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Densification of glass at very high pressure

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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 secondorder 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⁾

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

When thin discs of silicate glasses are subjected to pressure in a uniaxial pressure-transmitting device⁽²⁸⁾ 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

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imagine that the elastic compression is not entirely released when samples are removed from a highpressure 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 SiO₂ and other selected glasses.

Experimental procedure

Preparation of glasses

The following glass compositions were studied: SiO₂; GeO₂; a series of R₂O.0·1MgO.2·9SiO₂ (R=Li, Na, K); a series $(2-X)Na_2O.XAl_2O_3.(6-2X)SiO_2$ where X=0·5, 1·0, 1·1; 1·2 Li₂O. SiO₂; NaPO₃; LiRb(PO₃)₂; and Li₂Rb₂(P₂O₇). All compositions reported are batch compositions.

The SiO₂ glass was taken from tubes of commercial 'Satin Surface Vitreosil' obtained from the Thermal American Fused Quartz Company, Dover, New Jersey. GeO₂ glass was obtained by fusion at 1400°C in platinum of 'spectroscopic' grade GeO2. Preparation of the glasses in the series R2O.0.1MgO.2.9SiO2 is described by Ryder.(13) Preparation of the glasses in the series Na₂O.XAl₂O₃.(6-2X)SiO₂ is described by Day.⁽¹⁴⁾ A glass of the composition 1.2Li₂O. SiO₂ was prepared by melting crystalline Li2SiO3 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 1.2Li2O. SiO2. Three phosphate glasses of composition NaPO₃, LiRb(PO₃)₂, and Li₂Rb₂(P₂O₇) 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 $(40-150 \mu \text{ particle} \text{size})$ 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 SiO₂ glass as a function of the pressure of the run $\bigcirc 25^{\circ}C$

● 600°C

nAll

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 $\pm 5^{\circ}$ 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 $40-80^{\circ}$ C/ 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 $2-25 \mu$ 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

150 Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

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 is 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 gass 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 $500^{\circ}C$ of glasses in the series R_2O . $0.1MgO.2.9SiO_2$ as a function of the pressure of the run

 $\bigcirc R = \text{lithium} \\ \blacksquare R = \text{sodium}$

 \triangle R = potassium

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965



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

○ 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 SiO₂ glass appears to approach a maximum value. Further, the maximum density appears to be the same at 600 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 GeO₂ glass was discussed in a previous paper.⁽⁵⁾ The maximum density to which GeO₂ 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 $(2-X)Na_2O.XAl_2O_3.(6-2X)$ SiO₂ 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

151



Index of refraction



Temperature in degrees Celsius

20 kilobars

O 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 NaPO₃, LiRb(PO₃)₂, and L₂iRb₂(P₂O₇) 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 LiRb(PO3)2 and Li₂Rb₂(P₂O₇) 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 LiRb (PO₃)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.



Figure 5. Densification at 40 kilobars as a function of the temperature of the run for glasses in the series $R_2O.0.1MgO.2.9SiO_2$

- \bigcirc R = lithium
- R = sodium

 \triangle 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 SiO₂ glass and Figure 5 presents results for glasses in the series $R_2O.0.1MgO.2.9SiO_2$, 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).

Table	1.	Densif	ication	of	some al	kal	i pho	spł	nate ;	glasses

Composition (Molar ratio)	Pressure (Kilobars)	Temperature (°C)	Index of refraction ± 0.003	Density (g/cm³ ±0.003)	,s Remarks
NaPOs	Atmospheric pressure		1.479	2.484	and the second second second
	80	450	-	-	Sample devitrified
LiRb(PO ₃)s	Atmospheric pressure	200	1·494 1·496	2.769	
	80	450	1.508	2.887	Sample contained a few per cent crystals
LisRbs(PsO7)	Atmospheric pressure 100	25	1·513 1·513	2.990	
	40	450	1.524		

