

P1246
4337

C10034
40789



BIBLIOTHEEK TU Delft
P 1246 4337



C

344078

ON THE INTERNAL FRICTION IN ION-EXCHANGED SODIUM SILICATE GLASSES AND IN SODIUM ALUMINOBORATE GLASSES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE TECHNISCHE WETENSCHAPPEN AAN DE
TECHNISCHE HOGESCHOOL DELFT OP GEZAG VAN
DE RECTOR MAGNIFICUS Dr.Ir. C.J.D.M. VERHAGEN,
HOOGLEERAAR IN DE AFDELING DER TECHNISCHE
NATUURKUNDE, VOOR EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP WOENSDAG 1 NOVEMBER 1967
TE 16 UUR.

DOOR

HENDRIKUS DE WAAL

NATUURKUNDIG INGENIEUR
GEBOREN TE AMSTERDAM



1246 4337

DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE
PROMOTOR PROF. Dr. M.J. DRUYVESTEYN

ON THE INTERNAL FRICTION IN ION-EXCHANGED SODIUM SILICATE GLASSES AND IN SODIUM ALUMINOBORATE GLASSES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE TECHNISCHE WETENSCHAPPEN AAN DE
TECHNISCHE HOGESCHOOL DELFT OP GEZAG VAN
DE RECTOR MAGNIFICUS Dr.Ir. C.J.D.M. VERHAGEN,
HOGLERAAR IN DE AFDELING DER TECHNISCHE
NATUURKUNDE, VOOR EEN COMMISSIE UIT DE SENAAT
TE VERDEDIGEN OP WOENSDAG 1 NOVEMBER 1967
TE 16 UUR.

DOOR

HENDRIKUS DE WAAL

NATUURKUNDIG INGENIEUR
GEBOREN TE AMSTERDAM



DIT PROEFSCHRIFT IS GOEDGEKEURD DOOR DE
PROMOTOR PROF. Dr. M.J. DRUYVESTEYN

AAN MIJN VROUW

De in dit proefschrift beschreven experimenten zijn verricht in het laboratorium van de Technisch Fysische Dienst TNO-TH. Gaarne betuig ik de directie van dit laboratorium mijn erkentelijkheid voor de mij geboden gelegenheid dit werk te verrichten. Voorts wil ik op deze plaats mijn dank betuigen aan allen, die in enige vorm aan de tot stand koming van dit proefschrift hebben medegewerkt.

CONTENTS	page
I. GENERAL INTRODUCTION	7
References	13
II. EXPERIMENTAL PROCEDURE	14
II.1. Internal friction measurements	14
II.1.1. General remarks on the determination of internal friction .	14
II.1.2. Theoretical background of the applied measuring methods	17
II.1.3. Definition and use of the quantities "relaxation time" and "activation energy"	21
II.1.4. Description of the torsion pendulum apparatus for measurements of the rate of free decay	26
II.1.5. Modification of the torsion pendulum apparatus for measurements of energy dissipation during forced vibration	31
II.1.6. Performance of the measurements	36
II.2. Thermal expansion measurements	38
II.3. Selection and preparation of the glasses	38
II.4. Preparation and special treatments of the specimens	40
II.5. Analysis of the chemical composition of the specimens	41
References	44
III. EXPERIMENTS ON ION-EXCHANGED SODIUM SILICATE GLASSES	45
III.1. Introduction and review of the literature	45
III.2. Experimental results	49
III.2.1. Internal friction of mixed-alkali glasses in the composition range $x\text{Na}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot 2\text{SiO}_2$.	49
III.2.2. Internal friction of sodium disilicate glass after ion exchange with lithium ions	55
III.2.3. Internal friction of sodium disilicate glass after ion exchange with silver ions	58
III.2.4. Effect of etching on the internal friction of sodium disilicate glass after ion exchange with silver ions	62

III.2.5.	Experiments on sodium trisilicate glass	66
III.2.6.	Determination of activation energies	68
III.3.	Discussion of the results	69
III.3.1.	On the internal friction of the mixed-alkali glasses	69
III.3.2.	On the internal friction of the ion-exchanged fibers after annealing	70
III.3.3.	On the internal friction of the ion-exchanged fibers before annealing	72
III.3.4.	Suggestions for the mechanisms responsible for the phenomena recorded	76
III.4.	Survey of the results	78
	References	81
IV.	EXPERIMENTS ON SODIUM ALUMINOBORATE GLASSES	82
IV.1.	Introduction and review of the literature	82
IV.2.	Experimental results	89
IV.2.1.	The Nabal system	89
IV.2.2.	Glasses in series 1: $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$.	91
IV.2.3.	Glasses in series 2: $x\text{Na}_2\text{O} \cdot (0.9-x)\text{B}_2\text{O}_3 \cdot 0.1\text{Al}_2\text{O}_3$.	94
IV.2.4.	Glasses in series 3: $0.17\text{Na}_2\text{O} \cdot (0.83-y)\text{B}_2\text{O}_3 \cdot y\text{Al}_2\text{O}_3$.	96
IV.2.5.	Glasses in series 4: $x\text{Na}_2\text{O} \cdot (1-2x)\text{B}_2\text{O}_3 \cdot x\text{Al}_2\text{O}_3$.	96
IV.2.6.	Internal friction measurements on some Nabal and Cabal glasses	99
IV.3.	Discussion of the results	99
IV.3.1.	Thermal expansion measurements	99
IV.3.2.	Internal friction measurements	102
	References	107
V.	ON THE MECHANISM OF THE INTERNAL FRICTION IN GLASSES CONTAINING MONOVALENT METAL IONS	108
V.1.	Introduction	108
V.2.	Literature	110
V.3.	Energetic conditions for the occurrence of internal friction in glasses	115
V.4.	Discussion of a mechanism accounting for the "low-temperature peak" in alkali-containing glasses	118
V.5.	Discussion of a mechanism accounting for the "intermediate-temperature peak" in mixed-alkali silicate glasses	125
V.6.	Suggestions for the mechanisms accounting for the "high-temperature peak" and the "extra-high-temperature peak" in alkali silicate glasses	132
	References	134
	SUMMARY	135
	SAMENVATTING	138

CHAPTER I

General Introduction

Glasses formed from metal oxides and either silicon oxide or boron oxide have played a dominant role in the theories of glass structure. The number of glass-forming systems and the variety of possible structures, however, are tremendous, especially if we adopt the encompassing definition that any solid substance, having a structure without long-range order, is a glass. It should thus be emphasized that whatever is learned about the structure of a particular glass should not, without questioning, be presupposed to hold true for any other glass. The experiments presented in this thesis are performed on glasses in the $\text{Na}_2\text{O}-\text{SiO}_2$ system, in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ system and in the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ system. A brief survey of the most dominant theories that have been developed concerning the structure of these glasses is therefore indispensable.

SiO_2 as well as B_2O_3 belong to the oxides, with which it is possible to construct a three-dimensional framework. Zachariasen¹ called these oxides "glass-forming oxides", in distinction of other oxides that may be found in glasses, such as the alkali oxides, which he called the "network-modifying oxides". Al_2O_3 belongs to a third group of oxides, called the "intermediates", since they do not form glasses themselves, but can enter into the network in polycomponent glasses. Zachariasen proposed the so-called random network theory to account for the structure of these glasses and the conditions of glass formation. The ultimate general requirement for forming oxide glasses was stated by Zachariasen as the ability to form an extended three-dimensional network lacking periodicity with an energy content comparable to that of the corresponding crystalline network. This essentially requires that the first coordination number of each ion be very nearly the same in the glass as in the crystal. Furthermore, it means that the second coordination cannot be a large contributor to the total structure energy. For example, the crystalline forms of SiO_2 are made up of networks in which each silicon is surrounded by four oxygen ions; these are quite open networks, in contrast to close-packed oxides. Making this network random does not greatly change the total structure energy. For these general requirements to be satisfied, Zachariasen suggested the following rules for the formation of an oxide glass:

1. Each oxygen ion should be linked to no more than two cations.

2. The coordination number of oxygen ions about the central cation should be small, 4 or less.
 3. Oxygen polyhedra can share corners with one another so as to form three-dimensional networks, but cannot share edges or faces.
 4. At least three corners of each polyhedron should be shared.
- Figs. I-1a and b show how the imaginary oxide A_2O_3 may form either a crystal or a glass with AO_3 triangles in both cases, the crystal having perfect regularity of structure and the glass sufficient distorted bond angles to produce a random ion distribution without any long-range periodicity.

For polycomponent glasses it is not essential that all constituents be glass-forming oxides. A glass is formed as long as the composition contains a high percentage of cations which are surrounded by oxygen in triangular or tetrahedral coordination, these polyhedra share corners, and at least some oxygen ions are bonded to two cations and do not

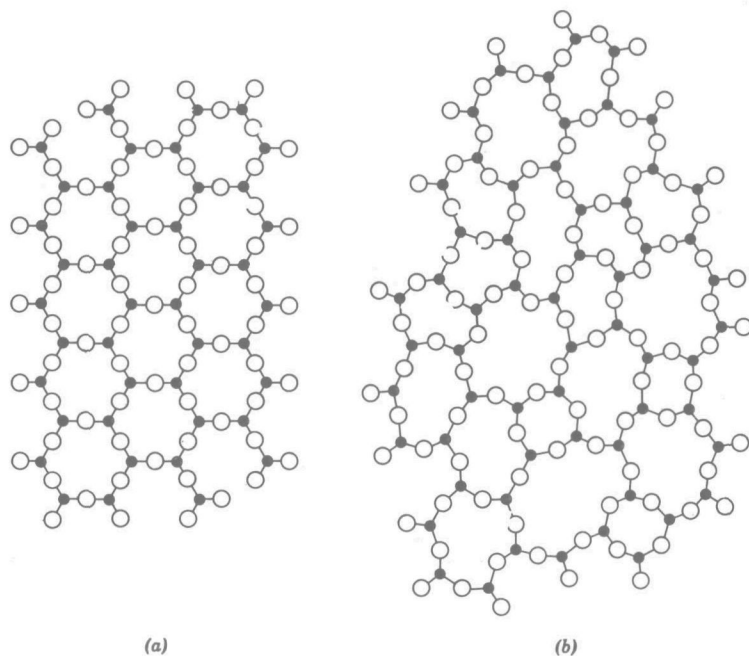


Fig. I-1. Two-dimensional representation of (a) regular crystalline lattice and (b) corresponding irregular glassy network. After W.H.Zachariasen¹.

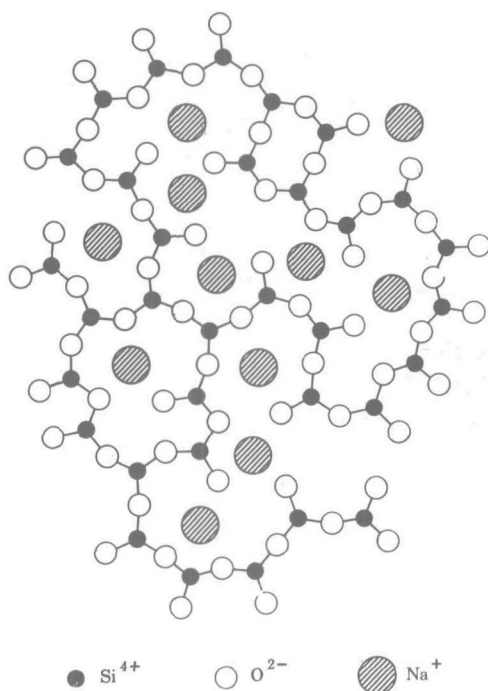


Fig. I-2. Schematic representation in two dimensions of a sodium silicate glass. After B.E.Warren¹⁹.

share bonds with other cations. Thus, for example, a sodium silicate can form a glass in which sodium ions do not contribute to the network formation, but essentially sit in holes in the network. The oxygen addition, involved in the addition of Na_2O , increases the O:Si ratio and requires that the infinite network be broken at several points, corresponding to oxygen ions bonded to a single silica. These oxygen ions are called nonbridging oxygen ions. They possess a net negative charge, providing an ionic bond with the sodium ions (a bond much weaker than the covalent bond they replace). A schematic two-dimensional representation of such a structure is given in Fig.I-2.

In borate glasses the situation is somewhat different. B_2O_3 forms a glass in which the oxygen ions are in triangular coordination about each boron ion. As Na_2O is added to B_2O_3 to form sodium borate glasses, some of the boron ions are believed to become tetrahedrally coordinated by oxygen ions. This would mean that each newly added oxygen

ion is bound to two boron ions. The rigidity of the network is enhanced by this mechanism. The sodium ions are situated in holes in the structure. Beyond a certain percentage of Na_2O nonbridging oxygen ions are believed to appear, giving rise to a looser structure. In Chapter IV this subject will be discussed more closely.

Zachariasen pointed out that we should not be led to believe that the framework is formed first and that the holes are filled afterwards; naturally the holes are filled as the framework is formed during cooling, so that the dimensions of the holes are determined by the size of the cations occupying them

Various aspects of the random network theory have been subjected to severe criticism. The belief that a network must be present, if a compound is to form a glass, is found to be untenable. Glasses have been found in oxide systems where no three-dimensional network is possible^{2,3}. Another dubious aspect of the unaltered Zachariasen theory is the assumed distribution of network-modifying cations at random in holes in the network. More recent investigations of silicate and borate glasses^{4,5,6,7,8} indicate that network-modifying cations occur with definite interatomic distances. These distances must be determined by the arrangement of the network over distances of several coordination shells. Therefore, the results point out to a considerable degree of short-range order in the glass.

In the Russian literature the problem of the structure of oxide glasses has been approached from another point of view. Lebedev⁹ originally proposed the so-called crystallite theory, in which the glass phase of quartz was considered to be a highly disperse aggregation of crystallites. Multicomponent glasses were believed to be composed of crystals of differing stoichiometry. At present the crystallite theory in its primitive form is no longer supported by glass scientists, but some aspects of the theory remain in the recent literature^{10,11,12}. The concept of partial ordering in glass could equally well have been developed from the network theory as from the crystallite point of view. The extreme standpoints of both theories actually have been abandoned. Today it is generally agreed that real glasses are more ordered than predicted by the random network theory and less ordered than expected from the crystallite theory.

New investigations have shown that certain glasses may possess a granular noncrystalline structure in the 10 Å to 100 Å range. The regions are not separated by observable boundary surfaces.

A second and well-established fact in several multicomponent glasses is the metastable liquid immiscibility following a heat treatment at temperatures between the transformation and the liquidus temperature.

It is nowadays believed that the oxide glasses are best described in terms of certain regions having a greater order than complete randomness, bound together by regions having a higher degree of randomness. In both regions the theory of Zachariasen may hold to a certain extent, but at the same time the grainlike structure found with an electron microscope is accounted for. This picture leads to the existence of a structural microinhomogeneity in glass.

It has also been suggested that a chemical inhomogeneity may occur. Porai-Koshits¹³ maintains that sodium silicate glasses with 0-50% of sodium oxide are composed of regions of SiO_2 and of metasilicate ($\text{SiO}_2\cdot\text{Na}_2\text{O}$), interconnected by zones which are gradually disordered, physically and chemically. Charles¹⁴ concluded from his observations that at concentrations between 5 and 25 mol.% Na_2O the sodium silicate glasses were composed of SiO_2 - and sodium disilicate regions. According to Tran¹⁵, however, the chemical composition of the sodium-rich regions would be closer to $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$, whereas the disilicate would appear only in glasses containing more than 25 mol.% Na_2O . At the moment it does not seem very fruitful to discuss this further. It is clear that even the question of the structure of glasses as simple as the alkali silicates is far from being solved. The only conclusion that may be drawn is that the distribution of the sodium ions is certainly not at random throughout the glass. There are certain density fluctuations of sodium ions. Some regions contain more sodium ions than other regions. Within each region the sodium-sodium distance seems to be fairly constant. This effect is particularly predominant in glasses of low sodium content (below 25 mol.%).

Microinhomogeneities have also been discovered in sodium borate glasses, although the glasses in this system have not yet been studied as intensively as the sodium silicate glasses. Vogel¹⁶ observed a granular structure, especially in glasses containing about 16 mol.% Na_2O .

It is not too surprising that alkali ions have a tendency to segregate in glasses. Weyl and Marboe¹⁷ pointed out that the formation of a superstructure in which the nonbridging oxygen ions are distributed as evenly as possible is very favourable from the view-point of the screening demands of the Si^{4+} ions. Such a structure, however, does not offer maximum screening to the sodium ions. When the sodium concentration is low each sodium ion would have to be screened by a group of oxygen ions, which may contain no more than one nonbridging oxygen ion. The tendency of the sodium ions to surround themselves with nonbridging, better screening, oxygen ions introduces a principle

which opposes the even distribution of nonbridging oxygen ions. The principle favours a segregation into regions of higher and lower concentration of sodium ions. At high sodium concentrations the tendency to develop such submicroscopic segregation should be smaller than in glasses with a low sodium content.

Since the silicate glasses, investigated in this thesis, contain at least 25 mol.% Na_2O , we do not believe segregation to have played a role in our glasses. Moreover, our investigation is mainly concerned with the secondary internal friction peaks, occurring in these glasses at temperatures below the transformation range. It is generally accepted that these peaks are to be related to the relatively high mobility of the metal ions at low temperatures. Since only the first coordination shells are involved in this mechanism we are mainly concerned with the environmental conditions of the metal ions, and it does not seem to be very important whether there are microinhomogeneities in the glass or not. Such in contrast to another property that can be related to the mobility of the metal ions, namely the ionic conductivity. Here a displacement of the ions over several atomic distances is involved, so that the overall distribution of sodium ions comes into question. Charles¹⁴ pointed out that in phase-separated glasses the dc conductivity will be much higher when the alkali-rich phase is continuous than when the alkali-rich phase is discontinuous. He attributes the phenomenon of the low ionic conductivity in mixed-alkali glasses (known as the "mixed-alkali effect") to a phase separation, in which the most mobile ions are situated in the discontinuous phase¹⁸. From our experiments on the mixed-alkali effect, presented in Chapter III, it seems rather improbable that the effect can be explained by supposing a phase separation. We prepared mixed-alkali glasses in a quite unusual way, namely by an ion-exchange treatment. From the internal friction measurements obtained on these glasses it can be deduced that another mechanism must be considered responsible for the mixed-alkali effect in mixed-sodium-lithium and sodium-silver silicate glasses. A discussion of this mechanism will be given in Chapter V.

References

1. W.H.Zachariasen, J.Am.Chem.Soc., 54, 3841 (1932).
2. K.H.Sun, A.Silverman, J.Am.Ceram.Soc., 25, 101 (1942).
3. H.J.L.Trap, J.M.Stevens, 5th Intern.Conf.on Glass, Glastechn. Ber., 32 K, VI, 31 (1959).
4. T.Forland, Office Naval Res., Techn.Rep., No. 63 (1955).
5. J.Krogh-Moe, Phys.Chem.Glasses, 3, 101 (1962).
6. C.Brosset, VIIIth Int.Ceram.Congr., Copenhagen 1962.
7. J.Krogh-Moe, H.Jurine, Phys.Chem.Glasses, 6, 30 (1965).
8. S.M.Ohlberg, J.M.Parsons, "Physics of Non-Crystalline Solids", p.31, North Holland Publ Co., Amsterdam, 1965.
9. A.A.Lebedev, Arb.Staatl. opt.Inst. Leningrad, 2, no. 10 (1921).
10. E.A.Porai-Koshits, Glastechn.Ber., 32, 450 (1950).
11. R.Hoseman, S.N.Bagchi, "Direct Analysis of Diffraction by Matter", North Holland Publ.Co., Amsterdam, 1962.
12. F.Oberlies, A.Dietzel, Glastechn.Ber., 39, 37 (1957).
13. E.A.Porai-Koshits, "The Structure of Glass", 1, 25 (1958).
14. R.J.Charles, J.Am.Ceram.Soc., 49, 55 (1966).
15. T.L.Tran, Glass Technol., 6, 161 (1965).
16. W.Skatulla, W.Vogel, H.Wessel, Silikattech., 9, 51 (1958).
17. W.A.Weyl, E.C.Marboe, "The Constitution of Glasses", Vol.II, Part I, John Wiley and Sons, New York, 1964.
18. R.J.Charles, J.Am.Ceram.Soc., 48, 432 (1965).
19. B.E.Warren, J.Am.Ceram.Soc., 24, 256 (1941).

CHAPTER II

Experimental Procedure

II.1. Internal friction measurements

II.1.1. General remarks on the determination of internal friction

Internal friction can be defined as the dissipation of energy in a material after application of an elastic strain or stress.

In glass it can be demonstrated in several ways, e.g.:

- a. The sudden application of a stress to the material not only causes an instantaneous strain, but also an anelastic strain, gradually approaching an asymptotic value. After removal of the stress this strain relaxes, with a certain relaxation time, to zero.
- b. When the material is subjected to an oscillating stress the strain lags behind the stress and per cycle of vibration a certain amount of energy is dissipated.
- c. During free oscillation there is a gradual decay in amplitude.

The equation that describes the properties of a material showing this type of internal friction can be written as:

$$(II-1) \quad \sigma + \alpha_1 \dot{\sigma} = E_R (\epsilon + \alpha_2 \dot{\epsilon}),$$

where σ represents the stress, ϵ the strain and E_R , α_1 , and α_2 are constants.

Eq. (II-1) is a linear homogeneous equation in stress, strain and their first time derivatives. A solid obeying this equation is therefore called a "standard linear solid".

It must be kept in mind that this equation applies to each element of volume of the material separately. As we shall see in Chapter III this can be important in cases where the composition of the specimen is not uniform.

Now suppose an element of volume be subjected to a periodic stress:

$$\sigma(t) = \sigma_0 e^{i\omega t}$$

Substitution of this expression in equation (II-1) results in the differential equation:

$$\varepsilon + \alpha_2 \dot{\varepsilon} = \frac{\sigma_0}{E_R} [1 + i\omega t] e^{i\omega t}$$

The periodic solution of this equation is:

$$(II-2) \quad \varepsilon = \frac{\sigma_0}{E_R} \cdot \frac{1 + i\alpha_1 \omega}{1 + i\alpha_2 \omega} e^{i\omega t}$$

As can be seen from this result a phase angle δ occurs between σ and ε , which can also be expressed as $\varepsilon = \varepsilon_0 e^{i(\omega t - \delta)}$.

It is simple to see that

$$e^{i\delta} = \frac{1 + i\alpha_2 \omega}{1 + i\alpha_1 \omega} = \frac{1 + \alpha_1 \alpha_2 \omega^2}{1 + \alpha_1^2 \omega^2} \left[1 + i \frac{\omega(\alpha_2 - \alpha_1)}{1 + \alpha_1 \alpha_2 \omega^2} \right]$$

So that

$$(II-3) \quad \tan \delta = \frac{\omega(\alpha_2 - \alpha_1)}{1 + \omega^2 \alpha_1 \alpha_2}$$

The relationship between σ and ε may be written in a simple way by making use of the so-called complex modulus \bar{E} , which is defined as:

$$(II-4) \quad \bar{E} = E_R \frac{1 + i\alpha_2 \omega}{1 + i\alpha_1 \omega} = E_R \cdot \frac{1 + \alpha_1 \alpha_2 \omega^2}{1 + \alpha_1^2 \omega^2} (1 + i \tan \delta)$$

This leads to the relation:

$$(II-5) \quad \sigma = \bar{E} \varepsilon$$

From equation (II-1) it can be seen that α_1 is the time of relaxation of stress under conditions of constant strain, and that α_2 is the time of relaxation of strain at constant stress.

