

Glass

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Some Studies of Effect of High Pressure on a Lithia-Alumina-Silica Glass

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The effect of near-hydrostatic pressure on the synthesis of a lithia-alumina-silica glass was studied. It was found that the fusion of the oxides to form a glass melt was seriously impeded. A study also was made of the effect of hydrostatic pressure on the crystallization of a previously synthesized glass of similar composition. The approach to equilibrium in the system was found to be more rapid than at atmospheric pressure. In addition, a minor amount of a phase which could not be synthesized directly from the melt (α -spodumene) was found.

In choosing a system, it was desired that it should (1) melt readily at relatively low temperatures (below 1000°C) because it was expected that pressure would increase the melting

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* Purely hydrostatic conditions are attainable only in equipment using fluid pressure-transmitting media. 30,000 bars is an upper limit for such devices. In the system used in this study solid pressure-transmitting materials were employed which possessed relatively low shear moduli under pressure. Although shear components do exist, they have been found to be small by observation of deformation.

I. Introduction

THE effect of near-hydrostatic pressure* on the synthesis and devitrification of a glass-forming system has been studied.

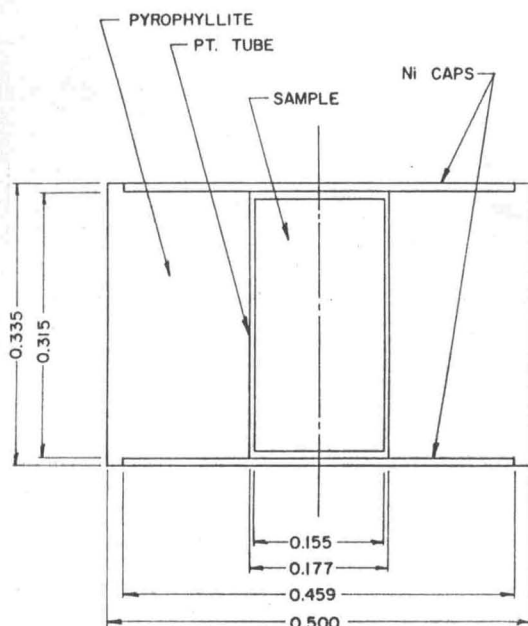


Fig. 1. Sample assembly. All dimensions given in inches.

point considerably, (2) be readily formable into a good-quality glass, (3) be readily devitrifiable, and (4) be well understood.

A system which easily meets all these criteria is the system lithia-alumina-silica. A great deal of information is available in the literature on this system.¹ It is readily formed as a glass and is as readily devitrified. For these reasons, the following composition was chosen for the study: Li_2O 20, Al_2O_3 10, and SiO_2 70% (wt).

The equilibrium crystalline phases are lithium metasilicate and β -spodumene. When crystallized from the glass, however, these phases appear only after treatment at elevated temperatures (600° to 900°C) for several (~16) hours, through recrystallization of a previously crystallized mixture of lithium metasilicate and β -quartz solid solution (i.e., silica "O").

II. Apparatus

The superpressure apparatus at the U. S. Army Signal Corps Laboratories was used for these experiments. This device, which has already been described,² consists, essentially, of two sets of symmetrically opposed stepped cemented carbide pistons and a cylinder assembly consisting of a double-bore cemented carbide member surrounded by a series of hardened-steel bands.

¹ (a) S. D. Stookey, "Method of Making Ceramics and Product Thereof," U. S. Pat. 2,920,971, January 12, 1960; *Ceram. Abstr.*, 1960, June, p. 142a.

(b) Rustom Roy and E. F. Osborn, "The System Lithium Metasilicate-Spodumene-Silica," *J. Am. Chem. Soc.*, **71** [6] 2086-95 (1949); *Ceram. Abstr.*, 1950, May, p. 111d.

