CHANGE IN THE SUPRAMOLECULAR STRUCTURE OF SODIUM-SILICATE GLASS DURING HEATING

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Abstract

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CHANGE IN THE SUPRAMOLECULAR STRUCTURE OF SODIUM-SILICATE GLASS DURING HEATING

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To study the dependence of the supramolecular (submicroscopic) structure of sodium-silicate glasses on heat treatment, the method of small-angle X-ray scattering (SAXS) was applied to glass with 14 mol.% Na_2O, heated in a gradient furnace over the temperature range 570–790° for 2.5 hours. To obtain information on the kinetics and completeness of structure formation, one glass sample was heated under the same conditions for 0.5 hour. After quenching in air, the samples were ground to a thickness of 0.2 mm, and for 30 points over the entire temperature interval SAXS intensity curves were obtained on the apparatus described in (^{1}). After correcting the curves in accordance with the experimental conditions, the following structural characteristics were calculated (^{2}): 1) the radii R of spherical regions of inhomogeneity*; 2) the values of the specific interfacial surface $\tilde{S}$ between these regions and the matrix surrounding them; and 3) the values of the mean square of the electron-density fluctuations $(\Delta\rho)^2$ for those points at which the values of R did not exceed 300 Å (^{3}).

In (^{4}) it was shown that for all low-alkali sodium-silicate glasses there exists a temperature zone of opalescence, a zone of rapid decrease in the intensity of visible-light scattering, and a zone of complete clarification of the glass; moreover, for the sample with 14 mol.% Na_2O the following temperature intervals of these zones were established: 600–735°, 725–775°, and above 775°. The temperature 735° was called the temperature of maximum opalescence T_m, and the temperature 775° the clarification temperature T_p; the latter, evidently, coincides with the liquidus temperature. All these values could depend on the conditions of sample preparation, and therefore in the present work the preparation conditions coincided, as far as possible, with those adopted in (^{4}).

In the opalescence zone, which for the sample studied by the SAXS method extended approximately from 580° to $T_\mathrm{m} \geq 710°$, the sizes of the regions of inhomogeneity increased with increasing temperature from $R = 115$ Å to $R = 730$ Å, and the structure was, within the accuracy of the experiment, monodisperse. Between the temperatures T_m and $T_\mathrm{p} = 770°$, two types of regions could be de-

Fig. 1

Figure 1: Fig. 1

termined from the SAXS curves—with maximum sizes $R = 730$ Å and $R \leq 100$ Å. Above the temperature $T_{\mathrm{p}} = 770°$ there is one type of region, having the same sizes $R \approx 90$ Å.

When the glass was heated in the gradient furnace for 0.5 hour, the sizes of the regions of inhomogeneity at $T \approx 600°$ were noticeably smaller; this difference decreased with increasing temperature, which is readily explained by the decrease in the viscosity of the glass and the acceleration of diffusion processes leading to coarsening of the regions of inhomogeneity.

* The closeness of the shape of the regions of inhomogeneity to spherical followed from the slope of the straight lines in the plot of the logarithmic dependence of the SAXS intensity on the scattering angle and was also found with the aid of an electron microscope (^{4}).

The generalized phase-interface surface area S was determined from plots of the dependence of $\lg I$ on $\lg \varphi$ (I is the intensity in relative units, φ is the scattering angle), some of which are shown in Fig. 1. The figure shows a linear dependence with a slope tangent of -3 (confirmation of the sphericity of the regions), a gradual increase in the size of the regions with increasing temperature from 575 to 710° (as indicated by the shift of the straight lines toward smaller angles φ), the appearance and development of a bidisperse structure (727

Fig. 1. Curves of the dependence of the logarithm of the intensity, in relative units, on the logarithm of the scattering angle, revealing monodispersity of the supramolecular structure of glass when it is heated to 725°, and above 765°, and bidispersity at these temperatures. From the intercepts cut off by extending the straight lines to the ordinate axis, the values of the generalized phase-interface surface area S were calculated.

and 765°), a gradual decrease in the number of large regions without a change in their size and an increase in the number of small regions, and, finally, the disappearance of the large regions with the small ones remaining (780°). From the intercepts cut off by extending the straight lines to the ordinate axis, the values of S were determined; these values, obviously, will be appreciably smaller for larger regions of heterogeneity (the lower straight lines). The values of S in the opalescence region decrease rapidly with increasing temperature, which agrees with the growth of the values of R (Fig. 2, curves 1*a* and 2*a*). At $T = 770°$ the value of S is very small, but with a further increase in temperature it rises abruptly to values that determine the generalized interface surface of the small regions (curve 2*b*). Thus, the entire curve 2*a* corresponds only to large regions of heterogeneity, even in the region of bidispersity, since they scatter much more intensely than the small regions with $R \simeq 90$ Å (curve 1*b*).

