

# Crystallization of Lithia-Silica Glasses at High Pressure

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The powdered lithia-silica glasses of the compositions,  $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  and  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$ , were loaded to various pressures reaching to 30 kilobar (Kb) with the uniaxial high-pressure apparatus, and the crystalline phases produced in the glasses, the crystallization temperatures and the stability of the crystallization products were investigated. In all of the glass samples, lithium metasilicate crystals and silica crystals (quartz or coesite) were found to be produced by the application of high-pressures in place of lithium disilicate crystals, which precipitate at atmospheric pressure. The crystallization temperature of the glasses was greatly lowered by the application of high-pressure. The crystallization of the glasses was markedly enhanced by the presence of water. The lithium metasilicate-coesite mixtures produced from the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass changed, when heated at atmospheric pressure, first into lithium metasilicate-quartz mixtures at the temperature from  $750^\circ\text{C}$  to  $850^\circ\text{C}$  and then into lithium disilicate crystals at the temperature from  $900^\circ\text{C}$  to  $950^\circ\text{C}$ .

## I. INTRODUCTION

After the new high-pressure polymorph of silica, "coesite", was discovered by Coes<sup>1)</sup>, many studies have been made of synthesis and transformation of high-pressure modifications of silica and silicates. Some of these deal with the process of crystallization of silicate glasses. Roy *et al.*<sup>2,3)</sup> made systematic studies of the effects of high-pressure on the rate of crystallization of glasses with various compositions: Zeto, Dachille and Roy<sup>2)</sup> confirmed experimentally that the crystallization rate of  $\text{SiO}_2$  glass is markedly increased by the application of high-pressure in excess of 10 kilobar (Kb) and also by the presence of water vapor. Blinov and Roy<sup>3)</sup> studied the crystallization of glasses of the system,  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , under the pressures up to 100 Kb and at temperatures up to  $800^\circ\text{C}$ , and found that eucryptite-and spodumen-composition glasses are converted, by application of pressures as low as 10 Kb, to various crystals which can not be obtained under the same time-temperature conditions.

The high-pressure experiments of Roy *et al.*, were made by using the opposed-anvil type apparatus by which the pressure involving a fairly high degree of shear are applied to the specimens<sup>4)</sup>. Using the high-pressure apparatus which generates the pressure of near hydrostatic nature, Eppler, Giardini and Tyding<sup>5)</sup> obtained the results which contradict those of Roy *et al.*; i.e., the high-pressure decreased the rate of crystallization of the glass of the composition,  $\text{Li}_2\text{O}$  20,  $\text{Al}_2\text{O}_3$  10, and  $\text{SiO}_2$  70 by weight percent.

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The present article deals with the effects of high-pressure on crystallization of a series of  $\text{Li}_2\text{O}-\text{SiO}_2$  glasses, whose crystallization processes at atmospheric pressure were already well investigated by many researchers. At atmospheric pressure the glasses of this series crystallize at about  $600^\circ\text{C}$ <sup>6)</sup>, the precipitated crystalline phase being lithium disilicate for the glasses of silica rich compositions ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$ , etc.) whereas lithium metasilicate and lithium disilicate for the glasses of low-silica composition ( $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$ )<sup>7)</sup>.

The high-pressure apparatus used in the present experiment is of the uniaxial simple squeezer type previously used by the authors for the study of the refractive index changes of the glasses under high-pressure<sup>8)</sup>.

## II. EXPERIMENTAL PROCEDURE

### Preparation of Glasses

The molecular compositions of the glasses prepared were  $\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  and  $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$ . The  $\text{SiO}_2$  glass samples were obtained from a commercial clear fused quartz (Toshibadenko Product; the coefficient of linear thermal expansion is  $5.4\times 10^{-7}$ ). The other glasses were prepared in the authors' laboratory. Batch materials used were lithium carbonate of high purity (Nippon Chemicals Product; the  $\text{Li}_2\text{CO}_3$  content was over 99%) and potter's flint powders purified for use in manufacture of ordinary optical glasses. Batches to yield 100 gram glass were melted in platinum crucibles at  $1370^\circ\sim 1420^\circ\text{C}$  for 2 hours in an electric furnace with silicon-carbide heating elements. The melts were poured on a steel plate and, after cooled to room temperature, pulverized into powders of less  $70\ \mu$  in diameter.

