

H. M. COHEN AND R. ROY: DENSIFICATION OF GLASS AT VERY HIGH PRESSURE

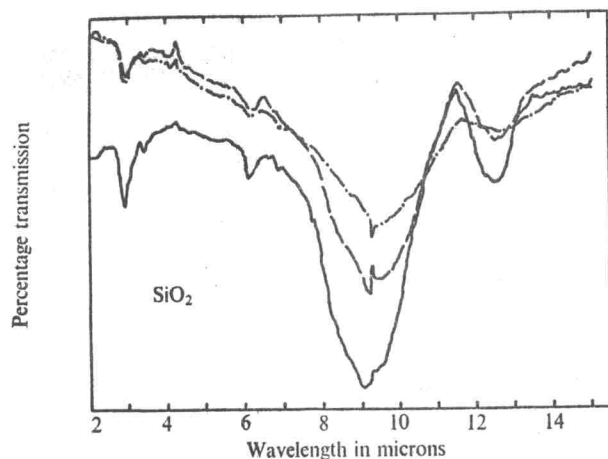


Figure 9. Infra-red absorption spectra in the 2-15 μ spectral region for progressively densified SiO_2 glass: 'd' represents the density in g/cm^3

Density (g/cm^3)	Absorption (microns)
2.20	9.10
2.53	9.32
2.60	9.50

band as the density increases. The positions of the absorption maxima are given in the legend to Figure 9. The absorption bands in the 12.5 and 21 μ region are significantly broadened as the glasses become denser, but there is no measurable spectral shift.

Figure 10 shows the absorption spectra in the 2-15 μ spectral region for glasses in the series $(2-X)\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$. It is seen that the absorption band in the 9 μ region is broadened as the glasses become more dense, but not as much as the absorption band in the corresponding spectral region for the SiO_2 glass. It also appears as if the relative intensity of the absorption decreases as the glasses become more dense. There is, however, no noticeable shift of the position of this band. There is no measurable shift of the 13 and 22 μ bands as the glass becomes more dense, but there is a very significant broadening and an apparent lowering of total absorption.

Discussion of results

An hypothesis concerning the densification of glass

Before the data which have been presented are discussed in detail, it is necessary to relate the nature of the data to what is believed to happen to the glass structure as pressure is applied to a sample and then released. In Figure 13 the density of silica glass at 25°C is given as a function of pressure. Curve AB represents the measured density of the glass, after the pressure has been released, plotted as a function of the pressure of the run. It is not the density at pressure.

Curve AC represents the calculated density of the glass under the applied pressure. This density was calculated using the compressibility data given by Birch *et al.*⁽¹⁸⁾ The glass is presumably elastically compressed along the line AC while pressure is being applied. However, in addition to this compression, the glass undergoes a continuous structural change in response to its pressure-temperature environment. This structural change involves the rearrangement of the tetrahedra to use up some of the void space. At a given pressure the structural change adjusts the density to a point corresponding to D. Upon release of pressure, however, the structural change in the reverse direction is extremely difficult; hence the glass does not return from D to A—instead the elastic compression which is stored in D is released and the density returns to position E. This is illustrated schematically by the curve DE. Finally, the density is plotted as a point on a graph at the pressure of the run corresponding to B. Figures 1-6, therefore, are generated by a sequence of points corresponding to B. Inherent in the above explanation is the hypothesis that densification is independent of the compressibility and involves a structural change in the network of the glass.

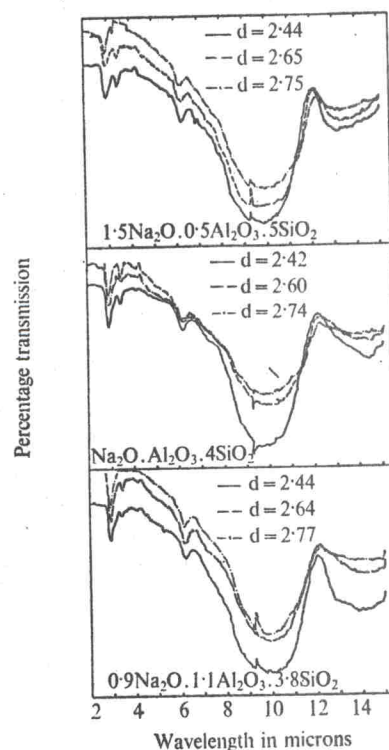


Figure 10. Infra-red absorption spectra in the 2-15 μ spectral region for progressively densified glasses in the series $(2-X)\text{Na}_2\text{O} \cdot X\text{Al}_2\text{O}_3 \cdot (6-2X)\text{SiO}_2$: 'd' represents the density in g/cm^3