152 Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

An exact comparison of results from samples subjected to hydrostatic pressure with results from samples subjected to pressure in the uniaxial pressure transmitting device is not possible since densification of SiO₂ glass cannot be recorded below 20 kilobars in the uniaxial pressure-transmitting device. However, one point obtained from a sample of silica glass subjected to 20 kilobars pressure in the uniaxial pressure-transmitting device. However, one point obtained from a sample of silica glass subjected to 20 kilobars pressure in the uniaxial pressure-transmitting device at $\sim 700^{\circ}$ C is shown in Figure 6. The curve for the data obtained from runs subjected to hydrostatic pressure has been extrapolated to 20 kilobars and seems to be in the same region as the 20 kilobar point from the sample subjected to pressure in the uniaxial pressure-transmitting device.

Additional results from runs of silica glass samples which were subjected to hydrostatic pressure are tabulated in Table 2. These results establish beyond doubt that silica glass can be substantially densified when subjected to hydrostatic pressure at temperatures greater than approximately 500°C.

One further experiment was made to see if a large sample of glass could be densified. A glass sample $(0.12 \times 0.25 \times 0.60$ in) of approximate window glass composition was wrapped in gold foil and subjected to nine kilobars hydrostatic pressure at 600°C for 18 hours. The index of refraction and density were measured in the laboratories of Bausch & Lomb, Incorporated, Rochester, New York. The initial index of refraction at the sodium D line and density were respectively 1.51721 and 2.5280 g/cm³, whereas these values for the densified sample were respectively 1.52981 and 2.5925 g/cm³.



Figure 6. The densification of SiO₂ glass which has been subjected to hydrostatic pressure

O Hydrostatic pressure-vessel

Uniaxial pressure-transmitting device

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

 Table 2. Results from SiO₂ glass samples densified under hydrostatic pressure

Pressure (Kilobars)	Temperature (°C)	Index of refraction* of sample after removal from the pressure vessel		
4.0	300	1.458		
4.0	400	1.458		
3.9	690	1.461		
4.9	876	1.469		
6.8	612	1.462		
6.7	847 .	1.470		
7.2	600	1.464		
7.3	10	1.459		
7.3	675	1.467		
7.4	675	1.466		
7.9	600	1.469 *		
9.3	720	1.472		

*The index of refraction was measured at the sodium D line. The values are accurate within ± 0.002 of a unit.

Kinetics of densification

At a given temperature and pressure the densification proceeds very rapidly and the glasses attain a density which is apparently characteristic of the pressuretemperature conditions to which they are exposed. For silica glass this 'characteristic' density is attained in less than one minute. This was shown by a series of runs from 15 seconds to several days. Typical results are tabulated in Table 3. The initial refractive index of silica glass is 1.458.

The sample was first heated to the temperature indicated in Table 3, the pressure applied, the sample quenched, and the pressure released. The 'Duration of the run' refers to the time which elapsed between the application of the pressure and the quench.

The alkali silicate glasses which were studied also densified rapidly, although not quite as rapidly as silica glass. The rate of densification of Na₂O.0·1MgO. 2·9SiO₂ glass is shown in Figure 7. The index of refraction for glasses of this composition which were subjected to 26 kilobars pressure at 300 and 500°C is plotted as a function of the time of the run. It is seen that the rate of densification is more rapid at 500 than 300° C.

Reversibility of densification

In order to prove that there is a metastable equilibrium structural state for glass which is a function of the

Table 3. Rate of densification of silica glass

Pressure (Kilobars)	Temperature (°C)	Duration of run	Refractive index after pressure is released
40	25	15 seconds	1·470 ±0·005
40	25	22 hours	1.470 ± 0.006
40	25	5 days	1.470 ± 0.005
30	600	15 seconds	1.475 ± 0.005
30	600	2 minutes	1.480 ± 0.006
30	600	6 minutes	1.480 ± 0.005
30	600	50 minutes	1·482 ±0·005

