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 & Simon[1] 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.

Experimental

Virtually all the work to be reported upon has been conducted in opposed anvil-type apparatus. The general principles involved in the construction of the apparatus and the anvils themselves as well as details of the performance and calibration of such apparatus are given elsewhere.[2,3] A recent paper[3] describes various modifications and gives evaluations of different piston materials, etc. In another paper to be presented at this Symposium (see p. 77), criticism of calibration procedures and the evaluation of the opposed anvil pressure by utilisation of the Bi_I–Bi_{II} transition is presented. In apparatus of the type used, pressures up to 175 kb were reproducibly and very simply achieved at room temperature. Pressures near 150 kb have been sustained for several hours at temperatures below 400° and pressures near 100 kb may be sustained for several hours at temperatures as high as 600°.

Experimental procedure

In general, the glasses were ground to pass a 200-mesh sieve and were pre-pelleted as a very thin wafer of approximately 8 mils thick into a nickel ring of the same thickness (see Dachille & Roy[2a]). The wafer is surrounded on both sides by platinum–rhodium discs so that the entire system is quite free from contamination except by platinum or nickel. The system is usually taken to the derived temperature and the pressure applied for a short period ranging from $\frac{1}{2}$ minute to a few minutes. The pressure is released and then the temperatures lowered rather quickly. For certain runs it was necessary to make a series of experiments with times extending into 24 or 48 h. under these same conditions. In most cases, the glasses were recovered as a continuous transparent film which could then be examined for certain optical properties as a film or crushed for measurement of density and/or refractive index, etc. Densities were determined by a simple procedure with the usual heavy liquid media and centrifugation. Refractive indices were measured by the Becke line technique under a polarising microscope. Infrared spectra were obtained with the Perkin Elmer, Model 21, and visible spectra with a Beckman DK 2 spectrometer. For the studies on the kinetics of crystallisation, quantitative X-ray diffraction procedures were employed with use of a Norelco diffractometer, and standardisation with mixtures of the glass and the crystalline phase being formed.

Results

Data on densification of glass

Fig. 1 shows a graph of the refractive index of silica glass plotted as a function of the pressure to which the sample was exposed. It should be made quite clear that this is a refractive index of the glass after the entire quenching procedure and removal from the sample holder, etc. It is not, of course, the refractive index at pressure. Through frequent repetition and through storage of the samples for over 2 years, it is quite clear that there is no change in the silica glass caused by normal processing in the examination procedure. The variation in the refractive index of the product glass, if the sample is treated as a whole, can be quite large, ranging up to ±0.006, although most of the material may fall within a much narrower range. It appears in the data in Fig. 1 that silica glass may be compressed to a new structural form with a linearly increasing density and refractive index, depending on the pressure. The variation of refractive index across the sample is undoubtedly due to inhomogeneities in the pressure. Although the glass, when removed from the sample chamber, is indeed birefrequent, the change of refractive index is quite
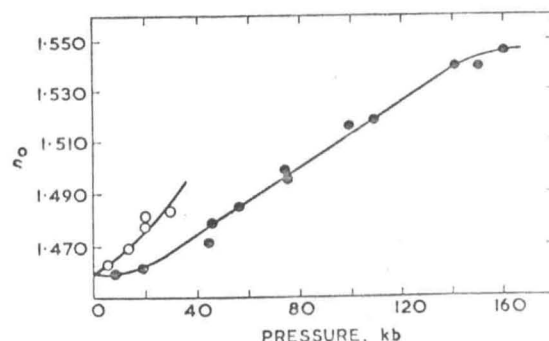

Fig. 1. *Refractive index of silica glass measured at atmospheric pressure and room temperature as function of the pressure of the run*
○ 600°   ● 25°

