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STUDY OF STRUCTURAL TRANSFORMATIONS IN CRYSTALLIZING GLASSES FROM UV ABSORPTION SPECTRA

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The investigation of the absorption spectra of glasses in the UV region is a structure-sensitive method for studying glasses. The absorption spectrum in the UV region is determined entirely by electronic absorption; moreover, in glasses the most weakly bound electrons—namely, the valence electrons, which play the principal role in the formation of bonds in glass—participate in absorption. Therefore, the slightest changes in the bonds in a glass, or any redistribution of electron densities, are registered as a change in absorption at one wavelength or another, depending on the natural frequency of the electrons that have changed their state. Those bonds that most readily change their state under various kinds of external action on the glass are characterized by us as defects of the glass.

As will be shown, the restructuring of the glass structure leading to its crystallization is accompanied by a change in such defective bonds, weak in structural terms.

In the present study, mainly readily crystallizing glasses are considered, since it is precisely during crystallization that a fundamental restructuring of the glass structure occurs.

In work (1) it was shown that the change in the absorption spectra of spodumene glass with an addition of TiO_2 during precrystallization heat treatment is associated with the crystallization ability of the glass. It was of interest to trace, during heat treatment, the change in the absorption spectra of a group of glass-ceramic glasses of another composition, qualitatively different from that investigated earlier (1). In the present work, the object of study was an alkali-free glass in the system $SiO_2{-}Al_2O_3{-}CaO{-}MgO$ with an addition of TiO_2, which was introduced in amounts of 1, 3, and 6 parts by weight per 100 parts by weight of the base glass (glasses No. D1, D2, D3).

The main investigations were carried out on glass No. 3, which is optimal for obtaining glass-ceramic. Glass No. 3 was melted in a gas-fired batch furnace of 300 kg capacity, lined with quartz refractory. An oxidizing atmosphere was maintained in the furnace. For the investigations, samples from one day of

Figure 1

Figure 1: Figure 1

production were taken in order to guarantee the same thermal history of the glass.

For a comparative study of glasses with different TiO_2 contents, as well as of glass D1, D2, D3 melted under different oxidation-reduction conditions, the glasses were melted in a crucible gas furnace in quartz crucibles of 1 l capacity under oxidizing and reducing conditions. The glass was pressed in the form of plates measuring 150 × 60 × 5 mm at 1450°. The plates were annealed in a muffle electric furnace at 700° for 1 hour and cooled to 400° at a rate of 200°/h. Measurements were carried out on polished specimens measuring 30 × 30 × 0.5 mm.

Absorption spectra of the uncrystallized samples were recorded on the SF-4 with the FEU-18. To reduce as much as possible the scattering of light when measuring the absorption spectra of partially crystallized (clouded) glass plates No. 3, the samples were placed in a holder at a distance of 1-2 mm from the FEU-19, whose photocathode was covered with a thin layer of vacuum oil. With this

Fig. 1. *a*—absorption spectra of glasses with different TiO_2 content, recorded relative to air: 1—glass D1, 2—glass D2, 3—glass D3. *b*—absorption spectra of glasses D1, D2, D3, melted under oxidizing conditions, recorded relative to the same glasses melted in a reducing atmosphere

method of measurement, all the light transmitted and scattered into the rear hemisphere of the sample falls on the photomultiplier. At the same time, diaphragms prevent light scattered into the front hemisphere of the sample from reaching the FEU-19. As in work (1), an increase in the titanium content in glass D causes an increase in absorption at the edge of the intrinsic absorption and a shift of the latter into the long-wavelength part of the spectrum (Fig. 1a). Fig. 1b gives the absorption spectra of glasses D1, D2, D3, melted under oxidizing conditions, recorded relative to those melted in a reducing atmosphere. As can be seen from the figure, the former have greater absorption. The maxima of the added absorption are formed at the edge of the intrinsic absorption. It is interesting to note that the influence of the atmosphere is somewhat weaker in glasses with a high titanium content.

To study the kinetics of structural transformations in glass, manifested in changes in the ultraviolet absorption spectra, absorption spectra were recorded for samples of glass D3 subjected to thermal shock at various temperatures (from 750 to 900° at intervals of 50°) for 1 min (Fig. 2). In subsequent works it will be shown that, on the curves of the change in the absorption minimum with time, saturation is observed. To compare the rates of the process, we chose a time of 1 min, when saturation still does not occur at any of the

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

temperatures. From Fig. 2 it is seen that heat treatment of glass D3 leads to bleaching in the differential absorption spectra, in contrast to spodumene glass, where precrystallization heat treatment causes the appearance of maxi-

Fig. 2. Differential absorption spectra of glass D3, heat-treated for 1 min at various temperatures: 1—at 750°, 2—at 800°, 3—at 850°, 4—at 900°

minimums. At the same time, the minima in the absorption spectra of glass D3 are located, like the maxima in spodumene glass C-6, at the edge of intrinsic absorption. The appearance of transparencies during precrystallization heat treatment does not contradict the ideas expressed earlier about the structural changes occurring in the glass: it only emphasizes the specificity of the mechanism of these transformations depending on the composition of the glass.

