The Effect of γ-Radiation on Glasses of the $\mathrm{Na_2O}$–$\mathrm{Al_2O_3}$–$\mathrm{SiO_2}$ System

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Abstract

Full Text

Chemistry

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The Effect of γ-Radiation on Glasses of the Na_2O –Al_2O_3–SiO_2 System

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The study of the influence of composition on the absorption spectra of glasses of the Na_2O–Al_2O_3–SiO_2 system irradiated with γ-radiation is of interest in connection with the large glass-forming regions in these systems, and also because the Al^{3+} ion can act both as a glass former and as a modifier ([1,2]).

Glasses were melted containing from 13 to 40 mol.% Na_2O and from 0 to 35 mol.% Al_2O_3. SiO_2 in the initial sodium silicate glasses was replaced by Al_2O_3 in equimolecular amounts. The iron content was about 0.005%. Samples of thickness 0.5–1.0 mm were prepared. The power of the γ-source was 10^4 r/hour, and the integral irradiation dose was $5 \cdot 10^6$ r, and in some cases $3 \cdot 10^7$ r. Measurement of the absorption spectra before and after irradiation was carried out on an SF-4 spectrophotometer in the wavelength interval 210–1100 mμ. The data obtained are presented graphically. Along the ordinate was plotted the difference in optical densities after and before irradiation (ΔD), and along the abscissa–the wavelength (λ), expressed in electronvolts. The absorption spectrum of sodium silicate glass with 15 mol.% Na_2O consists of five absorption bands located at about 2; 2.8; 4.2; 5; 5.6 eV (Fig. 1, 1). With an increase in the concentration of Na_2O, the bands at 5 and 5.6 eV disappear. At the same time, there occurs a decrease in the intensity of the 4.2 eV band and its shift into the long-wavelength region (4 eV). The 2 eV band becomes more intense with increasing Na_2O content, while the band at 2.8 eV shows a more complicated dependence. The effect of irradiation on sodium silicate glasses has been studied by a number of authors ([3,4]), who found analogous absorption bands.

Fig. 1. Influence of Al_2O_3 content on the spectral absorption of irradiated glasses. $l = 1$ mm, dose $5 \cdot 10^6$ r

Fig. 2 and Fig. 3: spectral absorption curves of irradiated glasses

Figure 2: Fig. 2 and Fig. 3: spectral absorption curves of irradiated glasses

No.	Na_2O (%)	Al_2O_3 (%)	SiO_2 (%)
1	15	—	85
2	15	0.15	84.85
3	15	0.31	84.69
4	15	0.62	84.38
5	15	5.00	80

When a small amount of Al_2O_3 (0.15 mol.%) is introduced into glass with 15 mol.% Na_2O and 85 mol.% SiO_2, there is a sharp decrease in the intensity of all absorption bands (Fig. 1, 2). Further replacement of SiO_2 by Al_2O_3 leads to the complete disappearance of the bands at 5 and 5.6 eV (Fig. 1, 3, 4, 5). The remaining bands change only slightly. Thus, the introduction of both Na_2O and Al_2O_3 leads to the disappearance of the bands at 5 and 5.6 eV.

To clarify the question of the existence of absorption bands in the ultraviolet region at a relatively high content of Na_2O and Al_2O_3, glasses of three compositions were irradiated with a dose of $3 \cdot 10^7$ r (Fig. 2, 1, 2, 3). Here, as in the case of glass with 15 mol.% Na_2O, 5 absorption bands were found at 2; 2.8; 4; 5 and 5.6 eV, which is also confirmed by the data on thermal bleaching. It is also seen from the figure that an increase in the Al_2O_3 content is accompanied by a decrease in the intensity of all absorption bands, except

Fig. 2. Spectral absorption of irradiated glasses of the Na_2O–Al_2O_3–SiO_2 system. $l = 0.5$ mm, dose $3 \cdot 10^7$ r

