 2b). The structure of radiation defects in the aluminoborosilicate matrix does not exhibit any changes, either: the EPR spectrum of radiation-induced intrinsic defects is characteristic of hole (boron-related) and electron (E') centers. Interestingly, the number of defects in glasses codoped with Sm, Gd and Sm, Eu (Figs. 3a and 3b) varies with the ratio between the codopants in the same way as the dependences of $I(Gd_{[n < 6]})/I(Gd_{[n > 6]})$, $I(Eu_{[n < 6]})/I(Eu_{[n > 6]})$ do (Figs. 2a and 2b).

With the results obtained in studies of aluminoborosilicate glasses doped with Sm, Gd, and Eu

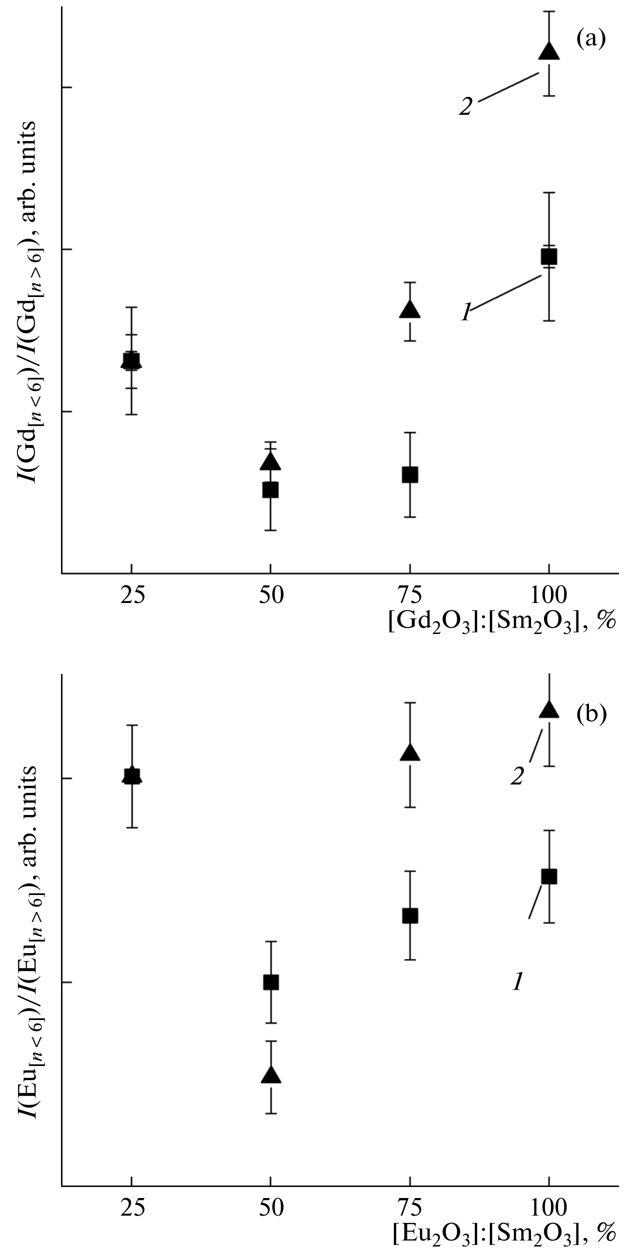

Fig. 2. Relative amounts of (a) Gd^{3+} and (b) Eu^{2+} ions localized in positions with $n \leq 6$ in aluminoborosilicate glass irradiated at a dose of 10^9 Gy in relation to the ratio of the codopants at their total concentrations of (*1*) 1 and (*2*) 2 wt %.

ions [6–8] taken into account, it is reasonable to assume that the mixing of two dopants should have led to a steadily decreasing dependence on the REE codopant concentrations on going from gadolinium to samarium both for the relative amounts of Gd or Eu ions localized in the positions with $n \leq 6$ and for the number of radiation defects. However, the observed evolution of the concentration of radiation defects has nothing in common with the dependences reported for the earlier considered REE dopants [6–8]. For all aluminoborosilicate glasses doped with REEs (REE = Gd, Sm, Ce, Nd, and Eu), a steady decrease in the number of radiation defects with increasing concentration of REE ions has been observed [6–8]. The minimum defect concentration corresponds to the situation in which the number of REE ion positions with $n > 6$ is at a maximum. The decrease in the concentration of radiation defects is attributed to the weaker migration of sodium ions in the structure of irradiated aluminoborosilicate glass doped with a REE impurity [12]. It has been suggested that radiation-defect precursors localized near an alkali ion occupying the modifier position activate its migration under irradiation. Thus, the 1 : 1 dopant ratio corresponds to the

