

# Effects of High Pressure on the Properties of Glass

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Glass powders of various compositions were compressed at 10 to 65 kilobars with a simple squeezer type apparatus, and after release of the pressure changes in their refractive index, light absorption spectrum and crystallization tendency on reheating were examined. On the basis of the experimental results, permanent shrinkage of glass in bulk caused by high pressure and its release on reheating, local shrinkage of glass in the neighborhood of transition elements (cobalt ions) or color centers, effects of high pressure on crystallization of glass and effects of high pressure in reducing silver ions in glass were discussed.

## 1. INTRODUCTION

Application of high pressure to glasses consisting of voluminous networks of atoms causes decrease in atomic distance and changes in atomic bond angle, leading to the shrinkage of the glasses in bulk. The glasses expand when the pressure is released, but do not regain their initial volume. The amount of residual shrinkage or permanent shrinkage is known to depend on the method of application of pressure<sup>1,2</sup>: It is larger for specimens pressed with a simple squeezer type apparatus than for those pressed with a piston cylinder type apparatus. Its cause has been attributed to shearing forces produced inevitably together with the hydrostatic forces in the specimens compressed with a simple squeezer type apparatus<sup>3</sup>.

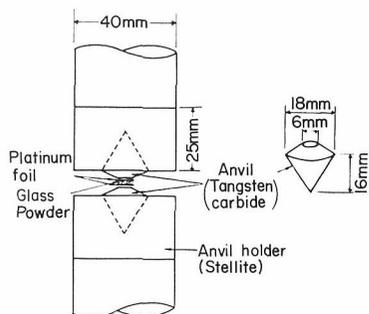
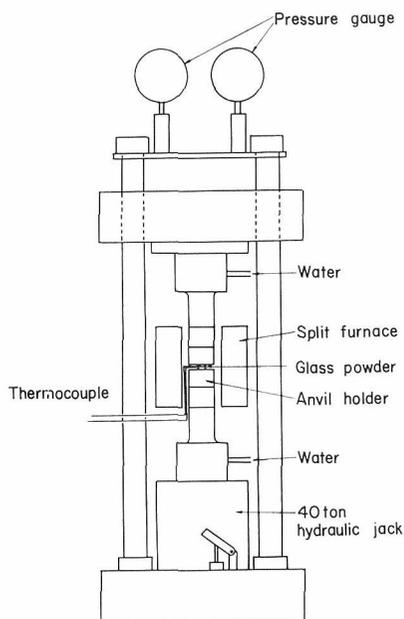
The present article describes results of a series of investigations on some physical behavior of glasses subjected to high pressure produced by a simple squeezer type apparatus.

## 2. HIGH PRESSURE APPARATUS

The apparatus used is the same in principle as that developed by Kennedy<sup>4</sup>. As shown schematically in Fig. 1, it consists of a pair of symmetrically opposed cemented tungsten carbide anvils each embedded in a stellite holder. The glass to be compressed was pulverized into powders of 40 to 80  $\mu$  in diameter. 0.3 gram of the powders were weighed out, wrapped in a 0.02 mm thick platinum foil, being placed between the opposed circular surfaces of 6 mm in diameter of the tungsten carbide anvils. The pressure actually applied to the glass particles depended on the spot where the particles were placed. In order to determine the actual pressure distribution on the surface of the anvils a quartz powder was employed as a pressure calibration substance<sup>1</sup>.

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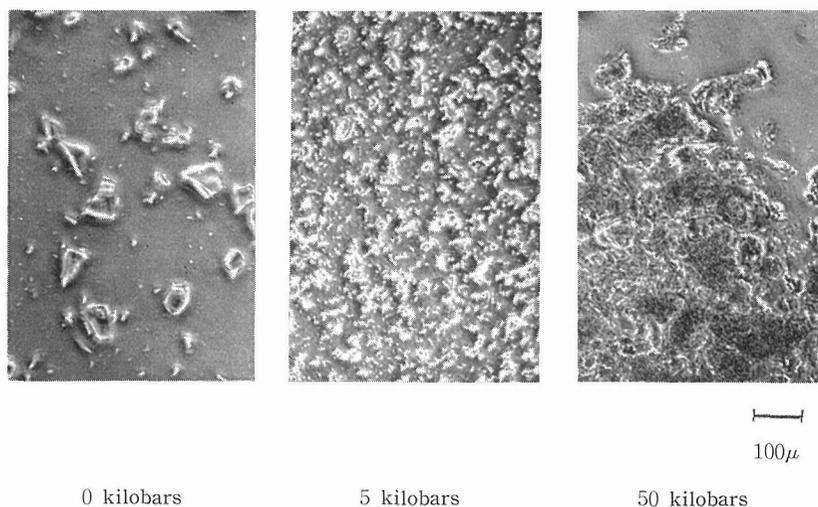
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↑ Fig. 1(b). Schematic figure of high pressure apparatus (cell).

← Fig. 1(a). Schematic figure of high pressure apparatus.

The powdered glass specimens, when subjected to the high pressure, broke into finer particles. The pressure at which their break started was about 5 kilobars, and their size became about  $5\mu$  at 10 kilobars. The break of the particles did not continue by further compression at elevated pressures, but, instead, they began to stick each other, forming thin flakes. The adhesive strength of the glass particles in the flakes was not markedly high but in a degree that their agglomerate could be loosened by soft grinding in an agate mortar. The process of break of the glass particles under elevated pressures is shown by a series of photographs in Fig. 2.