Specimen Nos.	Na_2O (%)	Al_2O_3 (%)	SiO_2 (%)
1	25	5	70
2	25	10	65
3	25	15	60
4	25	15	60; (10 min, 100°)
5	25	15	60; (20 min, 100°)
6	25	15	60; (50 min, 100°)
7	25	15	60; (80 min, 100°)

Fig. 3. Influence of the Al_2O_3 content on the spectral absorption of irradiated glasses. $l = 0.5$ mm, dose $5 \cdot 10^6$ r

Specimen Nos.	Na_2O (%)	Al_2O_3 (%)	SiO_2 (%)
1	13	8	79
2	13	13	74
3	13	18	69
4	13	22	65
5	13	26	61
6	13	18	69; (30 min, 150°)
7	13	22	65; (30 min, 150°)

the 4 eV band, whose intensity remains constant. Bands near 5 and 5.6 eV have been found in fused quartz and, apparently, are caused by defects of bridging oxygen (5). The decrease in the intensity of the bands and their complete disappearance with increasing concentration of Na_2O and Al_2O_3 may be associated with a decrease in the amount of bridging oxygen.

However, at an $Al_2O_3 > Na_2O$ content these bands reappear (Fig. 3, 3, 4, 5, 6, 7). The 2 and 2.8 eV bands are due to the presence of nonbridging oxygen, and the decrease in their intensity is associated with a decrease in the amount of nonbridging oxygen. At the ratio $Al_2O_3 > Na_2O$, these bands disappear completely, and at the same time a new absorption band appears at 3.4 eV (Fig. 3, 2, 3, 4, 5). Thus, it is evident that, as the Al_2O_3 content changes, both a quantitative and a qualitative change in the absorption spectrum occurs, which, in our view, is explained by the fact that the Al^{3+} ion tends to be incorporated into the network of SiO_4 tetrahedra and in doing so uses nonbridging oxygen, caused by the pres-

by the action of Na_2O, for the construction of its own tetrahedra. At the ratio $Al_2O_3 : Na_2O = 1$, all non-bridging oxygen proves to be bound in AlO_4^- tetrahedra; in this case a quartz-like network is formed, consisting of SiO_4 and AlO_4^- tetrahedra, while the Na^+ ions are located near the AlO_4^- tetrahedra for charge compensation.

An amount of Al_2O_3 in excess of Na_2O leads to the appearance of Al^{3+} in sixfold coordination, which lacks oxygen for the construction of tetrahedra ([2]). The appearance in this case of the absorption band at 3.4 eV, in our opinion, is associated with Al^{3+} in sixfold coordination. As thermal bleaching shows, in these glasses there is a "hidden" band near 4 eV (Figs. 3, 6, 7).

Thermal bleaching of glasses irradiated with a dose of $3 \cdot 10^7$ r (Fig. 2, curves 4, 5, 6, 7 for glass with 15 mol.% Al_2O_3) shows that the thermal stability of the 2 and 2.8 eV bands increases upon the introduction of Al_2O_3, while the 4, 5, and 5.6 eV bands are least stable in the glass with 10 mol.% Al_2O_3, i.e., as the quartz-like structure is approached, the glass network is strengthened, although initially the stability of the 4, 5, and 5.6 eV bands decreases somewhat from the

glass with 5 mol.% Al_2O_3 to the glass with 10 mol.% Al_2O_3.

Thus, in glasses of the Na_2O—Al_2O_3—SiO_2 system, two series of absorption bands are observed: 1) at a content $Na_2O > Al_2O_3$, the bands are 2; 2.8; 4; 5 and 5.6 eV; 2) at a content $Na_2O < Al_2O_3$, the bands are 3.4; $\sim$ 5; 4 and 5.6 eV; the last two bands are detected only upon thermal bleaching. Observation of the qualitative and quantitative change in the induced-absorption spectra as a function of glass composition makes it possible, on the one hand, to better understand the nature of the absorption centers and, on the other, to detect changes in the glass structure.

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Note: Figure translations are in progress. See original paper for figures.