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Dependence of the Crystallization of Photosensitive Glasses on the Method of Producing Crystallization Centers

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It is known that in heterogeneous crystallization the structure of the final product is determined by the nature, number, and size of the crystallization centers (⁀1). In the present work, the processes of heterogeneous crystallization of a photosensitive glass (⁀2) of the lithium aluminosilicate system on centers produced by various methods were investigated. In the glasses studied, particles of colloidal silver serve as the crystallization centers. Electron-microscopic studies of the crystallization products showed that their structure depends on the dose of irradiation with ultraviolet light (⁀3), but is not determined entirely by this factor, since even at the optimum irradiation time the structure often proves to be inhomogeneous. The structure of the crystallized glass depends substantially on the heat treatment in the period preceding crystallization, since it is precisely this treatment that determines the formation of crystallization centers. In the present work it is shown how, by varying the conditions of precrystallization treatment, it is possible to obtain centers of different number and size.

Samples in the form of plates of polished glass measuring $30 \times 12 \times 0.5$ mm were irradiated with a PRK-7 mercury lamp at a distance of 420 mm at a temperature of 80°. The precrystallization treatment consisted of the following. The irradiated samples were heated in a muffle furnace at a rate of 4–5° per minute, which led to the appearance of coloration with a maximum in the absorption spectrum at 405 mμ. The absorption spectra were recorded on an SF-4 spectrophotometer. During heat treatment of irradiated samples in the temperature range 300–450°, atomic silver centers are formed in them, while heat treatment above 450° leads to the formation of colloidal silver particles, which is reflected in the position of the maximum of the glass absorption spectrum (⁀4). In addition to slow heating, sharp heating of the sample (thermal shock) and holding in the above-mentioned temperature intervals were used as precrystallization heat treatment. It was established that thermal shock results, after subsequent holding at the corresponding temperature, in the formation of large colloidal particles, and in the absorption spectrum a strong shift of the maximum is observed (Fig. 1a).

Fig. 1

Figure 1: Fig. 1

By repeated multiple irradiation and subsequent thermal shock, it is possible to regulate the number of atomic centers produced (Fig. 1b).

To carry out thermal shock, the sample was rapidly introduced into a furnace heated to the appropriate temperature (400–500°) and was held there for 3 minutes. This time must ensure, on the one hand, the necessary heating of the sample and, on the other, the absence of growth of colloidal particles.

Crystallization of the samples was carried out according to two regimes: by gradual heating to 750° at a rate of 4°/min and subsequent holding (slow regime), and by rapidly introducing the sample into the furnace at the specified temperature (fast regime).

The structure of the samples was examined with a Tesla BS-242A electron microscope at electron-optical magnifications of about 14000×. The replica method was used, the replicas being obtained by simultaneous oblique deposition of

platinum and carbon onto a preliminarily etched specimen. The replicas were detached in hydrofluoric acid ([5]). The investigations showed that crystallization after preliminary treatment of the specimen by slow heating leads to the formation of a nonuniform structure. Holding at the temperature of formation of colloidal centers does not improve the structure (Fig. 2b). The observed large scatter in the sizes of the crystals and their shapes is associated with the nonuniformity of the growth of crystallization centers during precrystallization treatment. Fig. 2a presents the structure of a specimen brought to the onset of crystallization; the nonuniform distribution of crystalline particles and the etch pits associated with them is clearly visible, indicating nonuniform growth of crystallization nuclei ([5]).

Fig. 1. Absorption spectra of photosensitive glasses.
a —shift of the maximum in the absorption spectrum of glasses subjected to thermal shocks, after holding: *I* —after four thermal shocks, *II* —after four thermal shocks and holding at 500° for 4 h; *b* —increase in the intensity of the absorption maximum with increasing number of thermal shocks: *I* —2 thermal shocks, *II* —4 thermal shocks, *III* —5 thermal shocks, *IV* —8 thermal shocks.

Such a precrystallization structure determines the nonuniformity of the structure of the specimen after crystallization. A change in the precrystallization structure toward greater uniformity can be achieved if, instead of slow heating, one or several thermal shocks of the specimen are carried out (Fig. 2c). As was to be expected, such heat treatment predetermines a dense and homogeneous structure of the crystallized

Fig. 2. Influence of thermal shocks on the formation of the precrystallization and final structure of photosensitive glass.
a –precrystallization structure of a specimen held for 4 h at 540°; *b* –final structure of the same specimen after crystallization by the slow schedule at 750°; *c* – precrystallization structure of a specimen subjected to 5 thermal shocks at 400°; *d* –final structure of the same specimen after crystallization

Fig. 3. Structure of crystallized specimens after two (*a*), four (*b*) and eight (*c*) thermal shocks; rapid schedule

Fig. 4. Structure of specimens crystallized by the slow schedule. *a, b* – specimens with preliminarily separated atomic centers by means of, respectively, two and eight thermal shocks; *c, d* –specimens with preliminarily separated colloidal centers by means of, respectively, two and eight thermal shocks and holding for 4 h at 500°

Fig. 2

Panels: **a**, **b**, **c**, **d**, **e**. Scale mark: **1 μm**.