Fig. 2. Change in R (1), S (2), and $\overline{(\Delta\rho)^2}$ (3) upon heating the glass in the temperature interval 575-790°. Below is shown the curve of the temperature dependence of the intensity of light scattering according to the data of work (4).

Figure 2: Fig. 2. Change in R (1), S (2), and $\overline{(\Delta\rho)^2}$ (3) upon heating the glass in the temperature interval 575-790°. Below is shown the curve of the temperature dependence of the intensity of light scattering according to the data of work (4).

The antibatic character of curves 1 and 2 indicates that, in the opalescence region, the process of change in the supramolecular structure of the glass proceeds through coarsening of the heterogeneity regions without any noticeable change in their composition or total volume. The disruption of such a simple relation between R and S at high temperatures may be caused both by a change in the composition of the heterogeneity regions (i.e., by a change in ρ_1 and ρ_2—the difference in the mean electron densities of the particles and the matrix) and by a change in their volume, or by both factors. An answer to this question can in principle be obtained by studying the temperature dependence of $(\Delta\rho)^2$, which is also shown in Fig. 2. As stated above, the values of $(\Delta\rho)^2$ could be determined only

for regions of inhomogeneity whose dimensions do not exceed 300 Å.

As was to be expected, in the temperature interval 570-650° the values of $\overline{(\Delta\rho)^2}$ change little: the composition of the coarsening regions of inhomogeneity changes hardly at all (curve 3a). Since at $T_\mathrm{p} = 770°$ the large regions disappear, for them at this point $(\Delta\rho)^2 = 0$, and curve 3a may be approximately extrapolated to a zero value (the dashed part of curve 3a).

Separating the small-angle scattering curves into parts due to scattering by large and small regions, one can determine the temperature dependence of $\overline{(\Delta\rho)^2}$ for small regions, which appear only at $T > T_\mathrm{m}$ (Fig. 2, curve 3b). Thus, although the values of $(\Delta\rho)^2$ for the large regions in the interval 650-770° were not calculated, it proved possible approximately to outline the entire course of the change of $\overline{(\Delta\rho)^2}$ with temperature over the whole interval studied (curve 3a—3b—part of curve 3b).

Fig. 2. Change in R (1), S (2), and $\overline{(\Delta\rho)^2}$ (3) upon heating the glass in the temperature interval 575-790°. Below is shown the curve of the temperature dependence of the intensity of light scattering according to the data of work (4).

Thus, the following description may be given of the change with temperature in the supramolecular structure of sodium silicate glass with 14 mol.% Na_2O. When the temperature is raised from 570 to 710°, the dimensions of the regions of inhomogeneity arising over one and the same interval of time increase. Since the Na_2O content in the glass investigated exceeds its content in the glass with the maximum degree of inhomogeneity (11.5 mol.% Na_2O, according to (3, 7)), the composition of these regions, which have a purely liquation origin, is enriched in SiO_2. As the regions grow, their composition approaches somewhat that of the surrounding matrix, which is reflected in the gradual decrease of $\overline{(\Delta\rho)^2}$ and the decrease in the volume of the regions of inhomogeneity up to their complete disappearance at the temperature T_p.

Above and below T_p, a "fine" inhomogeneous structure arises with sharply different characteristics $\overline{(\Delta\rho)^2}$ and $\tilde{S}$. Several assumptions may be made concerning the nature of this structure. Its origin may be fluctuation-related (5), which is partly confirmed by its formation near the liquation boundary (near T_p). It is possible that it forms as a result of secondary chemical separation within one of the separating phases, in this case the matrix; this can be checked by ordinary X-ray structural analysis, which previously confirmed the probability of such an interpretation (8), revealing a chemically inhomogeneous structure not only in low-alkali sodium silicate glasses, but also in more alkaline ones, up to

to sodium metasilicate. Further, for interpretation one may invoke the idea of special "microliquation" processes ([9]), a characteristic feature of which is the independence of the dimensions of the regions of inhomogeneity from heat treatment. However, it is first of all necessary to check whether the "fine" structure arises as a result of the finite rate of cooling from rather high temperatures (at which the viscosity of the glass is still low) and, consequently, of the passage of the glass through the temperature region of opalescence.

Understanding the nature of the emergence of the fine inhomogeneous structure, whose appearance has been noted not only in sodium-silicate glasses ([3,6,9]), and studying the kinetics of its formation and the kinetics of the transformation of the fine structure into an ordinary liquation structure are tasks for the immediate future.

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