independent of this birefringence, most of which is lost when the glass is crushed. It will be noted from the data on anvil runs that very little change appears to have been effected below 20 kb. To confirm the fact that this effect is not due to the uniaxial nature of the pressure, as well as to extend the range to lower pressures, samples of silica glass sealed into gold capsules were placed in hydrostatic environment at 4 and 7 kb under argon pressure. The refractive index of the glass was extremely homogeneous and was raised to approximately 1·461 and 1·464 for 4 and 7 kb respectively at 600° (see Fig. 2). The results for germania and a few other glasses in Fig. 3, show a comparable magnitude of change of refractive index. The densities of most of these glasses have also been measured and the relationship between density, the refractive index being nearly linear. If one calculates the molar refraction of silica glasses from the refractive index and density data and the Lorentz–Lorenz equation, it is found that the refractivity for silica decreased from a value of 7·45 for ordinary silica glass to 7·19 for the very dense silica glass obtained. This latter glass has a refractive index essentially identical with that of quartz and its molar refractivity, it will also be seen, is identical to that of quartz (7·19).
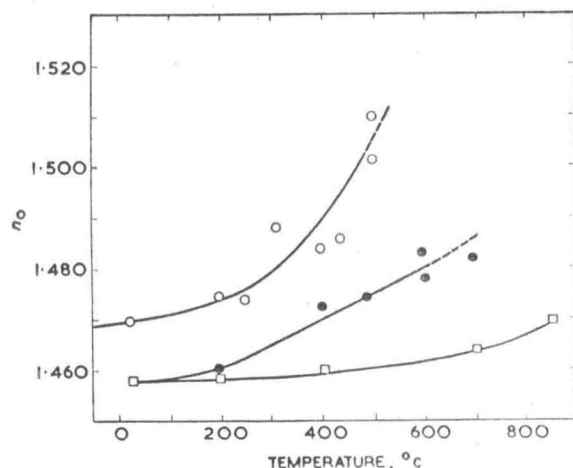

Fig. 2. *Refractive index of silica glass measured at atmospheric pressure and room temperature as function of the tenperature of the run*

pressure	○ 40 kb	◐ 20 kb	□ 4 kb
error	± 0·005	± 0·005	± 0·001

Fig. 3. *Refractive index measured at atmospheric pressure and room temperature of germania 25—200° (curve 1), dosimeter-type phosphate 500° (curve 2), window 25° (curve 3) and boron trioxide 25° (curve 4), glasses as function of pressure of the ram*
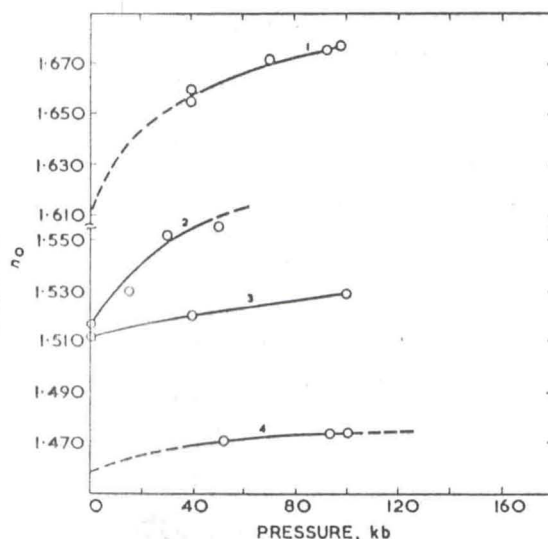
Before proceeding further, it is necessary to relate the nature of the results being presented to what we believe is actually happening in the relationship. In Fig. 4 is plotted the refractive index of the glass being examined versus the pressure. When the glass is compressed, the density presumably moves along the line AC'C. The slope of this line may be obtained from the compressibility data on silica glass as given by Birch *et al.*[5] and this is the slope actually shown. Thus

the glass is being elastically compressed along the line AC'C while pressure is being applied. However, in addition to this compression, the glass is also capable of a continuous structural change in response to its new pressure–temperature environment. This change also involves densification, due to a rearrangement of the tetrahedra so as to use up some of the void space. At the given pressure, the structural change adjusts the density to a point corresponding to D. The kinetics of such a change are extremely rapid. Upon release of pressure, however, the structural change in the reverse direction is extremely difficult, and hence, the glass does not return from D to A: instead, the elastic compression which is stored in D is released and the glass returns to a position E. Finally, it is plotted as a point in graph of the type of Fig. 1 at the pressure of the run corresponding to B'. Figs. 1 and those like it, therefore, are generated by a sequence of points corresponding to B'.
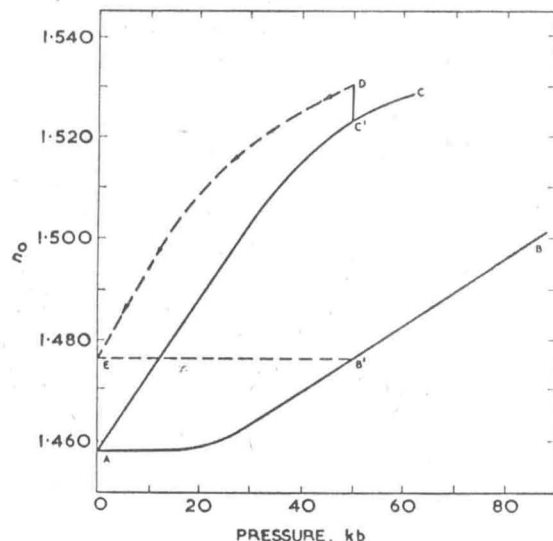

Fig. 4.   Curve AB'B represents the measured index of refraction of quenched silica glass as function of pressure. Curve AC'C represents the calculated index of refraction of the glass under the applied pressure.