E_R is the ratio of stress to strain after all relaxation has occurred and is called the relaxed elastic modulus. It can be shown that

$$0 < \frac{\alpha_2 - \alpha_1}{\alpha_1} \ll 1 \text{ (or } \alpha_1 \approx \alpha_2 \text{)}.$$

We can derive an unrelaxed elastic modulus E_U , which gives the relation between changes in σ and ϵ occurring so rapidly that no relaxation has time to take effect:

$$\Delta \sigma = E_U \Delta \epsilon.$$

From (II-1), however, we find for a very short time interval δt :

$$\alpha_1 \Delta \sigma = E_R \alpha_2 \Delta \epsilon,$$

which leads to:

$$E_U = E_R \frac{\alpha_2}{\alpha_1},$$

E_U being the modulus for high frequencies ($\alpha_1 \omega \gg 1$).

This transforms equation (II-4) into:

$$(II-6) \quad \bar{E} = E_U (1 + i \tan \delta)$$

Introducing: $E = (E_U E_R)^{\frac{1}{2}}$ and $\tau = (\alpha_1 \alpha_2)^{\frac{1}{2}}$, equation (II-2) can be transformed into:

$$(II-7) \quad \tan \delta = \frac{E_U - E_R}{E} \cdot \frac{\omega \tau}{1 + (\omega \tau)^2}.$$

The second factor gives the frequency variation of $\tan \delta$. It has a maximum value of $\frac{1}{2}$ when $\omega \tau = 1$, which means that

$$(\tan \delta)_{\max} = \frac{E_U - E_R}{2E}.$$

This result indicates that in a torsion experiment the value of $(\tan \delta)_{\max}$ may well be different from the value found in a tension experiment. In a torsion experiment the modulus of rigidity G is involved, whereas in a tension experiment the Young's modulus must be considered. Calling the maximum internal friction values in these two cases $(\tan \delta)_{\max, G}$ and $(\tan \delta)_{\max, E}$ respectively the relation between the two values may be deduced in a simple way if it is assumed that a hydrostatic pressure does not give rise to internal friction. In that case the compressibility χ will not show relaxation and we may write (for an isotropic material):

$$\chi = \frac{9}{E_R} - \frac{3}{G_R} = \frac{9}{E_U} - \frac{3}{G_U},$$

where the indices R and U refer to a relaxed and an unrelaxed modulus respectively.

With equation (II-7) this leads to:

$$(II-8) \quad \frac{(\tan \delta)_{\max, E}}{(\tan \delta)_{\max, G}} = \frac{E}{3G} = \frac{1+\mu}{1.5} \approx 0.8-0.9,$$

since the Poisson's ratio μ can be written as $\mu = \frac{E}{2G} - 1$.

In view of this result we will not further distinguish between the values of $\tan \delta$, found in torsion and in tension experiments.

II.1.2. Theoretical background of the applied measuring methods

In our experiments two methods were used to measure $\tan \delta$. The experimental details of these methods will be described in the Sections II.1.4. and II.1.5. Here we shall discuss the theoretical relationship between the measured quantities and $\tan \delta$. The first method involves the measurement of the gradual decay in amplitude of the torsional vibration in a fiber, supporting an auxiliary inertia member, in free oscillation. Since a relatively large inertia member is attached to the fiber the mass of the fiber may be neglected.

In that case the equation of motion is :

$$(II-9) \quad J \ddot{\Theta} + M_1 = 0,$$

where Θ represents the angle of twist of the fiber (or the angular displacement of the inertia member), J the inertia of the auxiliary member and M_1 the torque exerted upon this member by the specimen. The shear strain γ in a fiber of length L and radius R is

$$\gamma = \frac{\Theta r}{L},$$

if r is the distance to the torsion axis.

Assuming that the specimen is homogeneous it is obvious that the shear stress $\tau = r \max. \frac{\tau}{L}$. From equation (II-5) it follows that $\tau = \bar{G} \gamma$,

where \bar{G} is the complex torsion modulus, or $\tau = \bar{G} \frac{r}{L} \Theta$ and $\tau_{\max} = \bar{G} \Theta$. With this equation we can express M_1 in Θ as follows:

$$M_1 = \int_0^R \int_0^{2\pi} \tau r \cdot r dr d\theta = 2\pi \int_0^R \tau r^2 dr = 2\pi \int_0^R \frac{\bar{G} \Theta}{L} r^3 dr = \frac{\pi R^4}{2L} \bar{G} \Theta.$$

Substitution of this result into the equation of motion gives:

$$J \ddot{\Theta} + \frac{\pi R^4}{2L} \bar{G} \Theta = 0$$

This equation can be solved with a solution of the form:

$$\Theta = \Theta_0 e^{i\tilde{\omega}t}; \tilde{\omega} = \omega(1 + i \frac{\lambda}{2\pi}),$$

which represents exponentially damped oscillations.

λ is a constant and is called the logarithmic decrement. It represents the natural logarithm of the ratio of amplitudes in two successive vibrations, as can easily be shown:

Suppose at the time t_1 the amplitude of the vibration is $A(t_1)$, which is proportional to

$$\Theta(t_1) = \Theta_0 e^{-\frac{\lambda}{2\pi} \omega t_1} \cdot e^{i\omega t_1}$$

One period later the amplitude will be given by $A(t_1 + T)$, which is proportional to

$$\Theta(t_1 + T) = \Theta_0 e^{-\frac{\lambda}{2\pi} \omega(t_1 + T)} \cdot e^{i\omega(t_1 + T)};$$

if T is the oscillation time.

Since $\omega = \frac{2\pi}{T}$ we can write:

$$\ln \frac{A(t_1)}{A(t_1 + T)} = \ln \frac{\Theta(t_1)}{\Theta(t_1 + T)} = \ln \frac{\Theta_0 e^{-\frac{\lambda}{2\pi} \omega t_1} e^{i\omega t_1}}{\Theta_0 e^{-\frac{\lambda}{2\pi} \omega(t_1 + T)} e^{i\omega(t_1 + T)}} = \ln(e^{\lambda - 2\pi i}) = \lambda.$$

When the solution $\Theta = \Theta_0 e^{i\tilde{\omega}t}$ is substituted into the equation of motion we obtain:

$$\tilde{\omega}^2 = \frac{\pi R^4}{2LJ} \cdot \bar{G}.$$

If real and imaginary parts are separately equated and use is made of equation (II-6) it is found that:

$$\omega^2 - \left(\frac{\lambda}{2\pi}\right)^2 \omega^2 = \frac{\pi R^4}{2LJ} G_U.$$

and
$$\lambda = \frac{\pi R^4}{2LJ} G_U \frac{\pi}{\omega^2} \tan \delta.$$

If we neglect second-order terms in the internal friction we find:

$$(II-10) \quad \omega^2 = \frac{\pi R^4}{2LJ} G_U \quad \text{and} \quad \lambda = \pi \tan \delta$$

This relation correlates the logarithmic decrement λ with the internal friction $\tan \delta$. λ is easily obtained from experiments by counting the number of vibrations N between an amplitude A_0 and an amplitude A_N , using the equation:

$$(II-11) \quad \lambda = \frac{1}{N} \ln \frac{A_0}{A_N}$$

The second method used in our experiments is based on the determination of the dissipation of energy in forced torsional vibration. In a vibrating object there is a periodical conversion of potential energy into kinetic energy and vice versa. The potential energy in each element of volume, caused by its distortion, is converted into kinetic energy. However, internal friction causes not all the potential energy to be converted into kinetic energy. There is a certain dissipation of energy in every period.

It is convenient to indicate the internal friction in terms of $\frac{\Delta W}{W}$, denoting the energy dissipated in a volume element per period divided by the total energy that enters the element of volume during that period. (Note that ΔW is the decrease of W .)

The dissipated energy ΔW is the work done in one period on the element of volume.

The energy W that enters the element of volume in one period is the maximum amount of work that has been done on the element of volume during that period.

The work that has been done during a time t can be written as:

$$A(t) = \int_0^t \tau \, d\gamma = \int_0^t \tau \dot{\gamma} \, dt.$$

τ and γ are respectively the shear stress and shear strain on the element of volume under consideration.

For τ and γ we can write:

$$\begin{cases} \tau = \tau_0 \sin \omega t \\ \gamma = \gamma_0 \sin (\omega t - \delta) \end{cases}$$

Substituting this into the integral for A(t) gives:

$$A(t) = \tau_0 \gamma_0 \left\{ -\frac{1}{4} \cos (2\omega t - \delta) + \frac{1}{4} \cos (-\delta) + \frac{1}{2} \omega t \sin \delta \right\}$$

A(t) reaches its maximum value for $\omega t = \frac{\pi}{2} + \delta$:

$$W = A_{\max} = \frac{1}{2} \tau_0 \gamma_0 \left\{ \cos \delta + \left(\frac{\pi}{2} + \delta \right) \sin \delta \right\}$$

To find ΔW we must realize that A(t₁) consists of two parts, viz. the potential energy in the element of volume at the time t₁ and the dissipated energy between t = 0 and t = t₁.

According to the theory of elasticity this potential energy can be written as:

$$\begin{aligned} A_P(t_1) &= \frac{1}{2} \tau_1 \gamma_1 = \frac{1}{2} \tau_0 \gamma_0 \sin \omega t_1 \sin (\omega t_1 - \delta) = \\ &= \tau_0 \gamma_0 \left\{ -\frac{1}{4} \cos (2\omega t_1 - \delta) + \frac{1}{4} \cos (-\delta) \right\}. \end{aligned}$$

This means that the energy dissipated at the time t₁ is:

$$A_D(t_1) = \frac{1}{2} \tau_0 \gamma_0 \cdot \omega t_1 \sin \delta.$$

The energy dissipated in one period can be found from this by taking $t_1 = \frac{2\pi}{\omega}$:

$$\Delta W = A_D\left(\frac{2\pi}{\omega}\right) = \pi \tau_0 \gamma_0 \sin \delta$$

So

$$\begin{aligned} \frac{\Delta W}{W} &= \frac{\pi \tau_0 \gamma_0 \sin \delta}{\frac{1}{2} \tau_0 \gamma_0 \left\{ \cos \delta + \left(\frac{\pi}{2} + \delta \right) \sin \delta \right\}} \\ &= \frac{2\pi \sin \delta}{\cos \delta + \left(\frac{\pi}{2} + \delta \right) \sin \delta} \approx 2\pi \sin \delta \approx 2\pi \tan \delta. \end{aligned}$$

(for small values of δ)

or

$$(II-12) \quad \tan \delta = \frac{\Delta W}{2\pi W}$$

We must, however, realize that $\frac{\Delta W}{W}$ is the relative energy dissipation in one element of volume. Experimentally $\frac{\Delta W^*}{W^*}$, the dissipation of the specimen as a whole, is measured.

Only under certain conditions these quantities may be interchanged. Assuming the principle of superposition to be valid we may write:

$$\frac{\Delta W^*}{W^*} = \frac{\int_{\text{vol.}} \Delta W \, dv}{\int_{\text{vol.}} W \, dv},$$

when integrating over the volume of the specimen.

In a torsion pendulum the stress is not homogeneous throughout the specimen, which means that we must write: $W = W(v)$.

Since in a torsion pendulum the vibration can be specified by one periodic function we may write:

$$W^* = \int_{\text{vol.}} W(v) \, dv.$$

We then obtain:

$$(II-13) \quad \frac{\Delta W^*}{W^*} = \frac{\int_{\text{vol.}} \left(\frac{\Delta W}{W} \right) \cdot W(v) \, dv}{\int_{\text{vol.}} W(v) \, dv}.$$

This expression shows that only when $\frac{\Delta W}{W}$ is independent of the position in the specimen we may write:

$$\frac{\Delta W^*}{W^*} = \frac{\Delta W}{W}.$$

More specified this means that the internal friction of the specimen must be amplitude independent and that the specimen must be homogeneous. The second condition was only fulfilled in a part of our experiments. The consequence of the inhomogeneity of a specimen will be discussed in Section III.3.3.

II.1.3. Definition and use of the quantities "relaxation time" and "activation energy"

In Section II.1.1. we introduced α_1 and α_2 the relaxation times of a solid, obeying equation (II-1).

For convenience we also introduced a mean relaxation time τ defined

$$\text{as } \tau = \sqrt{\alpha_1 \alpha_2}.$$

In practice τ is referred to as the relaxation time of a process that

causes a certain internal friction peak. Essentially it is the mean time for the appropriate rearrangements to occur, which lead to the attainment of a new internal equilibrium after the application of an elastic stress or strain.

Whenever atomic movements of any kind are involved in a relaxation process it is to be expected that τ will be strongly temperature dependent, according to the Arrhenius equation

$$(II-14) \quad \tau = \tau_0 e^{\frac{\Delta H}{RT}},$$

where τ_0 is the relaxation time at infinitely high temperatures, ΔH the heat of activation, R is the gas constant and T is the absolute temperature.

This relationship can be of great use in obtaining an internal friction peak experimentally.

From equation (II-7) we learn that $\tan \delta$ is dependent only on the product $\omega \tau$, so the same end can be achieved if $\tan \delta$ is observed as a function of τ at constant ω as by a study of $\tan \delta$ as a function of ω at constant τ .

Locating an internal friction peak by varying the frequency requires measurements over two or three powers of ten in ω , which experimentally is very difficult. Therefore $\tan \delta$ is usually measured as a function of T , which is allowable if τ obeys equation (II-14). This, however, is not as self-evident as is sometimes suggested.

Several conditions must be satisfied. One has already been mentioned: the internal friction peak must be due to some atomic movement. In glasses we may expect this condition to be met.

Since there are no dislocations in glass we can hardly expect any other mechanism. Only for measurements near the softening temperature the occurrence of clusters has sometimes been mentioned as the cause of an internal friction peak, probably on the analogy of the damping attributed to the grain boundaries in metals.

Secondly the system must be in equilibrium. In a glass this condition is not strictly fulfilled. Thermodynamically the glassy state is a typical non-equilibrium state. In a less or greater time (depending on the temperature) the system will move irreversibly to its stable or metastable equilibrium state (the liquid and super-cooled liquid respectively). However, in the temperature range where the secondary internal friction peaks occur this time is almost infinitely long. For glasses with a certain degree of stabilization we may therefore ignore this deviation from true internal equilibrium, although we must keep in mind that there is a weakness in this treatment and that we must not try to compare glasses with a different degree of stabilization.

Another objection can be raised against the use of the Arrhenius equation. Theoretically the Arrhenius equation has not been derived for cases where cooperative effects or interactions between particles are involved. In most glasses the concentration of alkali ions is far too high to ignore the possibility of cooperative effects. Nevertheless the equation has always successfully been used to describe experimental results. The internal friction is always measured as a function of temperature and a frequency rise always causes the peaks to shift to higher temperatures. From this shift an energy of activation ΔH may be calculated with the relation:

$$(II-15) \quad \ln \frac{f_2}{f_1} = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right),$$

where T_1 is the temperature of the peak at a frequency f_1 and T_2 the temperature of the peak at a frequency f_2 .

It seems that the mutual interaction between the ions in the glass does not influence the equation at all. We can also say that interaction effects do not seem to occur.

In Chapter V it will be pointed out that it is not unreasonable to assume that only a small fraction of the alkali ions is involved in the internal friction mechanism. If this is accepted, the absence of interaction effects can be understood.

In spite of all the objections we believe that the Arrhenius equation is useful to describe the results of the measurements.

In connection herewith it is interesting to recollect the suggestion of Kirby¹, who rewrote the equation, using a theory by Eyring², as follows:

$$(II-16) \quad \tau = \frac{h}{kT} e^{-\frac{\Delta S}{R}} e^{\frac{\Delta H}{RT}},$$

where ΔS is the entropy of activation, h the Planck constant and k the Boltzmann constant. Kirby, speaking in terms of a movement over an energy barrier, interpreted a change in ΔS as a change in the shape of the barrier, whereas he regarded a change in ΔH as a change in the height of the barrier.

There is one thing that must be mentioned before leaving this section. When describing the internal friction of glass it is incorrect to speak of "the" relaxation time, since there is always a distribution of rela-

xation times. The existence of such a distribution leads to a broadening and a lowering of the internal friction peaks. The distribution may consist of a discrete set of τ values or of a continuous distribution. In general it seems more sensible to assume a continuous distribution. It is convenient to define the distribution in terms of the variable $\ln \tau$, rather than in τ itself. Eq. (II-7) then transforms into:

$$(II-17) \quad \tan \delta = \frac{E_U - E_R}{E} \int_{-\infty}^{+\infty} \Psi(\ln \tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d \ln \tau,$$

where $\Psi(\ln \tau) d \ln \tau$ is the relative number of contributing processes for which the logarithm of the relaxation time falls in the range between $\ln \tau$ and $(\ln \tau + d \ln \tau)$. Usually $\Psi(\ln \tau)$ is defined in such a way that

$$(II-18) \quad \int_{-\infty}^{+\infty} \Psi(\ln \tau) d \ln \tau = 1,$$

so that $\Psi(\ln \tau)$ represents the normalized distribution function.

Several distribution functions have been proposed in the literature, usually on empirical grounds. Nowick and Berry³ pointed out that the shapes of the internal friction peaks are not very sensitive to the choice of the distribution function, up to values of the peak width about twice that of a single relaxation. A satisfactory description of the experiments can be obtained by adopting the assumption that the relaxation times are distributed according to a Gaussian (or normal) distribution in $\ln \tau$. This distribution, which is also known as the lognormal distribution, was originally suggested by Wiechert⁴ in 1893 and was later applied to dielectric relaxation by Wagner⁵ and Yager⁶. Using the lognormal distribution and introducing a variable $z = \ln(\tau/\tau_m)$, where τ_m is the most probable value of τ , the normalized distribution function $\Psi(\ln \tau)$ may be written:

$$(II-19) \quad \Psi(z) = \frac{1}{\beta \sqrt{\pi}} \exp \left[- \left(\frac{z}{\beta} \right)^2 \right],$$

where β measures the half-width of the distribution at the point where $\Psi(z)$ falls to $1/e$ of its maximum value, $\Psi(0)$.

In view of the Eqs. (II-14) and (II-16) it is clear that a distribution in $\ln \tau$ is due either to the existence of a distribution in $\ln \tau_0$ (which is thought to be linearly related to the entropy of the activation), or in the

activation energy ΔH , or in both. Nowick and Berry³ have shown that the parameters β_1 and β_2 for the distribution in $\ln \tau_0$ and in the activation energy respectively may be determined separately. If it is possible to measure the parameter β at different temperatures β_1 and β_2 can be separated with the relation:

$$(II-20) \quad \beta = \beta_1 + \frac{\beta_2}{RT}.$$

Several investigators have tried to analyse their internal friction measurements in this way. The results are not very promising. Kirby¹ concluded that a distribution in $\ln \tau_0$ (or ΔS) was responsible for the broadening of the internal friction peak at low temperatures in sodium silicate glasses. Hilbert⁷, on the other hand, found evidence for a distribution in ΔH and a single ΔS value, whereas the results of Forry⁸ seem to be best explained if a distribution in both quantities is accepted.

The contradictory character of these results indicates that an analysis of the distribution parameters from internal friction measurements in glass is not very reliable. It seems that the accuracy of the determination of the parameter β is too low to allow such an analysis.

In the first place this may be due to a partial overlapping of internal friction peaks and to the background absorption increasing with temperature.

Secondly we must remember that β stands for the half-width of an internal friction peak, measured as a function of frequency. The internal friction peaks, however, are usually measured as a function of temperature. Of course a theoretical relationship exists between these quantities, but in general the change-over from the frequency to the temperature variable leads to complications resulting from the fact that the elastic moduli, the frequency and the distribution parameter may each be temperature dependent. Besides, the value of the mean activation energy (i.e. the most probable value of the activation energy in a Gaussian distribution), which is involved in this transformation, can hardly be attained with sufficient accuracy from internal friction measurements.

Finally the separation of β_1 and β_2 with Eq. (II-20) involves knowledge of the value of β at different temperatures, which means that the widths of the internal friction peaks must be obtained at different frequencies (when measuring as a function of temperature). Most internal friction devices do not allow large changes in the measuring frequency, so that the relation between β and T can be determined in only a small temperature range. This may reduce the accuracy of the separation of β_1 and β_2 considerably.

An analysis of the distribution parameters involved in the internal friction peaks can be performed with sufficient accuracy only, when an appa-

ratus is used that is especially constructed to cover a large frequency range. As will be shown in the following sections our apparatus is not particularly suited for the determination of the peak-widths at different frequencies. We will not attempt to analyse our results in terms of distribution parameters. Nevertheless it must be remembered that whenever in this thesis there is spoken of "the" relaxation time or "the" activation energy the mean values of these quantities, as defined above, are meant.

II.1.4. Description of the torsion pendulum apparatus for measurements of the rate of free decay

The internal friction measurements were performed on glass fibers with a diameter of about 1.0 mm and a length of 100 mm. These fibers were placed in a torsion pendulum, where the decay of free torsional oscillation was measured as a function of temperature. The frequency of the vibrating system was about 5 cps.

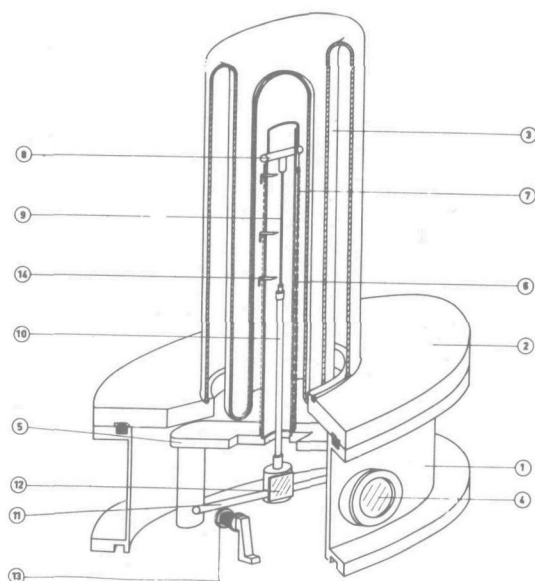


Fig. II-1. Cutaway view of the pendulum apparatus (simplified).

The pendulum was very similar to the one described by J.M. McCormick⁹.

Fig. II-1 shows a (simplified) cutaway of the apparatus. On a very heavy and rigid table (especially constructed to reduce external vibrations) an annular steel ring (1), with a diameter of 25 cm, is placed. On this ring an aluminium disk (2) is clamped. The disk has a circular hole in its centre and supports a triple-walled pyrex cover (3), closing the hole. The inner volume of this assembly can be evacuated to a pressure of less than 10^{-3} mm Hg. According to K.H. Karsch and E. Jenckel¹⁰ this precaution is sufficient to eliminate air damping. Our own measurements confirmed this, even at high temperatures.