0 kilobars                      5 kilobars                      50 kilobars  
 Fig. 2. Glass particles compressed under various pressures.

### 3. PERMANENT SHRINKAGE CAUSED BY COMPRESSION AND ITS REMOVAL BY HEATING

There are some discrepancies among experimental results reported in the literatures<sup>1,2)</sup> concerning the release of the permanent shrinkage of glass by heating. For example, Cohen and Roy<sup>1)</sup> reported that the silica glass after subjected to a high pressure did not show any change in volume by the subsequent heating at and below 600°C, whereas Mackenzie confirmed later the gradual expansion of the compressed glass at temperatures even below 600°C. Mackenzie used a piston cylinder type apparatus for compressing glass specimens in his experiments to disprove the result of Cohen and Roy instead of using a simple squeezer type apparatus which Cohen and Roy used. The followings are the results of experiments conducted by the present authors, in order to reexamine their results.

The glasses examined were a silica glass and a sodium borosilicate glass of the composition, Na<sub>2</sub>O 7.5, B<sub>2</sub>O<sub>3</sub> 22.5, SiO<sub>2</sub> 70 in weight per cent. They were subjected to the pressure of 30 kilobars at room temperature (25°C) and also at 300°C for various times, and after cooled to room temperature the pressure was released and their refractive indices were measured. Figure 3 shows changes in refractive

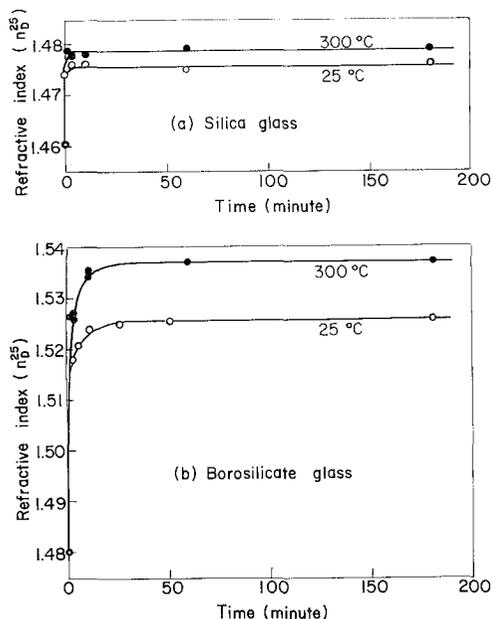


Fig. 3. Increase in refractive of glasses compressed under 30 kilobars for various times.

index with time. The glass specimens compressed at 30 kilobars at room temperature and 300°C respectively for 60 minutes were then reheated under an atmospheric pressure at various temperatures for various times. Their recovery in refractive index with time is shown in Fig. 4.

The reason for having conducted the refractive indices measurements in the present experiments in place of density measurements was that the measurements

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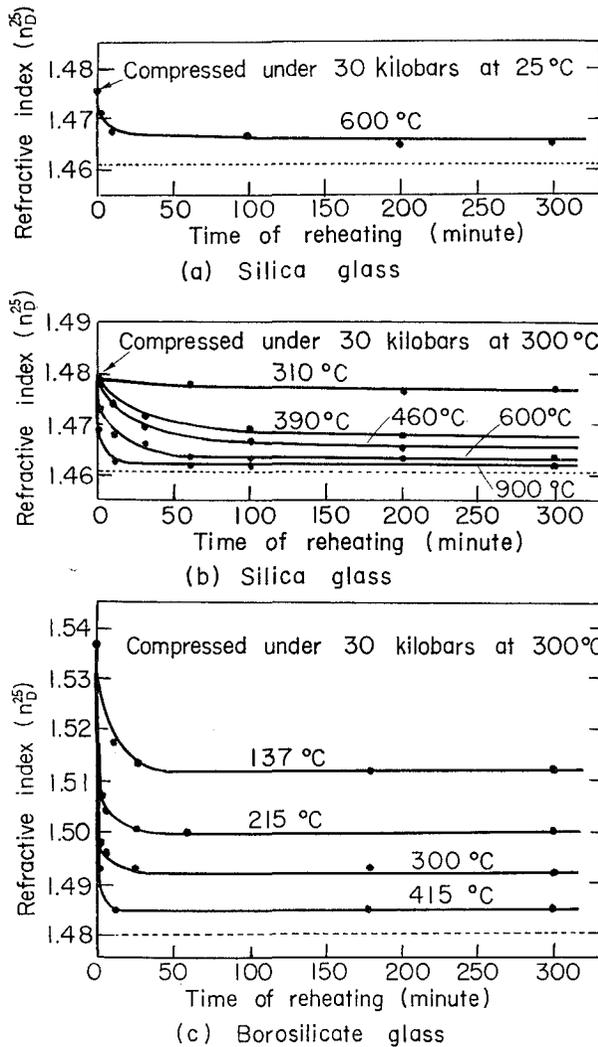


Fig. 4. Recovery in refractive indices of compressed glasses occurred by reheating at various temperatures under atmospheric pressure.

of density of glass specimens appeared to be difficult because they, after compressed, were in the state of agglomerate of fine glass powders involving air bubbles, and in addition the change in refractive index of glass is generally proportional to its density change.

Figure 5 is a schematic figure deduced from Figs. 3 and 4, showing a general tendency of recovery in refractive indices of glasses with times.

Since the changes in refractive index of glass are generally proportional to the changes in its density, the following conclusions can be drawn from the above described experimental results.