The step C'D represents, schematically, the resultant structural change which may in fact have taken place across a more complex path from A to D.

Curve DE represents, schematically, the release of the compression of the densified silica glass when the external pressure is quenched

The index of refraction was calculated, from the compressibility data given by Birch et al.[5], from the molar refraction relation

Influence of temperature

From the fact that silica glass has an extremely low thermal expansion, it might have been predicted that the densification would not be increased if the temperature of the run was increased a few hundred degrees Celsius. The facts, however, prove to be quite different. The temperature of the run had a profound influence on the final density of the glass. This is shown in Fig. 2 where the density of the resultant silica glass has been plotted against temperature in isobaric runs. The results so far might suggest that temperature was merely serving to accelerate the reaction and bring the glass to its equilibrium value more quickly. This is true to a certain extent, and is illustrated by the inability to obtain a measurable change in the silica glass at room temperature at 10 kb, while at 7 kb and 675° an increase in refractive index to 1·467 was recorded. However, the main effect of temperature is quite different. It appears that at each pressure and temperature there is an equilibrium or pseudoequilibrium structure of the glass which is attained very rapidly and then hardly changes at all. One can hardly explain otherwise the fact that silica glass heated to, say, 200° at 60 kb comes to equilibrium in 1 or 2 min., and does not change thereafter, even in a period of days, while heating to 400° at the same pressure also gives a psuedo-equilibrium value within a minute or two which is distinctly higher. The structural state of the glass therefore appears to be a rather sensitive indicator of both its pressure and temperature environment.

Structural aspects of densification process

If the hypothesis is correct that the densification of the glass by high pressure is achieved at the expense of the rearrangement of the tetrahedra to use up void space in the structure, then it ought to be possible to check the hypothesis by a study of the influence of pressure on glasses in which the percentage of voids is different. A systematic study has been attempted by a thorough evaluation of three glasses of the compositions R_2O, $0·1$ MgO, $2·9$ SiO_2 with the alkali ion changing from lithium to potassium. The results of the measurements are shown in Figs. 5

and 6. Here one finds that the saturation value for the densification, as well as the difference in the percentage densification, depend on the size of the cation. A most interesting calculation may be made for the packing density of all the saturated or maximum-density phases which have been achieved. It is found that the ratio volume of ions divided by molar volume is, in most of these cases, approximately 51 %, irrespective of the ratio for the original glass.
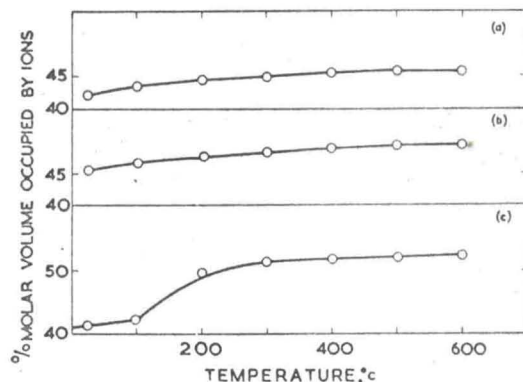

Fig. 5. *Ratio of volume of the ions (Goldschmidt's radii) to the molar volume of the glass composition, measured at atmospheric pressure and room temperature, as a function of the temperature of the run*
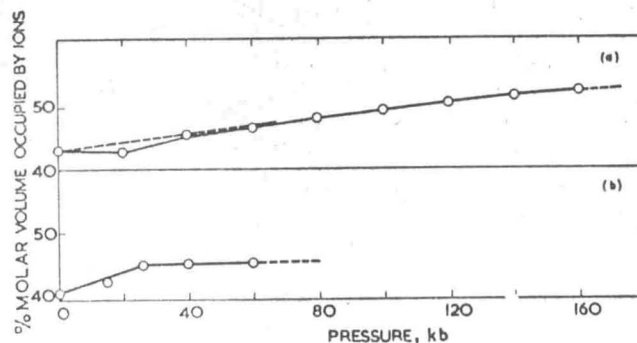
densification at 40 kb
(a) $K_2O,0\cdot1MgO,2\cdot9SiO_2$,
(b) $Na_2O,0\cdot1MgO,2\cdot9SiO_2$
(c) $Li_2O,0\cdot1MgO,2\cdot9SiO_2$