### Application of High Pressure

The high-pressure apparatus used consisted, essentially, of a high-pressure cell having a pair of symmetrically opposed cemented tungsten carbide pistons each embedded in a stellite holder, a 40 ton hydrostatic press and a split furnace with the nichrome resistance heater for external heating. The high-pressure cell is schematically shown in Fig. 1.

The application of high-pressure to the glass samples at high temperatures were conducted by the following procedure: The pulverized glass sample of about 0.3 gram was wrapped in a 0.02 mm-thick platinum foil, being placed between the opposed surfaces of the tungsten carbide pistons. Pressure was applied at room temperature up to about one thirds of the desired final pressure, and, under the pressure, the sample was raised to the desired temperature within about 20 minutes, the pressure was further increased to the final desired value. After the glass sample was compressed at the desired pressure and temperature for the desired duration, the split electric furnace was removed from a set of apparatus to allow the glass sample to cool. When the temperature of the sample fell to about  $200^\circ\text{C}$  the pressure was released. The cooling rate of the glass sample was fairly high; i.e., about  $20^\circ\text{C}/\text{min}$ . from  $500^\circ$  to  $300^\circ\text{C}$ , and about  $15^\circ\text{C}/\text{min}$ . from  $300^\circ$  to  $200^\circ\text{C}$ . In some experiments a drop of water was added to the sample powders wrapped in a platinum foil in order to investigate the effects of water on the

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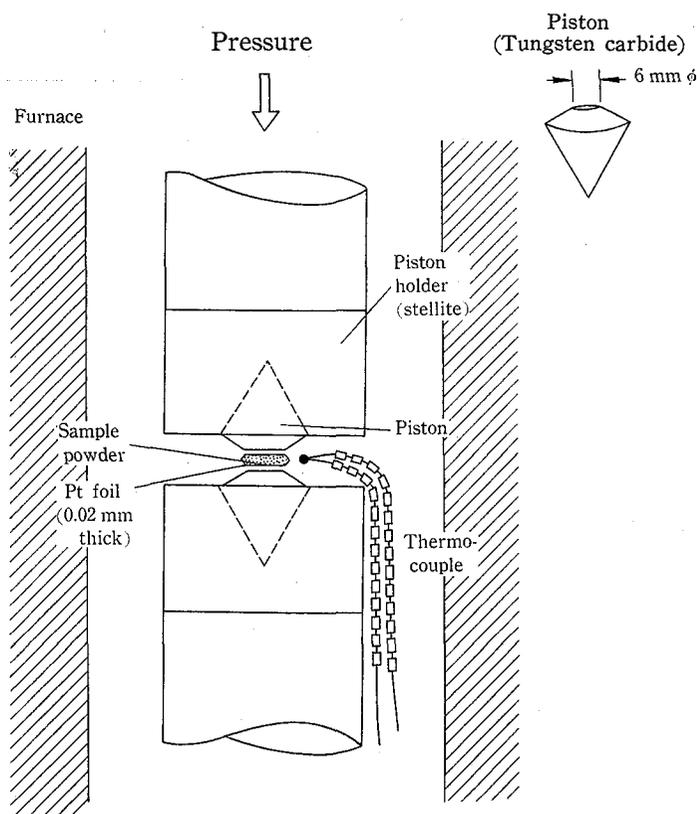


Fig. 1. High-pressure cell.

crystallization of the glass during compression. The temperature of the sample was measured by a chromel-alumel thermocouple mounted as shown in Fig. 1. In the present paper, the pressure applied to the sample was given in terms of total thrust divided by the cross sectional area of the piston.

The x-ray diffractometer used for the identification of crystals separated in the glass particles was of the type GX-2A of Shimadzu Co. with Cu  $K\alpha$  radiation.

