ON THE LIQUATION NATURE OF THE CHEMICALLY INHOMOGENEOUS STRUCTURE OF LOW-ALKALI SODIUM SILICATE GLASSES

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON THE LIQUATION NATURE OF THE CHEMICALLY INHOMOGENEOUS STRUCTURE OF LOW-ALKALI SODIUM SILICATE GLASSES

(Presented by Academician A. A. Lebedev on 30 VII 1965)

In works ([1–3], [7]) the clearing temperatures T_p of a number of low-alkali sodium silicate glasses were determined, and for some of them the values of the mean square of fluctuations of the electron density $\overline{(\Delta\rho)^2} = C\int I(\varphi)\varphi\, d\varphi$, where $I(\varphi)$ is the intensity of x-ray scattering at small angles (s.m.a.); φ is the scattering angle; C is a constant; $\Delta\rho = \rho - \bar{\rho}$ is the deviation of the electron density from its mean value over the volume. For a two-phase system $\overline{(\Delta\rho)^2} = (\bar{\rho}_1 - \bar{\rho}_2)^2 w_1 w_2$, where ρ_1 and ρ_2 are the mean values of the electron density of the two phases, and w_1 and w_2 are their specific volumes. The dependence of $\overline{(\Delta\rho)^2}$ on temperature was determined more fully in ([7]) for glass Na 14*.

Figure 1 gives the curve of the dependence of T_p on the composition of the glasses according to the results of works ([1], [3]). Experimentally it was determined for compositions from Na 20 to Na 5 (because of the difficulty of melting glasses with a lower Na_2O content). If the nature of the regions of inhomogeneity is liquational (as was assumed in ([4], [8])), then the curve in Fig. 1 may be regarded as the binodal curve of metastable liquation and continued (arbitrarily) toward lower Na_2O contents (dashed part of the curve). A similar curve was considered in ([5], [9]). To it one may apply the well-known "lever rule" and calculate, for any composition and at any temperature, the compositions and volumes of the separated phases and, from the densities of the corresponding glasses, which are given in ([10]), the absolute values of $\overline{(\Delta\rho)^2}$, and compare them with those determined from the s.m.a. curves.

Fig. 1. Dependence of the clearing (liquation) temperature on the composition of sodium silicate glasses

Figure 2

Figure 2: Figure 2

Fig. 3

Figure 3: Fig. 3

Fig. 2. Temperature dependence of $\overline{(\Delta\rho)^2}$ for glass Na 14. 1 –experiment, 2 –calculation. *a* –experimental values obtained in the present work; *b* –values obtained earlier ([3])

* Here and below, for glasses containing X mol.% Na_2O, the notation NaX is adopted.

Using a collimation system with higher resolving power ($\varphi_{min} = 2.8'$ instead of $5.5'$ in (11)), we were able to determine the values of $\overline{(\Delta\rho)^2}$ for the entire temperature range up to T_p.

Figure 2 gives the curves of the dependence of $\overline{(\Delta\rho)^2}$ on temperature for glass Na14, obtained on the basis of the small-angle X-ray scattering curves (curve 1) and by calculation using the binodal curve (curve 2). It should be noted that the presence of a "bidisperse structure," arising below the temperature T_p (below 770°) (7), could not noticeably affect the course of the experimental curve, since the weak intensity of small-angle scattering by small regions was almost not recorded with narrow slits. Undoubtedly, the curves agree qualitatively. Quantitative agreement can be judged only after determining $\overline{(\Delta\rho)^2}$ from the small-angle scattering curves in absolute units and determining T_p for glasses with a Na_2O content below 5%.

Fig. 3. Dependence of $\overline{(\Delta\rho)^2}$ on the composition of sodium-silicate glasses at temperatures 580° (1), 660° (2), 685° (3), 715° (4), and $T \geq T_p$ (5). *a* – experiment, *b* –calculation