Fig. 6. *Ratio of volume of the ions (Goldschmidt's radii) to the molar volume of the glass composition, measured at atmospheric pressure and room temperature, as function of the pressure of the run*
(a) SiO_2 25°
(b) $K_2O,0\cdot1MgO,2\cdot9SiO_2$ 500°

Changes in optical absorption spectra and electrical properties of glasses

Although the results in these areas are far from complete, some are recorded to show the magnitude of the effects to be expected. From the structural work recorded above, it was clear that one could not expect a change of major co-ordination number of the network-forming cation. It was hoped however, that perhaps a change in the co-ordination of the network-modifying cations may be effected as a by product of the densification process. Co^{2+} and Ni^{2+} ions were used as colour indicators. It was hoped that, even though a complete co-ordination change of these ions may not be effected, it might be possible to find a lattice contraction effect analogous to that reported by Schmitz-Du Mont *et al.*[6] in the shift of the absorption maximum in spinels as a function of the general lattice parameter. No major changes were observed.

Recent interest in the dispersion of the dielectric loss offers the possibility of confirming the mechanism of the change hypothesised in Fig. 4. For this purpose, it will be necessary to be able to make measurements both at high pressure and high temperature as well as to repeat the measurement after quenching. Glasses of the composition $(2-x)Na_2O,xAl_2O_3,(6-2x)SiO_2$ have been prepared and cast into nearly bubble-free blocks by heating in iridium crucibles at 1800°, and thin wafers have been cut and polished from these. The dielectric properties of the glass were determined as a function of frequency at atmospheric pressure and the experiment has been repeated at pressures as high as 30 kb. Finally after release of the pressure (and after densification of the glass) the experiment has been repeated. Since thorough evaluation of the results is not yet complete, it would be misleading to present the data at this time.

Crystallisation of glass under pressure

It has been pointed out above that the glass appears to undergo a continuous structural change in the direction of increased density by rearrangement of the tetrahedra of the network formers. Quite clearly, if this rearrangement is carried to equilibrium rather than to a meta-stable equilibrium, the glass must crystallise to the crystalline phase stable under the given *P–T* conditions. Silica glass cannot be crystallised at a finite rate below approximately 600° in our apparatus. In early studies,[2a] silica glass was used as starting material to obtain either quartz or coesite. In the equilibrium field of those respective crystalline phases, crystallisation occurred in a few hours, even at pressures as low as 20 kb when very small amounts (not detectable by weighing) of water are present. In the present study, it was found that if the silica glass was very thoroughly dried, it does not crystallise at pressures up to 100 kb at temperatures below 600°. Under these conditions, either coesite or stishovite might be the stable crystalline phase. Barely perceptible crystallisation is achieved if the temperature is increased to 700° at pressures of 80 kb in several hours. Since the limit of the apparatus is very close to these conditions, a thorough study of SiO_2 crystallisation was considered infeasible. Germania glass was used for a more exhaustive study, since it was found that it could be crystallised well within the range of experiment. Thoroughly dried germania glass cannot be crystallised at temperatures below 150° at pressures near 100 kb.

The rate of crystallisation at fixed temperatures (near 500°) and fixed time appears to vary approximately linearly with pressure, at least below total crystallisation of less than 50%.

In the development of the new technology based on the crystallised glasses, the system lithia–silica plays a very important role. A great deal of work has been done on the crystallisation of glasses of the composition $Li_2O,Al_2O_3,2SiO_2$ and $Li_2O_3,Al_2O_3,4SiO_2$. Blinov & Roy[7] have made a study of the rate of crystallisation of glasses of such compositions and obtained some most remarkable results. Fig. 7 shows the percentage of β-eucryptite crystallised out as a function of time in glasses of the composition of eucryptite which has been treated in the following manner.

The powdered glass is loaded on to the anvils (see above) and the anvils are brought together, but no pressure is applied and the furnaces heated up to the given temperature—a process usually taking 45 min. to 1 h. The pressure is then applied for the length of time which is plotted as the abscissa, the pressure is released instantaneously and the sample is cooled as rapidly as possible. The formation of a maximum of crystallisation with time in this curve poses a most difficult problem. At present, it is believed that the explanation for this is as follows. The initial phase, which is nucleated from the eucryptite composition is a silica-rich phase which may be called silica-O, according to the terminology suggested by Roy[8] earlier. This phase subsequently reacts with the remaining glass—first dissolving and then re-precipitating a phase poorer in silica. The analogous situation without pressure has already been reported by Ruiz & Roy.[9]
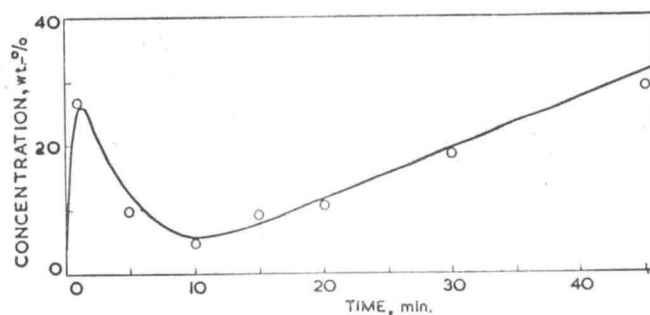