### III. EXPERIMENTAL RESULTS

#### Crystallization at High Pressures

##### (a) $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ glass

The results obtained with this glass are summarized in Table 1. The temperatures and pressures to which the samples were subjected, the crystals separated out in the glass powder and effects of addition of water are all given in the table. Durations of compression were 20 min. for all runs. Run was made only at the temperatures between 500° and 600°C. Below 500°C crystallization did not occur even under the pressure of 30 Kb. Over 600°C severe oxidation of the tungsten carbide pistons occurred. Fig. 2 shows some examples of the X-ray diffraction patterns of the crystals precipitated in the compressed samples.

Table 1. Crystallization of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass under high-pressure (duration of compression was 20 min).

| Pressure (Kbar) | Temperature |             |                |          |
|-----------------|-------------|-------------|----------------|----------|
|                 | 500°C       | 500°C       | 550°C          | 600°C    |
| (atm. pressure) | no water    | water added | no water       | no water |
| 0.001           | Glass       | Glass       | Glass          | L2S      |
| 0.5             | Glass       | Glass       | L2S (trace)    | —        |
| 1               | Glass       | Glass       | L2S+LS+Q       | —        |
| 2               | Glass       | Glass       | L2S+LS+Q       | —        |
| 5               | Glass       | Glass       | LS+Q           | —        |
| 10              | Glass       | Glass       | LS+Q           | —        |
| 20              | Glass       | LS+Q        | LS+Q+C (trace) | —        |
| 30              | Glass       | LS+Q        | LS+C           | —        |

Glass: Not crystallized    L2S: Lithium disilicate crystal ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ )  
 LS: Lithium metasilicate crystal ( $\text{Li}_2\text{O}\cdot \text{SiO}_2$ )    Q: Quartz ( $\text{SiO}_2$ )    C: Coesite ( $\text{SiO}_2$ ).

