Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1958

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1958. Volume 118, No. 4

PHYSICAL CHEMISTRY

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CHEMICALLY HETEROGENEOUS STRUCTURE OF SODIUM BOROSILICATE GLASSES

(Presented by Academician A. A. Lebedev on 27 VII 1957)

The structural homogeneity of glasses of complex composition, postulated by the Zachariasen–Warren random-network hypothesis ([1], [2]), has in recent years repeatedly been called into question ([3]–[8]). Especially convincing data indicating the chemically heterogeneous structure of glasses have been obtained for certain sodium borosilicate glasses ([9]–[14]). However, most of these data are indirect in character, and the experiments underlying them admit of interpretation from the standpoint of the random-network hypothesis. In particular, the attempts to substantiate and detail the chemically heterogeneous structure of sodium borosilicate glasses on the basis of studying the submicroscopic structure of the porous products of their leaching have met with the sharpest objections. For example, N. V. Belov asserts that the formation of pores, "which even geometrically were not outlined in the initial glass," occurs in the process of the action of acids on chemically homogeneous initial glasses ([15], [16]). Therefore the detection, by some direct structural method, of a chemically heterogeneous structure of glass is of fundamental interest.

For this purpose we used the method of small-angle X-ray scattering. A new vacuum chamber was constructed, based on the principle of the "frame camera" proposed by Kratky ([17]). With the aid of this chamber we succeeded in obtaining distinct and reproducible small-angle diffraction from a glass containing (mole percent): Na_2O 7, B_2O_3 23, and SiO_2 70, and not subjected to any chemical action.

Owing to the slight difference between the electron densities of the heterogeneous regions, the intensity of small-angle scattering by unleached glasses is very low, and attempts to record such weak scattering on X-ray film when preparing powdered glass samples ended unsuccessfully because of purely surface effects on the glass grains, which have nothing in common with the internal structure of the object under investigation. This scattering was almost independent of the composition and heat treatment of the glass, but depended strongly on the degree of dispersion of the powder. Noticeable scattering in the region very close to the primary beam was observed, for example, for grains 0.1 mm in diameter

Fig. 1. Intensity curves of small-angle scattering by unleached (solid curves) and porous (dashed curves) glasses, showing the effect of annealing at 600° (I) and at 650° (II); r is the distance from the center of the primary beam in millimeters

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with a 2-hour exposure. In this connection it should be noted that this effect may have introduced significant distortions into the results of Hoffman and Statton, who recently obtained small-angle X-ray scattering from glassy silica and sodium magnesium silicate glass, but investigated the samples in powder form ([18]).

We therefore used glass samples in the form of polished plates about 0.2 mm thick, and the absence of a surface effect was checked by changing the thickness of the samples. X-ray photography was carried out with filtered copper radiation (BSVI tube,

operating conditions—10 mA, 30 kV) at a distance from the specimen to the film of 350 mm. Small-angle scattering was obtained for 9 glass specimens subjected to various heat treatments. The initial specimen was specimen No. 1, annealed at a temperature of about 500°; the remaining specimens were heated at 600 and 650° for various times (from 1 to 8 hr) and quenched in air. The exposure, depending on the size of the regions of inhomogeneity, ranged from 15 hr (for the specimen heated for 6 hr at 650°) to 100 hr (for specimen No. 1). Glasses annealed at 600° remained, like specimen No. 1, transparent, whereas glasses annealed at 650° had various degrees of opalescence, increasing with increasing annealing time. The intensity of scattering of visible light (λ = 5400 Å) was measured on a special apparatus using an FEU-19 photomultiplier and a direct-current amplifier.

Fig. 1. Intensity curves of small-angle scattering by unleached (solid curves) and porous (dashed curves) glasses, showing the effect of annealing at 600° (*I*) and at 650° (*II*); r is the distance from the center of the primary beam in millimeters.

At the same time we studied porous glasses obtained from the same specimens by the action of HCl and KOH under the conditions described earlier ([1]). These specimens were studied in powder form. The guarantee that a surface effect was of no significance in this case was the short exposure times (of the order of several minutes) and the dependence of the diffraction pattern on the heat treatment of the initial glasses, but not on the degree of dispersion of the powder.

In Fig. 1, *I*, the solid lines show the intensity curves for the initial glass No. 1 and for glasses annealed at 600° for 4 and 8 hr (Nos. 2 and 3, respectively).

