BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1676—1680 (1973)

The Internal Friction of Glasses Containing Alkali under an Electric Field

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(Received May 31, 1972)

The change of the internal friction of sodium silicate and sodium borate glasses under an electric field was studied by means of a torsion pendulum technique. It was found that the internal friction increased under an electric field and that the increase was related to the numbers of vibration, the strength of the electric field, and the Na_2O content. The increase in internal friction in the glasses with a high Na_2O content was large because of the electrolysis of the glasses, which resulted in the removal of sodium ions. It was proposed that the internal friction increased because the removal of sodium ions was promoted by torsional oscillation under an electric field and that the deformation of the network took place around holes which were left behind by the removal of the sodium ions.

In an experiment with a glass containing alkali, an internal friction peak caused by the diffusion of sodium ions has been observed near room temperature over a period of the order of seconds.[1,2] When an alternating voltage is applied to a glass containing alkali, an electric loss with an activation energy and relaxation time almost the same as those of the internal friction has been observed.[3] In this case, alkali ions under electric stress move back and forth through the network structure of a glass. When an electric field is applied to a glass, an absorption current appears first, and then a constant current flows. The former causes polarization in a glass. The latter is due to ionic conduction. Alkali ions move to the cathode side under an electric field, some of them, however, stop within the network. Though alkali ions are forced to move within a glass by external force, their movement is controlled by the glass network structures. It is interesting to study the combined effect of electric and mechanical forces on glasses.

In Copley's experiment, an electric field was applied between the center and the surface of a glass bar sample and electrolysis was carried out for a constant time at 250 °C.[4] We are, however, interested in the polarization phenomenon, so we measured the internal friction by applying an electric field between the two ends of a glass bar sample.

Experimental

The apparatus used in this work is almost the same as Forry's except that a torsion pendulum is hung by means

1) J. V. Fitzgerald, *J. Amer. Ceram. Soc.*, **34**, 339 (1951).
2) L. C. Hoffman and W. A. Weyl, *Glass Ind.*, **38**, 81 (1957).
3) H. E. Taylor, *J. Soc. Glass Technol.*, **41**, 350 (1957); **43**, 124 (1959).
4) G. J. Copley, *J. Amer. Ceram. Soc.*, **51**, 667 (1968).

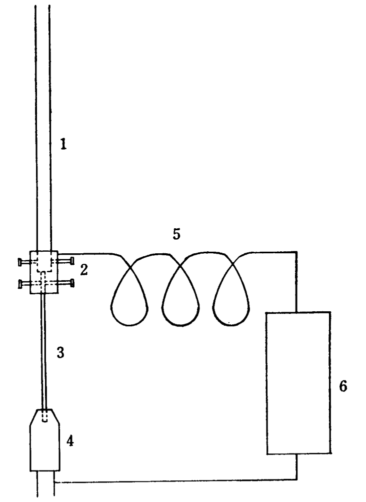

Fig. 1. Schema of a sample holder.
1: Pyrex tube, 2: Connector, 3: Sample, 4: Chuck, 5: Copper wire, 6: Voltage generator.

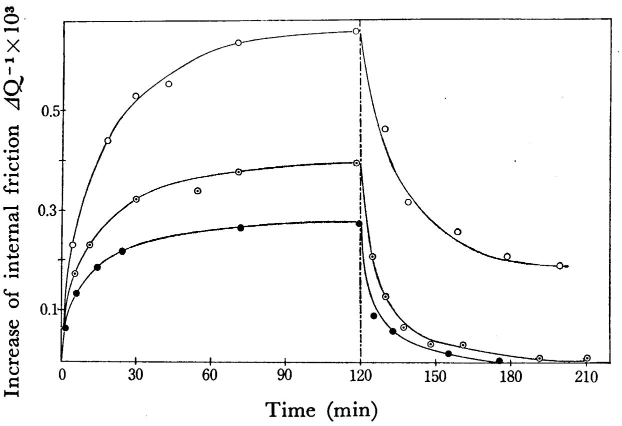

Fig. 2. Increase and decrease of internal friction as a function of time for the system SiO_2-Na_2O glasses under an electric field (3000 V/cm) and those after the removal of electric field. Period is 0.4 Hz and temperature 18± 0.1 °C.