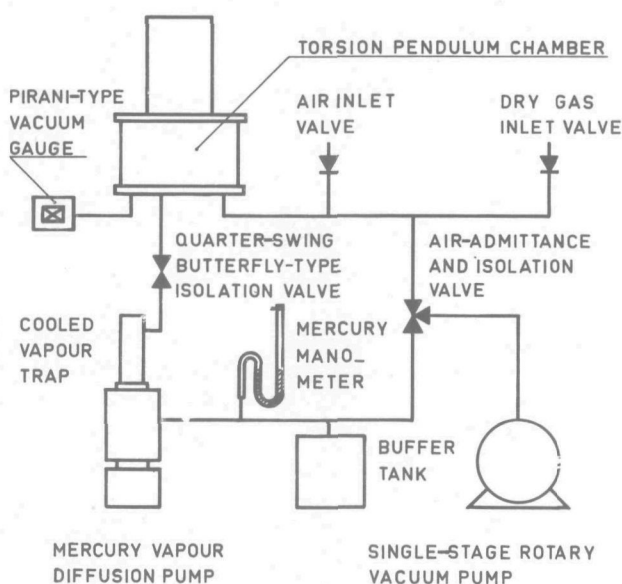


Fig. II-2. Diagram of the installation to evacuate the torsion pendulum chamber.

At temperatures below room temperature the assembly was sometimes filled with dry nitrogen gas to a pressure of 3 or 4 mm Hg. This did not interfere with the measurements and permitted a faster adjustment of a constant temperature. A diagram showing the vacuum installation is shown in Fig. II-2. It needs no further explanation. Fig. II-1 further shows that the re-entrant shape of the pyrex cover provides a small cylindrical working space. This space contains a copper tube (6), supported by a bridge (5) made from a heatproof insulating

material, The tube supports a heating winding(7), thus forming a furnace around the sample (9) situated in the axis of the tube.

The upper end of the copper tube is fitted with two V-shaped notches, serving to support the T-shaped extension(8) cemented to the upper end of the sample. The lower end of the sample is cemented to a pyrex bar(10), extending outside the temperature-control zone and carrying an inertia member(11) and a plane mirror(12).

To start the torsional vibration two solenoids(13), wound on nonmagnetic cores, are placed near the ends of the iron inertia member.

The temperature of the sample is measured by three iron-constantan thermocouples(14), located at different places along the sample. The average of the three values thus determined is considered to be the temperature of the sample. The difference between the three temperatures was kept as small as possible by arranging the windings of the furnace in the most satisfactory way and by making use of radiation shields. In this way we succeeded in keeping the temperature difference between the three measuring points smaller than 2°C in the whole temperature range, that is from -110° till $+500^{\circ}\text{C}$.

Close to the heating winding, inside the copper tube, a platinum resistance thermometer is located (not shown in Fig II-1), being the sensing part of a fully proportional temperature controller (A.E.I. type RT3R/MK2).

The controller is completed by a self-made programmer, so that the temperature of the sample cannot only be varied stepwise, but can also be lowered and raised linearly with time at different rates.

The temperature range below room temperature is covered by filling the annular cavity in the pyrex cover that surrounds the working space with liquid nitrogen. The temperature of the sample then decreases till -110°C . Intermediate temperatures are attained by using the heater.

The decay of oscillation is measured by observing the change of the amplitude of a beam of light reflected from the mirror on the pendulum. This is done as follows: a parallel beam of light, produced by a low dc voltage incandescent lamp with a flat filament and a condenser lens, passes a rectangular diaphragm with extremely sharp vertical edges. This diaphragm is made photographically; its dimensions are 2.0×0.4 mm. (the long edges are placed horizontally). The diaphragmed light beam then passes a long-focus lens (Kern-Paillard, Macro Ivar, 1:2.8; $f=100$ mm), a window(4) in the cylindric ring(1), reflects from the mirror(2) on the pendulum, and leaves the vacuum chamber through a second window(4) (not shown in Fig. II-1).

At a distance of about 3 meters the beam of light is focussed on the amplitude-measuring unit. In order to reduce the influence of external

vibrations it was desirable to place the measuring unit on the same table as the pendulum. To achieve this the beam of light was reflected several times before reaching the unit. A photograph of the assembly is shown in Fig. II-3.

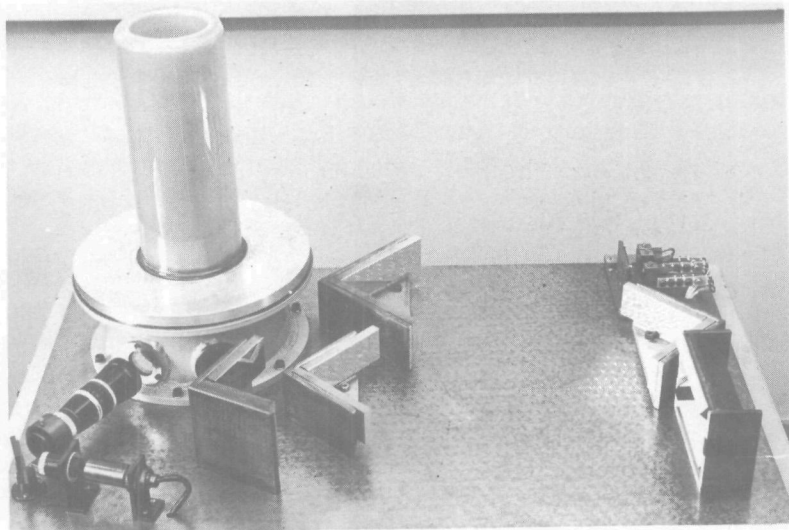


Fig. II-3. Overall view of equipment for internal friction measurements during free torsional oscillation, showing vacuum chamber and amplitude-measuring assembly.

The measuring unit consists in principle of a nontransparent glass plate with three vertical slits, placed on a carriage allowing only horizontal displacement in the direction perpendicular to the beam of light. The three vertical slits each have a width of 0.1 mm and a height of 10 mm. The two outer slits are at a mutual distance of 50 mm. The third slit lies in between, at 20 mm from the slit on the left-hand side, (see Fig. II-4).

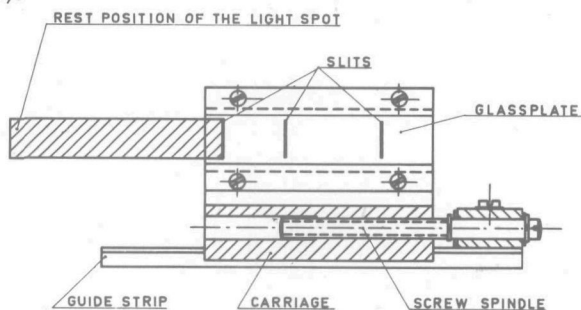


Fig. II-4. Front view of the amplitude-measuring unit with light spot in equilibrium position.

The image of the diaphragm is focussed on the glass plate and is large enough to cover all three slits simultaneously. However, the rest position of the pendulum mirror, together with the position of the glass plate on its carriage, is such that the vertical edge of the beam of light on the right-hand side exactly coincides with the slit that is most on the left, so that the two other slits get no light at all, as is shown in Fig. II-4.

The torsional vibrations of the pendulum cause the light beam to vibrate around its equilibrium position. This means that every half period the rectangular light spot on the amplitude-measuring unit moves to the right and - if the amplitude is large enough - temporarily covers the two slits on the right.

The narrow band of light that passes a slit is focussed on the sensitive part of a photomultiplier. The signal from the photomultiplier behind the slit on the left is used to adjust the equilibrium position of the light spot. To perform this the signal from this photomultiplier is led to a voltmeter. The position of the light spot is adjusted in such a way that the reading of the voltmeter attains half of its maximum value. The signals from the two other photomultipliers are led to digital counters to registrate the number of crossings of each slit by the leading edge of the light spot when this edge is moving to the right.

As long as the amplitude is large enough for the light spot to cover both slits both counters will count, but as soon as the amplitude has decreased so much that the light spot does no longer reach the outer slit the corresponding counter stops, whereas the other counter keeps counting until the amplitude has become too small to reach the inner slit. The difference between the numbers, read from the counters, is a measure for the internal friction, as has been explained in Section II.1.2.

The frequency of the oscillating motion is obtained directly as the time interval between alternate crossings of the slit at the rest position by the leading edge of the light spot. Use has been made of a Venner digital frequency and time counter.

There are of course certain sources of error to be found in this measuring method. For instance, the photomultipliers are arranged to respond to a change of illumination, but the amount of light necessary for the photomultipliers to respond may not always be the same. This means an uncertainty in the magnitude of the amplitude at which the counter stops counting.

Beyond that there is always an uncertainty in the determination of the number of vibrations, because of the discontinuous way of measuring the decay, i.e. an amplitude may be just too small or just large enough to reach a slit.

Nevertheless, from repeated readings of the number of vibrations be-

tween the two fixed amplitudes we learned that the scattering in the results did not exceed 2 %, except at very high values of $\tan\delta (>15 \times 10^{-3})$. To reduce the error the number of vibrations was always determined as the average of three individual readings.

The repetition of the readings also reduces the influence of an error of a quite different origin, viz. the presence of nontorsional vibrations.

The initial deflection of the system may cause transverse oscillations, even though the force couple is carefully balanced. This causes the light spot on the measuring unit to move vertically.

It was shown experimentally that a transverse vibration that caused a vertical amplitude of the light spot amounting to less than 2 mm did not interfere with the results. This value was rarely exceeded, but if so, the measuring unit stopped counting, because of the diminished illumination of the slits, and the measurement was rejected.

II.1.5. Modification of the torsion pendulum apparatus for measurements of energy dissipation during forced vibration

To determine the activation energy of an internal friction peak the temperature of the peak has to be measured at two different frequencies, preferably not too close together.

Searching for a method to perform this we found an article by P. Kofstad, R.A. Butera and R.S. Craig¹¹. The apparatus they describe is based on an (inverted) torsion pendulum, employs electromechanical principles, and can be used at frequencies ranging from about 50 to 500 cps. The method gives a continuous record of internal friction as a function of time on a strip chart recorder. With a few alterations the method could be adapted to our apparatus.

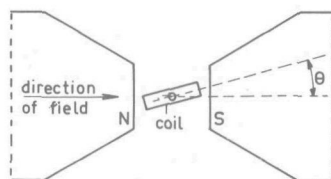


Fig. II-5. Orientation of the driver and pickup coils in the field of the permanent magnet. The axis of the specimen is perpendicular to the plane of the paper.

The inertia member and the mirror (11 and 12 in Fig. II-1) are replaced by two small coaxial coils, located in the field of a permanent magnet. The positioning is such that the direction of the magnetic field, the axis of the coils and the axis of the torsion pendulum are mutually perpendicular.

The coils are about 1 cm in diameter and are wound (from enameled copper wire) on the same core and appear as a single unit in Fig. II-5. An oscillatory motion of the pendulum induces an electromotive force in one of the coils (called the pickup coil).

The signal is amplified, converted into a square wave of constant amplitude, and fed into the other coil (the driver coil), producing a sustained oscillation at a frequency very close to the natural frequency of the system. The amplitude of the oscillations and the output voltage of the pickup coil are inversely proportional to $\tan \delta$, as will be shown in this section.

A schematic diagram of the electrical circuit is shown in Fig. II-6.

To avoid high-frequency oscillations due to the electrical coupling of the two coils the signal from the pickup coil first passes a low-pass filter, after which it is fed into a high-gain amplifying circuit.

The phase of the input signal from the pickup coil is affected by the filter and the coupling capacitors of the amplifier. It can be corrected by adjusting the potentiometer of the RC network before the output stage of the amplifier.

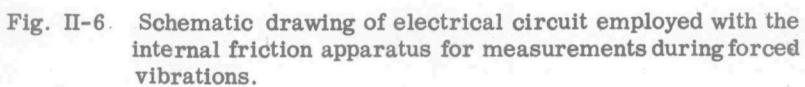
To perform this the emf's in the two coils can be compared with a double-beam oscilloscope connected to the measuring points E and P of Fig. II-6.

From the output of the amplifier the signal is fed into a pulse shaper (Philips PS 1), converting the sine wave into a square wave of constant amplitude (independent of the input signal). The symmetry of this square wave can be adjusted by varying the dc bias of the emitter follower preceding the pulse shaper. The square-wave output of the pulse shaper is applied to the driver coil via a stage consisting of two emitter followers, the output current of which can be adjusted by a potentiometer. This low-ohmic potentiometer serves as a potential divider controlling the amplitude of the vibrations.

The attenuating effect of the amplitude-control potentiometer can be eliminated by interrupting its earth connection with the push button S2, serving to start the vibrations.

The second circuit receiving the signal from the pickup coil is shown in the lower portion of Fig II-6. It serves to provide a dc voltage proportional to the amplitude of the vibration. It consists of two stages of amplification, the second transistor being followed by an emitter follower serving as a power stage. The output of the power stage is rectified to provide a signal to apply to a strip-chart recorder (Leeds and Northrup type H Speedomax with adjustable zero and range).

The output of the power stage can be connected directly to a Venner frequency meter.



To derive the relationship between the measured quantities and $\tan \delta$ we must consider the coil between the poles of the magnet as illustrated in Fig. II-5. The angle θ measures the displacement from the equilibrium position, and when the system is in oscillation the angle θ will vary in a sinusoidal manner about zero.

In Section II.1.2. we derived equation (II-12):

$$\tan \delta = \frac{1}{2\pi} \cdot \frac{\Delta W}{W}$$

We saw that W is the maximum torsional potential energy in the system and can be given by

$$(II-21) \quad W = \frac{1}{2} S \theta_m^2,$$

where S is the stiffness coefficient of the glass fiber and θ_m is the maximum angular displacement of the coil.

When the system is oscillating the flux intercepted in the driver coil is:

$$\Phi = (naB)_d \sin \theta,$$

where $(naB)_d$ represents the product of the number of turns of the driver coil, the area of the driver coil and the field intensity. We will denote this product as k_d .

The instantaneously induced voltage is:

$$E = \frac{d\Phi}{dt} = k_d \cos \theta \cdot \frac{d\theta}{dt}$$

Since both $\cos \theta$ and $\frac{d\theta}{dt}$ have their maximum when $\theta = 0$ the maximum induced voltage is given by the expression:

$$(II-22) \quad E_m = k_d 2\pi f \theta_m,$$

f being the frequency of the vibration.

We may combine Eqs. (II-21) and (II-22) to obtain the following expression for W :

$$(II-23) \quad W = \frac{S \theta_m E_m}{4\pi f \cdot k_d}$$

The energy lost per cycle is equal to the integral of the product of the current and the back emf. We will write this equal to twice the integral over a half cycle:

$$(II-24) \quad \Delta W = 2 \int_0^{2/f} i E dt$$

The current is a square wave of constant amplitude and will be represented by the constant k_i over the half cycle considered in the above integral.

The induced voltage may be expressed as $E = E_m \sin (2\pi ft + \varphi)$, where φ is the phase angle between current and voltage.

Integration of Eq. (II-24) then yields:

$$(II-25) \quad \Delta W = (2k_i E_m / \pi f) \cos \varphi \approx 2k_i E_m / \pi f$$

Direct observation by means of an oscilloscope shows the phase angle to be negligible, so that $\cos \varphi$ may be replaced by unity. An expression for $\tan \delta$ is now found by combining Eqs. (II-12), (II-23) and (II-25) as follows:

$$(II-26) \quad \tan \delta = \frac{4k_i k_d}{\pi S \Theta_m}$$

We now wish to express Θ_m as a function of the voltage induced in the pickup coil. Note that the maximum voltage induced in the pickup coil is given by an expression having the same form as Eq. (II-22), except that the factor $k_d = (nAB)_d$ is replaced by $k_p = (nAB)_p$, where the subscript p refers to the pickup coil.

Thus, the maximum induced voltage will be proportional to the product $f \Theta_m$. The voltage generated in the pickup coil is rectified and applied to the strip-chart recorder. The voltage read from the recorder chart may be expressed as follows:

$$(II-27) \quad E_r = k_p f \Theta_m$$

The final equation, relating $\tan \delta$ to the measured voltage, has the form:

$$(II-28) \quad \tan \delta = \frac{4k_i k_d k_p f}{\pi S} \cdot \frac{1}{E_r}$$

We did not determine the constants of proportionality. Since we wanted to measure only peak temperatures there was no need for a quantita-

tive determination of the internal friction and we recorded only relative values.

The frequency of the pendulum in this modified version fell into the range of 40 to 100 cps., depending particularly upon the diameter of the sample.

II.1.6. Performance of the measurements

Several investigators^{12,13} have pointed out earlier that the height and the position of the internal friction peaks in glasses are to a certain extent affected by the thermal history of the samples.

A peak in a chilled specimen is somewhat higher and lies at a lower temperature than the same peak in an annealed specimen with the same composition.

Some of our experiments were performed on glass fibers that had been subjected to an ion-exchange treatment. The internal friction of these fibers turned out to be very dependent on the thermal history. Actually the internal friction curve sometimes changed completely after the fiber had been annealed. Consequently it was very important to accept a standard annealing procedure, since otherwise the results on fibers with different compositions could hardly be compared.

The following method was chosen: The unannealed fiber ("as drawn") was placed in the pendulum apparatus and heated in vacuo to the temperature at which the background contribution of the internal friction starts to increase rapidly. From then on the temperature was raised carefully until the internal friction $\tan \delta$ had reached the (rather arbitrary) value 20×10^{-3} .

For three hours $\tan \delta$ was kept at that value as good as possible. During the first hours it was necessary to measure $\tan \delta$ every five or ten minutes and raise the temperature, because the steep rise of the background absorption has the tendency to shift to higher temperatures during the annealing treatment. This behaviour is demonstrated in Fig. II-7. After three hours some kind of equilibrium had been attained. Longer annealing had no detectable effect on the internal friction curves. We think that this method of "normal" annealing is better suited for the measurements executed than a normalization by using a constant time and temperature treatment.

The cooling rate also proved to be important, especially in the high-temperature range.

We adopted a cooling rate of $1^{\circ}\text{C}/\text{min.}$, and started the measurement on the same moment as the cooling period.

The measurements at a low frequency (5 cps.), using the method of free

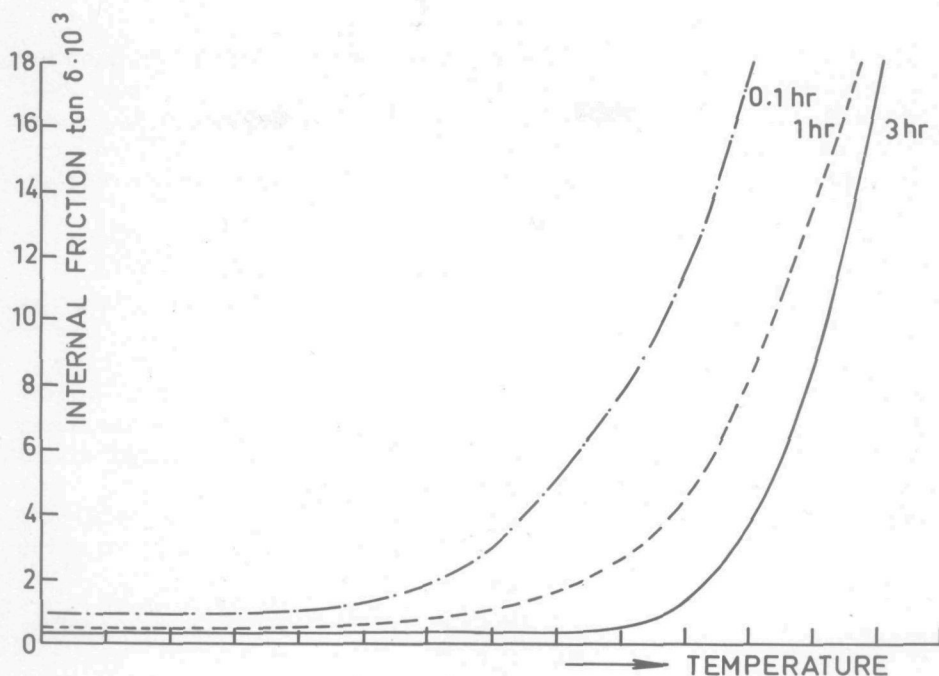


Fig. II-7. Trend of the background absorption after different times of annealing.

decay (Section II.1.4.), were performed discontinuously.

Every ten degrees centigrade, or - if necessary - more frequently, the internal friction was determined, while the temperature continuously decreased at a rate of $1^\circ\text{C}/\text{min.}$, until room temperature was attained.

Below room temperature it was difficult (and unnecessary) to change the temperature continuously. Therefore the fiber was cooled down to the lowest measuring temperature and raised about 10°C after each reading.

The measurements at a higher frequency (50 cps.), using the method of forced oscillation (Section II.1.5.), could be performed continuously above room temperature. Below room temperature the measurements were taken discontinuously.

In some cases the internal friction of an unannealed fiber was measured. The fiber was then heated to a suitable temperature (mostly to the temperature it had been exposed to during some preceding treatment) at least 100°C below the annealing temperature, after which the measurements were started at once, cooling at a rate of $1^\circ\text{C}/\text{min.}$ First the fibers were always measured at a low frequency. All the experimental curves presented in this thesis are in fact obtained at a low frequency, since the measurements in the higher-frequency range yield relative values of $\tan \delta$ only.

The fibers, used in low-frequency measurements, were also used for experiments at higher frequencies. From the 10 cm long fibers about 6 cm is used for the measurements at higher frequencies. Of course this part needs not be annealed any more and the measurements can be started immediately after the highest measuring temperature is attained.

It has been demonstrated experimentally that the internal friction is independent of the stress amplitude, up to shearing strains as large as 3×10^{-4} (cf. J.V. Fitzgerald¹²).

The maximum angular displacement of the inertia member that was permitted in our experiments never exceeded $1/50$ rad.; so the maximum shearing strain during measurement was 1.5×10^{-4} for the fibers with a length of 6 cm and 1.0×10^{-4} for the fibers with a length of 10 cm, which is inside the range mentioned by Fitzgerald.

We looked for deviations from the "standard linear solid" behaviour ourselves, but could not detect any dependence of stress amplitude at the strain levels employed in our apparatus.

II.2. Thermal expansion measurements

The coefficients of linear thermal expansion of several glass compositions were studied in the temperature range from 50° to 300°C with a Leitz dilatometer.

In this apparatus the thermal expansion is measured by a differential method, comparing the expansion of the specimen with that of a fused-silica rod. The test specimens have a round cross section with a diameter of about 3 mm and a length of about 50 mm.

Before the measurement a rod is transferred to a furnace, heated to its softening point, and subsequently cooled slowly to room temperature. After setting up the rod in the apparatus, but before proceeding to a measurement, the sample was first heated to its softening point and cooled at a rate of $1^{\circ}\text{C}/\text{min}$. In the subsequent measurement the rate of heating was always $1^{\circ}\text{C}/\text{min}$.

The coefficients are calculated under the assumption that the linear thermal expansion coefficient of fused silica amounts to 0.55×10^{-6} .

II.3. Selection and preparation of the glasses

All the glass compositions studied were prepared from raw materials of the highest purity available. If possible, "AnalaR" chemicals were

used. The glasses were melted in platinum-gold crucibles in an electric furnace with silicon carbide heating elements in air.

Two different types of glasses were studied.

The first group is based on the glass-forming oxide B_2O_3 . A number of binary glasses were made in the $Na_2O-B_2O_3$ system, the sodium being introduced as carbonate to the crystalline boric acid.