153



Figure 7. The rate of densification of Na₂O.0.1MgO.2.9SiO₂ glass

pressure-temperature environment to which the glass is exposed, it would be necessary to show that the curves in Figures 1-6 could be approached by samples whose initial densities, before application of pressure, were higher and lower than the assumed equilibrium density. However, the densified SiO2 glass samples were extremely 'stable', and it was not possible to decrease the density of densified SiO2 glass by subjecting it to pressures below which the glass was originally densified. This is, of course, analogous to the difficulty of causing a dense crystalline phase to revert to a less dense one at low temperature. Two samples of silica glass which had an index of refraction of 1.52 were subjected respectively to 20 and 30 kilobars pressure at 600°C for 12 hours; however, there was no perceptible change in the indices of refraction for these samples.

Densified samples of Na₂O.Al₂O₃.4SiO₂ glass could, however, be caused to revert to a lower density under pressure. Samples whose initial refractive indices were 1.500 ± 0.002 were subjected to 80 kilobars pressure at 600°C to increase their indices of refraction to 1.565 ± 0.002 . These samples were then subjected respectively to 20 and 40 kilobars pressure at 600°C, their indices of refraction decreased respectively to 1.527 ± 0.002 and 1.542 ± 0.002 . From Figure 3 it is seen that samples whose initial indices of refraction are 1.500 ± 0.002 will increase their indices of refraction to 1.522 ± 0.003 and 1.542 ± 0.003 when subjected respectively to 20 and 40 kilobars pressure at 585°C.

Physical properties of densified glasses: the relationship between the refractive index and density of progressively densified glasses

The relationship between the index of refraction and density of some progressively densified glasses in the system Na₂O. Al₂O₃. SiO₂ is shown in Figure 8. The relationship for SiO₂ glass and glasses in the series $R_2O.0.1MgO.2.9SiO_2$ has already been reported, and

154 Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

is linear within the experimental error.⁽¹⁷⁾ The relationship was determined by measuring the density of a cube of approximately one millimetre of the respective specimens and then measuring the refractive index of the same piece. The value of the refractive indices represents an 'average' value approximately centred around a spread of ± 0.005 of a unit for SiO₂ glass and ± 0.003 of a unit for the alkali silicate and sodium aluminosilicate glasses respectively. It is noted that the densified alkali silicate and sodium aluminosilicate glass samples were more homogeneous than the densified SiO₂ glass samples. The spread of the index of refraction in the respective glasses would reflect a spread in the density of approximately ± 0.02 g/cm³. Thus, the measured density of each specimen is actually an 'average' density.

Infra-red absorption spectra

Infra-red absorption spectra in the region from $2-25 \mu$ were obtained for progressively densified SiO₂ glass and glasses in the series $(2-X)Na_2O.XAl_2O_3(6-2X)$ SiO₂. The spectra from 2-15 μ are shown in Figures 9 and 10, and the spectra from 11-25 μ are shown in Figures 11 and 12.

Two significant changes occur in the SiO₂ absorption band in the 9 μ region and are shown in Figure 9. Firstly, the position of the maximum absorption shifts to higher wavelengths as the density increases; secondly, there is a very marked broadening of the



Figure 8. The relationship between the density and index of refraction of glasses in the series $(2-X)Na_2O \cdot XAl_2O_3 \cdot (6-2X)SiO_2$

0	х	-	0.2
Δ	х	-	1.0
n	x	-	1.1



Figure 9. Infra-red absorption spectra in the 2–15 μ spectral region for progressively densified SiO₂ glass: 'd' represents the density in g/cm³

	Density (g/cm ³)	Absorption (microns)
	2.20	9.10
<u>+</u>	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)Na₂O. XAl₂O₃. (6–2X)SiO₂. 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 SiO₂ 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.

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

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 Ainstead 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 $(2-X)Na_2O \cdot XAl_2O_3 \cdot (6-2X)SiO_2$: 'd' represents the density in g/cm³

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 $11-25 \mu$ spectral region for progressively densified SiO₂ glass. 'd' represents the density in g/cm³

 d = 2.20
 d = 2.53
 d = 2.60

156 Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965



Figure 12. Infra-red absorption spectra in the $11-25 \mu$ spectral region for progressively densified glasses in the series $(2-X)Na_2O.XAl_2O_3.$ $(6-2X)SiO_2:$ '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

for many solid-solid phase transitions could be extended to much lower temperatures than would be possible if no shear stresses were present. Since densification is a structural change, the results of this study are in concordance with these conclusions.