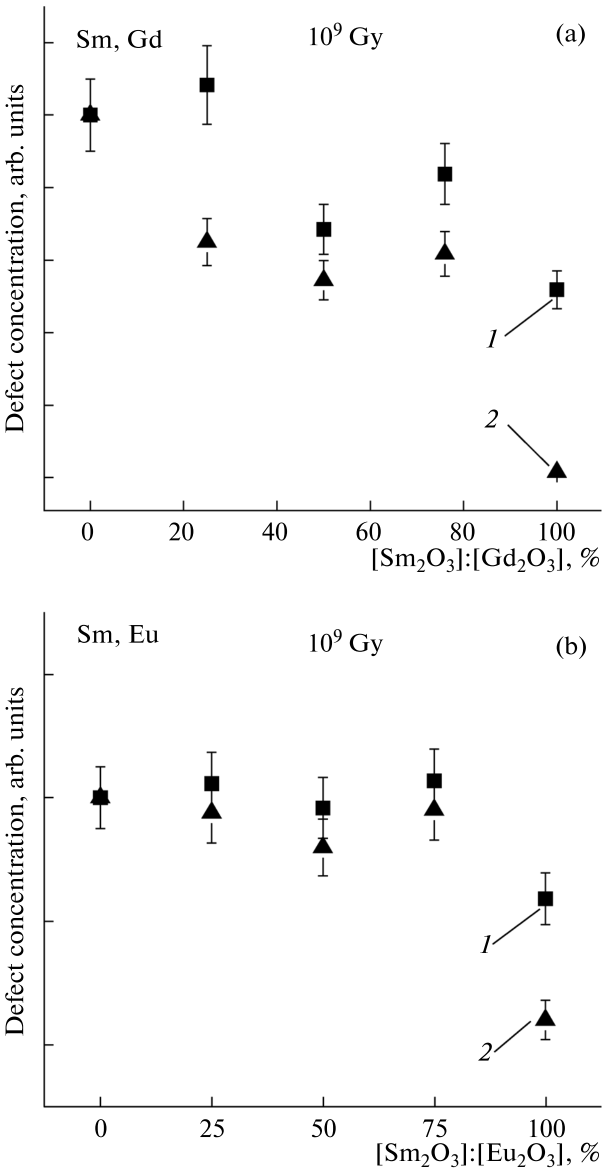

Fig. 3. Amount of radiation defects in aluminoborosilicate glass in relation to the ratio between (a) samarium and gadolinium and (b) samarium and europium oxides at their total content of (*1*) 1 and (*2*) 2 wt %.

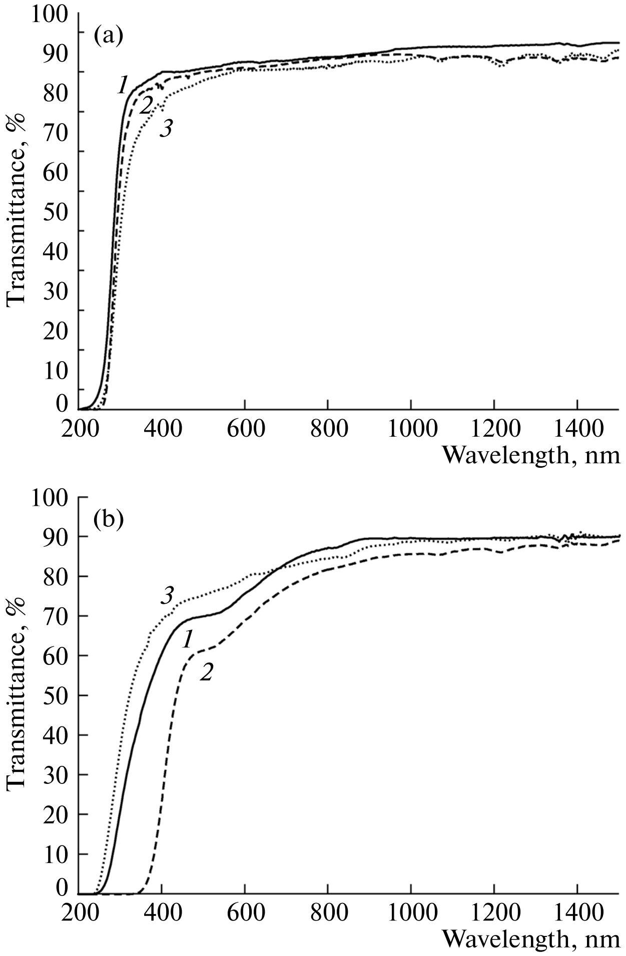

Fig. 4. Transmission spectra of (*1*) undoped and codoped with (*2*) Sm, Eu and (*3*) Sm, Gd samples in (a) the initial state and (b) upon irradiation at a dose of 10^9 Gy.