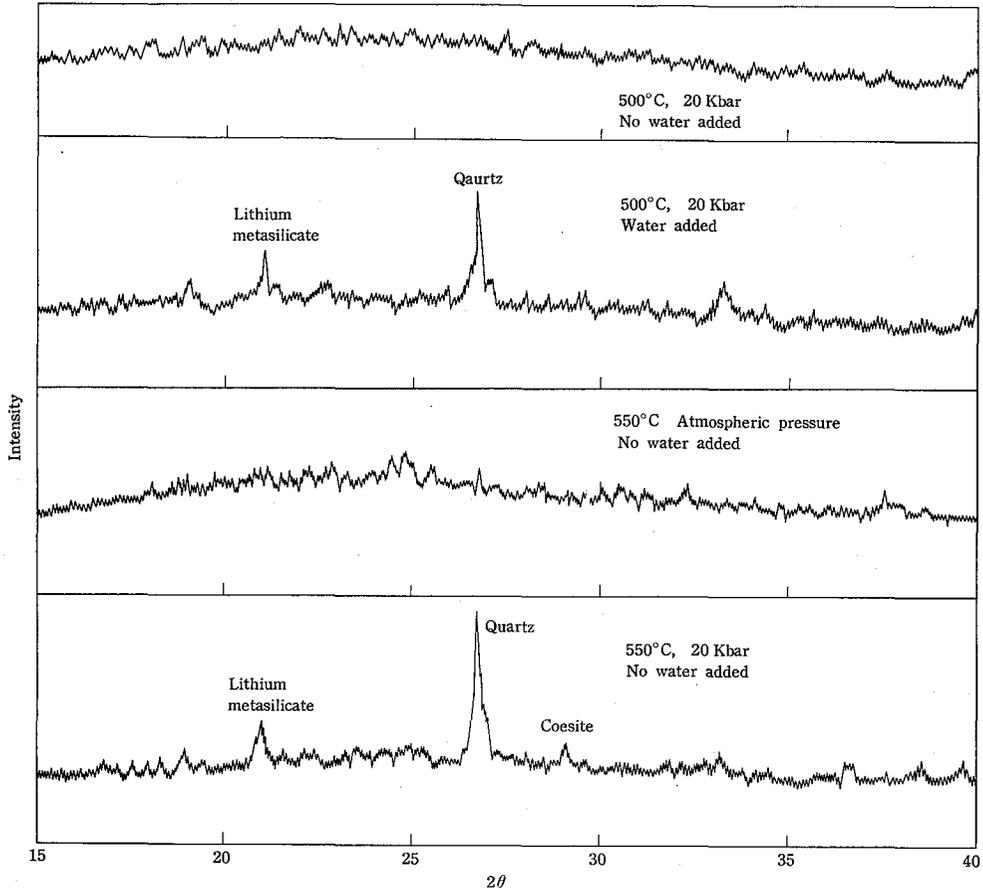


Fig. 2. X-ray diffraction patterns of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass heat-treated.

From Table 1 and Fig. 2 it can be seen that the application of high-pressure increases the rate of crystallization of this glass, especially in the presence of water. The combined effect of pressure and water is seen for the runs made

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at 500°C and at 20~30 Kb. In the presence of water, the  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  and quartz were found to crystallize out, whereas in the absence of water no crystals was observed.

The effect of pressure alone is seen for the runs made at 550°C. For both of the samples with and without water, the applications of pressures resulted in precipitation of various crystals in the glass samples:  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  plus  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  plus quartz at 1 to 2 Kb,  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  plus quartz at 5 to 20 Kb and  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  plus coesite at 30 Kb. Crystallization of the glass at atmospheric pressure was observed only on the runs made at 600°C. The crystallized product was lithium disilicate as already reported in the literature<sup>9</sup>.

Instead of using the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass as the starting material, in some experiments, the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystal, which was prepared by heating the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition glass at 600°C at atmospheric pressure, was subjected to the pressure of 20 and 30 Kb at 550°C. The resulting products were the same as those obtained from the glass of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition at the same temperature and pressure conditions: This result indicates that under such pressure and temperature the  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  crystal and the silica crystal (quartz or coesite) are equilibrium products of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition.

**(b) Glasses of the Compositions other than  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$**

The results obtained with the glasses of the compositions  $\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$ , and  $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$  are summarized in Table 2.

Table 2. Crystallization of  $\text{SiO}_2$ ,  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$  and  $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$  glasses under various high pressures (duration of compression was 20 min. with exception specially noted).

| Starting material                                | Pressure (Kbar)          | Temperature (°C)    | Water   | Product* |
|--|--------------------------|---------------------|---------|----------|
| $\text{SiO}_2$ glass                             | 30                       | 500                 | with    | Glass    |
|  | 30                       | 500<br>(for 90 min) | with    | C        |
| silica gel                                       | 30                       | 500                 | with    | C        |
| $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$ glass   | 0.001<br>(atm. pressure) | 550                 | without | Glass    |
|  | 0.001                    | 600                 | without | L2S      |
|  | 20                       | 500                 | without | Glass    |
|  | 20                       | 500                 | with    | Q+LS     |
|  | 20                       | 550                 | with    | Q+LS     |
|  | 30                       | 550                 | with    | C+Q+LS   |
|  | 30                       | 650                 | with    | C+Q+LS   |
| $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$ glass | 0.001                    | 500                 | with    | Glass    |
|  | 0.001                    | 550                 | with    | Glass    |
|  | 0.001                    | 600                 | with    | LS+L2S   |
|  | 20                       | 500                 | without | Glass    |
|  | 20                       | 500                 | with    | LS+C+Q   |
|  | 20                       | 550                 | without | LS+C+Q   |
|  | 30                       | 500                 | without | LS+C+Q   |

\* L2S; Lithium disilicate ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ )    LS: Lithium metasilicate ( $\text{Li}_2\text{O}\cdot\text{SiO}_2$ )  
 Q: Quartz ( $\text{SiO}_2$ )    C: Coesite ( $\text{SiO}_2$ ).

The results with the  $\text{Li}_2\text{O}\cdot 4\text{SiO}_2$  glass are similar to those for the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass described above: Although the glass did not crystallize up to  $600^\circ\text{C}$  at atmospheric pressure, it crystallized at the temperature as low as  $500^\circ\text{C}$  when the pressure of 20 Kb was applied in the presence of water. The crystals precipitated were the  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  crystal and quartz.