Having thus confirmed the validity of using the curve in Fig. 1 as a liquation curve, one can try, with its aid, to determine the dependence of $\overline{(\Delta\rho)^2}$ on composition for all glasses used in the small-angle scattering experiments. Obviously, at any fixed temperature (Fig. 1), $\rho_1 - \rho_2 = \text{const}$ for any glass composition and the behavior of $\overline{(\Delta\rho)^2} = (\rho_1 - \rho_2)^2 w_1 w_2$ is determined only by the factor $w_1 w_2$; therefore such curves must have a dome-like form with maxima at compositions where the volumes of the separated phases are equal. The curves obtained with the aid of Fig. 1 for the dependence of $\overline{(\Delta\rho)^2}$ on glass composition for temperatures 580, 660, 685, and 715°C are shown in Fig. 3 (dashed curves *b*). The solid curves *a* are drawn through points determined from the experimental small-angle scattering curves for glasses of different compositions (the compositions and temperatures used are marked in Fig. 1 by crosses). All glasses were held at these temperatures for 2.5 h, except for the Na16 specimen, which was heated not at $T_p = 715°$, but at 700° for 10 min, and the Na20 specimen, heated

at 540° for 20 h. The ordinates of the maxima of the calculated curves were taken equal to the ordinates of the maxima of the corresponding experimental curves. This led to undoubted qualitative agreement between the experimental and calculated curves, both in their shape and in the position (abscissae) of the maxima.* At low temperatures the position of the maximum coincides with that determined earlier in (1) (11.5 mol.% Na_2O); as the temperature is raised, the maximum shifts slightly (approximately to 10% Na_2O). If one takes into account the arbitrariness of the extrapolation of the curve in Fig. 1 and the possibility of using a nonequilibrium value of $\overline{(\Delta\rho)^2}$ for the given composition, temperature, and duration of heating, the agreement should be considered good.

Curve 5 in Fig. 3 was obtained from the small-angle scattering curves for glasses Na 7.5, Na 10, Na 11.5, and Na 14 after their heating at temperatures exceeding T_p (1). It is known that under these conditions large regions disappear and there remain in the glass

* A later determination of the absolute values of $(\Delta\rho)^2$ also led to quantitative agreement with an accuracy of up to 12-14% ($(\Delta\rho)^2 \approx 5.3 \cdot 10^{-4}$ (el/Å^3)^2).

only small ones ($R \leqslant 100$ Å) ([7]), for which the values of $\overline{(\Delta\rho)^2}$ are much smaller than for regions with $R \simeq 110$ Å, formed during low-temperature treatment of the glass (for example, at 580°). Indeed, in full agreement with this, the curve of $\overline{(\Delta\rho)^2}$ for transparent glasses held at 580° lies much higher than the curve of $\overline{(\Delta\rho)^2}$ for the same transparent glasses (clarified) held above T_p.

If only large regions of inhomogeneity were formed in the glasses investigated, then the dome-shaped curves of Fig. 3, with increasing temperature, would approach the abscissa axis and merge with it at the maximum value of T_p (for glass of composition Na 7.5). But at temperatures below T_p a bidisperse structure is observed; the small regions make their own contribution to the value of $\overline{(\Delta\rho)^2}$, slowing the decrease of the curves to zero at T_p. Therefore the limiting value of $\overline{(\Delta\rho)^2}$ for each of the glasses with increasing temperature will be its value for the fine structure at $T \geqslant T_p$. Thus, with increasing temperature, the curves of Fig. 3 will ultimately coincide with the curve due to the presence of only the fine high-temperature structure.

It was previously assumed that the appearance of the fine structure is connected with the passage of the glass, during cooling, through the liquation zone ([4]). The character of curve 5 in Fig. 3 confirms this. It therefore seems very probable that at high temperatures, before its cooling (quenching), the glass is either homogeneous* (at $T \geqslant T_p$) or monodisperse (at $T \leqslant T_p$). As a result of quenching, the glass rapidly, but nevertheless at a finite rate, passes through the liquation zone and separates with the formation of a fine structure existing either independently or together with the coarse structure.

If this is so, then the values of R and $\overline{(\Delta\rho)^2}$ characterizing this structure must depend strongly on the quenching rate. Indeed, such an effect was observed when glass Na 14 was quenched: upon quenching in air at room temperature, R

and $\overline{(\Delta\rho)^2}$ were appreciably lower for small pieces of glass, which cooled rapidly, than for large pieces, which cooled much more slowly.**

Thus, the results of the present work undoubtedly support the concept of a liquation origin of the high-temperature fine structure, and not the fluctuation origin previously proposed by Filippovich ([6]).

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* The absence of liquation regions of inhomogeneity larger than 80-100 Å is meant.

** The first results of electron-microscopic verification of this question, obtained by V. I. Averyanov, confirm the strong dependence of the high-temperature fine structure on the cooling rate.

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