

PAPERS

Densification of glass at very high pressure

H. M. Cohen* & R. Roy

*Materials Research Laboratory, The Pennsylvania State University,
University Park, Pennsylvania*

The pressure-temperature dependence of the densification of glasses subjected to pressure in a uniaxial pressure-transmitting device (20–200 kilobar range) at temperatures up to 600°C was studied.

The increase in the density of all glasses studied is a function of the pressure and temperature to which the glass is subjected. It appears that at each temperature and pressure there is an equilibrium (metastable) structure of the glass which is attained in a few minutes and then persists indefinitely at room temperature at atmospheric pressure. However, each glass composition studied attained a maximum density. The maximum density phase of most of the glasses studied showed a remarkable consistency at a value of 52% for the ratio 'volume of ions over molar volume'. Experiments with plastic balls showed that 'irregularly closest packed' tetrahedra can occupy only $55 \pm 2\%$ of a given volume, which is in interesting correspondence to the 52% figure found for the most dense glass phases.

A linear relationship between density and refractive index is obtained for most of the densified series. Infrared spectra show broadening of the stretching and bending mode bands.

It is concluded that the densification of glass is independent of the compressibility and involves a second-order structural change in the network of the glass. The data also suggest that the short-range order of the glasses studied decreases as the glass is progressively densified.

Certain glasses, when subjected to pressure, even at room temperature, undergo an increase in bulk density which persists at room temperature when the glass is removed from its high-pressure environment.^(1–6)

*Present address: Bell Telephone Laboratories, 555 Union Boulevard, Allentown, Pennsylvania 18103.

When thin discs of silicate glasses are subjected to pressure in a uniaxial pressure-transmitting device^(2a) densification at room temperature does not begin until the applied pressure exceeds a threshold value of 100 kilobars for SiO₂ glass and 40 kilobars for alkali silicate glasses. However, ground SiO₂ glass (40–80 μ particle size) can be densified at room temperature when subjected to pressure greater than 20 kilobars.⁽⁵⁾ Mackenzie^(6a) has pointed out the incongruity of results on densification of SiO₂ glass among different workers.^(2a, 5, 7) It had been suggested that this incongruity resulted from the varying degrees of shear inherent in the apparatus of different workers.^(7–12) Mackenzie^(6a) asserts that densification of SiO₂ glass at temperatures far below the glass transition region depends on the presence of shear, but Cohen & Roy⁽⁵⁾ maintain that shear affects only the rate of densification. Further, Cohen & Roy^(5a) maintain that there is a metastable equilibrium structure of the glass at each pressure and temperature, whereas Mackenzie^(6a) denies this. This paper will discuss further the role of shear in the densification of glass. Data will be presented which show that the existence of a pressure-temperature dependent metastable equilibrium structure of SiO₂ glass may not be ruled out.

Most crystalline materials which are exposed to high pressure and are elastically compressed appear to return to their original volume when the pressure is released. In some cases, however, a material will undergo a solid-solid phase transition, and if the activation energy for a reverse transformation is sufficient, the high-pressure form may be recovered under ambient conditions and will persist metastably. Glasses are formed from those materials which have very high activation energies for reconstructive changes between different structural arrangements. It is possible to

imagine that the elastic compression is not entirely released when samples are removed from a high-pressure environment. Alternatively, a continuous structural change, in response to the pressure-temperature environment, might take place, and these new structures persist metastably at room temperature and atmospheric pressure.

At present, the data on the pressure dependence of the densification of glass are limited to a few glass compositions. A systematic study was therefore undertaken to describe the influence of pressure and temperature, as independent variables, on the refractive index, density, molar refractivity, and certain other properties of SiO_2 and other selected glasses.

Experimental procedure

Preparation of glasses

The following glass compositions were studied: SiO_2 ; GeO_2 ; a series of $\text{R}_2\text{O} \cdot 0.1\text{MgO} \cdot 2.9\text{SiO}_2$ ($\text{R} = \text{Li}, \text{Na}, \text{K}$); a series $(2-X)\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$ where $X = 0.5, 1.0, 1.1, 1.2$ $\text{Li}_2\text{O} \cdot \text{SiO}_2$; NaPO_3 ; $\text{LiRb}(\text{PO}_3)_2$; and $\text{Li}_2\text{Rb}_2(\text{P}_2\text{O}_7)$. All compositions reported are batch compositions.