The results with the  $\text{Li}_2\text{O}\cdot 1.5\text{SiO}_2$  were also almost similar to those described above: The  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  and silica crystals (quartz and coesite) precipitated at above 20 Kb and above  $550^\circ\text{C}$  in the absence of water, and at above 20 Kb and above  $500^\circ\text{C}$  in the presence of water. At atmospheric pressure the crystals identified as the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  precipitated barely from  $600^\circ\text{C}$  in the presence of water.

Conversion of silica glass to coesite crystal was found to occur when compressed at 30 Kb at the temperature of  $500^\circ\text{C}$  for 90 min. A run made using silica gel as a starting material showed that it converts to coesite much faster (20 min.) than the silica glass at the same pressure and temperature condition.

### Conversion of High Pressure Phases at Atmospheric Pressure

The mixtures of lithium metasilicate plus coesite and lithium metasilicate plus quartz, which had been obtained by subjecting the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass to  $550^\circ\text{C}$  and 30 Kb and to  $550^\circ\text{C}$  and 10 Kb, respectively in the foregoing experiments, were

Table 3. Changes of high-pressure crystalline phases by heating at atmospheric pressure.

| High pressure phase                                     | Heating             |                     | Result*             |
|---|---------------------|---------------------|---------------------|
|   | Temperature         | Time                |                     |
| $\text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{Coesite}$ | $600^\circ\text{C}$ | 40 hr.              | No change           |
|   | 650                 | 40 hr.              | No change           |
|   | 700                 | 300 min.            | No change           |
|   | 750                 | 300 min.            | LS+Q+C              |
|   | 800                 | 100 min.            | LS+Q+C              |
|   | 850                 | 10 min.             | LS+Q                |
|   | 900                 | 30 min.             | LS+Q+L2S            |
| $\text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{Quartz}$  | 800                 | 100 min.            | No change           |
|   | 850                 | 100 min.            | No change           |
|   | 900                 | 30 min.             | LS+Q+L2S            |
|   | 900                 | 600 min.            | L2S+LS+Q            |
|   | 950                 | 60 min.             | L2S                 |
| Coesite   | 550                 | 40 hr.              | No change           |
|   | 650                 | 60 min.             | No change           |
|   | 750                 | 60 min.             | No change           |
|   | 800                 | 60 min.             | No change           |
|   | 850                 | 60 min.             | No change           |
|   | 900                 | 60 min.             | No change           |
|   | 950                 | 60 min.             | No change           |
|   | 1000                | 60 min.             | Coesite disappeared |
| 1050  | 60 min.             | Coesite disappeared |                     |

\* L2S: Lithium disilicate ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ) LS: Lithium metasilicate ( $\text{Li}_2\text{O}\cdot\text{SiO}_2$ )  
Q: Quartz ( $\text{SiO}_2$ ) C: Coesite ( $\text{SiO}_2$ ).

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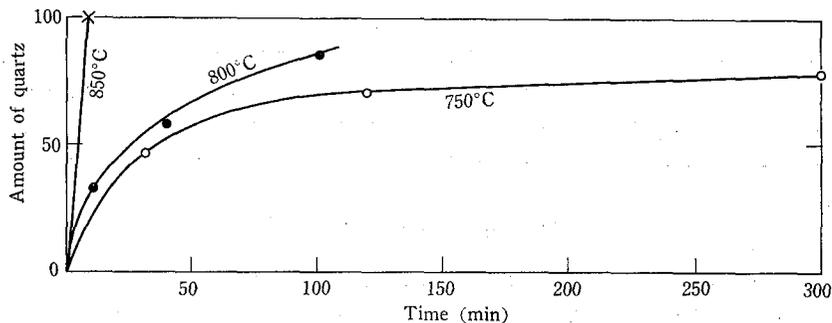


Fig. 3. The conversion,  $\text{Li}_2\text{O}\cdot\text{SiO} + \text{coesite} \rightarrow \text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{quartz}$  at atmospheric pressure.