(1) The magnitude of the permanent shrinkage of glass reaches, within a short period, to a value determined by the given pressure, temperature and chemical composition of glass.

(2) The rate of release of the permanent shrinkage of glass increases with

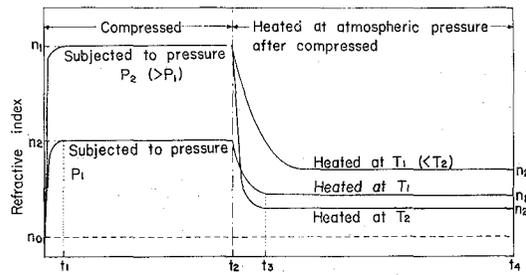


Fig. 5. Schematic representation of changes in refractive indices of glasses caused by application of high pressure and successive annealing.

reheating temperature. However, the complete recovery of its volume to the initial state is difficult even when reheated at high temperatures.

(3) In contrast to the results reported by Cohen and Roy<sup>13</sup>, the release of the permanent shrinkage of silica glass occurs even at 310°C.

#### 4. BULK AND LOCAL SHRINKAGES OF GLASSES SUBJECTED TO HIGH PRESSURE

The bulk permanent shrinkage of glass caused by high pressure can be determined by measuring changes in density or refractive index of glass. The shrinkage of glass, however, does not occur homogeneously throughout its bulk since the structure of glass is heterogeneous in the atomic scale. For example, the local structure around special glass constituent ions or defects such as color centers produced in glass might show a different shrinkage from the bulk shrinkage. The authors have determined the permanent shrinkage of the local structures around transition ions, especially, cobalt ions ( $\text{Co}^{2+}$ ) and also color centers produced in glasses by  $\gamma$ -ray irradiation.

Similar experiments were performed by Tischer and Drickamer<sup>15</sup>, but the local shrinkage they dealt with was not the permanent one remained after the release of compression but that measured while the glass specimens were still under compression.

##### (a) Local Shrinkage around Cobalt Ions

Compositions of glasses melted are given in Table 1. Light absorption spectra of these were measured with a microspectrophotometer (Type MSP-IV A, Olympus Co.) which enabled the use of glass powders or their agglomerate as small as  $50 \mu$  in diameter. As mentioned previously, the glass powders after subjected to the pressure of 55 kilobars were in the form of flakes about  $30 \mu$  in thickness consisting of an agglomerate of glass powders about  $5 \mu$  in diameter. The flakes were then loosened with an agate mortar to about  $50 \mu$  in size and subjected to the microspectrophotometric measurements. In order to eliminate effects of the pressure of air bubbles trapped in the agglomerate of glass powders on its light absorption, the glass powders of the same composition but without addition of  $\text{Co}^{2+}$  ions were prepared, compressed under the same conditions and used as a standard for comparison in the spectrophotometric measurements. Changes in absorption spectrum caused by compression measured for the glasses of the compositions  $\text{K}_2\text{O} \cdot 3\text{B}_2\text{O}_3$  and  $\text{K}_2\text{O} \cdot 9\text{B}_2\text{O}_3$  in mole ratio are shown in Figs. 6 and 7, respectively. Figure 6

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Table 1. Composition of Glasses.

Component	Silicate* glass	$K_2O \cdot 3 B_2O_3$ glass	$K_2O \cdot 9 B_2O_3$ glass
	Mole %	Mole %	Mole %
SiO <sub>2</sub>	72.0	—	—
Na <sub>2</sub> O	13.9	—	—
K <sub>2</sub> O	1.54	25.0	10.0
CaO	10.2	—	—
B <sub>2</sub> O <sub>3</sub>	1.33	75.0	90.0
Sb <sub>2</sub> O <sub>3</sub>	0.25	—	—
	wt. %	wt. %	wt. %
CoO	2.0	2.0	5.0

\* Corresponding to optical silicate glass.  
(Bureau of Standards 523/586)

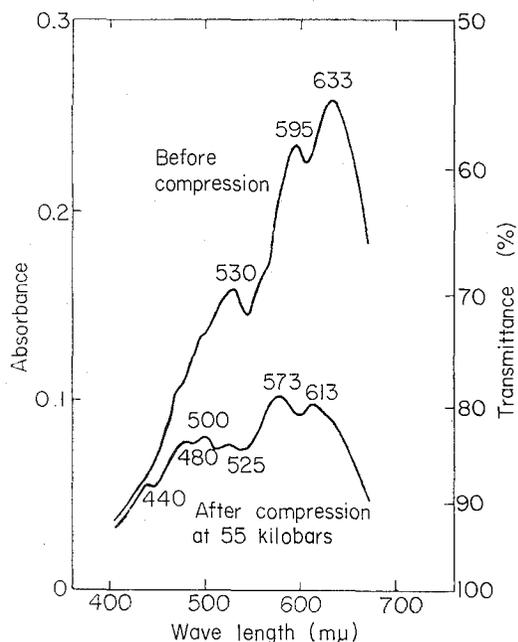


Fig. 6. Effects of high pressure on the spectra of  $Co^{2+}$  ions in a  $K_2O \cdot 3B_2O_3$  glass.

indicates that all three peaks at 530, 595 and 633  $m\mu$ , which are due to the  $Co^{2+}$  ions with fourfold coordinated oxygens, shift by 20 to 30  $m\mu$  to shorter wave length. More important was appearance of new three peaks at 440, 480 and 525  $m\mu$ , which were reported in the literature to be due to the  $Co^{2+}$  ions with sixfold coordinated oxygens<sup>9</sup>. This could be explained by assuming that a change in number of oxygens coordinated around  $Co^{2+}$  ions from four to six is caused by the high pressures. A possibility of such a change was already pointed out by Weyl *et al.* for a glass containing  $Ni^{2+}$  ions on the basis of the qualitative work by Förland<sup>10</sup>.

