

*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 metastable 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  $600^\circ$  in our apparatus. In early studies,<sup>2a</sup> 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  $600^\circ$ . Under these conditions, either coesite or stishovite might be the stable crystalline phase. Barely perceptible crystallisation is achieved if the temperature is increased to  $700^\circ$  at pressures of 80 kb in several hours. Since the limit of the apparatus is very close to these conditions, a thorough study of  $\text{SiO}_2$  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  $150^\circ$  at pressures near 100 kb.

The rate of crystallisation at fixed temperatures (near  $500^\circ$ ) 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  $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 2\text{SiO}_2$  and  $\text{Li}_2\text{O}_3, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ . Blinov & Roy<sup>7</sup> 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  $\beta$ -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<sup>8</sup> 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.<sup>9</sup>

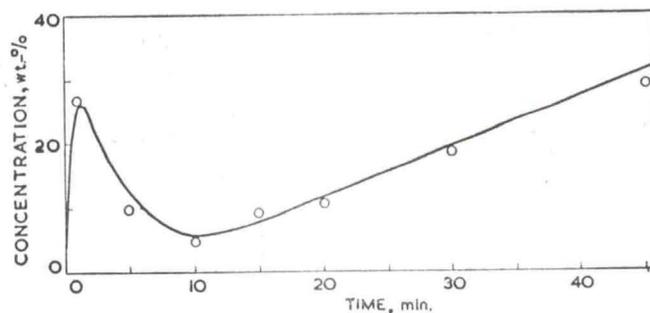


Fig. 7 %  $\beta$ -eucryptite crystallised out from glass as function of time at  $600^\circ$  at a pressure of 20 kb (no pressure applied during the heating-up period)

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  $\alpha$ -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