○: Na_2O 40 mol%, ⊙: Na_2O 35 mol%,
●: Na_2O 30 mol%

of a nylon string.[5-7] The influence from the twist of the string was minimized by using a long string (45 cm). Other advantages of hanging it with a nylon string are that the tension to a sample becomes smaller and the frequency of vibration can be easily varied as much as tenfold for the same sample.

The chuck holding a sample was insulated from metal parts by means of a Pyrex tube, as is shown in Fig. 1, lest an unnecessary vibration should be raised by coulombic force. A sample was connected with such thin copper wire lead (0.075 mm in diameter) that it affected nothing.

The glasses used were systems of SiO_2–Na_2O and B_2O_3–Na_2O. Each sample was about 1.5 mm in diameter and 30 mm in length. Since these glasses are hygroscopic and are apt to cause surface conduction, a drying box with silca gel was used, keeping the humidity low (below 10%).

Hot water within a plastic vessel was used instead of an electric furnace to raise the temperature. Below 0 °C,

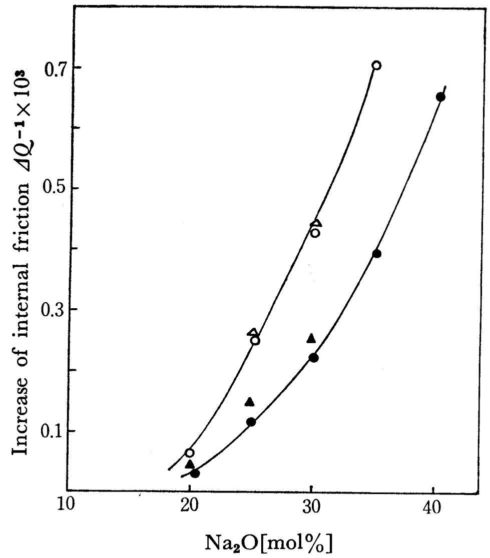

Fig. 3. ΔQ^{-1} value versus Na_2O content after an electric field (3000 V/cm) was applied for two hours. Period is 0.4 Hz and temperature 18±0 1 °C. Relative humidity is above 50% in atmosphere and below 10% in a drying box.

●: Silicate glasses in a drying box
○: Silicate glasses in atmosphere
▲: Borate glasses in a drying box
△: Borate glasses in atmosphere

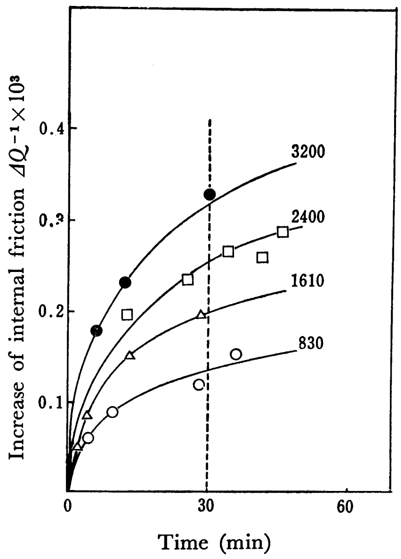

Fig. 4. Increase of internal friction as a function of electric field strength for 0.35 Na_2O+0.65 SiO_2 glasses Period is 0.4 Hz.

○: 830 V/cm, △: 1610 V/cm, □: 2400 V/cm,
●: 3200 V/cm.

even a very little moisture was frozen, electrified, and stuck on the surface of a sample, so the temperature range was limited to from 0 to 40 °C.

Results

The internal friction at a constant temperature and a constant voltage under continuous torsional oscillation increased gradually with the time finally reaching a constant value, as is shown in Fig. 2. ΔQ^{-1} is the difference between the internal friction under

5) K. E. Forry, *ibid.*, **40**, 90 (1957).
6) J. V. Fitzgerald, *ibid.*, **34**, 314 (1951).
7) G. J. Copley, *Phys. Chem. Glasses*, **8**, 38 (1967).