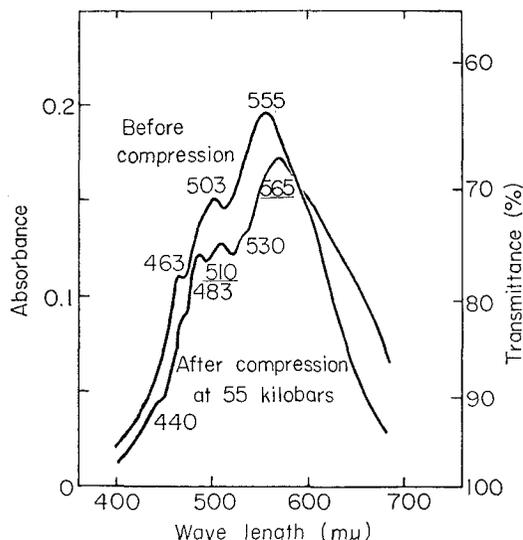


Fig. 7. Effects of high pressure on the spectra of  $\text{Co}^{2+}$  ions in a  $\text{K}_2\text{O}\cdot 9\text{B}_2\text{O}_3$  glass.

The  $\text{K}_2\text{O}\cdot 9\text{B}_2\text{O}_3$  glass is more basic than the  $\text{K}_2\text{O}\cdot 3\text{B}_2\text{O}_3$  glass and in such a glass the coordination number of oxygens around  $\text{Co}^{2+}$  ions are normally six<sup>6)</sup>. Three peaks at 463, 503 and 555  $\text{m}\mu$  observed in Fig. 7 for the  $\text{K}_2\text{O}\cdot 9\text{B}_2\text{O}_3$  glass before compression are due to such  $\text{Co}^{2+}$  ions. Similar to the case for the  $\text{K}_2\text{O}\cdot 3\text{B}_2\text{O}_3$  glass, these peaks shifted by about 30  $\text{m}\mu$  to shorter wave length by application of the high pressure (463 $\text{m}\mu \rightarrow 440\text{m}\mu$ , 503 $\text{m}\mu \rightarrow 483\text{m}\mu$ , and 555 $\text{m}\mu \rightarrow 530\text{m}\mu$ ).

Besides these shifts, new two peaks appeared at 510 and 565  $\text{m}\mu$  by application of high pressure. These are probably due to the elevation of symmetry in configuration of electrons around  $\text{Co}^{2+}$  ions caused by compression.

The shift of absorption peaks to shorter wave length is due to the change in energy level of 3d-electrons of  $\text{Co}^{2+}$  ions by compression. According to the Ligand Field Theory<sup>6)</sup>, changes in intensity of the coordination field created by  $\text{O}^{2-}$  ions coordinated around the  $\text{Co}^{2+}$  ions can be calculated from changes in the above described energy level. Furthermore, the ligand field parameter ' $Dq$ ' has the following relationship with the ionic distance ' $R$ ' between the center ion ( $\text{Co}^{2+}$  ion) and its coordinated ion ( $\text{O}^{2-}$  ion)

$$Dq \propto 1/R^5$$

Consequently, a change in local volume (local shrinkage) around the  $\text{Co}^{2+}$  ions in glass can be determined by measuring the shift in position of the absorption peaks caused by the high pressure.

A change in bulk volume of glass (bulk shrinkage) caused by compression can be determined by measuring a change in refractive index of glass using the Lorentz-Lorenz equation

$$d = [(n^2 - 1) / (n^2 + 2)] \cdot (M/R)$$

where  $d$  is the density of glass,  $n$ , the refractive index,  $M$ , the molecular weight, and  $R$ , the molecular refraction. The value of  $R$  should change by the compression of glass, but, according to the data reported by Cohen and Roy on silicate

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glass<sup>8)</sup>, its actual change is only about 3 per cent, being considered to be negligible in calculation of  $d$ . The bulk shrinkage of glass ( $\Delta v_b/v_b$ ) and the local shrinkage in the neighborhood of the  $\text{Co}^{2+}$  ions ( $\Delta v_l/v_l$ ) in glass are listed in Table 2.

Table 2. Comparison between Bulk and Local Shrinkages of Glasses Subjected to High Pressure of 55 Kilobars.

Glass	Bulk shrinkage ( $\Delta v_b/v_b$ )	Local shrinkage ( $\Delta v_l/v_l$ )
Silicate glass	0.021-0.050	0.005
$\text{K}_2\text{O}\cdot 3 \text{B}_2\text{O}_3$ glass	0.035-0.067	0.073
$\text{K}_2\text{O}\cdot 9 \text{B}_2\text{O}_3$ glass	0.030-0.062	0.078

The data shown above denote the shrinkages remained in glasses after the high pressure was released.

In the table, two values are given for bulk shrinkage; the left ones were obtained by assuming that molecular refraction of glasses does not change by their compression, whereas the right ones were obtained by assuming that its change is about 3 per cent. The table indicates that the bulk shrinkage is generally almost the same as that of the local shrinkage for the potassium borate glasses whereas the bulk shrinkage is much bigger than the local shrinkage for the silicate glass. Such comparisons, if be made further on various types of glasses, would bring valuable informations on their microstructures.