Fig. 3

Panels: **a**, **b**, **c**.

Fig. 4

Panels: **a**, **b**, **c**, **d**. Scale mark: **1 μm**.

sample (Fig. 2e). It may be assumed that thermal shock promotes the formation of centers of the same size and sets the same growth rate for the nuclei, as a result of which they simultaneously reach the dimensions critical for crystallization. Repeated thermal shocks lead to the formation of a larger number of centers, which at the crystallization temperature grow to critical dimensions. Further growth of the centers is limited by the crystallization process that has begun. Thus, in this case crystallization takes place on a large number of colloidal particles of small size. The final structure after crystallization depends on the number of these particles, i.e., on the number of thermal shocks, which is confirmed by electron-microscopic investigation (Fig. 3). Similar structural changes are observed in specimens in which the colloidal particles were grown by precipitation of unreduced silver on atomic centers at a temperature of 500°, when crystallization has not yet occurred ([4]). A decrease in crystal size and an increase in the density of the structure occur up to a certain limit: after five to six thermal shocks, stabilization of the structure sets in.

All the results described above were obtained on specimens crystallized by rapid introduction into a furnace heated to the crystallization temperature. Such a regime ensures fixation of the structure specified by the precrystallization treatment. To study the influence of the crystallization regime on the structure of specimens subjected to thermal shock, some of the specimens were crystallized according to a slow regime. It turned out that the structure of specimens crystallized according to the slow regime depends almost not at all on the type

of centers obtained as a result of the preliminary treatment (Fig. 4). This is explained by the fact that, during gradual heating of the specimen, colloidal particles have time to grow on the atomic centers separated in it.

In electron-microscopic photographs of all the specimens studied, needle-like crystals are observed; in the glass under study these constitute the principal crystalline phase and, according to X-ray structural analysis, were identified as lithium metasilicate. In some specimens, between the needle-like intergrowths of lithium metasilicate, a dense crystalline background is observed, which is identified with α-quartz (according to X-ray data). Electron-microscopic investigation showed that, depending on the nature of the centers, not only the structure of the specimen changes, but also the quantitative ratio of the precipitating crystalline phases. It indeed follows from the X-ray structural analysis data that two crystalline phases are precipitated, the quantitative ratio between which depends on the nature of the centers and on the crystallization regime. During crystallization, according to the rapid regime, of specimens with previously separated atomic centers, α-quartz appears simultaneously with lithium metasilicate (high-temperature α-quartz was also found at room temperature in lithium silicate glasses by other investigators ([6])). Depending on the holding time (in the range studied) at the crystallization temperature, the amount of lithium metasilicate increases up to a certain limit, while the amount of α-quartz continues to increase continuously. During crystallization on colloidal centers, lithium metasilicate is formed, the amount of which rapidly reaches a limit (at a holding time of 10 min), and only with very long holdings is α-quartz precipitated.

The difference in crystallization on colloidal and atomic centers is apparently explained by the fact that, in a specimen containing atomic centers, at the crystallization temperature colloidal particles grow to critical dimensions. The earlier precipitation of α-quartz in such specimens, as compared with specimens containing large colloidal particles, is probably connected with the fact that the nuclei for crystallization of α-quartz must have smaller critical dimensions than those for lithium metasilicate, although the latter is the primary crystalline phase for the given composition.

glass composition. During crystallization on large colloidal particles previously grown in the glass, lithium metasilicate is rapidly precipitated. The ratio of crystalline phases during crystallization under the slow regime does not differ from their ratio during rapid crystallization on colloidal particles.

Thus, it has been established that the nature of the precrystallization treatment determines the type, number, and size of the crystallization centers growing in photosensitive glass. It has been shown that, by means of a single or repeated thermal shock, a denser and more finely crystalline structure can be obtained, which remains unchanged under various crystallization regimes. It has been established that precrystallization heat treatment can be used to influence the quantitative ratio of the crystalline phases that precipitate, which is of practical interest for changing certain properties of the material.

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