

Density and boron coordination in heat-treated alkali-borosilicate glass

Thomas H. Elmer, Jan W. H. Schreurs and Roger J. Araujo

Corning Glass Works, Research, Development and Engineering Division, Corning, NY (USA)

The room temperature density of an alkali-borosilicate glass was determined as a function of heat treatment at 415 to 700 °C. It was found to decrease with temperature as expected on the basis of structural relaxation, but at temperatures above about 550 °C it was observed to increase. The increase is explained by the coarsening of the microphases in such glass.

NMR studies revealed that the fraction of 4-coordinated borons in the glass decreases on rapid cooling, but that the N_4 values are insensitive to subsequent annealing of the glass. Addition of alumina to such glass dramatically reduces the fraction of 4-coordinated borons, presumably due to competition for the Na^+ ions by Al^{3+} ions to form AlO_4 tetrahedra.

Dichte und Borkoordination in wärmebehandeltem Alkali-Borosilicatglas

Die Dichte von Alkali-Borosilicatglas bei Raumtemperatur wurde in Abhängigkeit von einer Wärmebehandlung bei Temperaturen zwischen 415 und 700 °C bestimmt. Die Dichte nimmt mit steigender Temperatur ab, wie auf Grund von Strukturrelaxationen im Glas zu erwarten ist, und steigt bei Temperaturen über 550 °C wieder an. Die Dichtezunahme wird durch das Wachstum von Mikrophasen in diesem Glas erklärt.

Untersuchungen der magnetischen Kernresonanzspektren ergaben, daß der Anteil an 4er-koordiniertem Bor im Glas durch schnelle Abkühlung verringert wird, daß aber die N_4 -Werte gegen eine nachfolgende Kühlung unempfindlich sind. Der Zusatz von Al_2O_3 führt zu einer starken Verringerung von Bor in 4er-Koordination, was wahrscheinlich auf die Bildung von AlO_4 -Tetraedern auf Grund vorliegender Na^+ -Ionen zurückzuführen ist.

1. Introduction

The role of heat treatment on density of an alkali-borosilicate glass was studied in efforts to determine how changes in density might relate to coarsening of the alkaliborate and silica-rich microphases.

Measurements of the boron coordination by means of a Varian wide-line NMR spectrometer (Varian, Sunnyvale CA (USA)) were made of water-quenched, hot-formed, and heat-treated glass to determine whether there are any significant changes in the fraction of 4-coordinated boron (N_4) with thermal history of the glass.

2. Experimental procedure

The specimens used in this study consisted of cast plates and fritted glass of the same composition (mol%: 70 SiO_2 , 23 B_2O_3 and 7 Na_2O). The latter was prepared by pouring the glass melt directly into cold water.

The glass plates were subjected to heat treatments at temperatures ranging from 415 to 700 °C and cooled in room atmosphere after a 3 h hold period at the desired temperatures. Densities of the samples were measured at room temperature in kerosene (to avoid leaching) in accordance with ASTM procedure in C373-72 [1].

NMR spectra, measured at 18.0 MHz, were taken [2] of as-formed and fritted glasses, both before and after annealing 3 h at 555 °C and cooling at a rate of 10 K/h. Additional N_4 data were obtained on an as-formed and an annealed glass plate that had the same molar ratio of SiO_2 , B_2O_3 and Na_2O but contained also Al_2O_3 (mol%: 65.9 SiO_2 , 21.7 B_2O_3 , 6.6 Na_2O and 5.8 Al_2O_3).

3. Results and discussion

The densities of the glass plates that had been heat-treated at temperatures ranging from 415 to 700 °C and cooled in room atmosphere are summarized in

Table 1. Room temperature density of heat-treated glass plates

temperature in °C	density in g/cm ³
415	2.2355
450	2.2354
500	2.2299
530	2.2272
555	2.2263
578	2.2266
603	2.2279
628	2.2295
654	2.2312
675	2.2323
700	2.2325

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table 1 and shown graphically in figure 1. The density at first decreases with increasing temperature, goes through a minimum, and then increases as shown. The maximum density change was 0.0092 g/cm^3 .

