

of glass would be the density. The precise measurement of the density of a small sample, however, is difficult and time-consuming, whereas the index of refraction is conveniently measured. Further, the measurement of refractive index allows one to observe small-scale sample inhomogeneity, whereas a bulk density measurement does not. Therefore, after the relationship between the density and index of refraction was determined for a given glass composition, the index of refraction was used as the parameter to measure the magnitude of densification.

Figure 1 shows the refractive index of silica glass plotted as function of the pressure to which the samples were exposed at 25 and 600°C respectively. It should be made quite clear that it is a refractive index of the glass after the entire quenching procedure and removal of the sample from the sample holder. It is not the refractive index at pressure. The variation of the refractive index of the product glass, if the sample is treated as a whole, can range up to ± 0.008 of a unit although the index of refraction of most of the material is within ± 0.005 of a unit. The birefringence of the powdered densified samples was less than 0.005.

Some of the densified silica glass specimens have been stored at room temperature for over two years, and they have not undergone any measurable decrease in their respective densities. No alteration to the density of the densified glass samples could be obtained by grinding in air or carbon tetrachloride. Thus, it is clear that normal processing in the examination procedure causes no change in the densified silica glass.

The absolute accuracy of high-pressure measurement is difficult to define because there is, at present, no satisfactory high-pressure scale. However, if a relative pressure scale for this work is defined by the linear portion of the curves shown in Figure 1, the precision of the pressure measurements reported in this paper is approximately ± 10 kilobars.

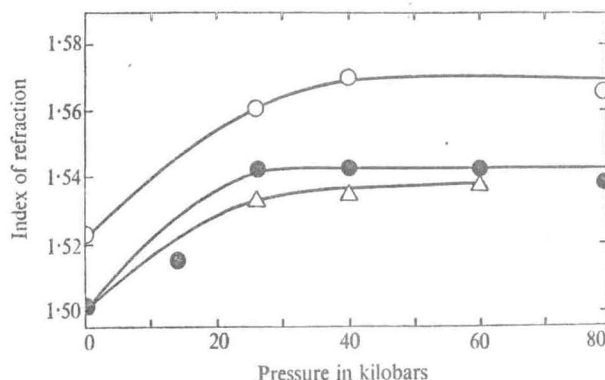


Figure 2. Densification at 500°C of glasses in the series $R_2O \cdot 0.1MgO \cdot 2.9SiO_2$ as a function of the pressure of the run

○ R = lithium
● R = sodium
△ R = potassium

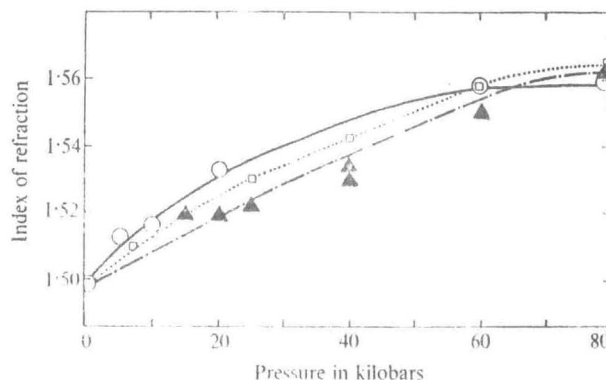


Figure 3. Densification of glasses in the series $(2-X)Na_2O \cdot XAl_2O_3 \cdot (6-2X)SiO_2$

○ X = 0.50; temperature 550°C
□ X = 1.0; temperature 585°C
▲ X = 1.1; temperature 595°C

Above approximately 120 kilobars at 25°C and 60 kilobars at 600°C, the density of the SiO_2 glass appears to approach a maximum value. Further, the maximum density appears to be the same at 600°C as at 25°C. As the densified glass samples approach the apparent maximum density, they become more homogeneous. The maximum spread of refractive index for these glasses in a given sample is ± 0.002 of a unit.

The densification of GeO_2 glass was discussed in a previous paper.⁽⁵⁾ The maximum density to which GeO_2 glass could be densified was 4.23 ± 0.02 g/cm³ (index of refraction 1.718 ± 0.002) compared to an initial density of 3.66 ± 0.02 g/cm³ (index of refraction 1.608 ± 0.002).

Figure 2 shows the refractive index of a series of alkali silicate glasses plotted as a function of the pressure to which the samples were exposed at 500°C. The variation of the refractive index of the respective samples was as high as ± 0.005 of a unit, but most of the material in a given run was within ± 0.003 of a unit. There was almost no noticeable birefringence of the densified glass samples. The glasses appeared to attain a maximum density at 500°C when the applied pressure exceeded approximately 40 kilobars. The same glasses were subjected to pressures up to 80 kilobars at 600°C, but it was not possible to densify them beyond the maximum values shown in Figure 2.