Ternary glasses were made in the $Na_2O-Al_2O_3-B_2O_3$ system, the glass-forming region of which is given in Fig. II-8. To allow for loss of B_2O_3 by volatilization an addition amounting to one-tenth of the desired weight proportion was introduced in all the borate melts.

The borate glasses were melted at a temperature between 1300° and $1400^\circ C$, depending upon the composition. After a melting time of 5 hours the furnace was switched off and furnace and melt were allowed to cool to room temperature.

The batches of the borate glasses were made up in quantities to give 30 g of glass per melt.

The second type of glasses that was studied is based on the glass-forming oxide SiO_2 .

Binary glasses were made in the Na_2O-SiO_2 system. Ternary glasses

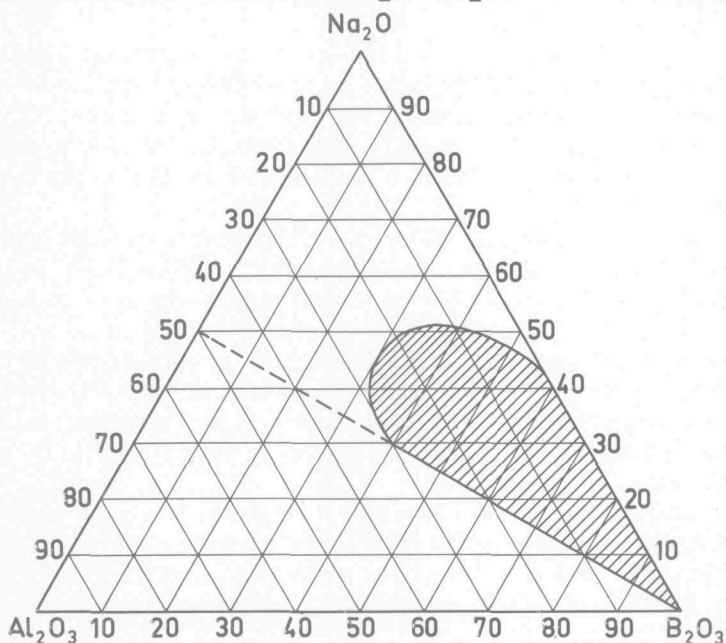


Fig. II-8. Glass-forming region in the $Na_2O-B_2O_3-Al_2O_3$ system. Glasses are formed in the shaded area.

were made in the $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{SiO}_2$ system. The alkalis were introduced as the respective carbonates and silica as high-grade sand, finely ground.

The glasses were melted at 1350°C . After 4 hours at that temperature they were withdrawn from the furnace, cooled and crushed. The material was then remelted at the same temperature for 7 hours. This was done to improve homogeneity.

The silicate glasses were weighed out in batches of a size to yield 75 g of glass.

II.4. Preparation and special treatments of the specimens

For the internal friction measurements glass fibers having a diameter of 1 mm had to be made. This was done by drawing a long fiber from a piece of the cooled melt, reheated with a gas-air burner. The best parts of those long fibers were selected to be used for the experiments. They did not contain any bubbles or particles of unincorporated material, nor devitrification products.

The selected fibers were stored in dry air before and after the measurements.

Some fibers were subjected to an ion-exchange treatment. Those fibers were immersed in a bath of molten salt, removed after a well-defined treatment time, cooled, rinsed with cold water, and carefully dried. Silver-nitrate melts were used for the exchange of sodium ions from the glass by silver ions from a salt melt at temperatures between 275°C and 295°C .

Molten lithium nitrate was used at 275°C and a eutectic mixture of lithium, potassium and sodium nitrate was used at 175°C to investigate the exchange of sodium ions from the glass by lithium ions from a melt.

From some ion-exchanged fibers thin layers were removed by etching. These fibers were immersed in a 10% solution of hydrofluoric acid for a certain period of time. The thickness of the layer removed in this way was determined by weighing the sample before and after etching.

The rod-shaped samples for the thermal expansion measurements were also made by drawing a piece of glass, heated with a burner. They were made from the same melts that were used for preparing the fibers for internal friction measurements. The rods were cut and ground to a length of approximately 50 mm.

II.5. Analysis of the chemical composition of the specimens

The compositions of the specimens for the internal friction measurements were determined analytically.*

Since the fiber-drawing treatment might change the composition of the glass we did not determine the composition of the cooled melts, but took the fibers for the determinations.

The alkali content was established with a flame photometer. The aluminium concentration in the borate glasses was determined with a spectrophotometer. The overall silver content of the fibers that had been immersed in a silver-nitrate melt was determined by means of neutron-activation analysis.

In the ion-exchanged fibers not only the concentration of the original ions was determined, but also the fraction of ions penetrated into the glass from the melt.

Table II-1 gives the results of the analyses of the fibers in the silicate system. In Table II-2 the results of the analyses of the fibers in the borate system are given. These tables also contain data on the annealing temperatures and on the treatments to which a part of the fibers have been subjected.

*The compositions of the specimens were determined by Drs. W. Brouwer of the „Analytisch Centrum-Centraal laboratorium TNO”

Table II-1. Data on the investigated silicate fibers

fiber	Analytically determined composition (Mol. %)				Successive fiber treatments					
					ion exchange			etching in HF		max. annealing temp. in
	SiO ₂	Na ₂ O	Li ₂ O	Ag ₂ O	melt	temp. (°C)	time (min.)	time (min.)	removed layer (μ)	int. fr. app. (°C)
A	67.0	33.0	-		-			-		435
B	67.2	30.9	1.9		-			-		430
C	67.0	23.0	10.0		-			-		400
D	66.9	16.6	16.5		-			-		400
E	67.0	10.0	23.0		-			-		410
F	66.8	2.0	31.2		-			-		430
A1	67.0	25.1	7.9		LiNO ₃	275	1	-		405
A2	67.0	30.6	2.4		(Li,Na,K)NO ₃	175	30	-		410
A3	67.0	32.3		0.7	AgNO ₃	275	5	-		420
A4	67.0	29.4		3.6	AgNO ₃	295	30	-		410
A5	67.0	32.5		0.5	AgNO ₃	275	5	-		420 *
A6	67.0	33.0		-	AgNO ₃	275	5	10	150	435
A7	67.0	32.8		0.2	AgNO ₃	275	5	1	15	430
A8	67.0	32.8		0.2	AgNO ₃	275	5	1	15	430 **
G	75.0	25.0			-			-		470
G1	75.0	23.1		1.9	AgNO ₃	295	30	-		430

* Annealed at 435°C (3h) before ion exchange

** Annealed at 435°C (3h) before ion exchange and reheated to 275°C after ion exchange

Table II-2. Data on the investigated borate glasses

Glass no.	analytically determined composition (Mol.%).			max. annealing temp. in int. fr. app. (°C).	annealing temp. for therm. exp. measurements (°C).
	Na ₂ O	B ₂ O ₃	Al ₂ O ₃		
1	9.0	91.0	-		360
2	15.0	85.0	-	380	400
3	16.9	83.1	-	410	430
4	20.8	79.2	-	430	450
5	23.6	76.4	-	432	450
6	28.0	72.0	-	438	460
7	32.3	67.7	-	440	460
8	10.0	80.0	10.0	370	390
9	12.5	77.5	10.0	390	410
10	17.2	72.9	9.9	402	420
11	22.0	68.0	10.0	415	435
12	26.0	63.9	10.1	425	450
13	16.9	83.1	-	410	430
14	17.1	80.4	2.5	403	425
15	17.0	78.7	4.3	402	420
16	17.2	72.9	9.9	402	420
17	16.9	70.0	13.1	410	430
18	17.0	66.3	16.7	415	440
19	10.0	80.0	10.0	370	390
20	12.5	75.0	12.5	390	410
21	17.0	66.3	16.7	415	440
22	19.4	61.4	19.2	422	440
23	20.9	58.3	20.8	430	450
24	25.0	50.2	24.8	430	450

References

1. P.L. Kirby, J. Soc. Glass Technol., 39, 385 T (1955).
2. H. Eyring, "The Theory of Rate Processes", Mc. Graw-Hill 1941.
3. A.S. Nowick, B.S. Berry, I B M Journ., p.297, oct. 1961.
4. E. Wiechert, Annalen d. Physik, 50, 335, 546 (1893).
5. K.W. Wagner, Annalen d. Physik, 40, 817 (1913).
6. W.A. Yager, Physics, 7, 434 (1936).
7. K. Hilbert, Silikattechn., 7, 394 (1956).
8. K.E. Forry, J. Am. Ceram. Soc., 40, 90 (1957).
9. J.M. McCormick, J. Am. Ceram. Soc., 38, 288 (1955).
10. K.H. Karsch, E. Jenckel, Glastechn. Ber., 34, 397 (1961).
11. P. Kofstad, R.A. Butera, R.S. Craig, Rev. Scient. Instr.,
33, 850 (1962).
12. J.V. Fitzgerald, J. Am. Ceram. Soc., 34, 388 (1951).
13. S.L. Blum, J. Am. Ceram. Soc., 38, 205 (1955).
14. J.V. Fitzgerald, J. Am. Ceram. Soc., 34, 339 (1951).

CHAPTER III

Experiments on ion-exchanged sodium silicate glasses

III.1. Introduction and review of the literature

The internal friction peaks in simple alkali glasses have been subjected to quite intensive study by several investigators since 1950.

The first internal friction measurements were performed on rather complex glasses^{1,2,3}, but soon it was realized that a better understanding of the underlying mechanisms could not be obtained without the use of glasses of simpler composition.

Simple alkali silicate glasses were the first to come into consideration, because of their resemblance to the technical glasses which were used before.

Even the results on these simple glasses were not easy to be understood. As a function of temperature two clear peaks were discovered in 1952 by Fitzgerald, Laing and Bachman⁴. Later on this result was confirmed in several publications, among others by Forry⁵, Hoffman and Weyl⁶, Rötger⁷, and by Mohyuddin and Douglas⁸.

At first it was not fully understood that the mere existence of internal friction peaks in glass is not self-evident. According to B.Eckstein²² the model of Zachariasen²¹ does not even allow internal friction peaks, since in a completely random network all relaxation times must have the same probability and the only internal friction we may expect is a continuous spectrum. It has been suggested therefore that some kind of short-distance order exists in glass. The environments of the "structural elements" that produce an internal friction peak cannot be too different from each other.

The first peak - sometimes called the low-temperature peak - is found somewhat below room temperature and the second peak - the high-temperature peak - at about 200°C, using a measuring frequency between 1 and 10 cps.

Both maxima become smaller when the alkali concentration decreases. According to Forry the peaks even disappear at an alkali concentration of 10 and 2.5 mol.% for borate and silicate glasses respectively.

At the same time the peak temperatures increase. The low-temperature peak, for instance, shifts to a 50°C higher temperature when the Na₂O concentration of a sodium silicate glass is lowered from 34 to 17 mol.%. The heat of activation at the same time increases from 15.8 to 19.6 kcal/mol, according to Forry.

The low-temperature peak is generally attributed to the "stress-induced diffusion" of the alkali ions, as Fitzgerald² calls it. This is a rather obscure statement and can easily be misunderstood. The word "diffusion" suggests the jumping of an ion through the network over a certain distance. This, however, is not necessary for an internal friction peak to be produced. It is sufficient when an ion spreads its presence over two equilibrium positions, while the probability of finding the ion in one of these positions is influenced by a macroscopic stress or strain. We will return to this in Chapter V.

For the moment we will confine ourselves to the remark that the existence of this peak has something to do with the presence of alkali ions in the glass.

There are two main reasons why this has been proposed in the literature.

Firstly the height and the temperature of this peak are directly related to the alkali-ion concentration in the glass.

Secondly the activation energy of the peak is about equal to the activation energy found for properties that are undoubtedly related to the presence of the alkali ions, such as the electrical conductivity and tracer diffusion.

The high-temperature peak has been attributed to several possible mechanisms.

Forry⁵ suggested that the high-temperature peak might be due to the cooperative action of two sodium ions. Jagdt⁹ similarly attributed the peak to an interchange of position of the alkali ions. Fitzgerald, Laing and Bachman⁴ however, suggested that the high-temperature peak might be due to a constrained movement of the silica tetrahedra or to nonbridging oxygen ions diffusion. Rötger¹⁰ concluded from his experiments on lithium, sodium and potassium silicate glasses as well as sodium borate glasses that the peak was due to the migration of the nonbridging oxygen ions associated with the alkali ions.

Ryder and Rindone¹¹ from their study on alkali silicate glasses containing alkaline-earth oxides, and Day and Rindone¹² from their study on soda aluminosilicate glasses, concluded that the high-temperature peak was caused by the movement of the nonbridging oxygen ions.

They observed that the addition of alkaline-earth oxides caused the high-temperature peak to shift to higher temperatures and to decrease in height and attributed this to the immobilization of a large proportion

of the nonbridging oxygen ions. By substituting Al_2O_3 for the Na_2O and/or SiO_2 they reduced the number of nonbridging oxygen ions and consequently found a decrease in height of the peak and a shift to higher temperatures.

Coenen¹³ postulated another explanation for the existence of the high-temperature peak. He called this peak an interaction peak, because in his opinion the high-temperature peak was due to the interaction of alkali ions and bridging protons.

Brückner¹⁴ supported this idea. He observed that the $4.25\text{ }\mu\text{m}$ -absorption (due to bridging protons) was directly related to the height and the temperature of the high-temperature peak. An increasing H_2O content meant an increase in the height of the high-temperature peak and a shift to lower temperatures. At the same time the low-temperature peak decreased in height and shifted to higher temperatures. He suggested that this peak was due to an interchange of the positions of alkali ions and bridging protons.

Some investigators extended their experiments to silicate glasses containing more than one alkali oxide. These glasses— often called mixed-alkali glasses— are of special interest, because they exhibit a certain anomaly.

When one alkali oxide in glass is partly replaced by another alkali oxide the electrical conductivity does not behave additively, but exhibits a minimum close to the 1:1 composition. This has been found by several investigators^{15,16}.

According to Stevels¹⁷ there is also a reduction in dielectric losses. Although many studies have been made of the effect, its occurrence in any one system has not yet been completely explained.

Several possible explanations have been proposed. Lengyel and Boksay¹⁵ tried to explain the phenomenon by pointing out the difficulties ions of different sizes must overcome to interchange their positions, Mazurin and Borisovskii¹⁶ showed that this was not sufficient to explain the effect. When in a simple sodium silica glass, containing 20% Na_2O , we replace 20% SiO_2 by K_2O the resistance does not drop nor remain constant, but increases by more than one order of magnitude. Thus the carrying of current by ions of one kind is not assisted by ions of another kind, but strongly hindered.

Stevels¹⁷ and Kobeko¹⁸ suggested that the reduction of dielectric loss resulted from a denser structure in mixed-alkali glasses than in glasses with a single alkali oxide. Caporali¹⁹, however, demonstrated that the mixed-alkali effect could also be found in glasses showing no increase in density compared with the single-alkali glasses.

Mazurin and Borisovskii¹⁶ suggest that the number of holes in the structure plays a predominant part. The looser the structure of a glass,

the easier it will be for the ions to be replaced. It appears that when SiO_2 is replaced by an alkali oxide the number of holes is considerably reduced. This can result in a considerable reduction of the electrical conductivity. They also state that the effect can be explained only by taking into account the interactions between alkali ions of different sizes.

Charles²⁰ offers another explanation, supported by experiments on Cs_2O -containing glasses. He suggests that partial alkali-ion substitution promotes or enhances metastable phase separation during cooling of the glass melts. The smaller and more mobile ions are scavenged into the discontinuous phase, so that the larger ions determine the dc resistivity.

An anomalous effect is also found in the internal friction of mixed-alkali glasses. Rötger¹⁰ reports the appearance of an extraordinarily high peak at temperatures between 100° and 200°C and the complete disappearance of the low-temperature peak in glasses with a concentration ratio of the alkali oxides near 1/1.

According to Mohyuddin and Douglas⁸ this peak is a summation of the low- and the high-temperature peak (although they noticed that the area under the combined peak was larger than might be expected).

Coenen²¹ suggests that the peak is originally a high-temperature peak. He observed that with the addition of a second type of alkali oxide to the glass the low-temperature peak shifts to higher temperatures and decreases in height, whereas the high-temperature peak shifts to lower temperatures and increases in height. At a concentration ratio 1 : 1 there is only one very high peak left, the height of which seems to be a function of the ratio of the radii of the two alkali ions present. Actually he considers this peak to be an interaction peak that can be compared with the high-temperature peak in single-alkali glasses, which - as we have seen - he believes to be due to interaction between alkali ions and protons.

It is generally accepted that the intermediate-temperature peak attains its maximum size at a concentration ratio 1 : 1. An extensive study on glasses with different alkali ratios, however, has never been performed as far as we know.

For this reason we started our experiments with a study of the internal friction of mixed-alkali glasses with various concentration ratios, restricting ourselves to the oxides Na_2O and Li_2O .

In connection with this we continued the investigations with a different approach of the problem. Starting with a soda silicate glass we introduced lithium oxide by an ion-exchange treatment. This was done at a temperature far below the annealing temperature, so that there was

no possibility for the network to adjust to the modified composition. From this it might be possible to decide whether the mixed-alkali effect is due to structural modifications or to the alkali ions themselves. The ion-exchange treatment takes place in a small surface layer only. This results in a concentration gradient in the glass, which no doubt influences the internal friction curve. By etching away the ion-exchanged layer the relative influence of this layer could be demonstrated experimentally.

It is to be expected that an annealing treatment influences the internal friction curve of the ion-exchanged glass to a great deal. The structure then has the opportunity to adjust to the composition and the concentration gradient will be modified by the enhanced diffusion. Consequently special attention was paid to this aspect of the investigation.

III.2. Experimental results

III.2.1. Internal friction of mixed-alkali glasses in the composition range $x\text{Na}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot 2\text{SiO}_2$

We investigated the compositions with a concentration ratio $\text{Na}/\text{Li} = x/1-x$ equal to ∞ , 15, 2.5, 1, 0.4 and 0.07. The fibers with these compositions are resp. called fiber A, B, C, D, E and F. The internal friction curves of these fibers are shown in the Figs. III-1 to III-6.

Fiber A (Fig. III-1), containing 33 mol.% Na_2O , is a simple sodium silicate glass. The internal friction curve as a function of temperature shows two peaks, a low-temperature peak at -33°C and a high-temperature peak at $+207^\circ\text{C}$. (measured at a frequency of 5 cps.). This is in complete agreement with the results of other investigators, as was discussed in the preceding section.

Curve A', representing the internal friction of the unannealed fiber of composition A, has the usual trend: the peaks are higher and shifted to a slightly lower temperature. There seems to be an indication of a small maximum at about 300°C in this glass. As far as we know this peak has not been described before in the literature. This may be due to the fact that we measured the internal friction in vacuo and used a careful annealing procedure which certainly reduced the background absorption in this temperature range.

As could be expected from previous investigations a new peak appears in the fibers where lithium oxide replaces part of the sodium oxide. As has been reported before^{7,9} this peak is extremely high at concentration ratios Na/Li approaching the value 1. From our experiments, however, it appears that even at concentration ratios as extreme as 15 (Fig. III-2) and 0.07 (Fig. III-6) the peak attains a considerable size. The exact data are given in Table III-1

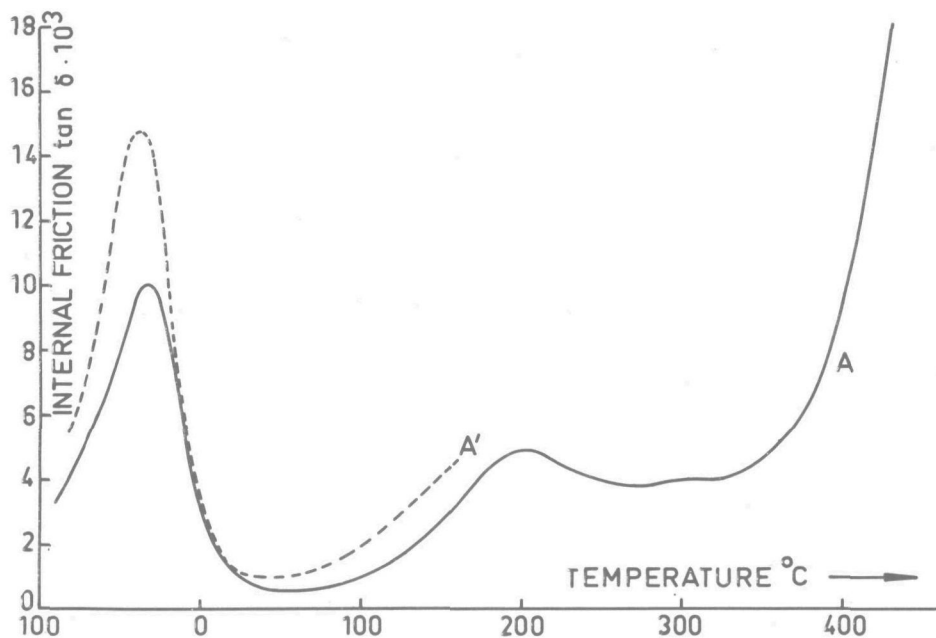


Fig.III-1. Internal friction curves of a fiber with the composition $0.33 \text{ Na}_2 \cdot 0.67 \text{ SiO}_2$ before and after annealing.

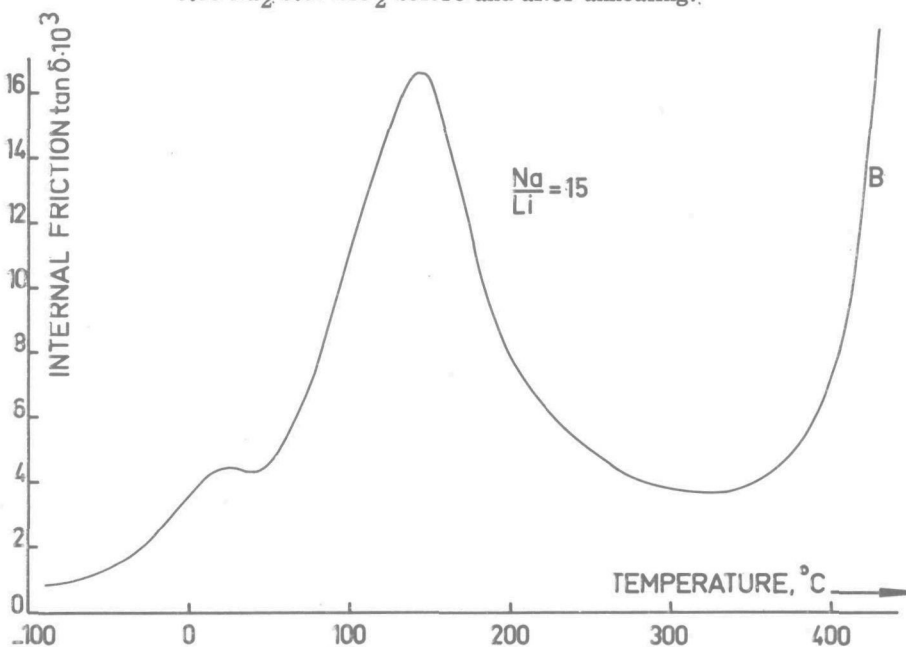


Fig.III-2. Internal friction curve of a fiber with the composition $0.31 \text{ Na}_2 \cdot 0.02 \text{ Li}_2\text{O} \cdot 0.67 \text{ SiO}_2$ after annealing.