Inherent in the above explanation is the question of whether there is a true metastable equilibrium structure for the glass at any given temperature and pressure. The most important criterion of equilibrium is reversibility. In order to prove that there is indeed a metastable equilibrium volume for glass which is a function of pressure, it must be shown that the purported metastable equilibrium density can be approached by glasses whose densities are respectively greater and less than the purported equilibrium density. This reversibility was demonstrated for the Na2O. Al2O3.4SiO2 glass but not for SiO2 glass. Apparently the activation energy necessary to cause densified samples of SiO2 glass to revert to a less dense phase is greater than the thermal energy available at 600°C.

The work of Douglas & Jones⁽²⁰⁾ and Douglas & Isard⁽²¹⁾ strongly supported the view that at a given temperature at atmospheric pressure a glass structure does approach a true metastable equilibrium and the data from the present study (Figures 1–6) firmly suggest that this conclusion can be extended to include the pressure variable.

Structural aspects of densification

Figure 8 and the data of Cohen & Roy⁽¹⁷⁾ show that the relationship between the index of refraction and the density of progressively densified silica glass, alkali silicate glasses, and the sodium aluminosilicate glasses which were studied is virtually linear. The molar refraction for the densified phases was calculated, and as expected from the linear relationship between the index of refraction and density, the molar refraction remains almost constant. Dachille & Roy⁽²²⁾ have



Figure 13. The relationship between the densification and compressibility of glass (Previously published⁽⁵⁾)

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

shown that a change in the primary co-ordination number of the silicon ions would require a change of 10-15% in the molar refractivity, whereas the largest change observed was 3.5% for silica glass and less for the other glasses. It is interesting to note that the molar refractivities of the normal silica glass (density, 2.203 g/cm³) and the most dense silica glass (2.624g/cm³) are equal to the respective molar refractivities of cristobalite and α -quartz. This calculation indicates that densification involves a change in the packing of tetrahedra rather than a major structural rearrangement of the first co-ordination sphere of the ions.

A significant feature of the data on the densification of glass is that each glass composition which was studied apparently attained a maximum density. Attempts to densify a glass beyond this maximum density by increasing the temperature and pressure either proved abortive or resulted in the devitrification of the glass. This maximum density strongly suggested a special structural significance. The maximum density phase for silica glass was attained near the pressure and temperature limits of the apparatus; however, the maximum density phases for all other glasses were attained well below this limit. The silica glass, which is difficult to devitrify when 'dry' (preheated to 800° C for half an hour and desiccated prior to being subjected to pressure), would invariably begin to devitrify at 650° C (within two to three minutes) at pressures which cause the glass to attain its apparent maximum density; it appears therefore that the attainment of a maximum density for the silica glass is structurally significant.

Lacy⁽²³⁾ pointed out some interesting relationships in the atomic packing in silicate glasses. On the assumption that the region of influence of each ion is spherical and by using values of the ionic radii found in crystalline substances, he was able to calculate approximately the fraction of the molar volume which the ions in a glass occupied. It was shown that 43% of the total space in silica glass is occupied, which is considerably less than that theoretically possible for spheres of uniform size (74%). It was also pointed out that the closest overall packing that has been found is 52% for lithium metasilicate glass.

