

EFFECTS OF HIGH PRESSURE ON GLASS*

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Glasses provide a whole family of materials which can undergo continuous and substantial changes in properties with the application of ultra-high pressures in the range 20–200 kb, 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 germania and silica. For most glasses, the total permanent compaction reaches a maximum value independent of the actual temperature and pressure conditions. Below this maximum value the compaction is a function of both temperature and pressure. Qualitative calculations show remarkable consistency at a value of ~ 0.51 for the term 'volume of ions over molar volume' when various glasses are compressed to their maximum density. Molar refractivity calculations show that the compaction is realised at the expense of the void spaces in the structure and not by increasing the primary co-ordination of the network formers.

Preliminary results on experiments with dielectric loss dispersion *in situ*, at these pressures, show measurable changes. The influence of high pressure on the kinetics of glass crystallisation is quite profound. Dry silica glass can be crystallised as low as 700° (at a pressure of 60 kb). Glasses of the composition of eucryptite and spodumene show a remarkable nucleation behavior. Such glasses may be crystallised within a few minutes at temperatures near 500° and pressures of approximately 20 kb. The course and the products of crystallisation are dependent on whether or not the pressure is applied during the heating-up stage or only after the sample has attained high temperature. Nuclei of the low temperature-high density α -forms of both these minerals can be formed if the pressure is applied at very low temperatures. These nuclei will then grow in the higher temperature region to well-crystallised low-temperature spodumene or eucryptite.

Introduction

Bridgman & Simon¹ first reported the effect of very-high pressure on certain glasses. They reported that silica glass could be densified even at room temperature with an applied pressure exceeding 100,000 atm. They were also able to show that the percentage densification in a series of glasses containing different alkali ions is related to the composition of the glass. When one considers the nature of such a permanent compression in the glass, it is not immediately obvious how this is realised. Crystalline materials which have been exposed to very-high pressures and elastically compressed to approximately $\frac{2}{3}$ of their volume, appear to return to exactly their original volume. In some cases, of course, they undergo a phase transition, and if the activation energy for a reverse transformation is sufficient, the high-pressure form may be recovered under ambient conditions and persist metastably. Glasses are formed from those very materials which do have very high activation energies for reconstructive changes between different structural arrangements. Hence, it is possible to imagine that the elastic compression itself may somehow be frozen-in. Alternatively, one could imagine that a continuous structural change in response to the pressure-temperature environment takes place and these new structures may be quenched to ambient conditions. The nature of the latter structural change and its dependence upon temperature and pressure should provide very important data in the evaluation of theories on the structure of glassy materials. The results of Bridgman & Simon showing a threshold effect at 100 kb for silica glass might at first tend to indicate a sudden major structural change in the short range order phase. However, preliminary work along similar lines showed not only that there was no threshold effect at 100 kb, since the effect of pressure could be recorded continuously from 20 kb to 175 kb at room temperature, but also that the magnitude of the changes were considerably greater than those reported by Bridgman & Simon. A systematic study was, therefore, undertaken to describe precisely the influence of pressure and temperature (as independent variables) on the refractive index, density, molar refractivity and certain other properties. From the structural viewpoint it was considered desirable to explore in greatest detail the simplest glasses, but also to include glasses which represented various end member structural types.

Since glasses are always metastable phases below their liquidus temperature, it is quite clear that the structural arrangement which is proposed during the densification process must have a finite limit which must be reached before this phase crystallises to the stable crystalline form under the environments superimposed upon it. Hence, it is quite natural that we should proceed from an examination of the densification to an examination of the crystallisation of simple glasses under pressure. Here again, simple compositions are desirable, but in view of the extensive work on the crystallisation of the lithium alumina silicates and the technological importance of the same, considerable effort has been expended on studies of compositions corresponding to the minerals eucryptite and spodumene.

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