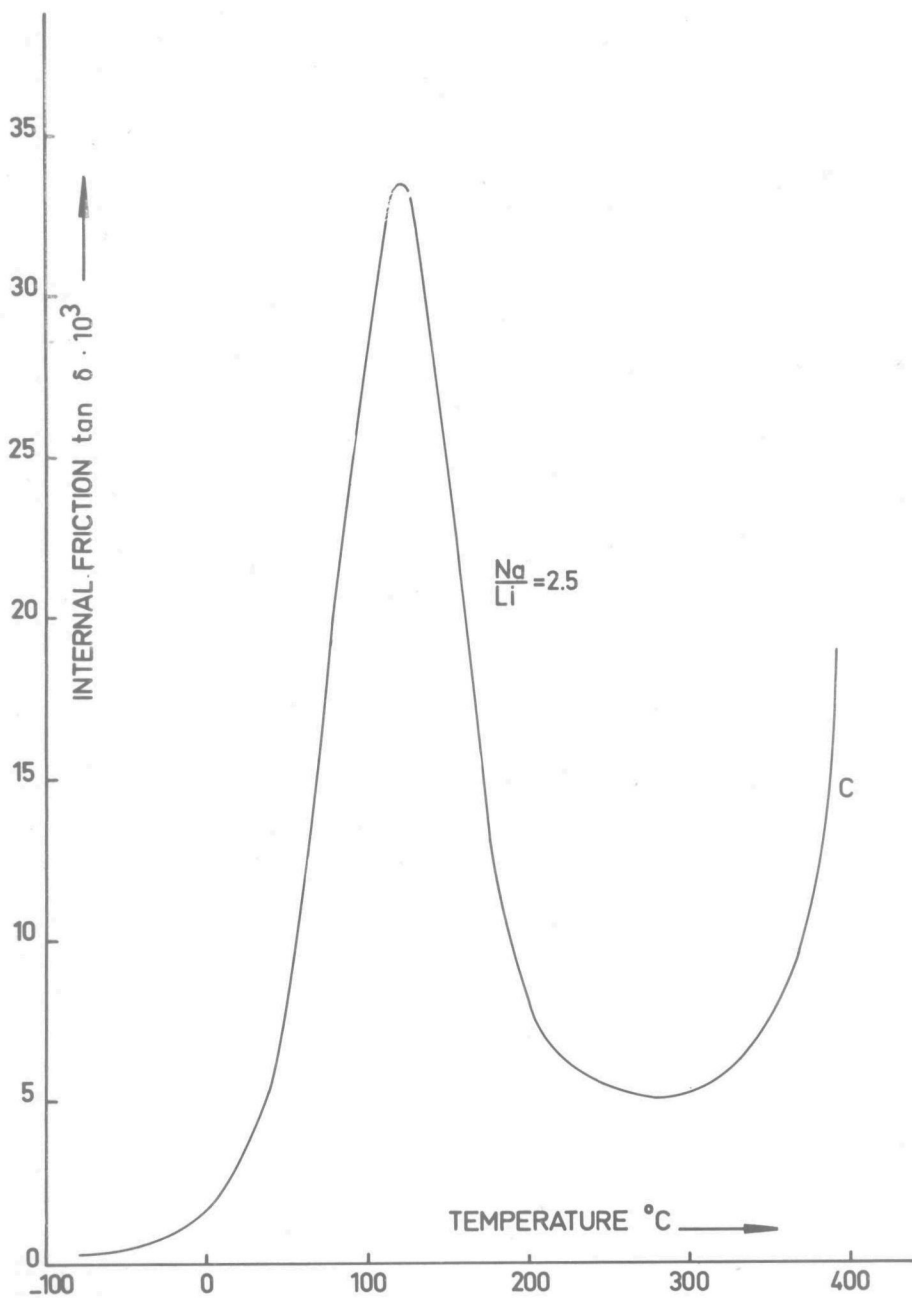


Fig.III-3. Internal friction curve of a fiber with the composition $0.23 \text{ Na}_2\text{O} \cdot 0.10 \text{ Li}_2\text{O} \cdot 0.67 \text{ SiO}_2$ after annealing.

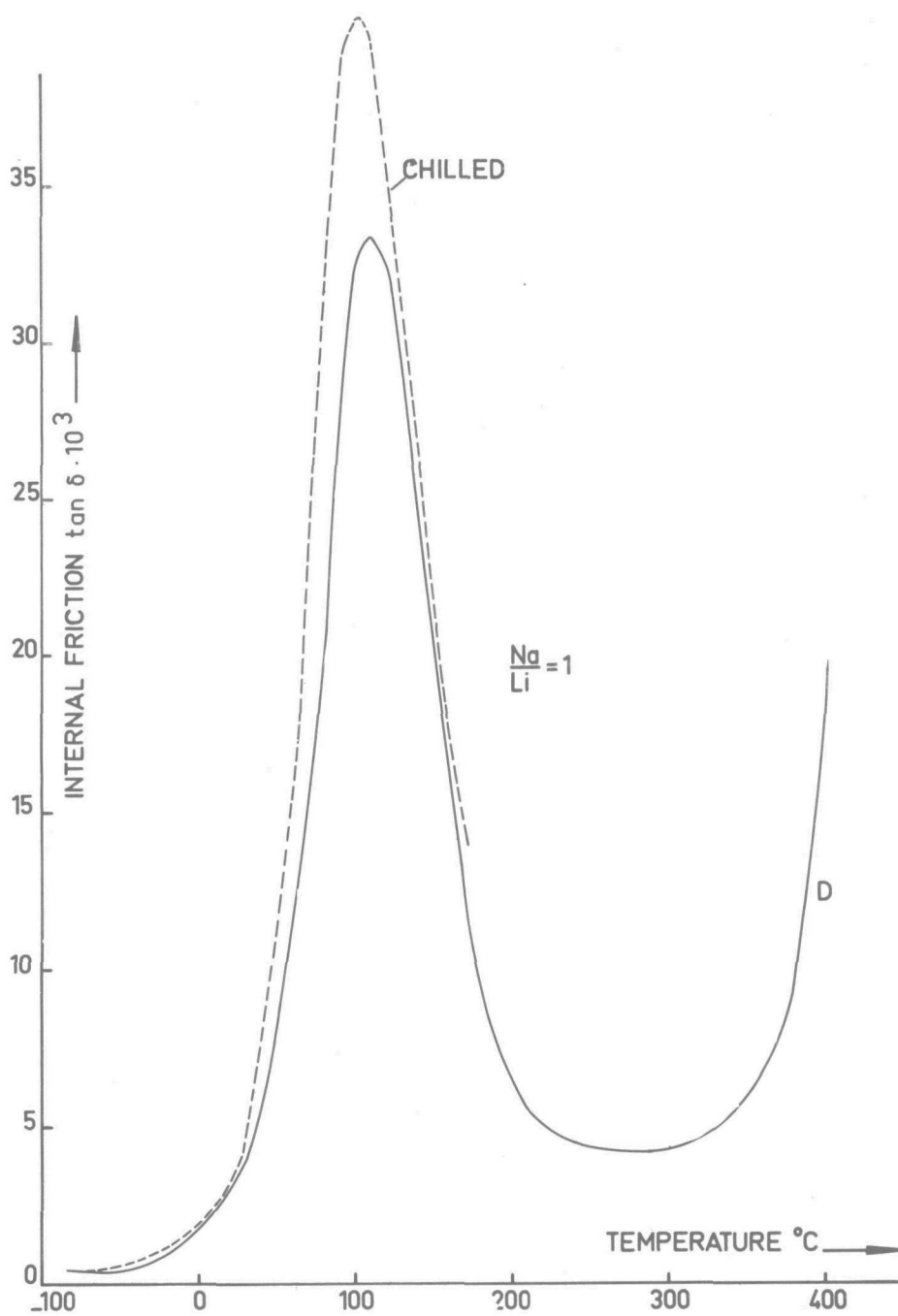


Fig.III-4. Internal friction curves of a fiber with the composition $0.165 Na_2O \cdot 0.165 Li_2O \cdot 0.67 SiO_2$ before and after annealing.

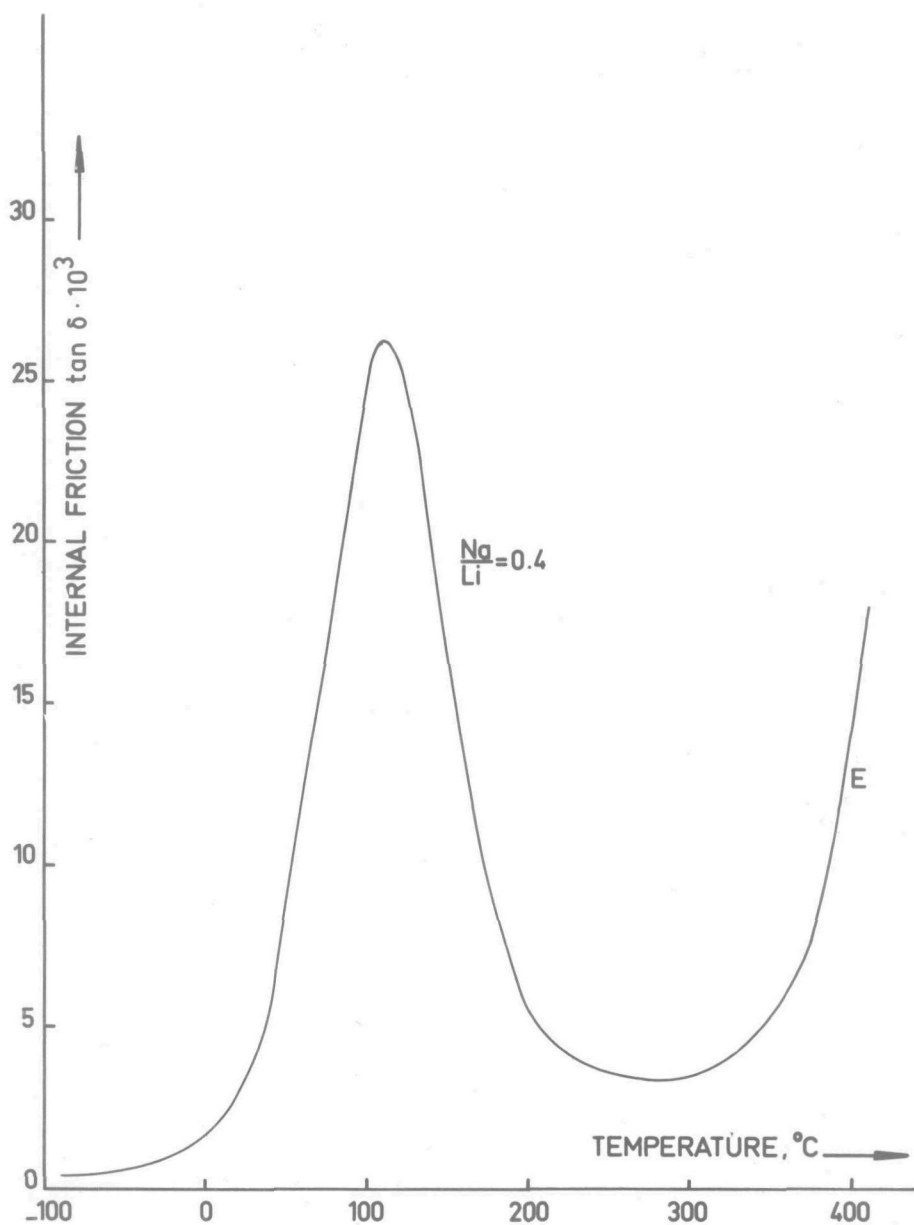


Fig.III-5. Internal friction curve of a fiber with the composition $0.10 \text{ Na}_2\text{O} \cdot 0.23 \text{ Li}_2\text{O} \cdot 0.67 \text{ SiO}_2$ after annealing.

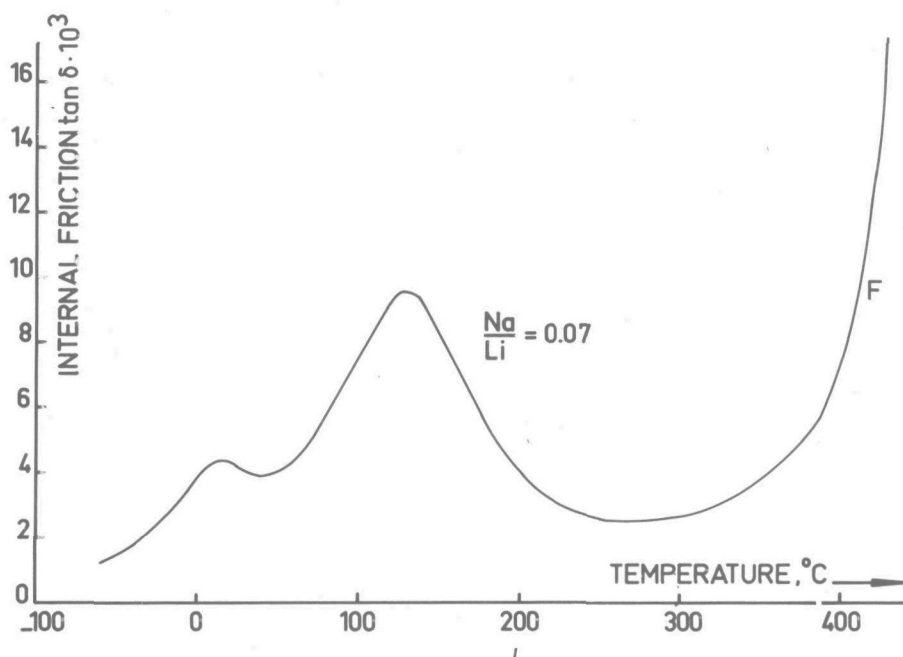


Fig.III-6. Internal friction curve of a fiber with the composition $0.02 \text{ Na}_2\text{O} \cdot 0.31 \text{ Li}_2\text{O} \cdot 0.67 \text{ SiO}_2$.

Table III-1. Data on the internal friction of mixed-sodium-lithium glasses

Fiber	concentration ratio Na/Li	Data on intermediate - temperature peak		
		temp.(°C)	max,height above background	width at half height
A	∞	-	-	-
B	15	143	16.6×10^{-3}	100 (°C)
C	2.5	121	33.4×10^{-3}	95
D	1.0	114	33.4×10^{-3}	85
E	0.4	115	26.2×10^{-3}	94
F	0.07	130	9.7×10^{-3}	106

It appears that the temperature of the intermediate-temperature peak is hardly affected by the concentration ratio. The temperature of the low-temperature peak, on the contrary, is very much influenced by the addition of lithium oxide. The replacement of 2% Na_2O by Li_2O causes the low-temperature peak to transform to not much more than an inflection of the intermediate-temperature peak, as can be seen in Fig. III-2. The peak not only decreases in height, but also makes a shift of about 50°C to higher temperatures. In the fibers C, D and E, containing resp. 10, 16.5 and 23 mol.% Li_2O , the low-temperature peak has completely vanished. (Figs. III-3, 4 and 5).

In Fig. III-6 it can be seen that in the glass with 31% Li_2O and no more than 2% Na_2O a low-temperature peak has reappeared that can be compared with the one in glass B, containing 2% Li_2O and 31% Na_2O . A glass containing 33% Li_2O could not be measured properly, because of crystallization phenomena during the annealing treatment. It could be demonstrated, however, that a glass of this composition contains no intermediate-temperature peak and has a low-temperature peak in the same temperature range as the glass containing 33% Na_2O .

III.2.2. Internal friction of sodium disilicate glass after ion exchange with lithium ions

The internal friction curve of sodium disilicate glass (Fig. III-1) changes markedly after an ion-exchange treatment in a lithium-containing melt.

Fig. III-7 shows the internal friction curve after a treatment in LiNO_3 for 1 min. at 275°C .

Before annealing (curve A1') the low-temperature peak has decreased in height, but the peak temperature has not changed. A peak appears at 120°C , smaller than the intermediate-temperature peaks we found in the mixed-alkali glasses, but in the same temperature range. After annealing the situation has changed; in curve A1 no low-temperature peak can be detected, whereas the intermediate-temperature peak has grown to a size that makes it comparable to those in the curves of the mixed-alkali glasses C, D and E.

In Fig. III-8 the internal friction is shown of a fiber subjected to an ion-exchange treatment in a melt consisting of a eutectic mixture of LiNO_3 , KNO_3 and NaNO_3 at 175°C for $2\frac{1}{2}$ h.

Here we followed a somewhat different procedure for the measurements. First we determined the internal friction below room temperature (curve A2''). The low-temperature peak that was measured in this way completely coincides with the low-temperature peak in the parent glass (curve A of Fig. III-1). After this the fiber was heated to 275°C . The curve that was measured down from this temperature shows only a

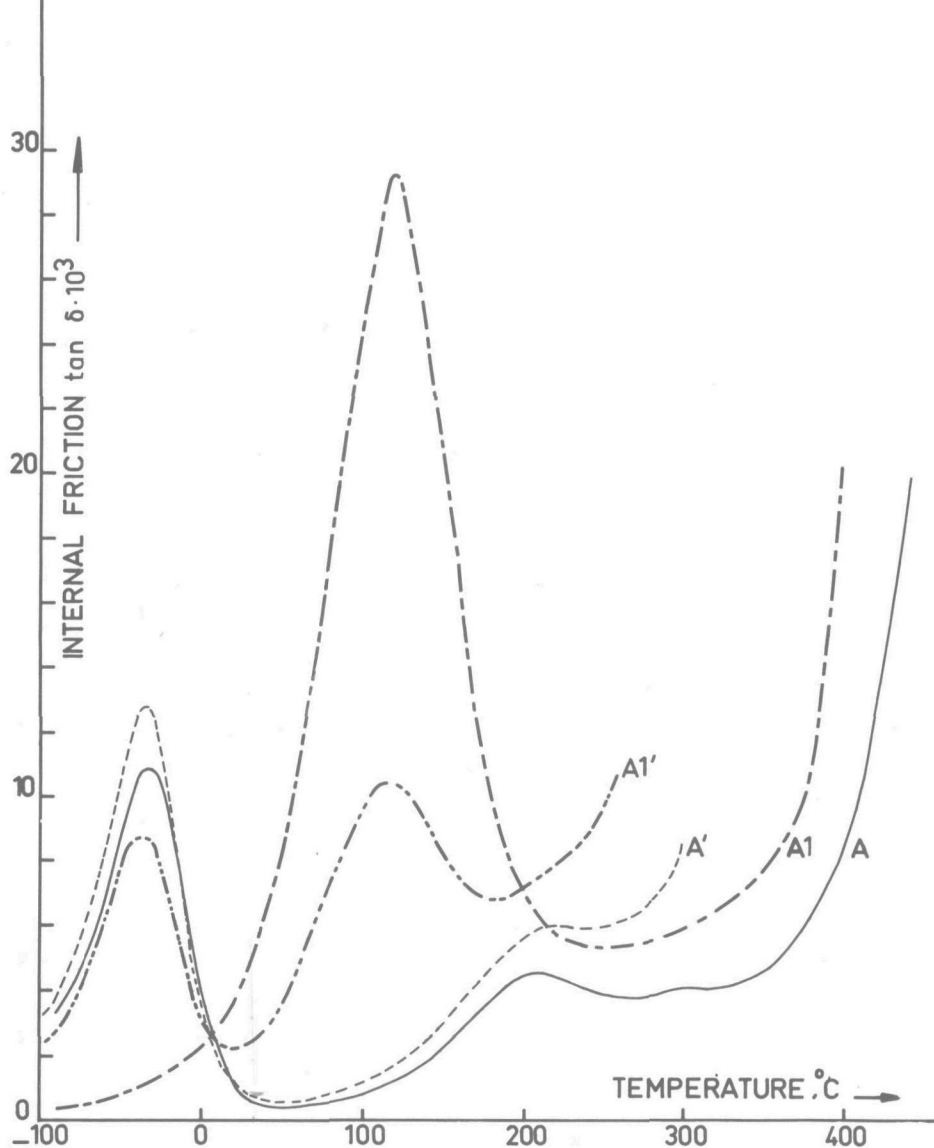
Fig.III-7. Internal friction of the glass $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ after 1 min. ion exchange in LiNO_3 at 275°C .

A' : original glass, unannealed.

A : original glass, annealed.

A1' : after ion exchange.

A1 : after ion exchange and annealing.



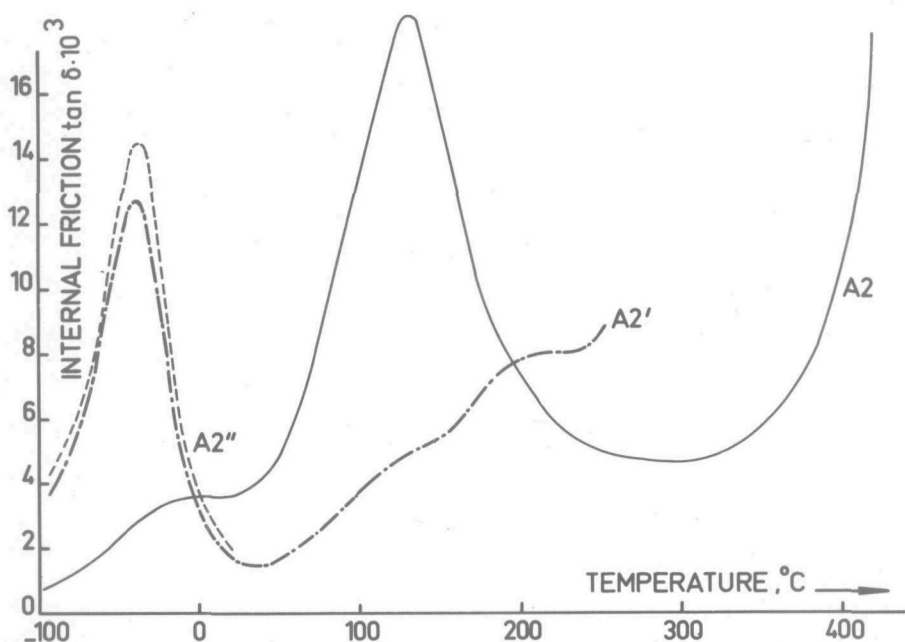


Fig.III-8. Internal friction of the glass $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ after $\frac{1}{2}$ h. ion exchange in $\text{LiNO}_3 + \text{KNO}_3 + \text{NaNO}_3$ at 175°C .

A2'': after ion exchange, measured down from 20°C .

A2': after ion exchange, measured down from 275°C .

A2 : after ion exchange and annealing.

small indication of an intermediate-temperature peak. The low-temperature peak has decreased slightly in height, but shows no temperature shift. After complete annealing the curve has changed completely, as is shown by curve A2. The low-temperature peak has become very small and has shifted to some 40°C higher temperature. The intermediate-temperature peak has grown, and actually the whole curve bears much resemblance to the curve in Fig. III-2, giving the internal friction of the glass containing 31% Na_2O and 2% Li_2O , prepared by melting.

During the experiments with lithium-ion-exchanged fibers it was noted that after the ion-exchange treatment the surface layer was cracked. This phenomenon, which is due to the internal stresses built into the layer when replacing a Na ion by the smaller Li ion, may obscure the results of the internal friction measurements.