Comparison of the magnitudes of the minima for different heat-treatment temperatures (curves 1-4) shows that the rate at which structural changes occur in the glass increases with temperature, especially intensively above 750°.

Different Ti contents in the glass do not change the nature of the changes in the absorption spectra during heat treatment, but lead only to a change in the magnitude of the transparency (Fig. 3). This confirms the opinion expressed earlier that the nature of the change in the absorption spectra in the UV region during precrystallization heat treatment is determined by the basic composition of the glass, which gives rise to one or another glass structure.

Fig. 3. Differential absorption spectra of glasses D1, D2, D3, heat-treated for 1 hour at 800°: a —glasses melted under reducing conditions; b —glasses melted under oxidizing conditions

Comparison of Figs. 3a and 3b shows that the change in the absorption spectra upon heat treatment is greater for glasses melted in a reducing atmosphere than for glasses melted under oxidizing conditions. This agrees with the data of thermographic analysis, which show that reduction of Ti4+ to Ti3+ increases the tendency of the glass to crystallize (crystallization begins 50° lower).

As is seen from Figs. 3a and 3b, with increasing Ti content in the glass the transparency in the absorption spectra increases. On the other hand, it is well known that with an increase in the amount of titanium in glasses of this system their crystallization ability increases. This confirms our supposition that the defectiveness of the glass, characterized by the magnitude of the minimum in the differential absorption spectra, is connected with the crystallization properties

Figure 4

Figure 4: Figure 4

of the glass.

In order to trace the further change in the structure of the glass at temperatures lying within the crystallization interval, absorption spectra were taken of samples treated at a temperature of 950° (Fig. 4, 1) and 1050° (Fig. 4, 2). As X-ray analysis showed, at 950° intensive crystallization takes place, while at 1050° crystallization is practically completed. We see that whereas in the precrystallization period the absorption spectra were characterized by transparencies, crystallization is accompanied—

is accompanied by the appearance of intense maxima, which grow with increasing crystallization temperature and shift into the longer-wavelength region (from 320 mµ at 950° to 360 mµ at 1050°).

The work carried out once again confirms that this method of investigation is highly sensitive.

First, the absorption spectra record changes in the structure of the glass that occur at temperatures lying far below the temperature of crystallization proper. Second, the absorption spectra make it possible to detect very subtle differences in the structural transformations of glasses of different composition during precrystallization heat treatment.

While for spodumene glass the change in the spectra during the precrystallization period was characterized by an increase in absorption, which appeared in the differential spectra as maxima, in the glasses considered here the precrystallization heat treatments cause bleaching, i.e., the appearance of minima on the absorption curves. However, the fact that both the maxima and the minima are located at the edge of the intrinsic absorption indicates that, despite the individual features of the process, determined by the basic composition of the glass, the nature of these structural rearrangements is the same and requires a unified approach to its explanation.

Fig. 4. Differential absorption spectra of glass D3, heat-treated for 0.5 h at various crystallization temperatures:
1 —at 950°, *2* —at 1050°

Obviously, precrystallization heat treatment causes, both in spodumene and in the present group of glasses, a certain rearrangement of bonds, accompanied by a redistribution of electrons between ions, which in one case leads to an increase in absorption, and in the other to bleaching.

The role of titanium in the observed precrystallization rearrangements for both groups of glasses appears to us to be analogous: namely, with an increase in the amount of titanium, the defectiveness of the glasses increases, predetermining their ability to crystallize. This is observed in the growth of the maxima in spodumene glass and of the minima in glass D3 with increasing TiO_2 content.

The proposed method of investigation helped explain the observed experimental fact that the reduction of Ti^{4+} to Ti^{3+} increases the crystallizing ability of the glass. As shown in the work, upon reduction of Ti the defectiveness of the glass increases at an unchanged TiO_2 content.

The investigations also showed that the structural rearrangements associated with crystallization, in the case of the present group of glasses, differ from the precrystallization ones. Whereas over a wide range of precrystallization temperatures we observe bleaching in the absorption spectra, during crystallization maxima arise that lie at another wavelength. For spodumene glass, crystallization was accompanied by an increase and a slight shift into the long-wavelength part of the spectrum of the maxima that had arisen during the precrystallization period.

Thus, this method of investigation is fruitful both for explaining features of the structure of crystallizing glasses and for studying the process of their crystallization.

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1. L. G. Baiburt, A. A. Gorbachev, DAN, **156**, No. 6, 1420 (1964).

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