Glasses in the series $(2-X)Na_2O \cdot XAl_2O_3 \cdot (6-2X)SiO_2$ were investigated; X being 0.5, 1.0, and 1.1. In Figure 3 the refractive index of these glasses is plotted as a function of the pressure to which the samples were exposed. The behaviour of these glasses is very similar to the behaviour of the alkali silicate glasses. The variation of the refractive index of a given respective sample was ± 0.003 , and there was no noticeable birefringence of the densified glass. The glasses appeared to attain a maximum density at approximately

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

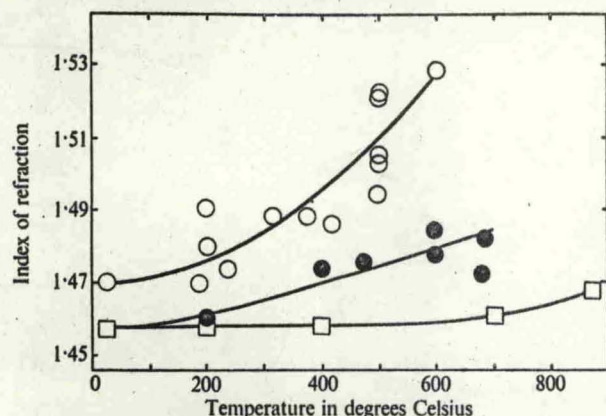


Figure 4. Densification of SiO_2 glass as a function of temperature

□ 4 kilobars hydrostatic
● 20 kilobars
○ 40 kilobars

550°C when the applied pressure exceeded approximately 70 kilobars. Samples were subjected to pressures greater than 100 kilobars at temperatures up to 600°C, but it was not possible to densify them beyond the maximum values shown in Figure 3.

Attempts to densify glasses of compositions NaPO_3 , $\text{LiRb}(\text{PO}_3)_2$, and $\text{Li}_2\text{Rb}_2(\text{P}_2\text{O}_7)$ at room temperature proved abortive, even when they were subjected to pressures higher than 100 kilobars. When heated under pressure to temperatures higher than 200°C, these glasses devitrified. By heating $\text{LiRb}(\text{PO}_3)_2$ and $\text{Li}_2\text{Rb}_2(\text{P}_2\text{O}_7)$ glass samples to 450°C as quickly as possible (15 min), applying 80 kilobars pressure for 15–30 s, and quenching, it was possible to obtain a sample which was about 50% glass and 50% crystal. However, the index of refraction of the glass had increased by only a few per cent. One sample of $\text{LiRb}(\text{PO}_3)_2$ glass was obtained by the above procedure which contained only a few per cent of crystals. The density of the resultant pellet was measured but is probably somewhat high because of the presence of admixed crystals. The densities and indices of refraction of the densified phosphate glasses are given in Table 1.

Table 1. Densification of some alkali phosphate glasses

Composition (Molar ratio)	Pressure (Kilobars)	Temperature (°C)	Index of refraction ± 0.003	Density ($\text{g/cm}^3 \pm 0.003$)	Remarks
NaPO_3	Atmospheric pressure	—	1.479	2.484	Sample devitrified
	80	450	—	—	
$\text{LiRb}(\text{PO}_3)_2$	Atmospheric pressure	—	1.494	2.769	Sample contained a few per cent crystals
	40	200	1.496	—	
	80	450	1.508	2.887	
$\text{Li}_2\text{Rb}_2(\text{P}_2\text{O}_7)$	Atmospheric pressure	—	1.513	2.990	
	100	25	1.513	—	
	40	450	1.524	—	
	60	450	1.524	—	

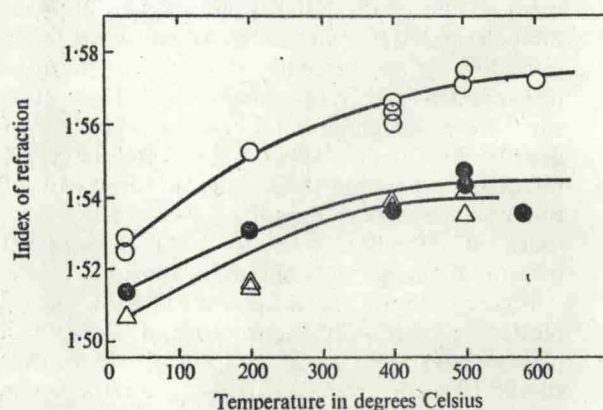


Figure 5. Densification at 40 kilobars as a function of the temperature of the run for glasses in the series $\text{R}_2\text{O} \cdot 0.1\text{MgO} \cdot 2.9\text{SiO}_2$

○ R = lithium
● R = sodium
△ R = potassium

Densification as a function of temperature. The change of refractive index of densified glass samples is plotted, at a given constant pressure, as a function of temperature in Figures 4 and 5. Figure 4 presents results for SiO_2 glass and Figure 5 presents results for glasses in the series $\text{R}_2\text{O} \cdot 0.1\text{MgO} \cdot 2.9\text{SiO}_2$, where R stands respectively for lithium, sodium, and potassium. It is clearly seen that thermal energy plays a very important role in the densification of glass.

Densification at low hydrostatic pressure

To determine if silica glass could be densified under purely hydrostatic pressure, several runs were made by sealing a few milligrams of powdered silica glass in gold capsules and subjecting these to a hydrostatic pressure-transmitting medium (argon gas) in an internally heated pressure vessel. Some of the results are plotted in Figure 6. The plot in Figure 6 is for approximately 700°C. The exact temperature of each run is shown adjacent to each point. No change in refractive index was observed for samples of silica glass subjected to similar pressures at 10°C. The samples which were densified by hydrostatic pressure appeared to be very uniform (within ± 0.002 index of refraction units).