The cracked layer is not likely to contribute to the internal friction peaks, because no elastic stresses can be built up in the layer. During annealing, however, the layer serves as a source of Li ions for the so far unaffected part of the fiber. The relatively high annealing temperature prevents cracking of this inner part during cooling, because the SiO_2 skeleton has the possibility to adjust to the new circumstances. In other words, the effective concentration of Li ions is not the same

before and after annealing, it may even be zero before and yet be very high after annealing.

For this reason, and also to see whether the phenomena recorded are exclusive for glasses containing only alkali metals, we extended the experiments to fibers exposed to an ion-exchange treatment with silver ions.

III.2.3. Internal friction of sodium disilicate glass after ion exchange with silver ions

The Figs. III-9, 10, and 11 show the influence of the exchange of sodium ions by silver ions in fibers of the sodium disilicate composition. Fiber A3 has been subjected to an AgNO_3 melt during 5 min. at 275°C , after which the Ag_2O content amounts to 0.7 mol.% (Table II-1). As shown in Fig. III-9 the internal friction curve is not essentially different from the curves in the preceding section. There is an intermediate-temperature peak at about 80°C in the unannealed fiber cooled from 275°C (curve A3'). The low-temperature peak has decreased in height, compared with the same peak in a fiber of the original composition (A), which is also shown in this figure. Before annealing there is no temperature shift. As a result of annealing the low-temperature

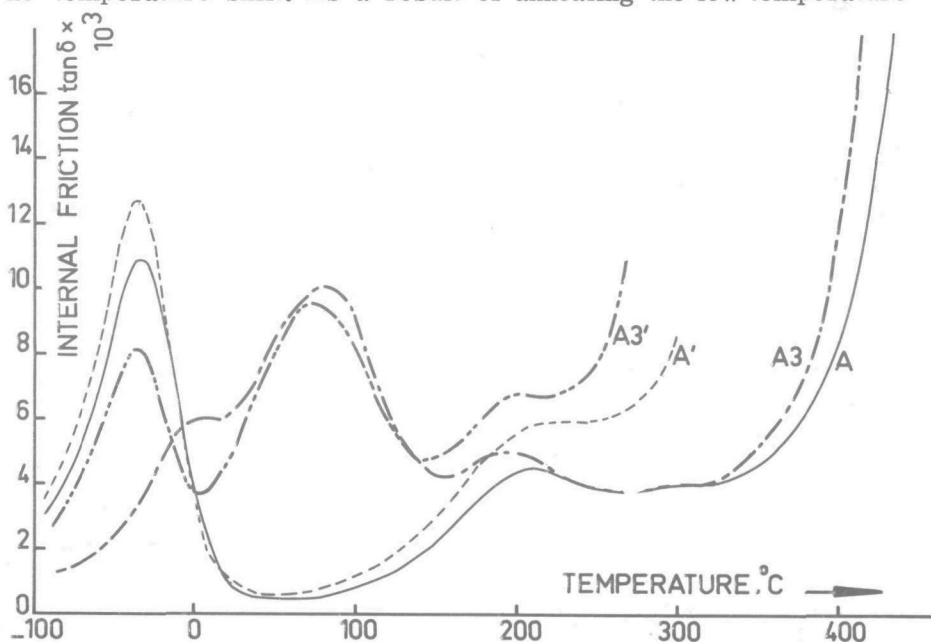


Fig. III-9. Internal friction of the glass $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ after 5 min. ion exchange in AgNO_3 at 275°C .

A' : original glass, unannealed.

A : original glass, annealed.

A3' : after ion exchange.

A3 : after ion exchange and annealing.

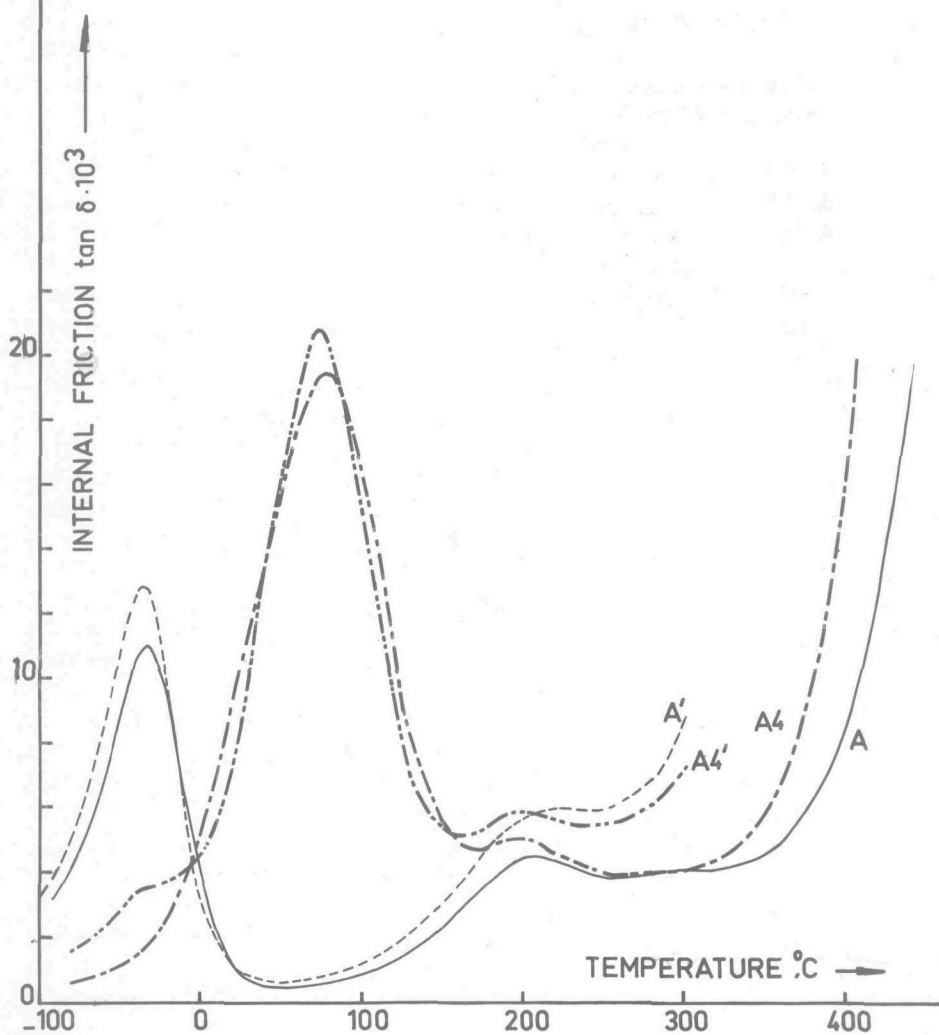
Fig.III-10. Internal friction of the glass $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ after $\frac{1}{2}$ h. ion exchange in AgNO_3 at 295°C .

A' : original glass, unannealed.

A : original glass, annealed.

A4' : after ion exchange.

A4 : after ion exchange and annealing.



peak shifts to a higher temperature and reduces further in height. It should be noted that the size of the intermediate-temperature peak is not noticeably influenced by the annealing treatment, unlike the results with the lithium-ion-exchanged fibers in the preceding section. The high-temperature peak seems not to be influenced by the ion-exchange treatment.

A similar, but more pronounced, behaviour is found in Fig. III-10 for fiber A4, containing 1.6 mol.% Ag_2O after $\frac{1}{2}$ h in the salt melt at 295°C . The intermediate-temperature peak is very high and its size is not affected by the annealing treatment. The low-temperature peak is very small, but still shows no temperature shift. After annealing the peak has disappeared. The high-temperature peak seems not to be influenced, although this is not quite certain, since the peak is partly overlapped by the intermediate-temperature peak.

The results of Fig. III-8 showed that no decrease in height could be detected in the low-temperature peak of a fiber that had been subjected to a lithium-ions-containing melt, when the peak was measured without heating to 275°C . We considered that this might be due to the cracking of the surface layer. Perhaps the "active" (i.e. uncracked) part of the fiber did not contain any lithium ions until it had been heated to a higher temperature.

Since the Ag-containing fibers did not exhibit any cracking - probably because of the more corresponding radii of the ions involved and the greater polarizability of the Ag ions - we thought it interesting to repeat the experiment, using silver ions instead of lithium ions. We did, however, use fibers that had already been annealed in a furnace at 420°C for 2 hours (cooling rate $1^\circ\text{C}/\text{min.}$) before exposing them to the ion-exchange melt. This was done to make sure that the height and the position of the low-temperature peak did not change during the experiments at the different temperatures (as we have seen the height and the position of the internal friction peak depend on the thermal history of the fiber, but after the annealing treatment this effect can be neglected). The results of this experiment are shown in Fig. III-11. The height of the low-temperature peak in the original glass amounts to $\tan \delta = 10 \times 10^{-3}$. In the ion-exchanged fiber we find that the height of the peak has decreased to 9.5×10^{-3} when cooling from 20°C , to 9.2×10^{-3} when cooling from 140°C , and to 9.0×10^{-3} when cooling from 200°C . When the fiber has been heated to 275°C , however, we suddenly find a sharp decrease and the peak reaches only a height of 6.8×10^{-3} . As usual a temperature shift occurs only after annealing at higher temperatures. For the intermediate-temperature peak the situation is also somewhat unexpected. Heating to 140°C results only in a weak indication of a very broad maximum. Cooling from 200°C results in a sharper peak, but still the magnitude of the peak is much

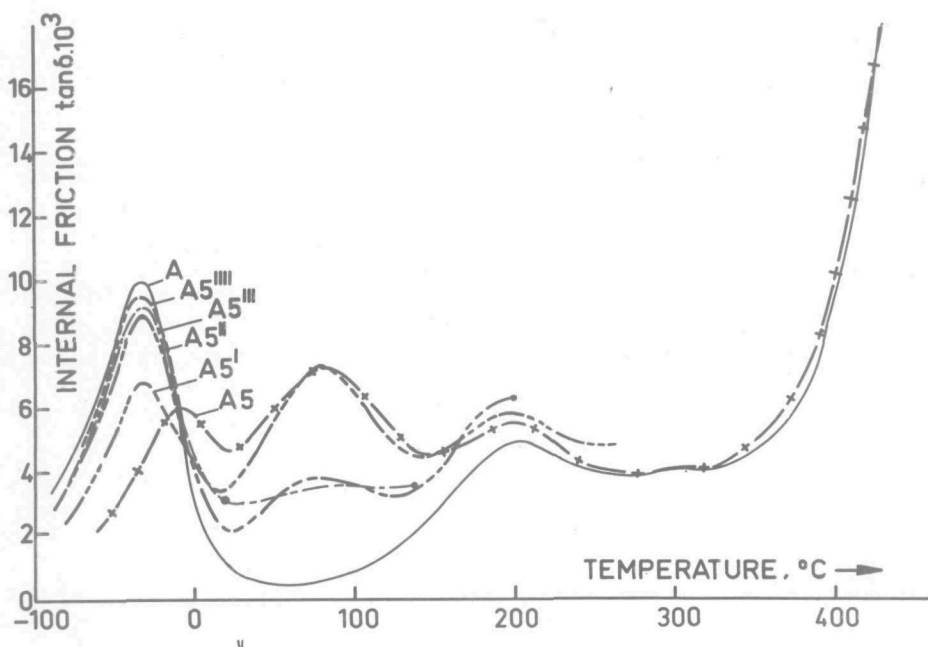


Fig.III-11. Effect of the starting temperature on the internal friction of the annealed glass $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ after 5 min. ion exchange in AgNO_3 at 275°C .

- A : original glass, annealed.
- A5'''' : after ion exchange, measured down from 20°C .
- A5''' : after ion exchange, measured down from 140°C .
- A5'' : after ion exchange, measured down from 200°C .
- A5' : after ion exchange, measured down from 275°C .
- A5 : after ion exchange and annealing.

smaller than was found before. Heating to 275°C again produces a significant change. The peak height increases to a more "normal" value. This seems to be its final size, since even annealing at 420°C does not result in changes in size or position.

As a conclusion we can say that a temperature of 275°C seems to be necessary to produce a significant change in the internal friction curve of the ion-exchanged fiber. It makes the low-temperature peak diminish in height and the intermediate-temperature peak grow considerably. It must be remembered that the upper temperature limits were only starting points for the measurements. The fiber was heated to the

concerning temperature and immediately cooled down at a rate of $1^{\circ}\text{C}/\text{min}$. It may be possible that a longer time at 200°C results in a curve, similar to the one found for a starting temperature of 275°C when cooled down immediately.

III.2.4. Effect of etching on the internal friction of sodium disilicate glass after ion exchange with silver ions

From the unannealed fiber A3' (Fig. III-9) we removed thin layers by etching in an HF solution. It might be expected that the internal friction curve returns to its original shape (fiber A') after removal of the entire ion-exchanged layer. This is exactly what happens, as is shown

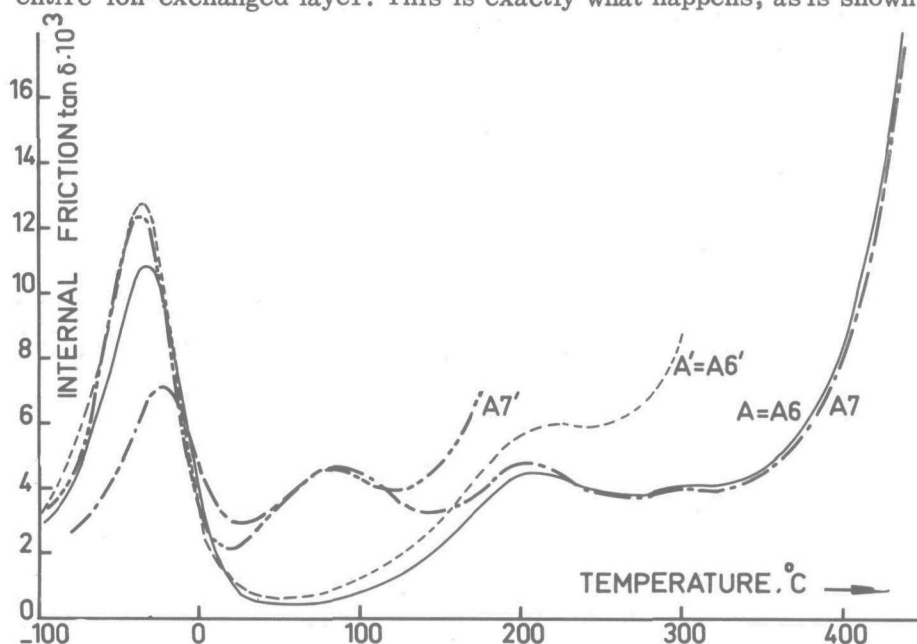


Fig. III-12. Effect of 5 min. ion exchange in AgNO_3 at 275°C and subsequently etching in HF on the internal friction of the glass $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$.

A' : original glass, unannealed.

A : original glass, annealed.

A6' : after ion exchange and removal of a 150μ layer.

A6 : after annealing.

A7' : after ion exchange and removal of a 15μ layer.

A7 : after annealing.

by the curves A6' and A6 (resp. before and after annealing) in Fig. III-12, where 150μ was removed from a fiber of the type A3'. The curves coincide completely with those of the sodium disilicate glass, shown in Fig. III-1.

What happens if the ion-exchanged layer is removed only partly is also shown in Fig. III-12. Curve A7' represents the internal friction of fiber A3' after removal of a layer of 15μ . According to Table II-1 less than 0.1 mol.% Ag_2O is left in this fiber. Evidently the intermediate-temperature peak is much smaller, but remains at the same temperature. The low-temperature peak, on the contrary, almost returns (in size as well as in temperature) to its original shape. After annealing of this fiber the higher-temperature part of the curve (A7) turns out to be identical to the one in the sodium disilicate glass. The intermediate-temperature peak is not influenced by the annealing treatment, but the low-temperature peak falls to a lower value and shifts to a higher temperature than does the same peak in the sodium disilicate glass after annealing.

In contrast with the previous results etching after an annealing treatment has no detectable effect on the internal friction curve. We annealed a fiber of the type A3' during three hours in a furnace at 420°C and afterwards removed successive layers from the fiber. The internal friction curve was not affected, not even after removal of 200μ . It is likely that this is due to the diffusion of the metal ions at the annealing temperature, resulting in a uniform Ag-ion concentration in the fiber.

To verify this it was necessary to determine the concentration gradient of the silver ions in a more direct way*. This was done by using a radioactive silver-nitrate melt for the ion-exchange treatment. Thin layers (5 to 10μ) were successively etched off with dilute hydrofluoric acid. The quantity of radioactive silver ions in each solution was counted. The thickness of the etched layers was calculated from the change in weight after etching.

The results of these experiments are shown in Fig. III-13a for fibers subjected to the radioactive melt for 5 min. at 275°C , and in Fig. III-13b for fibers subjected to this melt for $\frac{1}{2}$ h at 295°C . The curves A in these figures represent the concentration gradients in fibers that have not been heat treated after the ion-exchange treatment. The curves B represent the concentration gradients after reheating to 275°C and cooling at a rate of about $1^\circ\text{C}/\text{min}$. It can be seen that, although

* These experiments were performed by Drs. W.M.C.de Jong of the "Analytisch Centrum - Centraal Laboratorium TNO".

the ions have penetrated further into the glass, there still exists a concentration gradient, and a relatively large part of the fiber has not yet been affected. Curve C (only in Fig. III-13a) represents the concentration of silver ions as a function of the penetration depth after annealing at 420°C for 3 hours. No concentration gradient can be detected after this treatment. This confirms the suppositions we made in this section about the internal friction of annealed ion-exchanged fibers after etching.

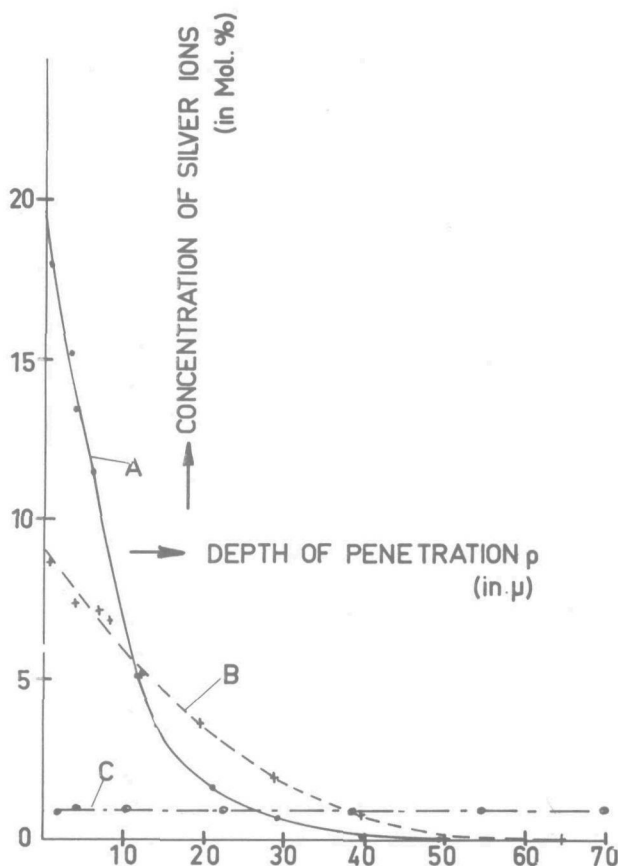


Fig.III-13a. Concentration profile of silver ions penetrated into an unannealed fiber of the composition $\text{Na}_2\text{O} \cdot 2 \text{SiO}_2$ during an ion-exchange treatment of 5 min. in AgNO_3 at 275°C.
 curve A : before reheating.
 curve B : after reheating to 275°C.
 curve C : after annealing at 420°C for 3 hours.

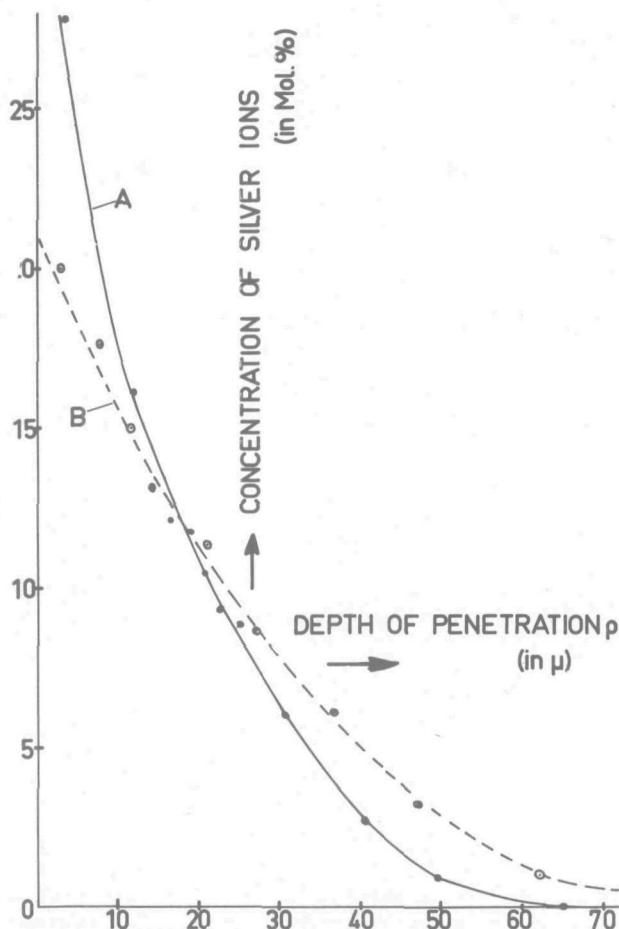


Fig.III-13b. Concentration profile of silver ions, penetrated into and an unannealed fiber of the composition $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ during an ion-exchange treatment of $\frac{1}{2}$ h. in AgNO_3 at 295°C .
 curve A : before reheating.
 curve B : after reheating to 275°C .

In view of the results shown in Fig. III-11 - where the great influence of the starting temperature was demonstrated - it seemed interesting to perform the following experiment: we took a fiber of the sodium disilicate composition, annealed it in a furnace at 420°C during 2 hours and cooled at a rate of $1^\circ\text{C}/\text{min}$. We then subjected this fiber to an ion-exchange treatment in AgNO_3 at 275°C for 5 min., heated the fiber to 275°C and cooled it down immediately at a rate of $1^\circ\text{C}/\text{min}$. From this fiber - which was then of the type A5' - we removed 15μ by etching. The internal friction of this fiber was measured down from 20°C (A8^{***}), 140°C (A8^{**}), 275°C (A8') and after annealing at 420°C (A8). The results are shown in Fig. III-14.