The influence of temperature, pressure, and shear on densification

It has already been pointed out that Bridgman & Simon^(2a) could not record densification below 100 kilobars at room temperature for silica glass discs subjected to pressure in an uniaxial pressure device. However, the results portrayed in Figure 3 of this study show that densification of powdered silica glass (particle sizes ranging from 40 M to 80 μ) can be recorded at room temperature when the applied pressure is greater than 20 kilobars. Microscopic examination of the powdered specimens shows that the index of refraction can vary from grain to grain by as much as ± 0.006 of a unit. This variation in index of refraction has been attributed to differences in shear stresses present when the pressure is initially applied to the powdered specimen. As major differences of the extent of densification are recorded for bulk samples and powdered samples, shear must play *some* role in the densification process. This has previously been suggested by Bridgman,⁽⁸⁾ Weir *et al.*,⁽⁹⁾ Weir & Spinner,⁽¹⁰⁾ Mackenzie,^(6a) Mackenzie & Laforce,⁽¹¹⁾ and Aboaf.⁽¹²⁾ However, the results portrayed in Figure 6 and Table 2 show that above 500°C, far below the glass transition temperature of SiO₂ glass, the silica glass can be densified under purely hydrostatic pressure. It is therefore established that the role of shear in the densification of glass is no different from its usual role in increasing the rate of solid-state reactions.⁽¹⁹⁾

Thus, shear in one sense plays a role similar to temperature—it supplies an activation energy for the densification reaction. However, shear cannot be equated to an increase in temperature caused by significant 'local heating'. This has been borne out by Mackenzie.^(6a) The inhomogeneity of the index of

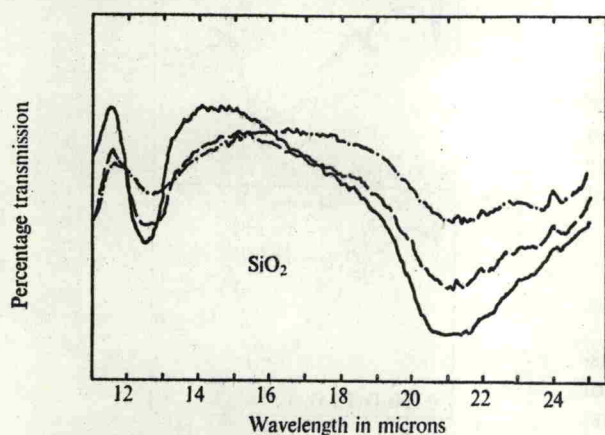


Figure 11. Infra-red absorption spectra in the 11–25 μ spectral region for progressively densified SiO₂ glass. 'd' represents the density in g/cm³

— d = 2.20
 - - - d = 2.53
 - · - · d = 2.60

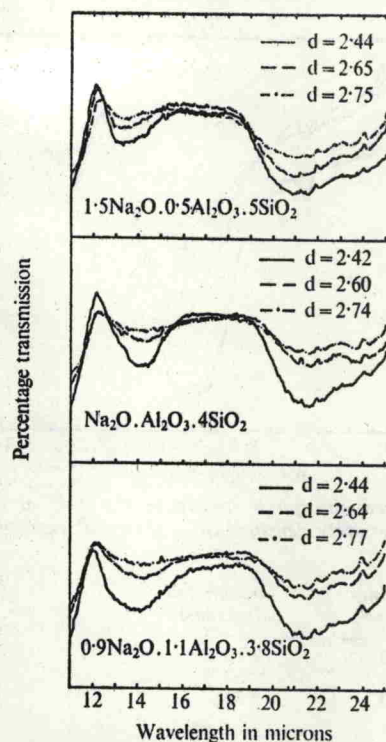


Figure 12. Infra-red absorption spectra in the 11–25 μ spectral region for progressively densified glasses in the series $(2-X)Na_2O \cdot XAl_2O_3 \cdot (6-2X)SiO_2$; 'd' represents the density in g/cm³

refraction of runs of SiO₂ glass along the 600°C curve in Figure 3 is just as great as the inhomogeneity of runs on the 25°C curve. This is an indication that the shear stresses at each temperature are of the same magnitude. However, the percentage densification at 600°C is significantly greater than at 25°C. These results suggest the following hypothesis. Shear forces as well as thermal energy serve to accelerate the densification reaction, but the main effect of temperature goes beyond that of a thermal activation agent. It appears that at each pressure and temperature there is a metastable equilibrium or pseudo-metastable equilibrium structure of the glass which is attained very rapidly and then persists. In other words, shear, at a given pressure, affects only the kinetics of densification; whereas temperature, at a given pressure, affects the kinetics of densification as well as the ultimate equilibrium or pseudo-equilibrium structure. Dachille & Roy⁽¹⁹⁾ have shown that, in crystal-crystal transformations, within their experimental limits, shear changes the kinetics of a structural transformation but not the equilibrium relations. They also showed that, using shear to overcome an activation energy barrier, the experimentally determined pressure-temperature equilibrium curves