(b) Local Shrinkage in the Neighborhood of the Color Centers Produced in Glasses

Color centers similar to F-center, V-center etc., produced in  $\gamma$ -ray irradiated KCl crystal can also be produced in glasses by irradiating with  $\gamma$ -ray. The glass specimens of the compositions, 20  $\text{R}_2\text{O}$ , 10 BaO and 70 mole per cent  $\text{SiO}_2$  ( $\text{R}_2\text{O}$ ;  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ), were exposed to  $\gamma$ -ray of  $1 \times 10^7$  roentgen at room temperature using a Cobalt-60 irradiator, and then subjected to the high pressure of 50 kilobars at room temperature. Light absorption spectra measured of the glass specimens before and after compression are shown in Fig. 8. For each spectrum, a left peak

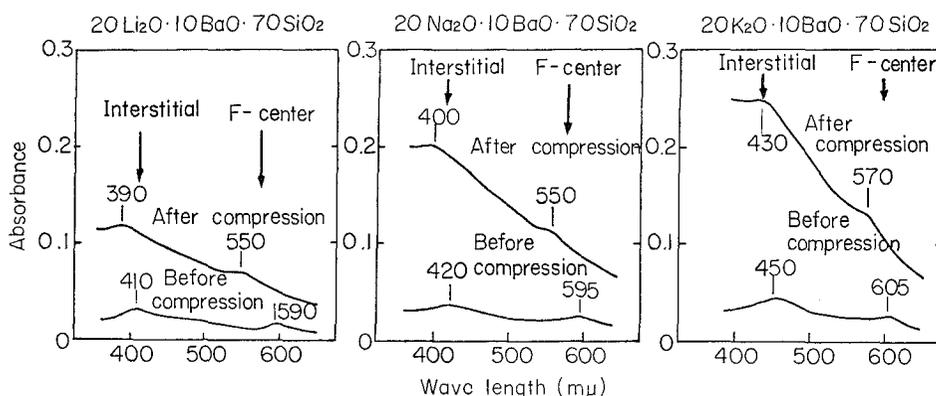


Fig. 8. Absorption spectra of  $\gamma$ -ray irradiated glasses before and after compression.

Exposure dose ;  $1 \times 10^7$  roentgen  
Pressure applied ; 50 kilobars

is the one due to the color center consisting of interstitial alkali ions associated with a trapped electron, and a right peak is the one due to the F-like color center<sup>9)</sup>.

Figure 8 indicates that, (1) for all compositions, the both peaks shift to shorter wave length by the compression of glass, and (2) the absorption spectra of all glasses rise broadly but especially markedly in short wave lengths by the compression of glass and this tendency is greater for the glasses containing alkali ions with a larger radius.

Shrinkage of the local structure in the neighborhood of a color centers in simple alkali halides subjected to compression can be calculated from the shift of their absorption peaks by the following formula

$$\nu \propto 1/A^2$$

where  $\nu$  is the frequency corresponding to the position of the peak of the color centers and  $A$  is a lattice constant of their structure<sup>10)</sup>. By assuming that this relation also holds approximately for the glasses investigated, the local shrinkage of the structures in the neighborhood of the color centers in the glasses could be determined. Their values obtained are listed in Table 3 together with the data

Table 3. Comparison between Bulk and Local Shrinkage of Glasses subjected to High Pressure of 50 Kilobars.

Glass	Bulk Shrinkage	Local shrinkage
Interstitial center		
Li <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.041	0.074
Na <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.025	0.075
K <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.014	0.074
F-like center		
Li <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.041	0.124
Na <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.025	0.111
K <sub>2</sub> O·BaO·SiO <sub>2</sub>	0.014	0.095

for the bulk shrinkage of the glasses obtained from the measurements of their refractive indices before and after compression. From the data given in Table 3, it can be seen that (1) the shrinkage of the F-like center with an oxygen vacancy is larger than that of the glass in bulk, (2) the shrinkage of the color center with an interstitial alkali ions is smaller than that of the F-like center, and (3) the bulk shrinkage is the smallest for the glass composed of a glass former network stuffed with the largest alkali ions, that is, the bulk shrinkage of the 20 K<sub>2</sub>O, 10 BaO and 70 mole per cent SiO<sub>2</sub> glass is the smallest.

Besides the shift of the absorption peaks due to the color centers in glasses, the broad rise of the absorption spectra over the region of short wave length was observed for all of the compositions as mentioned previously.

When the glass once subjected to the  $\gamma$ -ray irradiation and the high pressure was reheated, its absorption decreased as the temperature was raised. Figure 9 shows its process. It should be noticed that the small absorption peaks at 430 and

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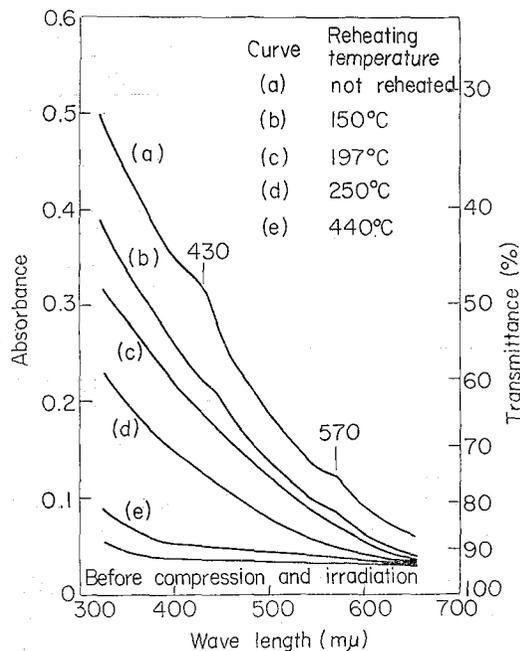


Fig. 9. Effects of reheating on the absorption spectrum of the glass once subjected to high pressure and  $\gamma$ -ray irradiation.