Fig. 7   *% β-eucryptite crystallised out from glass as function of time at 600° at a pressure of 20 kb (no pressure applied during the heating-up period)*

Quite a different phenomenon is found if the conditions of experiment are changed only slightly. In a second set of experiments, the pressure is applied during the heating-up process. Not only is the percentage of crystallisation of the glass dramatically changed, but also the phases which are crystallising. In the case of eucryptite, it was possible, for the first time, to synthesise α-eucryptite without the presence of any mineraliser. As for spodumene, the natural form of spodumene has never previously been synthesised reproducibly. In this study, it was

found that low or α-spodumene could be synthesised easily by crystallising the glass at temperatures above 750° and pressures in excess of 20 kb, if a pressure of 10 kb or more was maintained during the heating-up period. Fig. 8 shows plots of the percentage of α- and β-eucryptite crystallising out as a function of time under these conditions.
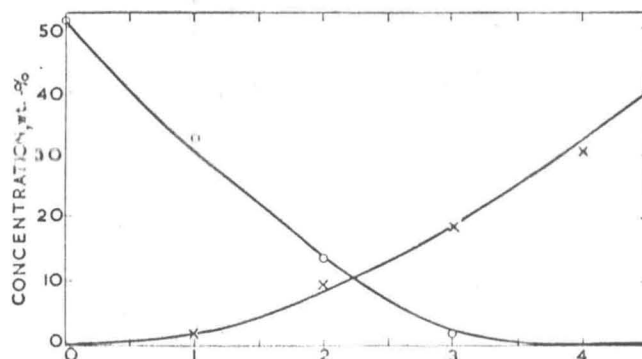

Fig. 8. *Crystallisation of α (×) and β-eucryptite (○) out of glass in a constant time period as function of the pressure applied during heating up*

The temperature and pressure of crystallisation are kept constant at 650° and 20 kb
Points along abscissa indicate pressure during heating 0, none; 1, 5; 2, 10; 3, 15; 4, 20 kb.

Clearly the nuclei of the high-density phases are formed at the lower temperature under pressure. However, these nuclei will *not* grow at appreciable rates below 400°, and, if the sample is heated at temperatures between 400 and 600°, the nuclei of the β-phase will form and grow faster. If the pre-formed nuclei are taken to a high enough temperature, then the growth of these α-phase nuclei predominates over the nucleation and growth of the β-phases.

Acknowledgment

References

[1] Bridgman, P. W., & Simon, I., *J. appl. Phys.*, 1953, 24, 405

[2] (a) Dachille, F., & Roy, R., *Z. Krist.*, 1959, 111, 451; (b) *idem.*, 'High-pressure Phenomena', 1960, pp. 441–46, in 'McGraw-Hill Encyclopedia of Science and Technology' (New York: McGraw-Hill Book Co. Inc.); (c) *idem.*, *Amer. J. Sci.*, 1960, 258, 225

[3] Dachille, F., & Roy, R., 'Opposed-Anvil Pressure Devices', in 'Modern Very High Pressure Techniques', (R. H. Wentorf, jun., ed.), 1962 (Washington: Butterworths Publications)

[4] Dachille, F., & Roy, R., this Symposium, p. 77

[5] Birch, F., Schairer, J. F., & Spicer, H. C. (eds.), 'Handbook of Physical Constants', *Geol. Soc. Amer.*, *Spec. Pap.*, 1942, No. 36, p. 51

[6] Schmitz-DuMont, Gossling, H., & Brokopf, H., *Z. anorg. Chem.*, 1959, 300, 159

[7] Blinov, V., & Roy, R., 'Catalysis of Glass Crystallisation under Extreme Pressure', Amer. Ceram. Soc. Mtg, May, 1962

[8] Roy, R., *Miner. petrogr. Mitt.*, 1959, III, 185

[9] Ruiz-Menacho, C., & Roy, R., *Bull. Amer. ceram. Soc.*, 1959, 38, 229 (Abstr. only)