

Fig. 3. Formation of a lithium aluminosilicate glass under pressure.

served with strontium titanate⁵ and with rutile crystals⁶ and is attributed to oxygen deficiency. Another possibility is that the effect is due to some undetected impurity.

(2) Experiments on Glass Crystallization

A series of experiments was made to study the effect of pressure on the crystallization of a glass at elevated temperatures but below the liquidus of the material. A glass of the composition described in Section I was melted at 1400°C for 4 hours in a platinum crucible, was cast in a steel mold, and was annealed at 400°C. A thin rod of this material was ground and loaded into the platinum heating element. On completion of the experiment the sample assembly was embedded in lucite and sectioned.

At atmospheric pressure, crystallization of this glass began as low as 600°C and was evident at all temperatures above this and below the liquidus at 930°C. At 30,000 bars crystallization did not begin until above 900°C and was very sluggish even at the higher temperatures. This is probably one of the few known methods of impeding the devitrification process. Figure 5 shows what this crystallization looks like. The glassy matrix remains. The crystallization is observed as a haze of microscopic nuclei within the glassy matrix.

The crystallites formed in an experiment at 30,000 bars and 1000°C over a period of 15 minutes were examined by X-ray powder diffraction. The resultant pattern could be interpreted as a mixture of β -spodumene, lithium metasilicate, and a lesser amount of α -spodumene by comparison with available patterns.^{7,8,9}

IV. Conclusions

Two conclusions can be gleaned from these results. First, at atmospheric pressure β -spodumene does not appear until after several hours under reaction conditions. Instead lithium metasilicate and β -quartz solid solution (i.e., silica "O") are the initial precipitants. These react only sluggishly to form the equilibrium products, β -spodumene plus lithium metasilicate. Thus it appears that high pressure hastens the approach to equilibrium in these systems.

Second, α -spodumene (or low-temperature spodumene) is a high-pressure phase. The only other synthesis of this material (from which the trace was obtained) was under hydrothermal conditions.⁹

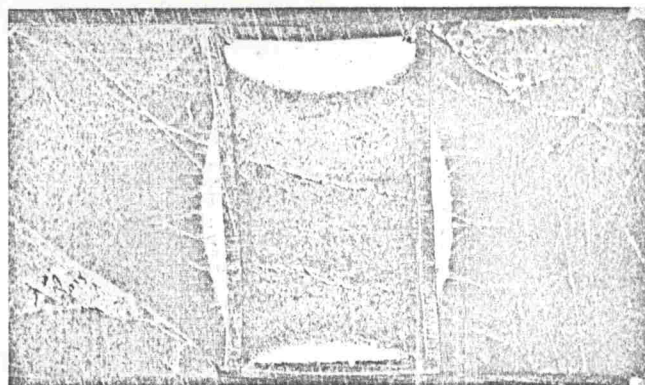


Fig. 4. Darkening of lithium aluminosilicate powder before melting

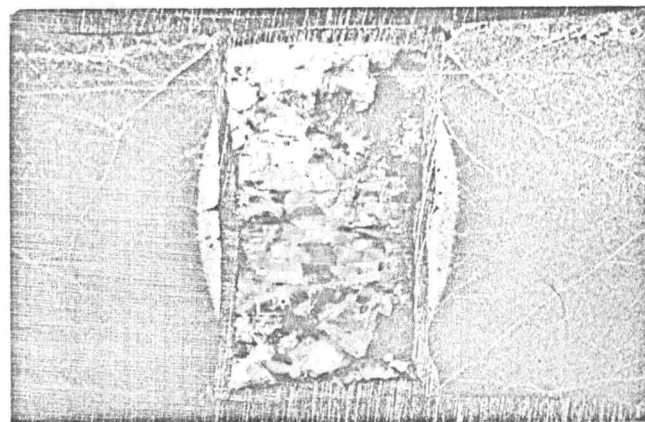


Fig. 5. Fracture and devitrification of a lithium aluminosilicate glass under pressure.

Figure 5 also illustrates the fracture pattern of a glass which had been subjected to superpressures. Almost all cracks are either normal or perpendicular to the pistons. They are interpreted as being due to the differential relaxation rate of axial and lateral components of stress during the descending portion of the high-pressure cycle. Differences in stress relaxation of the sample environment are caused by static surface frictional characteristics of the various movable and compressible components of the pressure apparatus.

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⁵ S. B. Levin, N. J. Field, F. M. Plock, and L. Merker, "Some Optical Properties of Strontium Titanate Crystal," *J. Opt. Soc. Am.*, **45** [9] 737-39 (1955).

⁶ (a) C. H. Moore, Jr., "Formation and Properties of Single Crystals of Synthetic Rutile," *Am. Inst. Mining Met. Engrs. Tech. Pub. No. 2617*; *Mining Eng.*, **1** [6, Sect. 3] 194-99 (1949); *Ceram. Abstr.*, 1949, September, p. 217i.

(b) D. C. Cronmeyer, "Electrical and Optical Properties of Rutile Single Crystals," *Phys. Rev.*, **87** [5] 876-86 (1952).

⁷ D. Evans, Corning Glass Works; private communication.

⁸ A. E. Austin, "X-Ray Diffraction Data for Compounds in the Systems $\text{Li}_2\text{O}-\text{SiO}_2$ and $\text{BaO}-\text{SiO}_2$," *J. Am. Ceram. Soc.*, **30** [7] 218-20 (1947).

⁹ R. M. Barrer and E. A. D. White, "Hydrothermal Chemistry of Silicates: I, Synthetic Lithium Aluminosilicates," *J. Chem. Soc.*, 1951, article 283, pp. 1267-78.