The presence of a maximum on these curves indicates fairly uniform sizes of the scattering regions and their sufficiently dense distribution. The intensity at the maxima was taken as unity. The shift of the curves with increasing annealing time indicates an increase in the size of the regions. In the same figure the dashed lines show the intensity curves for porous glasses obtained from the same specimens. These curves are very close to the curves for the corresponding initial glasses, which is convincing evidence of the similarity of the shape and size of the regions of inhomogeneity in the initial glasses and of the pores formed during the leaching process. Calculation of the radii of the inhomogeneities, carried out on the basis of the position of the interference maximum with the introduction of a collimation correction for the finite height of the primary beam (R_m) and by means of the "tangent method" (R), gave the following results for specimen No. 1: $R_m = 105$ Å, $R = 113$ Å for the initial glass and $R_m = 113$ Å, $R = 99$ Å for the porous glass. For specimen No. 3 the radius increases to 180 Å. The intensity of scattering of visible light increases, correspondingly, by a factor of 3-4.

In Fig. 1, *II* shows the intensity curves for the original and leached glasses for samples annealed at 650° for 1 hour (No. 4) and 6 hours (No. 5). The intensity at the minimum scattering angle (at a distance of 0.05 mm from the edge of the primary beam, i.e., at a scattering angle of $30'$) is taken as unity. No interference maxima were found in the accessible angular range. The somewhat greater discrepancy between the curves for the original and porous glasses is explained in this case by the different conditions of X-ray photography: the original glasses were photographed at 30 kV, whereas the porous ones were photographed at 15 kV, and the most intense short-wavelength part of the continuous spectrum, after passing through the filter, caused a shift of the intensity curves of the original glasses toward smaller scattering angles. This circumstance was checked by a special experiment. Therefore, here as well it may be considered that the shape and dimensions of the regions of inhomogeneity in the original glasses are close to the shape and dimensions of the pores in the leached glasses. As for the influence of heat treatment, it is the same as for the samples annealed at 600°, but the dimensions of the regions of inhomogeneity at 650° are considerably larger.

A calculation carried out by the tangent method (without introducing a collimation correction for the finite width of the beam) shows that, for sample No. 4, the average radius of the regions of inhomogeneity increased, in comparison with sample No. 1, to 380 Å (the intensity of visible-light scattering increased by approximately 30 times), and for sample No. 5, to 610 Å (the intensity of visible-light scattering increased by more than three orders of magnitude).

Thus, when the small-angle method was applied to unleached sodium borosilicate glasses heated at different temperatures for different lengths of time, the same regularities were revealed as in the study of porous glasses (⁀12). This convincingly confirms the earlier conclusion that submicroscopic regions of inhomogeneity exist in the original glasses. The growth of these regions upon heating

may be accompanied by an increase in the degree of ordering (crystallites), as is indicated by preliminary results of the investigation of the same glasses by the ordinary method of X-ray structural analysis. The role of such crystallization of the borate "component" of these glasses in the scattering of visible light and small-angle X-rays is currently being clarified. The question of the chemically inhomogeneous structure of sodium borosilicate glasses should be regarded as definitively resolved.

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Received
15 VII 1957

CITED LITERATURE

^1 W. H. Zachariasen, J. Am. Chem. Soc., **54**, 3841 (1932).
^2 B. E. Warren, Zs. Kristall., **86**, 349 (1933).
^3 W. A. Weyl, J. Soc. Glass Techn., **35**, 421, 448, 462, 469 (1951).
^4 A. G. Smekal, J. Soc. Glass Techn., **35**, 411 (1951).
^5 N. J. Kreidl, Glass Ind., **31**, 573 (1950).
^6 J. M. Stevels, Philips Techn. Rund., **13**, 350 (1952).
^7 E. A. Porai-Koshits, *Structure of Glass*, Acad. Sci. USSR Publishing House, 1955, p. 30.
^8 K. Griotheim, J. Krogh Moe, Glass, **33**, 465 (1956).
^9 T. Abe, J. Am. Ceram. Soc., **35**, 284 (1952).
^10 V. L. Indenbom, DAN, **89**, 509 (1953).
^11 D. I. Levin, S. P. Zhdanov, E. A. Porai-Koshits, Izv. Acad. Sci. USSR, Dept. Chem. Sci., **1955**, 31, 197, 395.
^12 E. A. Porai-Koshits, D. I. Levin, N. S. Andreev, Izv. Acad. Sci. USSR, Dept. Chem. Sci., **1956**, 287.
^13 F. Oberlies, Naturwiss., **43**, 224 (1956).
^14 D. P. Dobychin, N. N. Kiseleva, DAN, **113**, 372 (1957).
^15 N. V. Belov, *Collected Papers: The Structure of Glass*, Acad. Sci. USSR Publishing House, 1955, p. 334.
^16 N. V. Belov, Mineralogical Collection of the Lvov Geological Society, No. 8, 13 (1956).
^17 O. Kratky, Zs. Elektrochem., **58**, 49 (1954).
^18 L. C. Hoffman, W. O. Statton, Nature, **176**, No. 4481, 561 (1955).

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