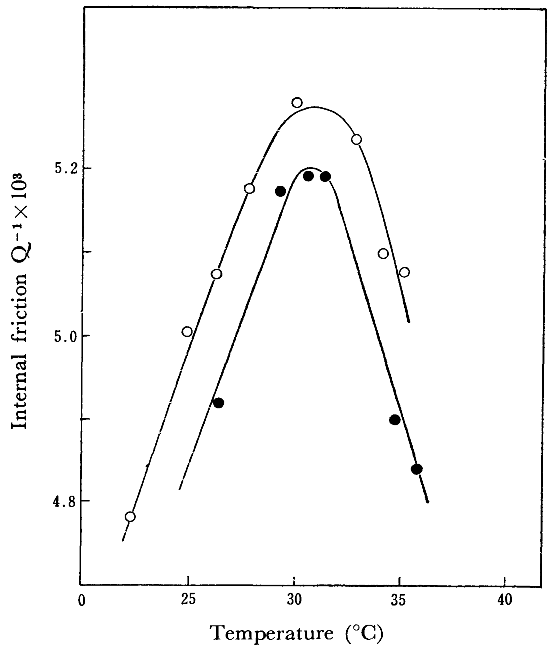

Fig. 5. Influence of electric field on the peak of internal friction for a 0.25 Na_2O+0.75 B_2O_3 glass at 0.4 Hz.
○: under an electric field (2700 V/cm)
●: after removal of an electric field

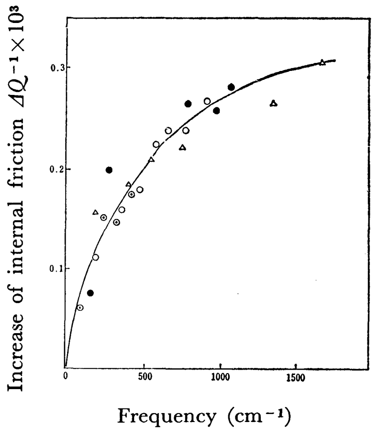

Fig. 6. Relationship between the increase of internal friction and numbers of vibration for a 0.35 Na_2O+0.65 SiO_2 glass at 18 °C. Electric field applied is 2700 V/cm.
○: 0.14 Hz, ⊙: 0.17 Hz, ●: 0.41 Hz, △: 0.69 Hz.

