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Abstract

Full Text

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STUDY OF THE CATALYZED CRYSTALLIZATION OF GLASS

(Presented by Academician A. A. Lebedev on 20 VI 1963)

The study of catalyzed crystallization was carried out on glasses of the Li_2O $-Al_2O_3-SiO_2$ system with the addition of 5 wt.% TiO_2 as a catalyst and a small amount of oxides of elements of groups I, I, and III of the periodic table of D. I. Mendeleev. In terms of the amounts of Li_2O, Al_2O_3, and SiO_2 oxides introduced, the glasses were close to spodumene. The specimens were subjected to heat treatment in air for 24 hours at various temperatures from 600 to 1000°.

Fig. 2. X-ray diffraction patterns of glasses subjected to various heat treatments

The investigations were carried out by electron-microscopic and X-ray structural methods, and also by studying changes in light absorption in the indicated temperature range.

The electron-microscopic investigation was performed by the replica method. A fresh fracture of the glass was etched in a 5% solution of hydrofluoric acid for 5 sec, washed in distilled water, and dried. The fracture was then shadowed with a Pt–Pd alloy at a small angle, and a carbon film was deposited, which was usually separated from the glass

gelatin. The gelatin dissolved in water, and the free carbon film was caught on the specimen grid.

After the electron-microscopic examination, the specimen was ground into powder and studied by the Debye–Scherrer method on a standard x-ray apparatus

Fig. 3. Light-transmission curves (λ 585 mμ) for glass as a function of heating time at temperatures: 1–630°, 2–710°, 3–850°

Figure 2: Fig. 3. Light-transmission curves (λ 585 mμ) for glass as a function of heating time at temperatures: 1–630°, 2–710°, 3–850°

with ionization recording of the URS-50I type. A tube with a copper anticathode was used as the radiation source, and nickel foil as the filter.

In studying changes in light absorption, a glass specimen with plane-parallel polished ends was placed in a tubular furnace equipped with quartz windows. A monochromatic parallel beam ($\lambda = 585$ mμ) was passed through the specimen, the intensity of which was recorded by a photoelement. The change in light absorption was measured at different temperatures as a function of heating time.

According to the results obtained, the process of catalyzed crystallization of glasses, depending on the heating temperature, proceeds as follows.

There are three temperature regions for which the transition from one to another is accompanied by a sharp change in the properties and structure of the glass. The first temperature region extends approximately up to 700°, the second from 700 to 830°, and the third from 830° and above.

Fig. 3. Light-transmission curves (λ 585 mμ) for glass as a function of heating time at temperatures: 1–630°, 2–710°, 3–850°.

In the first temperature region, at relatively low heat-treatment temperatures (up to 625°), no noticeable structural changes occur in the glass (Fig. 1a, see insert to p. 118). With increasing treatment temperature, against the background of the glassy phase, separate regions of inhomogeneity appear in the glass (Fig. 1b), about 0.5μ in size. The nature of these inhomogeneities does not change up to 680°, and as the heat-treatment temperature is raised further, small crystals form in individual regions of the glass (Fig. 1v, g); their appearance determines the beginning of bulk crystallization of the glass, which begins to develop vigorously at a temperature of about 700°.

The results of electron-microscopic studies in the temperature range up to 700° agree with the data of x-ray structural analysis. Specimens heated at temperatures below 625° give x-ray patterns with diffuse maxima, typical of glasses (Fig. 2).

On the x-ray scattering curve for glass specimens heated at temperatures above 625°, a weak peak ($\Theta \simeq 7°$) is observed, which can be explained by the presence in the specimens under study of a small amount of an ordered phase. Although it is not possible to identify this phase either electron-microscopically or x-raygraphically, it may be said that structurally, and perhaps also chemically, it has little in common with the principal crystalline phases that separate in the glass at temperatures above 700°.

Fig. 4. Increase in the content of the crystalline phase in the glass as a function of the heating temperature of the specimens (obtained by the method of quantitative X-ray phase analysis)

Figure 3: Fig. 4. Increase in the content of the crystalline phase in the glass as a function of the heating temperature of the specimens (obtained by the method of quantitative X-ray phase analysis)

Heating the specimens at temperatures below 700° over time leads to an intense increase in the light absorption of the glass, which can be explained by the formation of iron–titanium color centers ([1–3]). The results of measurements of light absorption in this temperature region show that structural changes in the glass proceed with a large activation energy (65 kcal/mol) and involve a relatively small mass of glass. This value of the activation energy is close to the energy values necessary for the switching of Si–O–Ti or Al–O–

Ti. Apparently, in the precrystallization region there is a process of formation of a phase containing titanium in its composition.

At temperatures above 700° the crystallization of the glass occurs throughout the entire volume; a fine-crystalline phase appears, consisting of crystallites up to 0.7 μ in size (Fig. 1d). A further increase in the heat-treatment temperature to 830° does not lead to substantial structural changes; no growth of crystallites in the glass is observed. X-ray diffraction records in these specimens the appearance of a crystalline phase that remains unchanged over the entire temperature interval from 700 to 830° (Fig. 2). At the same time the glass becomes clearer, as is seen from curve 2 in Fig. 3.

In a comparatively narrow temperature region (about 700°), a sharp increase occurs in the content of the crystalline phase, and subsequently, as the temperature rises, its increase is insignificant (Fig. 4).

Fig. 4. Increase in the content of the crystalline phase in the glass as a function of the heating temperature of the specimens (obtained by the method of quantitative X-ray phase analysis)

At heat-treatment temperatures above 830° the appearance of fractures of the glass, observed in the microphotographs, changes qualitatively. At first, small crystallites combine into blocks with dimensions of 0.2-0.4 μ, and then large crystals grow on their basis, the sizes of which reach 1 μ and more (Fig. 1e). Apparently, in the temperature region of 830° and above, recrystallization occurs in the glass, as a result of which the fine-crystalline structure of the glass characteristic of the second temperature interval disappears, giving way to a new, coarse-block structure. X-ray investigation showed that in this temperature region of heat treatment there is a change in the phase composition of the crystallized glass: the crystals characteristic of the second temperature interval of heat treatment disappear and are replaced by new ones (Fig. 2). The glass in this case becomes milky and opaque.

The structural changes in glass heated at high temperatures proceed sequentially: first a fine-crystalline phase is formed, characteristic of lower temperatures, and then it is transformed into a coarse-block high-temperature phase (Figs. 3, 3). Phase analysis carried out on the basis of the X-ray patterns obtained showed that in transparent crystallized glass there separates, apparently, a solid solution with a eucryptite-like structure, while in milky glass there separates a high-temperature modification of spodumene*.

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CITED LITERATURE

1. A. Dietzel, *Naturwiss.*, **29**, No. 9, 537 (1941).

2. W. A. Weyl, *Coloured Glasses*, Sheffield, 1951.

3. V. V. Vargin, DAN, **111**, No. 4, 848 (1956).

* To make an exact X-ray determination of the crystalline phase separating in transparent crystallized glass does not appear possible. There is some basis for the supposition that in the present case a new modification of spodumene is separating.

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