Glass specimen ;  $20 \text{ K}_2\text{O} \cdot 10 \text{ BaO} \cdot 70 \text{ SiO}_2$

Exposure does ;  $1 \times 10^7$  roentgen

Pressure applied ; 50 kilobars.

570  $m\mu$  due to the color centers in the glass disappeared already below about 200°C whereas the big and broad absorption over the region of short wave length remained at much higher temperatures.

The structure which causes the big and broad absorption remains obscure. It would be some type of defective structure accompanied with trapped electrons being much more stable than the color centers in the glass.

### 5. EFFECTS OF HIGH PRESSURE ON CRYSTALLIZATION OF GLASSES

Recently it has been confirmed by Blinov and Roy<sup>11)</sup> that crystallization of glasses during heating is enhanced by the application of high pressure, especially in the presence of water vapor. The present authors have investigated effects of high pressure on the kind of crystals formed in glasses.

The glasses investigated were lithium silicate glasses of the compositions,  $\text{Li}_2\text{O} \cdot n\text{SiO}_2$  in mole ratio where  $n=1.5, 2,$  and  $4$  whose crystallization behaviors under the atmospheric pressure were already well investigated by some workers<sup>12)</sup>. The glass powders were heated at various temperatures under various pressures, and after the powders were cooled to room temperature they were subjected to the X-ray diffraction analysis for identification of the crystals separated out in the glasses.

The results with the  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass are summarized in Fig. 10. This glass, when heated under an atmospheric pressure, started to crystallize homogeneously

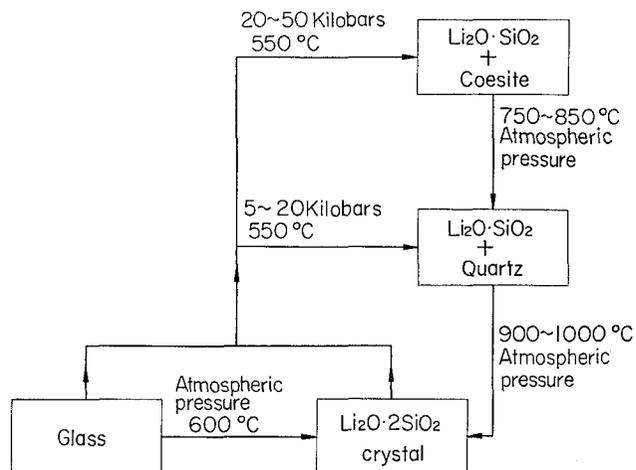


Fig. 10 Crystallization of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass and transformation of the crystallized products.

from about 600°C to give lithium disilicate ( $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ ) crystal. When heated under the pressure of 5 to 20 kilobars, however, the glass started to crystallize from 550 °C and the crystals separated out were lithium metasilicate ( $\text{Li}_2\text{O}\cdot \text{SiO}_2$ ) crystal and quartz. Under the high pressures, that is 20 to 50 kilobars, coesite crystals were separated out together with the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal in place of quartz. When the glass in which the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal and coesite were present was heated up to higher temperatures, that is 750° to 850°C, but under the atmospheric pressure, the coesite in the glass converted to the quartz at 750° to 850°C. At 900° to 1000 °C, the quartz thus formed converted with the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal to the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystal.

Similar experiments were carried out with the other lithium silicate glasses of various silica contents. Figure 11 is a schematic representation of the pressure versus composition relationship for the lithium silicate glasses derived from the results of the present experiments. As is shown in Fig. 11, the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal can be formed even in the glasses of the silica contents over 2 mole when the glasses are heated under high pressure. A reason why the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal are formed with the quartz in these glasses in place of a mixture of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystal and quartz under the high pressure is probably that a sum of the molecular volume of the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  and  $\text{SiO}_2$  crystals ( $35.7+22.7=58.4$ ) is smaller than the molecular volume of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  (61.2), and consequently the formation of the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  and  $\text{SiO}_2$  crystals is more favorable under high pressure.

In the present experiments, it was also ascertained that the crystallization of glasses under high pressure are markedly accelerated by the presence of water. For example, powders of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  glass did not show any crystallization when heated in dry state at 500°C under 30 kilobars whereas powders of the same glass, when wetted with water, started to crystallize at 500°C even under 20 kilobars to give the  $\text{Li}_2\text{O}\cdot \text{SiO}_2$  crystal and quartz. The similar effect of water is often observed in accelerating the material transport in silicate glasses. For its explanation, Weyl and Marboe<sup>13)</sup> used a concept that the screening of the  $\text{Si}^{4+}$  ions in the glasses is improved by the addition of water, that is, the addition of