The decrease in density in the low temperature regime is similar to that seen in silicates and is presumably related to the anharmonicity of the bonds. The increase in density above 550°C is not so readily explained. It almost certainly cannot be related to a change in the bonding of boron in a way that resulted in an increase in the number of non-bridging oxygen atoms. That would have led to a decrease in the density [3 and 4]. Nor is the increase in density related to a change in the bonding of boron to produce a decrease in the number of non-bridging oxygen atoms and an increase in the number of tetrahedrally bonded boron atoms. The development of opacity at the higher temperature and the electron micrographs in figures 2a and b show clearly the coarsening of separate phases. The decrease in the silica content of the alkali borate-rich phase which

accompanies this phase separation would be expected to decrease the number of tetrahedrally bonded boron atoms if it had any effect at all [5]. An increase in the number of tetrahedrally bonded boron atoms cannot be a direct result of a high-temperature structure. Calculations [6] show that 4-coordinated boron is thermodynamically less stable at high temperatures. Measurements (table 2) of the fraction

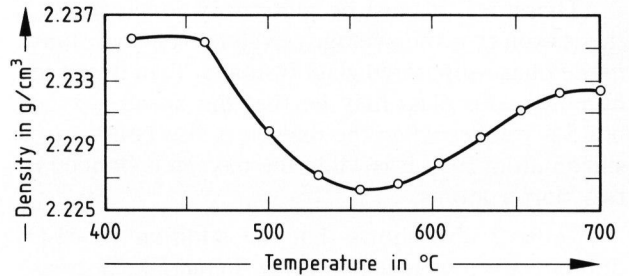
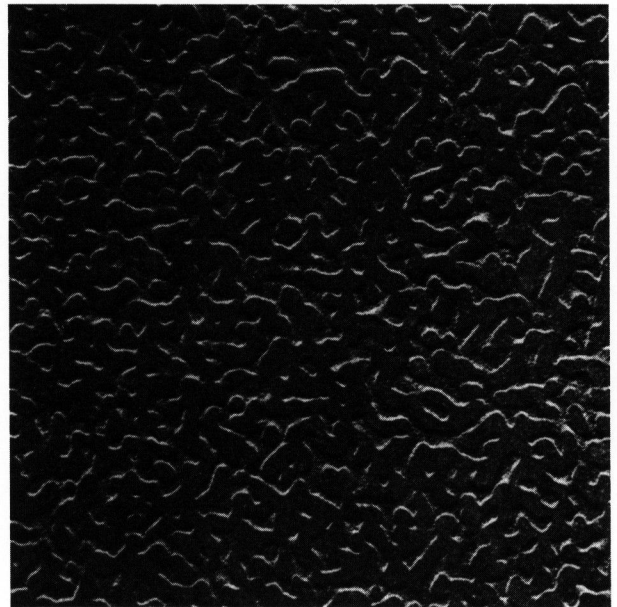


Figure 1. Room temperature density of alkali-borosilicate glass as a function of heat treatment temperature. Time at temperature = 3 h.



Figures 2a and b. Electron micrographs of alkali borosilicate glass. The silica-rich phase, which appears raised and smooth, has coarsened appreciably with temperature; a) after 3 h at 580°C , b) after 3 h at 650°C .

Table 2. Fraction of 4-coordinated boron in glass A and glass B before and after annealing

glass	N_4 content	glass history	composition in mol%			
			SiO_2	B_2O_3	Na_2O	Al_2O_3
A	0.36 ± 0.01	as-formed	70	23	7	—
	0.35 ± 0.01	annealed				
	0.31 ± 0.01	melt-quenched in water				
	0.31 ± 0.01	annealed				
B	0.04 ± 0.01	as-formed	65.9	21.7	6.6	5.8
	0.04 ± 0.01	annealed				

of boron atoms in 4-fold coordination in quenched glasses and as-formed glasses confirm this expectation. Furthermore, the changes in bonding required to increase the number of tetrahedrally coordinated boron atoms substantially are too slow to be observed in these experiments. Table 2 confirms that the fraction of tetrahedrally coordinated atoms is insensitive to annealing at 555 °C for both quenched and slow cooled glasses.

Therefore, it must be tentatively concluded that the reason that the average oxygen–oxygen distance in the phase-separated glass is smaller than it is in the homogeneous glass may be that the boron–oxygen bond is weaker when the oxygen is also bonded to a silicon atom than it is when the oxygen is bonded to two boron atoms.

Table 2 also shows that the addition of Al_2O_3 dramatically lowers the N_4 value. In fact, the decrease in N_4 is exactly that to be expected if all of the alumina is in tetrahedral coordination and only the alkali in excess of the alumina content is available for producing tetrahedral boron.

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4. References

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