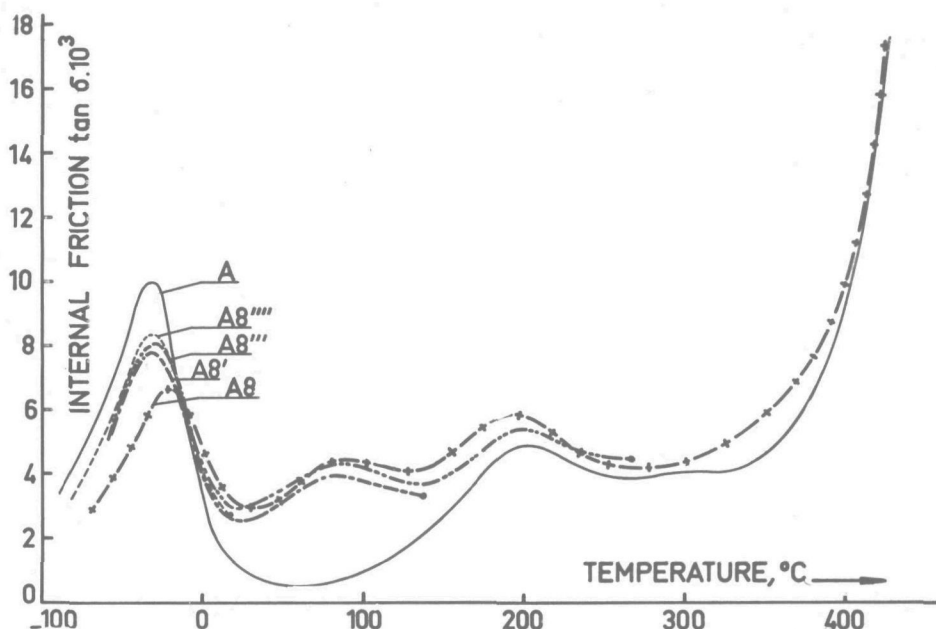


Fig.III-14. Effect of the starting temperature on the internal friction of the annealed glass $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ after 5 min. ion exchange in AgNO_3 at 275°C , reheating to 275°C and removal of a 15μ layer in HF .

A : original glass, annealed.

A8''': after ion exchange, reheating and etching; measured down from 20°C .

A8''': after ion exchange, measured down from 140°C .

A8' : after ion exchange, measured down from 275°C .

A8 : after ion exchange, after annealing.

Since this fiber had already been heated to 275°C we do not expect the great differences we found in Fig. III-11 between the curves with starting temperatures below 275°C and the curve started at 275°C . The height of the low-temperature peak is hardly influenced by the starting temperature, except after annealing, when the peak shifts to higher temperatures. The intermediate-temperature peak also is hardly influenced by the starting temperature. Even annealing has no effect. There can be no doubt, however, that after heating to 275°C there still exists a concentration gradient in the fiber; the low-temperature peak is higher and the intermediate-temperature peak is much lower than before etching. This completely confirms the results shown in Fig. III-13.

III.2.5. Experiments on sodium trisilicate glass

We performed some experiments with fibers of the composition $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ to see if the phenomena we found for the sodium disilicate glass could also be detected in glasses with a different soda content.

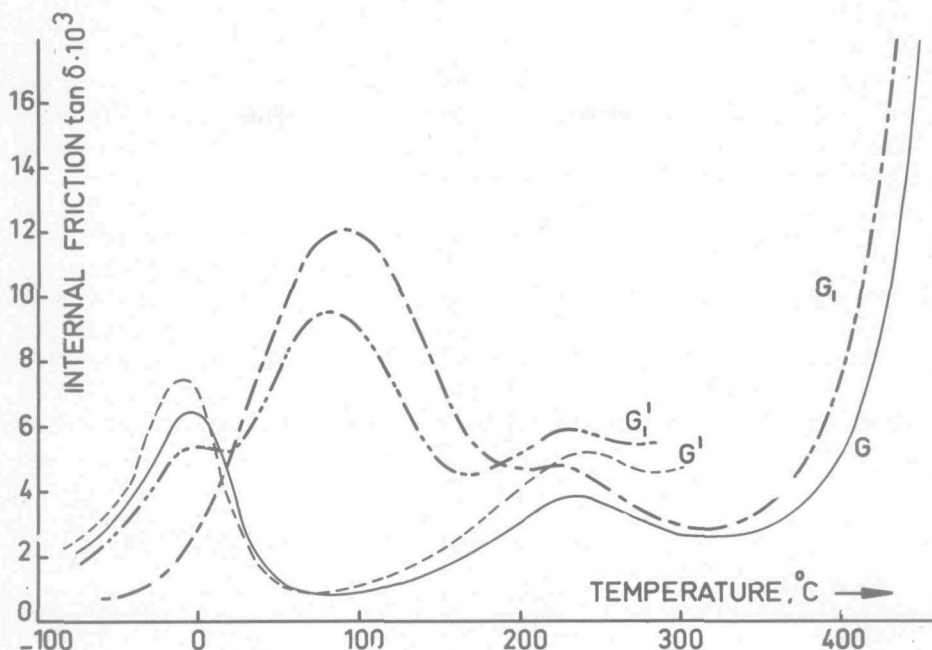


Fig.III-15. Internal friction of the glass $\text{Na}_2\text{O} \cdot 3 \text{SiO}_2$ before and after $\frac{1}{2}$ h. ion exchange in AgNO_3 at 295°C .
 G' : original glass, unannealed.
 G : original glass, annealed.
 $G1'$: after ion exchange.
 $G1$: after ion exchange and annealing.

In Fig. III-15 the internal friction curves are shown of the pure sodium trisilicate glass. Curve G' represents the internal friction measured down from 295°C and curve G the internal friction after annealing at 470°C . Compared with the curves we found for the sodium disilicate glass the two peaks are smaller and have shifted to higher temperatures, which confirms the results of other investigators^{5,6}.

In the same figure the internal friction is shown after an ion-exchange treatment of $\frac{1}{2}$ hour at 295°C in a silver-nitrate melt (curves $G1'$ and $G1$). Just like in the sodium disilicate glasses there is an intermediate-temperature peak ($80^\circ\text{--}90^\circ\text{C}$), which, however, increases in magnitude after the annealing treatment. The low-temperature peak decreases only in height, when measured down from 295°C , but disappears completely after annealing.

According to Table II-1 this fiber contains 1.9 mol.% Ag_2O . We removed a layer of 70μ by etching with HF and measured the internal friction. The curves completely coincided with the original curves of the sodium trisilicate glass, indicating that all the silver ions had been removed from the glass.

III.2.6. Determination of activation energies

From some of the investigated fibers the activation energies of the recorded peaks were determined with the modified internal friction apparatus described in Section II.1.5., using Eq. (II-15). The results of these determinations are shown in Table III-2.

The accuracy of the determinations depends of course on the resolution of the peaks, but as a rule the errors in the determinations of the activation energies of the peaks at low, intermediate, and high temperatures do not exceed 1.0, 1.6, and 2.0 kcal/mol. respectively. This means that the low-temperature peaks in the unannealed ion-exchanged fibers have an activation energy that equals the activation energy of the low-temperature peak of the pure sodium disilicate glass. After annealing of the ion-exchanged fiber A7 the activation energy increases from 14.3 to 16.5 kcal/mol.

Table III-2. Peak temperatures, measured at 5 cps. and mean activation energies of some ion-exchanged fibers of the series A

fiber	treatments	annealed or unannealed	low-temp. peak		intermediate- temp. peak		high-temp. peak	
			°C	kcal/mol	°C	kcal/mol	°C	kcal/mol
A'		unannealed	-37	14.0	-		200	27.5
A		annealed	-33	14.3	-		207	28.0
A1'	1 min. in LiNO ₃ melt	unannealed	-37	14.0	117	26.8	-	
A1	1 min. in LiNO ₃ melt	annealed	-		120	26.2	-	
A3'	5 min. in AgNO ₃ melt	unannealed	-37	14.1	75	24.7	(200) ⁺	
A3	5 min. in AgNO ₃ melt	annealed	(-10) ⁺		82	25.0	200	27.1
A4	$\frac{1}{2}$ h. in AgNO ₃ melt	annealed	x		78	25.0	(200) ⁺	
A6	5 min. in AgNO ₃ melt and 150 μ removed	annealed	-33	14.5	-		207	27.4
A7	5 min. in AgNO ₃ melt and 15 μ removed	annealed	-22	16.5	85	25.2	205	27.0

- : no peak.

+ : inflection; activation energy cannot be calculated.

x : in low-frequency run no peak; in high-frequency run inflection.

The activation energies of the intermediate-temperature peaks are much higher, but still somewhat lower than the values found for the high-temperature peaks.

It is sometimes thought that a higher peak temperature must correspond with a higher activation energy. This is true as long as the peak due to a certain mechanism is studied (although no linear relationship may be expected), but it needs not be true for peaks due to different mechanisms. Although the temperature of the intermediate-temperature peak is roughly in the middle between the two other peaks its activation energy is not much lower than the value found for the high-temperature peak.

III.3. Discussion of the results

III.3.1. On the internal friction of the mixed-alkali glasses

For the explanation of the internal friction curves of the mixed-sodium-lithium disilicate glasses two questions have to be answered.

- a. Why does the low-temperature peak disappear after the introduction of lithium?
- b. What is the reason of the occurrence of the intermediate-temperature peak?

Probably these questions are related to each other.

The first question can no doubt be correlated with the decrease of the ionic conduction in these glasses. Both the low-temperature peak and the ionic conductance exist because the alkali ions have a certain freedom to move through the glass. Somehow the jumping of the sodium ions is impeded by the presence of the lithium ions and vice versa. The reduction of the dielectric losses must also be due to this mechanism.

The second question cannot easily be correlated with other phenomena. The intermediate-temperature peak seems to be due to a mechanism that cannot be detected with dielectric measurements. This means that the structural elements that are involved must be electrically neutral. In spite of this important restriction of the possibilities it has not been possible to give a satisfactory and detailed description of the mechanism, responsible for this peak, so far.

Generally the structure of a glass, prepared by melting of raw materials, will not be identical with the structure of a glass, prepared by ion exchange, even if the compositions of the two were exactly the same. In a mixed-alkali glass, prepared by melting, the SiO_4 tetrahedra will

be able to link together in a way that satisfies the demands of the alkali ions as good as possible because of the low viscosity at the melting temperature. The alkali ions will - if possible - be surrounded by their favourite number of oxygen ions. Because of their smaller radius lithium ions prefer to be surrounded by a smaller number of oxygen ions than do the sodium ions, as can also be seen in Table III-3.

Table III-3. Data on the ions used in the experiments,
after weyl and marboe²³ and doremus²⁴

Ion	Na ⁺	Li ⁺	Ag ⁺	O ²⁻	Si ⁴⁺
Coordination number	6	4 or 6	6		4
Ionic radius (Å)	0.98	0.70	1.25	1.32	0.39
Polarizability (arb.un.)	0.21	0.15	0.40	3.1	0.04
Cation-oxygen distance a(Å)	2.30	2.10			1.60
Field strength z/a^2	0.19	0.23			1.57

In an element of volume, having the same composition, but prepared by an ion-exchange treatment at a temperature well below the annealing range, the SiO₂ structure will not be able to satisfy the demands of the ions that have entered the structure by ion exchange. These new ions enter the structure by diffusion and they migrate through a structure that has been "built" around ions with other demands. So these replacing ions will generally not be able to find holes in the network where their environmental demands are completely met. Annealing of such a glass composition in the transformation range will allow the structure to adjust to a certain extent to the changed composition, but it will never be possible to attain a complete reorganization of the structure (if this were necessary). Reorientation on a larger scale like clustering and microheterogeneity will not be able to appear or - if already present - to disappear. It will therefore be interesting to see if there is any fundamental difference between the internal friction curves of the fibers prepared by melting and the fibers prepared by an ion-exchange treatment, both unannealed and annealed.

III.3.2. On the internal friction of the ion-exchanged fibers after annealing

In view of the results on the determinations of the concentration

gradient in a silver-containing fiber, shown in Fig. III-13, the existence of a concentration gradient in the ion-exchanged fibers must be considered very unlikely, once the fibers are annealed. We are therefore allowed to compare the results on the ion-exchanged fibers after annealing with those on the mixed-alkali glasses prepared by melting, without being obliged to take into consideration a nonuniform composition.

The fibers that have been subjected to an ion-exchange treatment in a lithium-oxide-containing melt show an internal friction peak at intermediate temperatures. Fiber A1 (Fig. III-7) shows a peak at 120°C with a maximum height of 29.4×10^{-3} . Fiber A2 (Fig. III-8) shows a peak at 131°C with a maximum height of 18.4×10^{-3} . This is in complete accordance with the results on the mixed-sodium-lithium glasses prepared by melting, the data of which are given in Table III-1.

Fiber A1 contains 7.9 mol.% lithium oxide, according to Table II-1. This means that the concentration ratio Na/Li in this fiber amounts to about 3.2 after annealing. The curve of this fiber must be compared with the curve of fiber C (Fig. III-3) and as a matter of fact the similarity is striking. Even the widths at half height of the intermediate-temperature peaks are very close; we find 95°C for fiber C and 90°C for fiber A1.

Fiber A2 contains only 2.6 mol.% Li_2O . The concentration ratio thus amounts to about 11 in this fiber. The height and the position of the intermediate-temperature peak of fiber A2 are in accordance with this concentration ratio and are not different from what could be expected from a fiber with this concentration ratio in Table III-1.

The same remarks are valid for the low-temperature parts of the curves. Fiber A1 and fiber C show no low-temperature peak at all. The low-temperature peaks of the fibers A2 and B are shifted to higher temperatures and considerably reduced in height.

The fibers that have been subjected to an ion-exchange treatment in an AgNO_3 melt cannot be compared directly with silver-containing disilicate glasses prepared by melting, since it is not possible to prepare such glasses because of the reduction of Ag_2O to metallic silver at the high melting temperatures.

The results on the ion-exchanged fibers, however, leave little doubt that in these fibers the same mechanism is active. We find a shift and a reduction in height of the low-temperature peak, depending on the amount of silver ions penetrated into the fiber.

We also find an intermediate-temperature peak. This peak is situated in a somewhat lower-temperature range than was found in the lithium-containing glasses. This is not unexpected. Coenen reports that the

temperature of the intermediate-temperature peak is higher when the radii of the metal ions involved are more different from each other. The radius of a lithium ion is believed to differ more from the radius of a sodium ion than the radius of a silver ion. *)

There can be no doubt that the effects found in the internal friction of mixed-alkali glasses, prepared by melting, are also present in the ion-exchanged fibers after annealing. This means that the effect cannot be due to important structural changes.

III.3.3. On the internal friction of the ion-exchanged fibers before annealing

Before annealing there exists a concentration gradient in the ion-exchanged fibers. This is shown in Fig. III-13. We must take this into consideration when trying to explain the internal friction curves. We must distinguish between the surface layer, where the alkali ions have been partly replaced, and the inner part of the fiber, still having the original composition.

The inner part of the fiber will of course contribute to the internal friction curve and will be responsible for the existence of a low-temperature peak at -33°C , the temperature where the low-temperature peak of the sodium disilicate glass is situated at a measuring frequency of 5 cps. Naturally this peak will be smaller than in a fiber that is composed entirely of sodium disilicate. So we are not surprised finding a low-temperature peak at -33°C , reduced in height.

It does not surprise us either finding this peak more reduced at higher starting temperatures (Fig. III-11). The higher the temperature, where the measurements are started, the smaller will be the inner part with the original composition, because the replacing ions are brought into a position to migrate further into the glass and to level off the concentration gradient.

An ion-exchange treatment of 5 min. at 275°C in an AgNO_3 melt proved to be sufficient to produce a penetration depth of about 45μ . So it seems likely that the ions will diffuse further into the fiber when the fiber is reheated to that temperature, even if this is only for a short period of time. There is no doubt, however, that there is still a concentration gradient left in the fiber after reheating to 275°C once. The results of Fig. III-14, where a layer of 15μ was removed from a

*) From Table III-3 this is not obvious. The great polarizability of the silver ions has to be taken into account. Because of its great polarizability the "effective" radius of a silver ion decreases, since the ion may more easily be deformed.

fiber that had been reheated to 275°C once, are sufficient to prove this. The intermediate-temperature peak in this fiber is much smaller than it was before etching (Fig. III-11).

At starting temperatures below 275°C this effect may also appear, but since the diffusion rate will be smaller, not to such an extent. Nevertheless we are surprised to see how little the low-temperature peak has decreased in height in the curves with starting temperatures lower than 275°C. Especially at a starting temperature of 20°C we can hardly speak of a reduction at all.

It is true that we cannot expect this fiber to be penetrated by "new" ions to a depth as was measured in Fig. III-13. The fiber used for the experiments shown in Fig. III-13 was "as drawn" and it appears that the ion exchange proceeds faster in such a fiber than in a fiber that has been annealed. (This is in accordance with the observation that in a chilled fiber the internal friction peaks are situated at a lower temperature than in an annealed fiber. The structure of a chilled fiber must be somewhat "looser".)

This can be shown also by comparing the curves of the fibers A3 and A5. These fibers have been subjected to the same ion-exchange treatment, but in fiber A3 (which is "as drawn") the intermediate-temperature peak is obviously larger than in fiber A5 (which is annealed).

We may estimate that the depth of the surface layer of the fiber A3 will not be less than 30 μ . We can hardly imagine that - if the surface layer does not contribute to "the" low-temperature peak (like after annealing) - this would only result in such a slight reduction of the peak. These observations may bring on consequences, important enough to ask for a more quantitative approach.

It is possible to calculate the reduction of the height of the low-temperature peak that must be expected theoretically, supposing that the surface layer of the fiber does no longer contribute to this peak. To perform this we must find the relative contribution to the internal friction curve of each volume element in the fiber as a function of the position of the element.

We can take advantage of the results of Section II.1.2., where, among others, the following expression (Eq. II-13) was derived:

$$\frac{\Delta W^*}{W^*} = \frac{\int_{\text{vol.}} \left(\frac{\Delta W}{W} \right) \cdot W(v) dv}{\int_{\text{vol.}} W(v) dv}$$

This expression relates $\frac{\Delta W^*}{W^*}$, the energy dissipation of the specimen as a whole, with $\frac{\Delta W}{W}$, the relative energy dissipation of an element of volume dv .

From Eq. (II-12) we know that for each element of volume the relation $\tan \varphi = \frac{\Delta W}{2 \pi W}$ is valid, where $\tan \varphi$ represents the internal friction of the element of volume. We use the notation φ instead of δ here to indicate that $\tan \varphi$ is not the internal friction we measure.

The measured internal friction can be written as:

$$\tan \delta = \frac{\Delta W^*}{2 \pi W^*}.$$

We can rewrite Eq. (II-13):

$$\tan \delta = \frac{\int_{\text{vol.}} \tan \varphi \cdot W(v) dv}{\int_{\text{vol.}} W(v) dv}.$$

In the experiments with ion-exchanged fibers before annealing $\tan \varphi$ is not independent of the position of the element of volume in the specimen and $\tan \varphi$ cannot be placed before the integral sign.

In Section II.1.2. we derived the following expression for $W(v)$:

$$W(v) = \frac{1}{2} \tau_0 \gamma_0 \left\{ \cos \delta + \left(\frac{\pi}{2} + \delta \right) \sin \delta \right\}.$$

As long as δ is small we may replace this by:

$W(v) = \frac{1}{2} \tau_0 \gamma_0$, where τ_0 and γ_0 are the maximum shear stress and strain respectively.

In a torsion experiment stress, and strain linearly increase with the distance r to the central axis of the fiber.

The theory of elasticity gives the following expressions:

$$\tau_0 = \Theta_0 G r$$

$$\text{and } \gamma_0 = \Theta_0 r,$$

where G represents the modulus of rigidity and Θ_0 the maximum angular displacement of the fiber per unit of length.

Substituting this into the expression for $W(v)$ gives:

$$W(v) = \frac{1}{2} G \Theta_0^2 \cdot r^2.$$

In combination with Eq. (II-13) we obtain:

$$\tan \delta = \frac{\int_{\text{vol.}} \tan \varphi \cdot r^2 dv}{\int_{\text{vol.}} r^2 dv},$$

if for simplicity G is considered to be a constant along the fiber radius. From this we derive:

$$(III-1) \quad \tan \delta = \frac{4}{R^4} \int_0^R r^3 \tan \varphi \, dr$$

where R is the radius of the fiber.

Assuming that the outer layer of the fiber does not contribute to the low-temperature peak this leads to the following relation between the reduction factor $\frac{\tan \delta}{\tan \varphi}$ and the penetration depth ρ of the replacing ions:

$$(III-2) \quad \frac{\tan \delta}{\tan \varphi} = \left(1 - \frac{\rho}{R}\right)^4$$

In Fig. III-16 this relationship is represented graphically.

According to this result we expect the height of the low-temperature peak of fiber A5 to decrease to about 75% of its original value when measuring from a starting temperature of 20°C and assuming a penetration depth of 30 μ . The experimental curves, however, show a decrease of no more than 5%. This would correspond to a penetration depth of only 5 μ , which is out of the question, in view of the results on the etched fibers.

If it is accepted that somehow the sodium ions are responsible for the occurrence of the low-temperature peak this result strongly suggests that the sodium ions in the surface layer, which have not yet been replaced, do contribute to the low-temperature peak of the sodium disilicate glass, without being aware of the modified composition. This suggestion is supported by the behaviour of the intermediate-temperature peak. Fig. III-11 shows that at starting temperatures below 275°C this peak is very small. The mechanism that causes this peak seems not yet to be active, although the silver ions are already present. So there are reasons to assume that the mechanism that suppresses the low-temperature peak and the mechanism that causes the intermediate-temperature peak are related to each other in such a way that the effects occur simultaneously. Only at temperatures of 275°C and higher the conditions are changed in favour of the appearance of the mixed-alkali effect.

This is a second reason why the low-temperature peak falls to such a low value at a starting temperature of 275°C compared with lower starting temperatures. After reheating to 275°C the remaining sodium ions in the surface layer do no longer contribute to the low-temperature peak. Reheating to lower temperatures does not produce this effect.

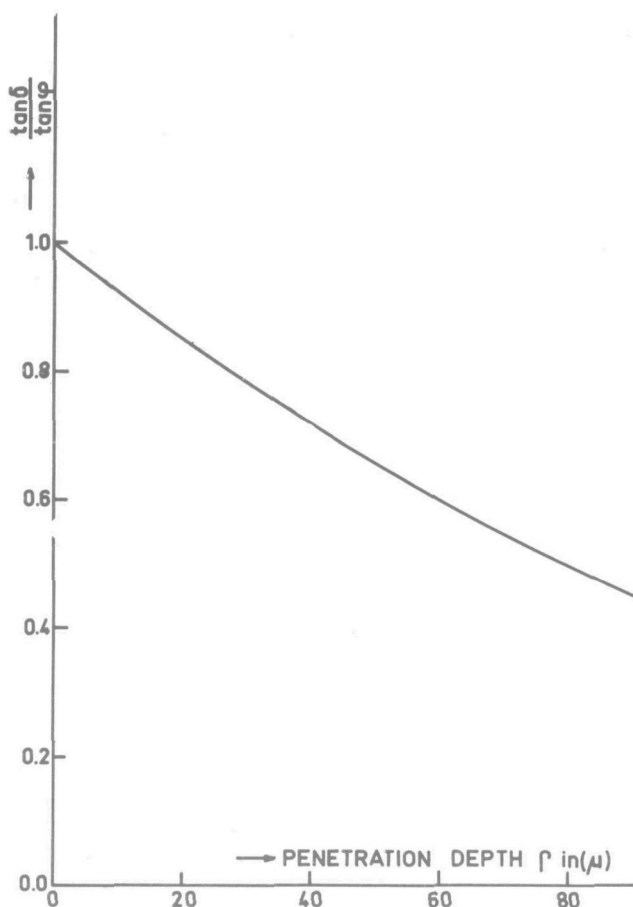


Fig.III-16. Reduction of peak height as a function of penetration depth ρ in a fiber with a radius of 500μ , assuming that the ions in the ion-exchanged layer do not contribute to the internal friction peak ($\tan\delta$ is the measured internal friction value, $\tan\varphi$ the internal friction of the unaffected inner part of the fiber.).