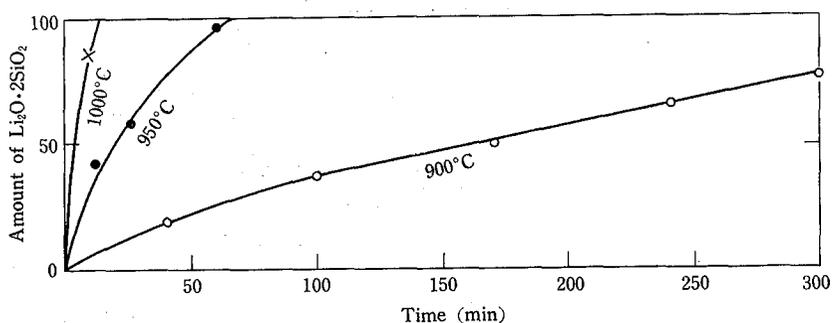


Fig. 4. The conversion,  $\text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{quartz} \rightarrow \text{Li}_2\text{O}\cdot 2\text{SiO}_2$  at atmospheric pressure.

heated in the air (at atmospheric pressure) and at temperatures over  $600^\circ\text{C}$  for various times, and the resulting materials were subjected to the X-ray diffraction analyses. The results are given in Table 3, Fig. 3 and Fig. 4. The same experiment was carried out on the coesite crystals prepared in the foregoing experiment by subjecting the silica glass to 30 Kb and  $500^\circ\text{C}$  for more than 90 min.. Its result is also given in Table 3. Fig. 3 and Fig. 4 show the changes in ratio of the amount of original crystal in the samples e.g., coesite, to that of the converted crystal e.g., quartz, with time at various temperatures. The change in amount of the crystals was determined by measuring the height of the characteristic peaks of the crystals in their X-ray diffraction patterns.

From Table 3 it can be seen that the coesite in the mixture of the  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  crystal plus coesite starts to convert to quartz from  $750^\circ\text{C}$ , completing its conversion at  $850^\circ\text{C}$ . Conversion of coesite alone to quartz, the process of which is also given in Table 3, is sluggish i.e., the coesite remained almost unchanged up to  $950^\circ\text{C}$ . This indicates that the conversion of coesite is facilitated by the presence of lithium metasilicate. The high stability of pure coesite at atmospheric pressure was already reported by Zeto, Dachille and Roy<sup>23</sup>.

The mixture of the  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  crystal plus quartz remained unchanged up to  $850^\circ\text{C}$ , began to convert partly from  $900^\circ\text{C}$  and completely at  $950^\circ\text{C}$  to the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystal.

From Fig. 3 and Fig. 4, the activation energies for the conversions were calculated using an equation,

$$E = K(1/T_1 - 1/T_2)^{-1} \log (r_2/r_1)$$

where  $r$  is the initial rate of conversion obtained approximately from tangents drawn to the conversion-time curves, and  $T$  is the absolute temperature. Their values were 0.9 kcal/mole for  $\text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{coesite} \rightarrow \text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{quartz}$  at 750° to 800°C and 5 kcal/mole for  $\text{Li}_2\text{O}\cdot\text{SiO}_2 + \text{quartz} \rightarrow \text{Li}_2\text{O}\cdot 2\text{SiO}_2$  at 900° to 950°C.

#### IV. SUMMARY AND DISCUSSION

The results of the present experiments may be summarized as shown in Fig. 5 and Fig. 6. Arrows in Fig. 5 given directions of transformation of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition in the given conditions for temperature and pressure. As

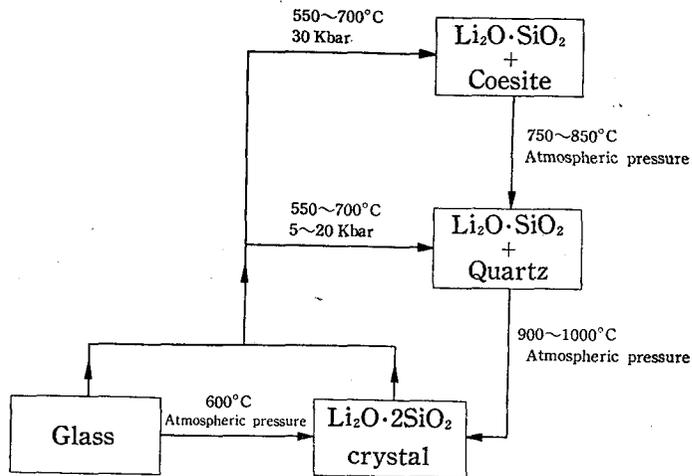


Fig. 5. Crystallization of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass and transformation of the crystallized products.