(c) M. K. Murthy and F. A. Hummel, "Phase Equilibria in the System Lithium Metasilicate- β -Eucryptite," *J. Am. Ceram. Soc.*, **37** [1] 14-17 (1954).

(d) R. A. Hatch, "Phase Equilibrium in the System $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$," *Am. Mineralogist*, **28**, 471-96 (1943); *Ceram. Abstr.*, **23** [1] 26 (1944).

(e) Rustom Roy, D. M. Roy, and E. F. Osborn, "Compositional and Stability Relationships Among the Lithium Aluminosilicates: Eucryptite, Spodumene, and Petalite," *J. Am. Ceram. Soc.*, **33** [5] 152-59 (1950).

² A. A. Giardini, J. E. Tydings, and S. B. Levin, "Very High Pressure-High Temperature Research Apparatus and Synthesis of Diamond," *Am. Mineralogist*, **45** [1-2] 217-21 (1960); *Ceram. Abstr.*, 1961, May, p. 132b.

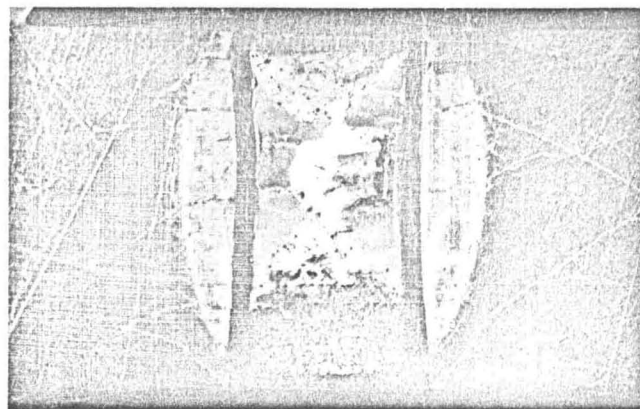


Fig. 2. Melting of a lithium aluminosilicate powder batch to form a glass.

The sample area is shown in Fig. 1. The sample itself is enclosed in a Pt20Rh tube with platinum caps at both ends. This in turn is placed into a pyrophyllite cylinder and capped at both ends with a thin nickel disk. The assembly is placed between the pistons of the superpressure apparatus for the experimental run.

Pressures were determined by extrapolation from the first two pressure-induced bismuth electrical resistance discontinuities³; the limits of error are approximately $\pm 5\%$ for the range of pressures used in this study. Temperatures were obtained by linear extrapolation of input power versus platinum melting point⁴ at the particular pressure employed; the accuracy is within $\pm 50^\circ\text{C}$ at 500°C and $\pm 100^\circ\text{C}$ at 2000°C for a given position in the sample capsule.

III. Experiments and Results

(1) Experiments on Glass Synthesis

A series of experiments was made to study the effect of pressure on the glass-melting process. The raw materials were Harshaw Chemical Company 325-mesh silica, Norton Company 38900 alumina, and Foote Mineral Company technical-grade lithium carbonate. The materials were carefully weighed out, intimately mixed, and compacted into the platinum heating tube. On completion of the experiment, the sample assembly was embedded in lucite and cross-sectioned to permit visual observation (see Fig. 2).

It was found that melting of the powder and subsequent formation of the glass was seriously impeded. The powder remained after subjection to temperatures well in excess of the normal melting point of the mixture at 900°C . The melting point appeared to increase with increasing pressure (see Fig. 3).

The alteration of the powder before melting was also investigated. As the temperature was increased the white powder turned to gray (see Fig. 4). During further heating the material became partly white again just before melting. Subsequent heating of the darkened powder at 600°C in air reversed the darkening. A similar darkening has been ob-

³ (a) P. W. Bridgman, "Resistance of Nineteen Metals to 30,000 Kg./Sq. Cm.," *Proc. Am. Acad. Arts Sci.*, **72**, 157-205 (1938).