The fraction of the molar volume which the ions occupy in the progressively densified glasses studied was calculated using Goldschmidt's values of ionic radii and the measured densities of the densified glasses. The results of the calculations for silica glass, the alkali silicate glasses, and the sodium aluminosilicate glasses studied are shown in Figures 14 and 15. In Table 4 the per cent molar volume occupied by the ions in a given glass before it was subjected to pressure is compared to the value for the most dense glass which can be produced. It is seen from Figures 14 and 15 that the value of per cent molar volume occupied by the ions tends toward an asymptotic maximum as the



Percentage molar volume occupied by ions

Figure 14. The pressure dependence of the per cent molar volume occupied by the ions for SiO_2 glass and glasses in the series $(2-X)Na_2O.XAl_2O_3.(6-2X)SiO_2$

glasses are progressively densified. It is also seen from Table 4 that the value for the most dense glasses is approximately 52% in most cases, irrespective of the value for the starting glasses. The notable exception is the potassium silicate glass. There is an interesting coincidence between this maximum figure of 52% with the figure of 52% for lithium metasilicate glass quoted by Lacy⁽¹⁹⁾ as the highest packing found in any glass investigated. Indeed, attempts to densify a lithium metasilicate glass were unsuccessful.

As the density of silica may be increased by 20%, it is somewhat surprising to realise that the most dense phase of silica glass has a very open structure; in fact, it is just as spacious as α -quartz, for its density is nearly the same. Why, then, is it not possible to produce a denser glass phase? Before attempting to answer this, it is necessary to review some experiments and proposals made by Bernal.⁽²⁴⁾

Bernal proposed a theory of the structure of simple monoatomic liquids based on a geometrical approach. He has recently given a more complete discourse on his theory,* but the substance of this has not been published. The portion of Professor Bernal's discourse which is of most interest to this paper is his description of an experiment he made to determine how closely similar sized spheres could be irregularly packed. This was determined by filling a container with steel balls and shaking the container until the balls no longer rattled, i.e. had achieved the closest possible irregular packing. The volume which the balls occupied could be measured; hence the packing density could be calculated. The balls could occupy approximately 68% of the total volume compared to 74% for cubic closest packing of the same size spheres.



Figure 15. The pressure dependence at 500 ° C of the per cent molar volume occupied by the ions for glasses in the series $R_2O.0.1MgO.$ 2.9SiO₂(R=Li, Na, K)

The fact that irregularly closest packed balls of the same size can fill up 68% of the available volume shows that the structure of even the most dense silica glass does not correspond to an irregular closest packed oxygen network.

It is now possible to return to the question: Why is it not possible to produce denser glass phases than found in this study? If the answer is related to a geometrical limitation of the packing of ions in the glass, the structure of the maximum density phases must consist, to a first approximation, of irregularly oriented close packed or closest packed structural units. The obvious structural unit to consider in silicate glasses is the SiO4 tetrahedron. The Si-O bond is several times stronger than the alkali- or alkaline earth-oxygen bonds, and it is not unreasonable to suggest that the Si-O tetrahedra will remain inviolate. To test this idea an experiment along similar lines to the experiment of Professor Bernal was performed. A large number of 1-in dia. plastic balls (6000) were glued together to form 1500 individual tetrahedra. The tetrahedra were placed in

Table 4. The per cent molar volume occupied by the ions

Composition	% Volume occupied before densification	% Volume occupied for maximum density phase		
SiO ₂	44	52		
GeO2	42 .	49		
Li2O.0.1MgO.2.9SiO2	47	52		
Na2O.0.1MgO.2.9SiO2	44	50		
K20.0.1MgO.2.9SiO2	41	46		
·5Na2O.0.5Al2O2.5SiO2	46	52		
Na ₂ O. Al ₂ O ₈ .4SiO ₂	46	52		
0.9Na20.1.1Al202.3.8SiO2	46	52		
·2Li2O.SiO2	52	52		
LiRb(PO ₃) ₂	50	50		
LizRb2(P2O7)	50	50		
NaPOs	51	51		

^{*}Symposium on Crystal Synthesis and Structure in Solid State Research, State College, Pennsylvania, 27–28 April 1962.

¹⁵⁸ Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

containers of various sizes and shapes. For a given experiment the container was tapped sharply with a rubber mallet until there was no audible rattling of the tetrahedra. The important result was that it was possible to fill only $55\pm 2\%$ of the space with the tetrahedra. There is an interesting correspondence between this figure and the maximum values of the per cent molar volume occupied by the ions which are listed in Table 4.

