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 $55\pm2\%$ 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 'co-ordinations'. 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 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 SiO_2 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 $Na_2O–Al_2O_3–SiO_2$ 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 Al^{3+} is substituted for Si^{4+} 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 0·2 μ 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 co-ordination 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 SiO_2 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 GeO_2 and SiO_2.

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: SiO_2; GeO_2; a series $R_2O.0.1MgO.2.9$ SiO_2 (R=Li, Na, K); a series $(2-X)Na_2O.XAl_2O_3.$ $(6-2X)SiO_2(X=0.5, 1.0, 1.1)$; $1.2Li_2O.SiO_2$; $NaPO_3$; $LiRb(PO_3)_2$; and $Li_2Rb_2(P_2O_7)$.

The relationship between the refractive index and density was determined for progressively densified SiO_2 glass, glasses in the series $R_2O.0.1MgO.2.9SiO_2$ (R=L, Na, K), and glasses in the series $(2-X(Na_2O.$ XAl_2O_3 $(6-2X)SiO_2$. 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 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 SiO_2 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 pressure-transmitting 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; $NaPO_3$, $LiRb(PO_3)_2$, and $Li_2Rb_2(P_2O_7)$ could be densified by only a few per cent, and $1.2Li_2O.$ SiO_2 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 $\pm2\%$ 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 $\pm2\%$ (plastic ball experiment)