The SiO_2 glass was taken from tubes of commercial 'Satin Surface Vitreosil' obtained from the Thermal American Fused Quartz Company, Dover, New Jersey. GeO_2 glass was obtained by fusion at 1400°C in platinum of 'spectroscopic' grade GeO_2 . Preparation of the glasses in the series $\text{R}_2\text{O} \cdot 0.1\text{MgO} \cdot 2.9\text{SiO}_2$ is described by Ryder.⁽¹³⁾ Preparation of the glasses in the series $\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$ is described by Day.⁽¹⁴⁾ A glass of the composition $1.2\text{Li}_2\text{O} \cdot \text{SiO}_2$ was prepared by melting crystalline Li_2SiO_3 in sealed platinum capsules and quenching the capsules in water; comparison of the index of refraction of the glass (1.562) with the data of Kracek⁽¹⁵⁾ showed the composition to be $1.2\text{Li}_2\text{O} \cdot \text{SiO}_2$. Three phosphate glasses of composition NaPO_3 , $\text{LiRb}(\text{PO}_3)_2$, and $\text{Li}_2\text{Rb}_2(\text{P}_2\text{O}_7)$ were obtained from M. K. Murthy of the Ontario Research Foundation.

Sample preparation

The uniaxial pressure-transmitting device was basically of the Bridgman-Basset design. The modification used has been described in full detail by Dachille & Roy.⁽¹⁶⁾

The glass samples were ground (40–150 μ particle size) in a dry air atmosphere, 8–10 mg of sample were placed between two platinum 10% rhodium-foil discs (one mil thick) and pre-pelleted into a disc 8–10 mils thick. The pellets were either 3/16, 3/8, or 1/2 in dia. The resultant pellet, sandwiched between the foils, was placed between two anvils. The diameter of the anvil was always the same as the diameter of the sample pellet. Thrust was applied to the anvils by a hydraulic jack connected to an oil pump and pressure-controlling system. The anvils were surrounded by a split furnace

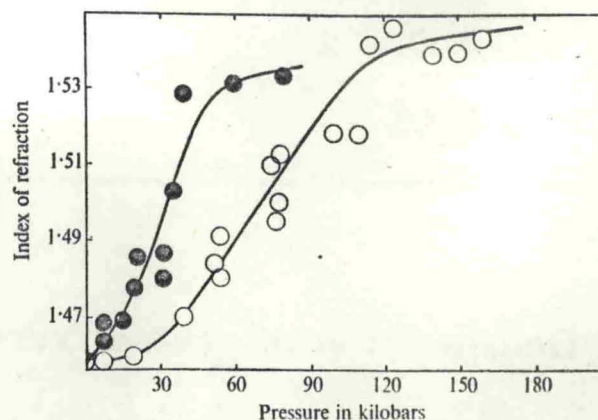


Figure 1. The densification of SiO_2 glass as a function of the pressure of the run

○ 25°C
● 600°C

and the temperature was regulated by a Minneapolis Honeywell 'pyrovane' temperature controller. The temperature was measured by a chromel-alumel thermocouple placed very close to the sample and shielded from the direct heat of the furnace by two steel cylinders. The diameter of the anvil was measured after a run was completed, and the pressure was calculated as the total thrust divided by the area of the anvil. The temperature control and accuracy was $\pm 5^\circ\text{C}$ and the load pressure was controlled within $\pm 5\%$ of the total pressure. The accuracy of the pressure measurement is discussed later.

The system was heated, and the pressure applied for a period ranging from 15 seconds to 30 days. The sample was quenched by directing an air blast at the anvils to give an approximate quench rate of $40\text{--}80^\circ\text{C}/\text{min}$. The pressure was released in less than one second after the temperature had cooled to 40°C or less.

Density and refractive index measurements

The refractive index was measured by the Becke line technique in white light. The index of the oils was corrected for thermal expansion to 25°C . The densities were measured by a sink-float technique.

Infra-red absorption spectra

Infra-red absorption spectra were measured from $2\text{--}25\ \mu$ with a Perkin-Elmer model 21 double-beam spectrophotometer using NaCl and KBr prisms. Between 0.6 and 1.0 mg of sample was ground with 300 mg of KBr and the mixture was pressed under vacuum into a pellet.

Presentation of results

Densification as a function of pressure and temperature

Densification as a function of pressure. The most direct parameter to measure the magnitude of densification