The plastic ball model of irregularly closest packed tetrahedra cannot necessarily be interpreted as the model of densified silica glass. The model, at first sight, appears to correspond to an orthosilicate (individual tetrahedra) rather than a tektosilicate (three-dimensional network). Further reflection and examination of the model reveals that, in fact, the irregular or 'heap packing' of tetrahedra creates a large percentage of octahedral sites. Further, tetrahedra share corners, edges, or faces plus a lower proportion of other 'coordinations'. Thus the resultant model is not at all 'orthosilicate' in character.

The important conclusion which can be drawn from the model is that there is a geometric limit to the amount of space which irregularly close packed structural units can occupy. This also supports the hypothesis that the densification of glass involves a second order or continuous structural change. This structural change is brought about by a rearrangement of structural units which constitute the glass structure. The size and type of structural unit or units which constitute a given glass would depend on the size, charge, and polarisability of the ions in the glass. The maximum density to which a glass may be densified is achieved when the strongest structural units have achieved an irregular closest packing. Further, the densification of glass is possible only because of the absence of long range order in the glass structure.

The concept that glasses contain structural units is, of course, not new. Huggins⁽²⁵⁾ has been able to explain some of the volume relations in sodium silicate glasses by postulating the existence of different types of 'structons' or structural units. Tilton⁽²⁶⁾ proposed a plausible model for silica glass by assuming the glass was made up of cages of pentagonal dodecahedra connected by an intermediate mesh. The silicon ions occupied the vertices of the pentagonal dodecahedra and the oxygen ions occupied the edges. He termed these cages 'vitrons'. These works serve as examples to illustrate the growing support for the concept that although there is a decided absence of long-range order in most glasses, there is an extent of short-range order. Thus, the hypothesis of densification of glass which assumes the existence of definite structural units is tenable.

In this study the basic unit proposed is the SiO_4 tetrahedron. In Table 4 it is seen that the most dense

Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

potassium silicate glass has a more open structure than any of the maximum density phases of the other glasses studied. As the potassium ion is too large for octahedral sites and has a relatively low polarising power, the type of structural units which might be present would be relatively open.

Changes in the infra-red absorption spectra for SiO₂ glass and some sodium aluminosilicate glasses

The assignment of absorption bands of silica glass has been discussed recently by Lippincott *et al.*,⁽²⁷⁾ and a review of the literature on the infra-red absorption of glasses in the system Na₂O-Al₂O₃-SiO₂ was given by Day.⁽¹⁴⁾ The spectrum of silica glass is characterised by strong bands at 9.05, 12.4, and 21.4 μ and may be assigned as the Si-O stretching, Si stretching, and Si-O-Si bending characteristic group frequencies. As Al³⁺ is substituted for Si⁴⁺ the spectral absorption at 9 μ shifts to longer wavelengths.

The infra-red reflection spectra of silica glass densified approximately 2% by neutron irradiation and pressure respectively have been examined by Simon⁽²⁸⁾ and Mackenzie.(6a) They observed an approximate shift of 0.2μ of the main Si–O stretching band in the 9 μ spectral region to higher wavelengths for progressively densified silica glass. This is in agreement with the results of this study. Simon(28) attributed this shift to a decrease in the Si-O-Si bond angle. However, if Lippincott et al.,⁽²⁷⁾ are correct in their assignments, such a change should appear in the Si-O-Si band, not in the main Si-O band. The shift could also be attributed to a small increase in the mean Si-O bond length reflecting a possible increase in the average coordination of some of the silicon ions. In this paper no further significance will be attributed to this shift. However, neither Simon⁽²⁸⁾ nor Mackenzie^(6a) reported any change in the shape of the reflection bands. It is seen from the absorption spectra of progressively densified silica glasses shown in Figures 10 and 12 that there is a very significant broadening and weakening of all the major absorption bands, but only the 9 μ band shows any measurable shift. A quantitative interpertation of this effect is not possible, but the broadening of the 12.5 μ band can be interpreted qualitatively as an increase in the distribution of bond angles possible due to a more 'random packing' of tetrahedral units. In other words, as the silica glass is progressively densified there may be a decrease in the extent of the short-range order.