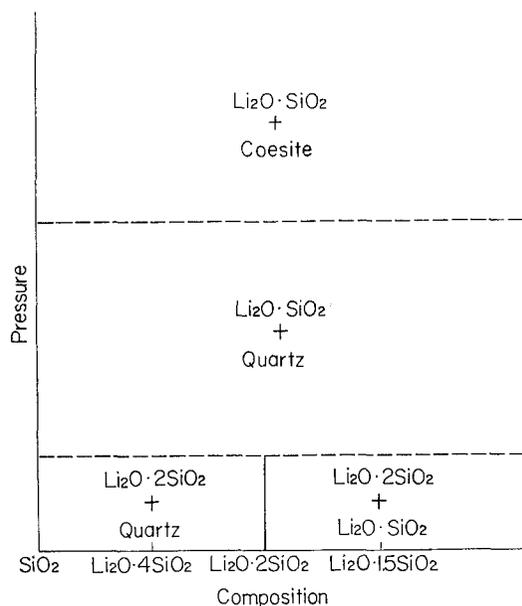


Fig. 11. Pressure versus composition relationship for the lithium silicate glasses.

the  $O^{2-}$  ions of water increases the coordination numbers of the  $O^{2-}$  ions around the  $Si^{4+}$  ions, thus making ease the movement of the  $Si^{4+}$  ions in the glass structure. This concept would also be applicable to the explanation of the effect of water in accelerating the crystallization of glasses under high pressures.

## 6. REDUCTION OF IONS IN GLASSES SUBJECTED TO HIGH PRESSURE

Silver ions in glasses can be reduced to metallic colloids by a combination of the high energy irradiation and the subsequent heat-treatment. The authors have found that a combination of the application of high pressure and the subsequent heat-treatment also has a marked effect in reducing these ions. Figure 12 shows absorption spectra obtained for the glass of the composition, 15  $K_2O$ , 10  $BaO$ , 75  $SiO_2$  and 0.45  $Ag_2O$  in mole ratio, first compressed at various high pressure for 30 minutes and then heat-treated at  $500^\circ C$  for 30 minutes. An absorption peak observed at  $415m\mu$  in each of the spectra is the same as that reported in the literature as being due to the metallic silver colloids of about  $30m\mu$  in diameter formed in glasses subjected to high energy irradiation and the subsequent heat-treatment. A curve marked with '0' was obtained for the specimen subjected only to the heat-treatment but not to any high pressure. The results shown in Fig. 12 indicate that the amount of the metallic colloids increases with increasing pressure applied.

Figure 13 shows the results of experiments made for the glasses, first irradiated with  $\gamma$ -ray of  $1 \times 10^7$  roentgen, then compressed at various pressures and finally heat-treated at  $500^\circ C$  for 30 minutes. The composition of glass is the same as that previously used but with no addition of cerium oxide, that is, 15  $K_2O$ , 10  $BaO$ , 75  $SiO_2$ , 0.45  $Ag_2O$  and 0.03  $CeO_2$  in mole ratio. A curve marked with '0' was obtained for the glass specimen subjected only to the  $\gamma$ -ray irradiation and the

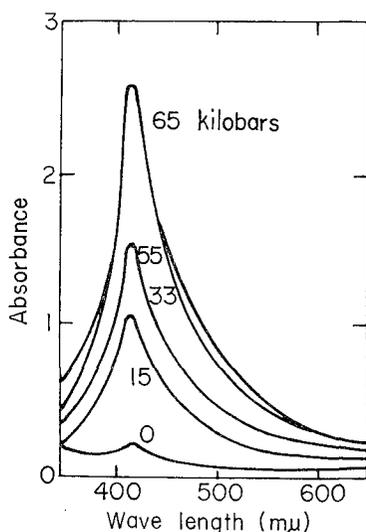


Fig. 12. Spectra of the 15 K<sub>2</sub>O, 10 BaO, 75 SiO<sub>2</sub> and 0.45 Ag<sub>2</sub>O in mole ratio glass, first compressed at various pressures and then heated at 500°C for 30 minutes.

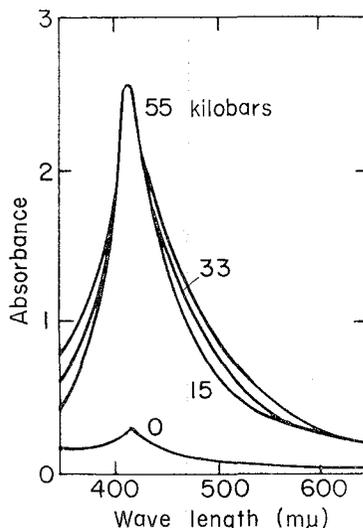


Fig. 13. Spectra of the 15 K<sub>2</sub>O, 10 BaO, 75 SiO<sub>2</sub>, 0.45 Ag<sub>2</sub>O and 0.03 Ce<sub>2</sub>O<sub>3</sub> in mole ratio glass, first irradiated with  $\gamma$ -ray of  $1 \times 10^7$  roentgen, then compressed at various pressures and finally heated at 500°C for 30 minutes.

heat-treatment but not to any high pressure. A big difference between the two results obtained for the glasses with and without cerium oxide was that for the glass with cerium oxide an application of the pressure as low as 15 kilobars was enough to bring its absorption peak to a saturated level.

The role of high pressure in accelerating the formation of silver colloids in glass may be explained in terms of contraction of the distance between the silver ions and the surrounding oxygen ions, which facilitates the transfer of the electrons of oxygens to the silver ions at the elevated temperatures. In case when the cerium ions are present in glass, the 4f-electrons of the Ce<sup>3+</sup> ions are captured by the silver ions. Since these electrons can be liberated from the parent ions much easier than the electrons of the oxygen ions, application of the pressure as low as 15 kilobars is satisfactory to bring the absorption spectrum of the glass to the saturated level.