(b) P. W. Bridgman, "Pressure-Volume Relations for 17 Elements to 100,000 Kg./Sq. Cm.," *Proc. Am. Acad. Arts Sci.*, **74** [13] 425-40 (1942).

(c) P. W. Bridgman, *Physics of High Pressure*. G. Bell & Sons, Ltd., London, 1949. 445 pp.

(d) F. P. Bundy, "Phase Diagram of Bismuth to 130,000 Kg./Sq. Cm., 500°C ," *Phys. Rev.*, **110** [2] 314-18 (1958).

⁴ H. M. Strong and F. P. Bundy, "Fusion Curves of Four Group VIII Metals to 100,000 Atmospheres," *Phys. Rev.*, **115** [2] 278-84 (1959).

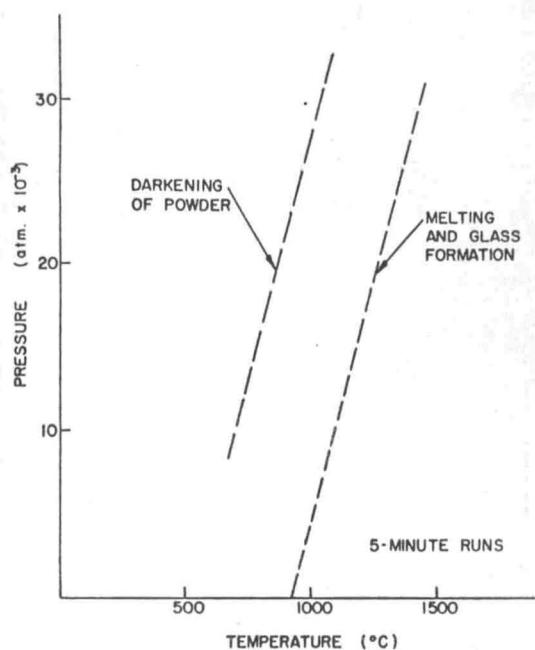


Fig. 3. Formation of a lithium aluminosilicate glass under pressure.

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

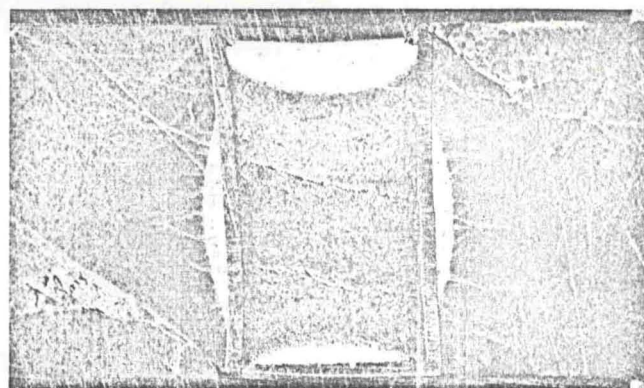


Fig. 4. Darkening of lithium aluminosilicate powder before melting

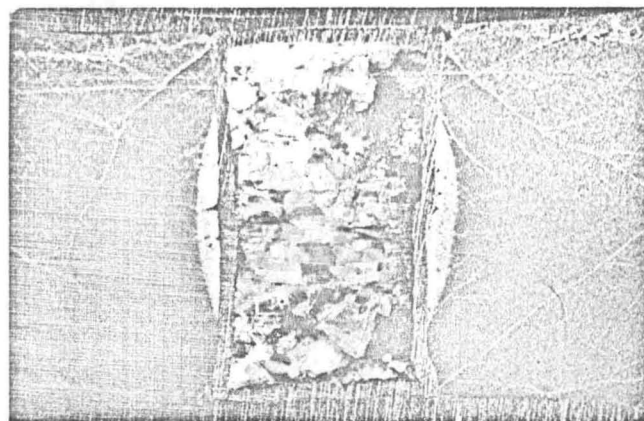


Fig. 5. Fracture and devitrification of a lithium aluminosilicate glass under pressure.

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. Cronemeyer, "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.