The absorption spectra for progressively densified $1.5Na_2O.0.5Al_2O_3.5SiO_2$, $Na_2O.Al_2O_3.4SiO_2$, and $0.9Na_2O.1.1AlO_3.3-8SiO_2$ glasses which are shown in Figures 11 and 13 also display a broadening of bands but no obvious shift in spectral position. The absorption band at 9-10 μ apparently decreases in intensity.

This anomalous decrease in intensity could be attributed to a change in co-ordination of a fraction of the aluminium or silicon ions. If this is true, a new absorption band should appear.⁽²²⁾ However, if any of the aluminium or silicon ions do increase their co-ordination number, the new co-ordination number would probably be averaged over a distribution. Any new infra-red activated absorption would be spread over a wide spectral region and positive detection would be difficult.

It was previously suggested that densification involved a second order structural change with no concomitant major change in the co-ordination of the network-forming ions. The anomalous decrease in intensity of the 9–10 μ band of the sodium aluminosilicate glasses and the shift of the 9 μ band of SiO₂ glass to higher wavelengths are, at best, marginal evidence in favour of a possible co-ordination change of a fraction of the network-forming ions. Thus, the above hypothesis must stand, but the possibility that a finite fraction of the network-forming ions increase their average co-ordination as the glass is densified cannot be discarded.

The very marked broadening of the absorption bands in the 14 and 22 μ regions for the densified sodium aluminosilicate glasses is, as in the case of silica glass, attributed to substantial changes in the Si-O-Si, Si-O-Al or Al-O-Al bond angles, affecting the stretching mode (14 μ) and the bending mode (22 μ).

Summary and conclusions

Summary

It has been shown that glasses can undergo continuous and substantial changes in density with the application of ultra-high pressures in the range 20-200 kilobars, even when these pressures are applied for a very short time and at room temperature. Increases in density of approximately 10-20% have been realised in simple glasses such as GeO₂ and SiO₂.

The temperature dependence of the densification of glass under pressure was also studied since this proved to be a most important variable.

Densification of the following glass compositions was studied: SiO₂; GeO₂; a series R₂O.0·1MgO.2·9 SiO₂ (R=Li, Na, K); a series (2-X)Na₂O.XAl₂O₃. (6-2X)SiO₂(X=0·5, 1·0, 1·1); 1.2Li₂O.SiO₂; NaPO₃; LiRb(PO₃)₂; and Li₂Rb₂(P₂O₇).

The relationship between the refractive index and density was determined for progressively densified SiO₂ glass, glasses in the series $R_2O.0.1MgO.2.9SiO_2$ (R=L, Na, K), and glasses in the series (2-X(Na₂O. XAl₂O₃ (6-2X)SiO₂. The relationship for each glass, within experimental error, is linear. The slope of the curves, i.e. ratio of the change in index of refraction to

160 Physics and Chemistry of Glasses Vol. 6 No. 5 October 1965

the change in density (g/cm³), for each glass is approximately five. The molar refractivity of the densified glasses was calculated from the density and index of refraction data. The maximum change in the molar refraction was 3.5% for SiO₂ glass which was densified (fractional increase in density) by 20%. The change in the molar refractivity of the other glasses studied is less than 3.5%. According to the criteria of Dachille & Roy,⁽²²⁾ a change of primary co-ordination (say, 9–6) involves a change of 10–15% in the molar refraction. Thus, densification of the above glasses does not involve a major structural rearrangement of the ions.

The per cent increase in the density of all glasses studied is a function of the pressure and temperature to which the glass is subjected. For glasses in the series $(2-X)Na_2O.XAl_2O_3(6-2X)SiO_2$ it appears that at each pressure and temperature there is a metastable equilibrium structure of the glass which is attained within a few minutes and then persists.