Figure 14 shows changes in absorption spectrum of the above described non-cerium oxide glass when compressed at 55 kilobars at room temperature, then heated at 500°C for 30 minutes and finally compressed again at 55 kilobars at room temperature. It should be noticed that the peak characteristic of metallic silver colloids in glass became lower and broader by the final compression.

Figure 15 shows the results of the experiment in which the order of compression and heating of the glass was changed, that is, the glass was first heated at 500°C for 30 minutes, then, after cooled to room temperature, compressed at 55 kilobars and finally heated at 500°C for 30 minutes.

In Figure 16 are shown replica electron micrographs of the surfaces of the two glass specimens above described etched with hydrofluoric acid, that is, the one compressed and then heated, and the other heated and then compressed, corre-

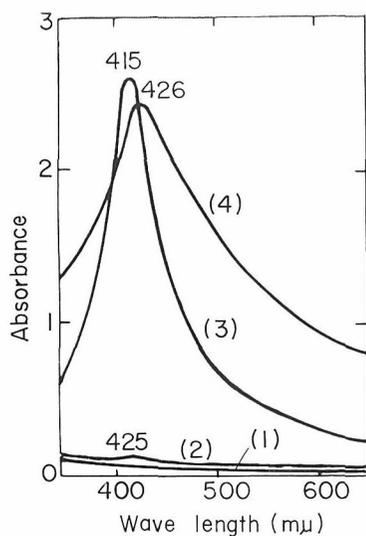


Fig. 14. Spectra of the 15 K<sub>2</sub>O, 10 BaO, 75 SiO<sub>2</sub> and 0.45 Ag<sub>2</sub>O in mole ratio glass, before treatment (1), first compressed at 55 kilobars (2), then heated at 500°C for 30 minutes (3), and finally compressed again at 55 kilobars (4).

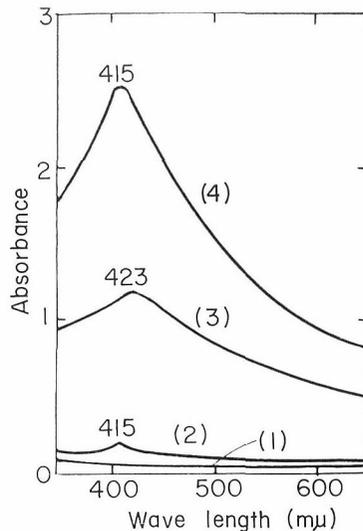
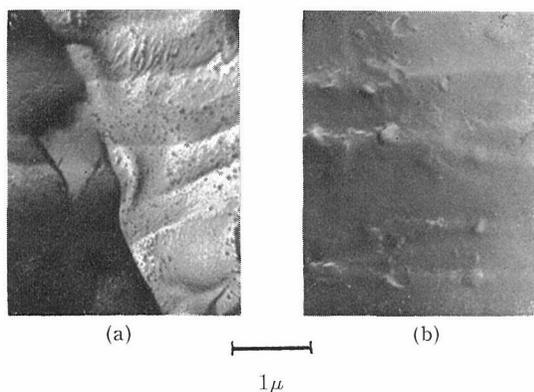


Fig. 15. Spectra of the 15 K<sub>2</sub>O, 10 BaO, 75 SiO<sub>2</sub> and 0.45 Ag<sub>2</sub>O in mole ratio glass, before treatment (1), first heat-treated at 500°C for 30 minutes (2), then compressed at 55 kilobars (3), and finally heated again at 500°C for 30 minutes (4).

sponding to the specimens for the curve (3) in Fig. 14 and the curve (3) in Fig. 15, respectively. Many, small black particles of less than  $0.05\ \mu$  in diameter observed on the surface of the glass specimen compressed and then heated ((a) in Fig. 16) are probably silver colloids remained after the hydrofluoric acid etching. On the surface of the glass specimen heated and then compressed, ((b) in Fig. 16) black particles are also observed, but their size is much larger, that is, about  $0.2\ \mu$  in diameter and their number is smaller. These results are consistent with the shape of absorption peaks of the glasses measured in the previous experiments; that is, the glass containing silver colloids of smaller size showed the sharp abs-



(a) Heated after compressed. Etched with 0.1% HF solution for 30 minutes.  
 (b) Compressed after heated. Etched with 0.1% HF solution for 5 minutes.

Fig. 16. Replica electronmicrographs of silver colloids on the surface of glass particles.

orption peak, whereas those containing the colloids of larger size showed the broad absorption peak.

The mechanism of formation of the large silver colloids remains unexplained. At present the authors consider it as follows. The silver ions in the glass are reduced to the atomic state or the likes by the first heat-treatment and, then, are squeezed out to the surface of the glass specimen or to defective structures in the glass produced by compression, where they agglomerate, resulting in the formation of the large metallic silver colloids as confirmed with the electron microscope.

## 7. SUMMARY

Glass powders of various compositions were compressed at 10 to 65 kilobars with a simple squeezer apparatus, and after release of the pressure changes in their physical properties were examined. The main results obtained can be summarized as follows.

(1) The permanent shrinkage of silica glass produced by the compression is released by reheating even at 310°C.

(2) The shrinkage, caused by the compression, of the local glass structure around special glass constituent ions (cobalt ions) or defects such as color centers, can be determined from the shift of position of light absorption peaks characteristic for these ions and centers.

(3) The compression facilitates the formation of  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  crystal in the glass of the  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition in place of the formation of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystal.

(4) The compression accelerates the reduction of silver ions to metallic silver colloids in glass.

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