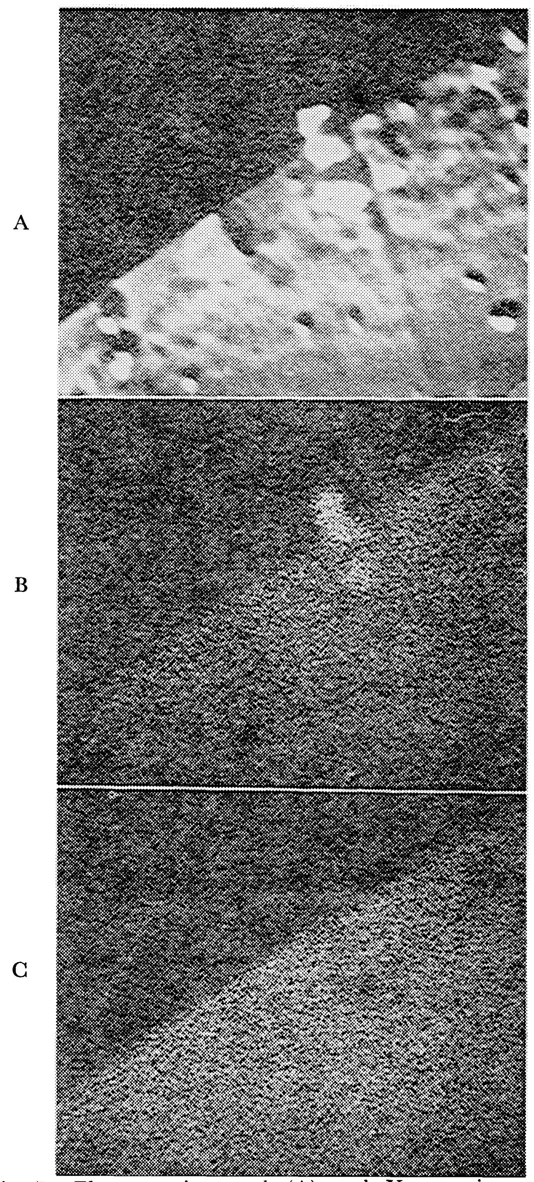

Fig. 7. Electron micrograph (A) and X-ray microanalysis by NaK_α (B) and Si-k_α (C) on the surface of a cut-edge of a 0.40 Na_2O+0.60 SiO_2 glass bar sample near cathode after an electric field was applied for a while. In B some sodium product can be seen at the edge of the surface but in C it can not be seen. Magnification is 1080.

the electric field and that without the electric field. When it reached a constant value, the electric field was removed. The ΔQ^{-1} value decreased gradually and approached zero under continuous torsional oscillation. The internal friction under an electric field was found to increase as the concentration of the sodium ion in a glass increased. The change in internal friction for the 0.4 Na_2O+0.6 SiO_2 glass was especially large, and the ΔQ^{-1} value did not return to zero after the removal of the electric field. This indicates that some irreversible change occurred in the sample.

Figure 3 shows the change in the internal friction versus the Na_2O content. There was little difference between the curves for the SiO_2–Na_2O and B_2O_3–Na_2O systems. Their curves were nearly parabolical. The internal friction, as measured in a drying box, was generally smaller than that in an ordinary room. The increase in internal friction was in proportion to the strength of the electric field. For instance, the ΔQ^{-1} values after the electric field was applied for 30 minutes were found to be proportional to the electric field in the range from 8×10^2 to 32×10^2 V/cm, as is shown in Fig. 4. The electric field had little influence on the peak position, but the background became higher than that obtained without an electric field, as is shown in Fig. 5.

When the ΔQ^{-1} values for various periods were plotted as a function of the numbers of vibration, it was found that the period had no influence, but that the numbers of vibration did influence the change in internal friction, as is shown in Fig. 6.

When a 0.4 Na_2O+0.6 SiO_2 glass was measured, a part of the sample near the chuck on the cathode clouded and then cracked before long. This is probably because of the presence of product obtained through electrolysis (see Fig. 7). This seems to be the reason why the curve of the internal friction for the 0.4 Na_2O+0.6 SiO_2 glass (Fig. 2) did not return to zero after the removal of the electric field.

Discussion

The curves in Fig. 2 were normalized at their saturated values, as is shown in Fig. 8. Among these curves for the increasing internal friction (solid lines), Curve 3 is quite different from Curves 1 and 2. The difference is caused by electrolysis. In the cases shown by Curves 1 and 2, very little electrolysis occurs, so their internal friction returns to the orginal value after the removal of the electric field. The returning curves 1 and 2, after the removal of an electric field (broken lines), are different from the increasing curves 1 and 2 (solid lines). During this experiment, torsional oscillation was always applied to a sample. If torsional oscillation is not applied under an electric field, the values of the internal friction will scarcely alter at all. The increase in internal friction will occur only when torsional oscillation and an electric field are applied to a sample simultaneously. When an electric field is removed after the internal friction reaches a saturated value, the internal friction decreases rapidly even without torsional oscillation. This suggests that sodium ions which have been raised to a higher potential energy level return to their original lower potential level by thermal vibration. This is one of the causes of the difference between a solid line and a broken line.