The effect of hydrostatic pressures up to 10 kilobars on silica glass was studied by sealing silica glass into gold capsules and placing the capsules in an internally heated pressure vessel utilising argon gas as a pressuretransmitting medium. It was possible to densify the silica glass at pressures greater than four kilobars and temperatures greater than 500° C. The results from runs subjected to hydrostatic pressure are consistent with the results from runs subjected to pressure in the uniaxial pressure-transmitting device.

Each glass composition which was studied attained a maximum density. Silica glass attained a maximum density at pressures greater than 120 kilobars at 25° C and 60 kilobars at 600° C. The alkali silicate glasses studied attained a maximum density at 500° C when the applied pressure exceeded 40 kilobars, and the sodium aluminosilicate glasses studied attained a maximum density at approximately 550° C when the applied pressure exceeded 70 kilobars. Alkali phosphate glasses; NaPO₃, LiRb(PO₃)₂, and Li₂Rb₂(P₂O₇) could be densified by only a few per cent, and $1\cdot 2Li_2O$. SiO₂ glass could not be densified.

The maximum density phase of most of the glass compositions studied shows a remarkable consistency, at a value of 0.52, for the ratio 'volume of ions over molar volume'. Notable exception to this is the glass $K_2O.0.1MgO.2.9SiO_2$, for which the ratio for the maximum density phase is 0.46. Thus, even the most dense glass phases which could be produced have relatively 'open' structures.

It was experimentally determined that tetrahedra, constructed by gluing plastic balls together, can occupy only 55 $\pm 2\%$ of the container when irregularly closest packed. This clearly illustrates that there is a geometric limit to the amount of space which irregularly close packed structural units can occupy. The correspondence of the figure 55 $\pm 2\%$ (plastic ball experiment)

with the 52% figure for the maximum molar volume which the ions in a glass could occupy led to the hypothesis that the densification of glass is achieved by a rearrangement of structural units which constitute the glass. The existence of structural units can be postulated on the basis of the experimental results; however, the data do not permit the delineation of specific types of structural units which might exist in a particular glass, but suggest that they may be as small as the SiO₄ tetrahedra.

The infra-red absorption patterns of progressively densified SiO₂ glass and (2-X)Na₂O.XAl₂O₃.(6-2X) SiO₂ glasses were recorded. The major changes in the spectra are:

- 1. SiO₂ glass. The 9 μ Si–O stretching frequency shifts to higher wavelengths. A shift of approximately 0.4μ is observed for a glass whose density increased from 2.20 to 2.60 g/cm3. The major absorption bands at 9, 12, and 21 μ are noticeably broadened and weakened.
- 2. (2-X)Na₂O. XAl₂O₃. (6-2X)SiO₂. The absorption band in the 9 μ spectral region apparently decreases in intensity, but no new absorption bands are noticed. The absorption bands in the 13 and 22 μ regions are noticeably broadened, almost disappearing in the most dense phases.

The broadening of the spectral absorption bands of silica glass and the sodium aluminosilicate glasses can be attributed to an increase in the distribution of bond angles and possibly to a more random arrangement of tetrahedral units. In other words, as these glasses are progressively densified there may be a decrease in the extent of short-range order. The anomalous decrease in the intensity of the 9 μ absorption band is considered weak but admissible evidence in favour of an increase in average co-ordination of a finite fraction of the network-forming ions.

Conclusions

The data suggest that at each pressure and temperature there is a metastable equilibrium structure of the glass, and that the short-range order of the glasses studied decreases as the glass is progressively densified.

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. This structural change is brought about by a rearrangement of small structural units which constitute the

glass structure rather than a major structural rearrangement of the first co-ordination sphere of the ions. The size and type of structural unit, or units which constitute a given glass depends on the size, charge, and polarisability of the ions in the glass. The maximum density to which a glass can be densified is achieved when the structural units are irregularly closest packed.

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