minimum number of defects, minimum mobility of sodium ions in the glass matrix, and maximum number of positions of Gd or Eu ions under the influence of the weak field of ligands. However, a subsequent increase in the dopant concentration ratio to the 3 : 1 proportion leads both to an increase in the number of radiation defects and to a decrease in the number of REE ion positions with $n \geq 6$. The observed dependence of the ratio between the numbers of Gd ion positions with various coordination numbers becomes understandable on taking into account the fact that Gd ions, first, can compete with sodium ions for charge compensator positions in the structure of the aluminoborosilicate glass and, second, are distributed among two environments in this matrix, the borate and silicate [13]. At low concentrations, Gd ions are predominantly incorporated into the borate environment. With increasing concentration of Gd ions, the positions with the borate environment are saturated, which leads to the introduction of Gd ions into the silicate environment [13]. With the aforesaid taken into account, the results obtained can be explained as follows. The increase in the number of Gd or Eu ion positions with larger coordination number is accompanied by a decrease in the diffusion capacity of sodium. After a certain excess concentration of these ions is reached, their distribution in the borate environment saturates and the silicate environment starts to be filled. In the process, sodium migration becomes more pronounced and the concentration of radiation defects grows. Therefore, it can be said that codoping strongly affects the process in which intrinsic radiation defects are formed in aluminoborosilicate glasses.

We have shown previously that the doping of an aluminoborosilicate matrix with REE ions suppresses the formation of intrinsic radiation defects. The reason for this is that electron–hole pairs formed under irradiation are involved with greater efficiency in the recharging of doping ions, compared with defect formation in the matrix via the breaking of bonds between glass-forming ions and oxygen. However, doping with REEs gives no way of increasing the radiation hardness, with the aluminoborosilicate matrix preserving its transparency under the action of ionizing radiation in the case of Sm- or Eu-doping. In the case of Gd-doping, the number of radiation defects decreases only slightly and the transparency of the glass is retained. Therefore, the present study has demonstrated that codoping may prove to be a useful procedure for obtaining a transparent and radiation-hard material.

3.2. Optical Transmission

The main issue in using glasses as protective covers for solar cells is the transparency of a glass in the spectral range of the sensitivity of photovoltaic converters and the change in the transparency under irradiation. The transmission spectra of glasses in the as-synthesized and irradiated states are shown in Fig. 4. It can be seen that the initial transmittance of the undoped glass in the visible and near-IR spectral ranges was 85% and more. A maximum transmittance of more than 92%, observed in the near-IR spectral range, was determined by reflection from the front and rear surfaces of the glass. With the wavelength decreasing from 1500 to 400 nm, the transmittance decreased, which may be due both to an increase in the refractive index of the glass and to an increase in light scattering at surface irregularities which remain because of the limited possibilities of the hand grinding.

The irradiation led to a decrease in the optical transmission of the undoped glass in the whole spectral range under study. The transmittance decreased most strongly at wavelengths shorter than 800 nm, which occurs because a wide variety of electron and hole defects related to boron, oxygen, and silicon are formed in the glass under the action of radiation [14]. At wavelengths exceeding 800 nm, rather weak, not exceeding 3%, changes in transmittance were observed.

The effect of codoping with the ratios [Sm]/[Eu] = 1 : 1 and [Sm]/[Gd] = 1 : 1 on the optical transmission of the glasses in the initial and irradiated states is illustrated by Fig. 4. It can be seen in Fig. 4a that, in the initial state, the transmittance of the codoped glasses in the visible and near-IR spectral ranges exceeded 77%. The most pronounced changes in the transmittance were observed for the sample codoped with Sm, Gd. The main changes occurred in the range from 300 to 500 nm, in which the decrease in the transmittance relative to the undoped sample reached a value of 10%.

Irradiation led to a decrease in the transmittance for all glasses under study (Fig. 4b). Absorption increased to the greatest extent for the glass codoped with Sm, Eu. At the same time, it can be seen in Fig. 4b that codoping with Sm, Gd led to an increase in the transmittance in the visible spectral range in the irradiated state, compared not only with the sample codoped with Sm, Eu, but also with the undoped sample. Thus, it can be assumed that codoping with Sm, Gd suppresses the formation of radiation defects responsible for the increase in optical absorption in the visible spectral range.

4. CONCLUSIONS

The effect of codoping with Gd, Sm or Eu, Sm ions on the structural and optical properties of aluminoborosilicate glass under the action of β radiation was studied. EPR spectroscopy demonstrated that the minimum number of radiation defects in aluminoborosilicate glasses codoped with Sm, Gd is obtained when the REE dopants are present in the 1 : 1 ratio. In the irradiated state, the glass fabricated with the codopant ratio [Gd]/[Sm] = 1 : 1 has the highest transmittance in the visible spectral range, compared with the undoped glass. The results obtained give reason to believe that, with appropriate choice of the content of the codopants, the radiation-optical resistance of the material used for radiation-protective covers of solar cells can be substantially raised.

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