The increase in internal friction was scarcely observed in the glass with a low Na_2O content, below 15 mol%, but in the glass of Na_2O above 20 mol% it increased considerably with the Na_2O content, as is shown in Fig. 3. In the glasses of the SiO_2–Na_2O systems, the background of internal friction is large in a glass with a low Na_2O content (below 100 °C) and is large in one with a high content (over 100 °C).[5] It may be supposed that the background below 100 °C is affected by the deformation of the porous frame structure of SiO_2 while over 100 °C it is affected by the increase in the flexibility of the Si–O network due to sodium ions. The background in the temperature range of this experiment seems to be affected mostly by the deformation of the porous frame structure of SiO_2 and very little by the flexibility of the Si–O network. In a higher-Na_2O-content glass, the three-dimensional network structure is destroyed and the background becomes lower. When an Na_2O-containing glass is subjected to torsional oscillation under an electric field, the network structure is apt to be deformed around holes which are left behind by the removal of sodium ions. Thus, the internal friction must increase. The network structure will deform more easily near continuous holes than near an isolated hole. Such continuous holes can be made more in higher-Na_2O-content glasses. Moreover, electrolysis is also apt to occur. This is the reason why the increase in internal friction is high in the glass with a high Na_2O content and very low in the glass with a Na_2O content of less than 15 mol%.

The results can almost all be explained in terms of Copley's proposal that the increase in background is characteristic of a more open, loosely-bound structure because of the removal of a certain number of sodium ions.[4] The internal friction was found to increase with the strength of the electric field. This means that the number of holes which are left behind by the removal of the sodium ions is proportional to the strength of the electric field, so that the background of internal friction rises in proportion to the number of holes. The characteristic of the increase in the background is, however, related to the network structure of glass composition. From the facts that the increase in background shows saturation with time and that it does not change with the period of torsional oscillation, but with the number of vibrations, a mechanism in which some of the sodium ions moving under an electric field are trapped somewhere in the network structure when the network is deformed can be proposed. As soon as an electric field is applied, some holes are produced by polarization, and hence the background increases, yet sodium ions are supposed to move from a hole to a hole which has nonbridging oxygen ions. When sodium ions are trapped somewhere in the network structure, the number of holes seems to increase. These sodium ions cannot slip easily from the traps without torsional oscillation after an electric field is removed. They can, however, slip gradually because of thermal vibration.

According to Copley's experiment, the peak position of the internal friction caused by sodium ions shifts slightly,[4] but we did not observe such a change. In Copley's experiment, the surface concentration of

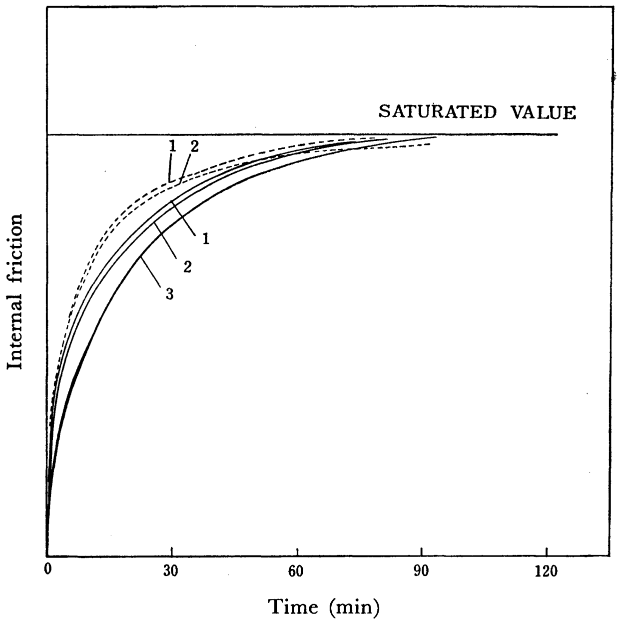

Fig. 8. Variation of internal friction with time. Each saturated value in Fig. 2 is normalized.
1: Na_2O 30 mol%, 2: Na_2O 35 mol%,
3: Na_2O 40 mol%
——: under electric field
----: after the removal of electric field

the sodium ions changed by electrolysis. In our experiment, the change in the concentration of the sodium ions is caused by polarization and electrolysis occurs only near the cathode in the axial direction of a sample. Therefore, there is probably no influence on the peak position.