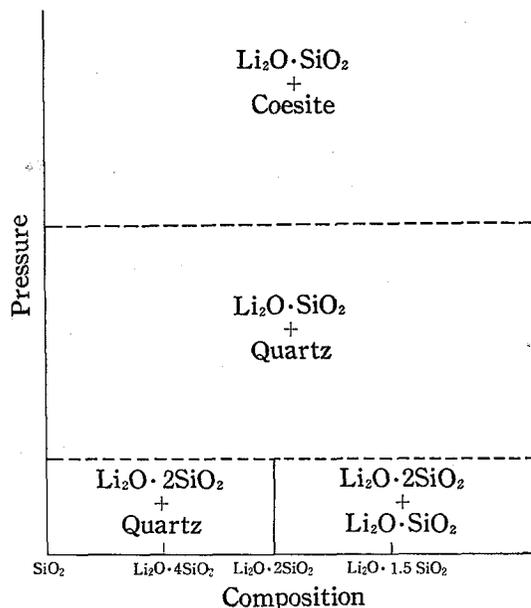


Fig. 6. Tentative diagram for the system  $\text{Li}_2\text{O}\text{-SiO}_2$ .

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shown in both figures, lithium disilicate crystal is not stable at high-pressure and decomposes to lithium metasilicate and silica (quartz or coesite). The higher stability of the mixture, lithium metasilicate and silica, at high-pressure can be explained on the basis of their molar volumes which are listed in Table 4. The phase transformation under high-pressure proceeds in such a direction that the total molar volume of the phase decreases. The transformation,  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2 \rightarrow \text{Li}_2\text{O}\cdot \text{SiO}_2 + \text{quartz}$ , is therefore understandable because the total molar volume decreases from 61.2 to 58.4  $\text{cm}^3$ .

Table 4. Density and molar volume of the crystals.

| Crystal   | Density <sup>9)</sup><br>d(g/cm <sup>3</sup> ) | Molar Volume<br>V=M/d (cm <sup>3</sup> ) |
|---|--|--|
| $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$                        | 2.454  | 61.2                                     |
| $\text{Li}_2\text{O}\cdot \text{SiO}_2$                         | 2.520  | 35.7                                     |
| $\text{SiO}_2$ (Quartz)   | 2.650  | 22.7                                     |
| $\text{Li}_2\text{O}\cdot \text{SiO}_2 + \text{SiO}_2$ (Quartz) |  | 58.4                                     |

The effect of high-pressure in accelerating the crystallization of glass or the phase transformation between two crystals can be explained, if the pressures applied involve a high degree of shear.

As described previously, the pressure apparatus used in the present experiment is of uniaxial type which generates the pressure involving a high degree of shear. The reconstruction of the glass or the crystal structure would be facilitated by the shearing force.

The effect of water in accelerating the crystallization of glass under high-pressure, which was already established with some other glasses by Roy et al, was also found to be noticeable with the glasses investigated in the present work. To its reasoning W. A. Weyl's screening theory<sup>10)</sup> would be feasible to be applied. "The addition of water to a silicate system can best be described as the addition of  $\text{O}^{2-}$  ions which increase its anion to cation ratio and of protons which can move from one  $\text{O}^{2-}$  ion into the electron cloud of the others. By temporarily lowering the anionic charge the proton weakens the binding forces between silicon and oxygen ions:  $\text{Si}^{4+}\text{O}^{2-}\text{Si}^{4+} \xrightarrow{\text{H}^+} \text{Si}^{4+}(\text{OH})^-\text{Si}^{4+}$ " and thus the conversion of glass to crystal would be facilitated.

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