III.3.4. Suggestions for the mechanisms, responsible for the phenomena recorded

We will now try to find the answers on the two questions we posed in Section III.3.1:

- a. Why does the low-temperature peak disappear after the introduction of lithium or silver ions?
 - b. Which mechanism causes the intermediate-temperature peak?
- We saw that silver ions can cause these effects just as well as lithium ions, so the name "mixed-alkali effect" may be misleading. The presence of two different types of monovalent ions seems to be sufficient. This, however, is not true either. One of the conclusions

in the preceding section was that the mere existence of silver ions in a sodium disilicate glass is insufficient to produce a mixed-alkali effect. Reheating to 275°C appears to be necessary to activate the process.

This is an important result. We cannot accept the idea that at 275°C large structural modifications are possible. For the time-scale used in our experiments the SiO₂ structure must be considered as "rigid" at this temperature, although minor displacements on an atomic scale cannot be excluded. The Si-O bond is a very strong bond, but the binding forces between monovalent metal ions and nonbridging oxygen ions are much smaller. A short reheating to 275°C enables these ions to migrate relatively fast through the network and undoubtedly the replacing metal ions will try to use this opportunity to establish a distribution that is energetically more suitable.

In connection with this the theory of W.A.Weyl and E.C.Marboe²³ is interesting. They point out that the screening demands of the Si⁴⁺ cores are best satisfied in a sodium silicate glass if the addition of Na₂O does not lead to a random distribution of the nonbridging oxygen ions, but to a structure in which the better screening, more polarizable, nonbridging oxygen ions are evenly distributed.

A random network would mean that a sodium disilicate glass would consist of a mixture of all possible tetrahedra (sharing zero, one, two, three or four corners) in some kind of a statistical distribution. According to Weyl and Marboe such a glass would consist of tetrahedra all of which share three corners, so that each tetrahedron contains one nonbridging oxygen ion. Such a distribution bears some resemblance to the superstructures, found in many crystalline materials.

Alkali ions contrapolarize bridging oxygen ions by drawing towards themselves electron density from the binding region between two silicon cores. This effect increases with increasing field strength of the alkali ions, so the introduction of a second type of alkali ions will disproportionate the binding forces in the glass. According to the theory of Weyl and Marboe these ions will also try to distribute as evenly as possible in the structure, because this reduces the disproportionation of the binding forces and leads to a maximum and most equal screening of the metal ions.

The theory of Weyl and Marboe may be valid for mixed-alkali glasses prepared by melting, but we can hardly expect it to be true for glasses prepared by ion exchange, especially before annealing. In the latter glasses a concentration gradient exists and first of all the migration of the metal ions will serve to reduce the chemical inhomogeneity in the fiber. Of course here too each replacing ion will tend to be surrounded by a number of sodium ions and replacing ions

in the proportion of the concentration ratio of the metal ions existing in that particular region, but since this concentration ratio is still changing with time we believe this to be a secondary effect.

Our experiments leave no doubt that reheating to 275°C is insufficient to produce a homogeneous fiber. The curves of Fig. III-13 and 14 make clear that a concentration gradient still exists. Nevertheless, it does not seem to make much difference for the mixed-alkali effect (as far as the internal friction is concerned), whether the network has been thoroughly annealed - or even constituted by melting - or just heated to 275°C . This suggests that an even distribution of metal ions in the fiber is not necessary for the mixed-alkali effect to occur. It seems that it is not the enhanced migration of the metal ions at 275°C that is responsible for the sudden changes in the internal friction curve that occur after reheating to that temperature.

We believe that the explanation of the phenomena can be found in the behaviour of the network structure itself. The ion-exchange treatment introduces foreign ions in a structure that is originally built around metal ions with a different radius, mass, polarizability, etc. It is clear that the network will try to adjust to the special demands of the foreign ions as good as possible. The small local distortions of the network, involved in this process, are only possible at higher temperatures and our results seem to indicate that at a temperature of 275°C this reorientation or rearrangement takes place fast enough to be completed during the reheating procedure applied in our experiments.

In this respect it may be remembered that there are indications²³ that at a temperature around 275°C the kinetic energy of the network of a sodium silicate glass reaches a value, which even permits an occasional exchange of position between a bridging and an adjacent nonbridging oxygen ion.

In Chapter V it will be shown that both the suppression of the low-temperature peak and the occurrence of the intermediate-temperature peak can easily be explained if the concept of the modifying network is accepted.

III.4. Survey of the results

Before leaving this chapter we want to give a brief survey of the most important experimental results and their interpretation.

- a. Two clear peaks are found in the internal friction curve of a sodium disilicate fiber. In the annealed glass the low-temperature peak is situated at -33°C (at 5 cps) and has an activation energy of 14.3

kcal/mol, whereas the high-temperature peak is situated at 207°C with an activation energy of 28.0 kcal/mol. At about 300°C there seems to be a third peak (extra-high-temperature peak), almost completely covered by the high-temperature peak and the increasing background absorption (Fig. III-1).

- b. In mixed-sodium-lithium disilicate glasses the low-temperature peak decreases in height and shifts to higher temperatures. At concentration ratios Na/Li that are not too extreme it is completely covered by a new high peak, occurring at about 120°C, called the intermediate-temperature peak (Figs. III-2 to 6).
- c. In sodium disilicate fibers that have been subjected to an ion-exchange treatment in LiNO_3 the phenomena mentioned under b. also occur, but there seems to be some unexpected influence of the temperature, to which the fibers are reheated (Figs. III-7,8). Since the interpretation of the results is obscured by the presence of cracks in the surface layers of the ion-exchanged fibers we did not proceed with these experiments, but changed to ion exchange with silver ions.
- d. After an ion-exchange treatment in AgNO_3 (at 275°C) the internal friction curve depends strongly on the thermal treatment that is given after the ion-exchange treatment. Three stages may be distinguished (Fig. III-11):
 - d1. When the fiber is annealed at 420°C for 3 hours an intermediate-temperature peak appears at about 80°C (activation energy 25 kcal/mol) and the low-temperature peak shifts to higher temperatures and decreases in height, compared to the peak in the base glass. (In fact this is the "normal" behaviour of a mixed-alkali glass.)
 - d2. When the fiber is not annealed, but reheated only to 275°C for a short period of time the low-temperature peak still has decreased considerably in height, but has not shifted to higher temperatures. The intermediate-temperature peak is not different from the one in the annealed fiber (Fig. III-9).
 - d3. When the fiber is reheated only to temperatures of 200°C or less the intermediate-temperature peak is very small in comparison to the peak found in the stages d1 and d2. The low-temperature peak has hardly decreased in height, compared to the peak in the original sodium disilicate glass, while no temperature shift can be detected.
- e. After etching the internal friction curve of an unannealed ion-exchanged fiber returns to the curve of the untreated fiber as soon as the ion-exchanged layer has been removed completely. Removal of a smaller layer results in a lowering of the intermediate-temperature peak and a heightening of the low-temperature peak, while

the latter also shifts back to lower temperatures. It seems as if the whole curve is "on its way" to the curve of the original glass (Fig. III-12). Etching of an annealed fiber, on the contrary, has no influence on the internal friction curve at all.

- f. To interpret the phenomena, described under d and e, the concentration gradient of the metal ions along the fiber radius has to be taken into account. In an unannealed fiber the inner part of the fiber is unaffected by the ion-exchange treatment. This explains why the low-temperature peak has not shifted in temperature: the peak is nothing but the contribution of the unaffected part of the fiber to the measured internal friction curve. After annealing at 420°C no concentration gradient is left and it appears that the internal friction curve of the resulting glass composition is in no way different from the curves found for mixed-alkali glasses, prepared by melting. Explanations of the mixed-alkali effect, based on large-scale structural deviations between single- and mixed-alkali glasses (like phase separation, clustering etc.) are thus ruled out.
- g. The behaviour of unannealed fibers and in particular the great influence of the reheating temperature (stages d2 and d3) suggests that the mixed-alkali effect, found in the internal friction, occurs only when the network has had the opportunity to adjust to the changed composition. It seems that at 275°C small local modifications in the structure are possible in a reasonable small period of time and that this reorientation or rearrangement results in a lowering of the low-temperature peak, a shift of this peak to higher temperatures, and the occurrence of the intermediate-temperature peak.

References

1. C.E.Guye, S.Vassileff, Arch.Sci.Phys.et Nat., 214, 301 (1914).
2. J.V.Fitzgerald, J.Am.Ceram.Soc., 34, 339 (1951).
3. P.L.Kirby, J.Soc.Glass Technol., 38, 383 (1954).
4. J.V.Fitzgerald, K.M.Laing, C.S.Bachman, J.Soc.Glass Technol., 36, 90 T (1952).
5. K.E.Forry, J.Am.Ceram.Soc., 40, 90 (1957).
6. L.C.Hoffman, W.A.Weyl, Glass Industry 38, 81 (1957).
7. H.Rötger, Silikattechn., 10, 57 (1959).
8. I.Mohyuddin, R.W.Douglas, Phys.Chem.Gl., 1, 71 (1960).
9. R.Jagdt, Glastechn.Ber., 33, 10 (1960).
10. H.Rötger, Glastechn.Ber., 31, 54 (1958).
11. R.J.Ryder, G.E.Rindone, J Am.Ceram.Soc., 43, 662 (1960).
12. D.E.Day, G.E.Rindone, J.Am.Ceram.Soc., 45, 496 (1962).
13. M.Coenen, Z.für Elektrochemie 65, 903 (1961).
14. R.Brückner, Glastechn.Ber., 37, 536 (1964).
15. B.Lengyel, Z.Boksay, Z.physik.Chem., 204, 157 (1955).
16. O.V.Mazurin, E.S.Borisovskii, Soviet Physics-Tech.Phys. (English Translation) 2, 243 (1957).
17. J.Stevens, Philips Techn.Rundschau, 13, 350 (1952).
18. P.P.Kobeko, "Amorphous Materials" Acad.Sci.U.S.S.R. Press, 1952
19. R.V.Caporali, J.Am.Ceram.Soc., 47, 412 (1964).
20. R.J.Charles, J.Am.Ceram.Soc., 48, 432 (1965).
21. W.H.Zachariasen, J.Am.Chem.Soc., 54, 3841 (1932).
22. B.Eckstein, Kolloid-Zeitschr. 194, 34 (1963).
23. W.A.Weyl, E.C.Marboe, "The Constitution of Glasses" Vol.II, Part I, John Wiley and Sons, New York, 1964.
24. R.H.Doremus in "Modern Aspects of the Vitreous State", Vol.2, (Ed.J.D.Mackenzie), Butterworths, London, 1962.

CHAPTER IV

Experiments on sodium aluminoborate glasses

IV.1. Introduction and review of the literature.

The structure of vitreous boric oxide bears little resemblance to that of vitreous silica. In pure boric oxide the boron ions have a triangular coordination of oxygen ions. The X-ray diffraction patterns taken by J.Biscoe and B.E.Warren¹ indicate that the addition of alkali causes a shift in the average coordination number of the boron ions from 3 to 4. This shift became the centre of all theories concerning the borate glasses.

It was recognized that many physical properties of binary borate glasses show unusual trends with changes in composition^{2,3} and this behaviour became known as the "boric-oxide anomaly". The linear thermal expansion coefficient in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$, for instance, goes through a minimum at about 16 mol.% Na_2O , according to E.J. Gooding and W.E.S.Turner⁴.

This type of behaviour is found in many physical properties of the binary borate glasses. There often is a critical composition where the measured property shows a minimum or maximum in its variation with composition. Other properties show a significant change in their trend or value as a function of composition.

For a long time it was thought that this behaviour was due to a mechanism causing the concentration of boron ions in fourfold coordination (BO_4 groups) to remain constant as soon as the alkali content had reached a certain value. At that concentration the first non-bridging oxygen ions would appear.

Several hypotheses have been put forward to account for the apparent saturation in the number of boron ions which can adopt fourfold coordination.

One of the most useful hypotheses has been the "screening theory" of T. Abe⁵. Abe proposed that the limiting concentration of BO_4 groups is determined by the requirement that each BO_4 group is screened by four BO_3 groups. This leads to the formation of certain structural units in the glass of the type shown in Fig. IV-1. Abe suggested that this structural unit is the result of the need to screen the BO_4 group, which has a net negative charge.

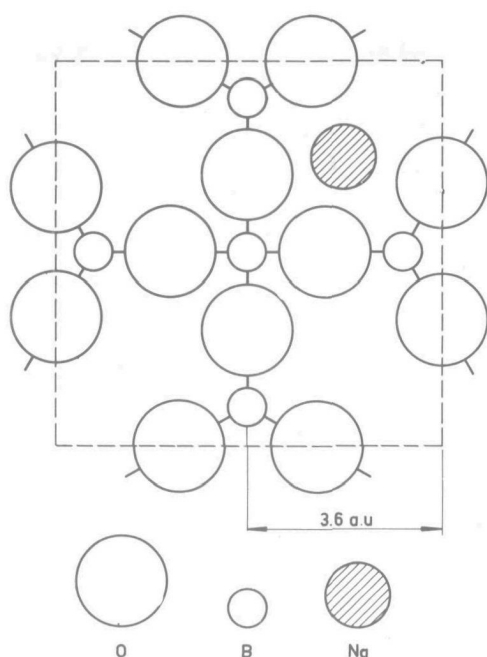


Fig.IV-1. Two-dimensional representation of a structural unit consisting of a BO_4 group, screened by 4 BO_3 groups (after Abe⁵).

Abe further assumed that one BO_3 group can share in the screening of one BO_4 group only. This hypothesis predicts that the critical concentration is given by the molecular formula $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$, i.e. the ratio of four-coordinated borons, to the total number of boron ions is 1 to 5.

Recently a new technique has been developed for the investigation of coordination numbers. With the technique of nuclear magnetic resonance (NMR) spectroscopy it is possible to examine the charge distributions (or the electric field gradient) in the neighbourhood of the boron nuclei. The electric quadrupole moment of a B^{11} nucleus ($\text{spin} = \frac{3}{2}$) interacts with the local electric field gradient, arising from electrons in the chemical bonds of the atom containing the nucleus, and from charges at further distances from the nucleus (the O^{2-} ions). The NMR technique enables us to measure this interaction. Since the environments of the boron nuclei in BO_3 groups differ from those in BO_4 groups it is clear that with this technique the number of BO_4 groups may be measured from the relative strengths of the absorption bands in the NMR spectra. The results of the NMR experiments^{6,7,8} seem to indicate that no saturation takes place at all at a concentration of 16 mol.% Na_2O .

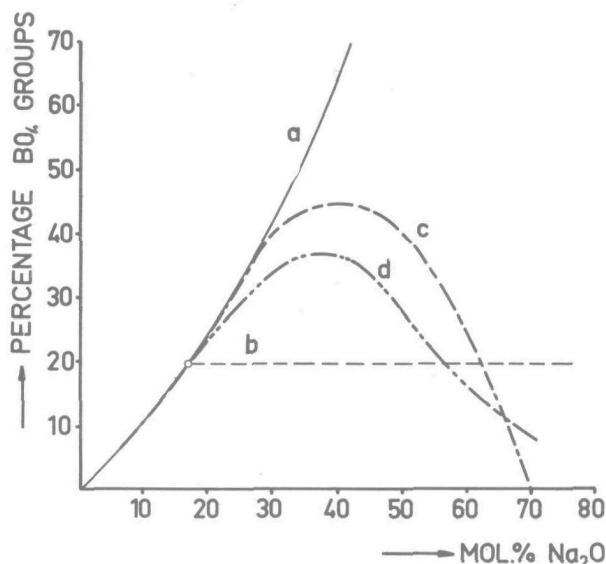


Fig.IV-2. Fraction of boron ions in fourfold coordination as a function of the soda content.

Curve a: without formation of nonbridging oxygen ions;

Curve b: after Abe⁵.

Curve c: after Bray⁶.

Curve d: after Beekenkamp⁹.

In Fig. IV-2 it is shown how the number of BO_4 groups would increase if every excess oxygen ion were used for the formation of a BO_4 group and no nonbridging oxygen ions occurred, even at high concentrations of Na_2O (curve a). The figure also demonstrates the trend in the number of BO_4 groups according to the theory of Abe (curve b). The results of the NMR experiments of Bray and Silver⁶ are represented by curve c. Curve c does not deviate from curve a until a concentration of about 30 mol.% Na_2O is reached. The experiments of Bray and Silver thus seem to indicate that no nonbridging oxygen ions are found at concentrations of Na_2O lower than 30 mol.%.

The results of Bray and Silver create serious difficulties with respect to the explanation of the boric-oxide anomaly, which usually occurs at Na_2O concentrations much lower than 30 mol.%. P. Beekenkamp⁹ tries to solve this problem by proposing a slight modification in the experimental curve of Bray and Silver. He states that, in view of the experimental errors in the values of the number of BO_4 groups given by Bray and Silver (and also by Krogh-Moe et al.⁸), the Na_2O concentration, given by the authors mentioned, where curve c starts to deviate from curve a in Fig. IV-2 is not likely to be very reliable. He suggests, on theoretical grounds, that curve d is more probable. In his opinion N_4 , the ratio of the number of BO_4 groups to the total number of boron ions, is governed by an equilibrium equation of the form:

$$N_4 = \frac{x}{1-x} \cdot \frac{1}{1 + e^{\frac{\Delta E}{kT}}},$$

where x is the mol fraction Na_2O , k the Boltzmann constant, T the absolute temperature (probably the softening temperature) and ΔE the energy that determines the difference in stability between a structure with BO_4 groups and a structure with BO_3 groups associated with nonbridging oxygen ions. To adapt this relation to the experimental results Beekenkamp substitutes $\Delta E/kT = 11.5x - 4.8$, which leads to curve d in Fig. IV-2.

Beekenkamp points out that the hypothesis of Abe can be improved by leaving out one of the rules Abe proposed for the structure of borate glasses. If it is accepted that BO_3 groups can serve to screen two BO_4 groups instead of one the fraction of boron ions in fourfold coordination can become much higher than $\frac{1}{5}$.

As can be seen in Fig. IV-2 curve d starts to deviate from curve a at a concentration of about 15 mol.% Na_2O . Beekenkamp points out that it is very probable that at this concentration the amount of nonbridging oxygen ions attains a detectable value. McSwain et al.¹⁰ observed a marked change in the absorption coefficient at about 2000 Å in the U.V. part of the optical spectrum of sodium borate glasses in the composition range of 0.15-0.20 mol Na_2O . They explain the increase of absorption in the U.V., appearing in the range of 4-7 eV, as due to the excitation of an electron of a nonbridging oxygen ion.

From colour-centre experiments, performed by Beekenkamp¹¹, it can also be concluded that at a concentration of 15 mol.% Na_2O a detectable amount of nonbridging oxygen ions begins to occur. So he concludes that, in spite of the increasing amount of BO_4 groups, properties that are sensitive to the occurrence of nonbridging oxygen ions will show an "anomaly" at concentrations of 15 mol.% Na_2O or higher. The thermal expansivity can be considered one of these properties. In this respect it is important to point out that the occurrence of BO_4 groups seems to increase the coherence of the network, whereas the nonbridging oxygen ions decrease its coherence. Therefore the composition range between B_2O_3 and $\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3$ is often called the accumulation region (A.R.). The composition range with an alkali oxide content higher than 15 mol.% is often called the destruction region (D.R.).

In view of the results of the NMR measurements this separation may not be fully correct, but we can still use it to indicate the composition

where the nonbridging oxygen ions start to occur. We must keep in mind, however, that in the destruction region also BO_4 groups are formed.

The internal friction of alkali borate glasses has been measured by M.Coenen¹² and some years later by K.H Karsch and E.Jenckel¹³. They established the occurrence of an internal friction peak in the temperature range between 50° and 200°C , depending in size and position on the concentration and the kind of the alkali ions in the glass. According to Coenen the boric-oxide anomaly affects the internal friction in such a way that the peak occurs only at concentrations of Na_2O

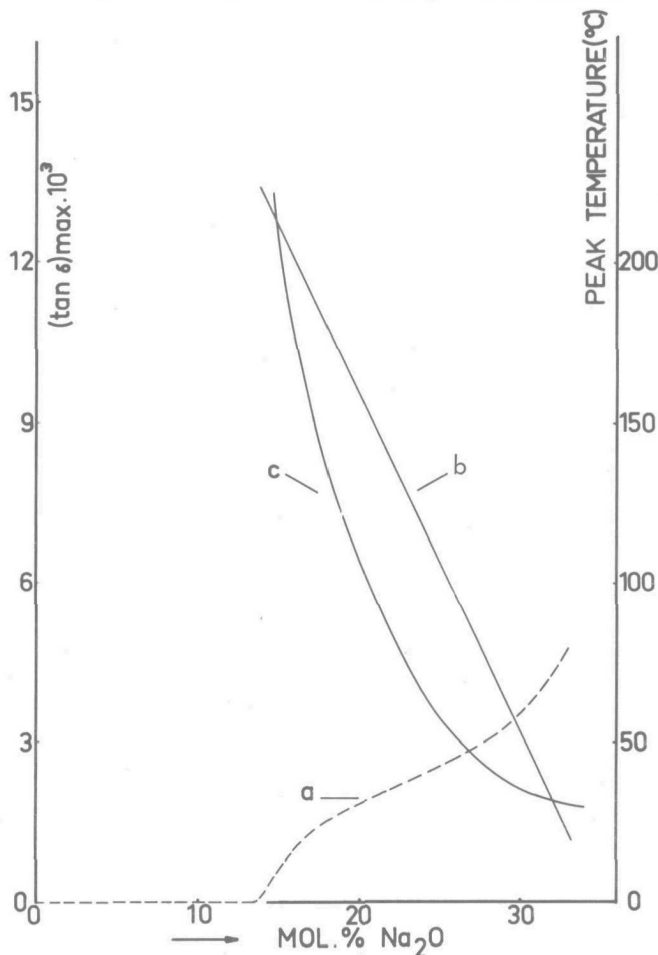


Fig.IV-3. Position and height above background of the internal friction peak in sodium borate glasses.

Curve a: height above background, after Coenen¹².

Curve b: position of the peak, after Coenen¹².

Curve c: position of the peak, after Karsch¹⁸.

higher than 13 mol.%. Height and position of the internal friction peak as measured by Coenen are represented in Fig. IV-3. As can be seen his measurements suggest a linear relationship between the temperature of the peak and the alkali content. This was not confirmed by Karsch and Jenckel. Their results are also represented in Fig. IV-3 (curve c).

Karsch and Jenckel ascertained a relationship between the type of the alkali ions incorporated and the minimum concentration at which an internal friction peak could be detected. Under the impression that the transition from accumulation region to destruction region as predicted by Abe had to occur at a fixed concentration of alkali ions, independent of the type, they questioned the relationship Coenen saw between the occurrence of an internal friction peak and the boric-oxide anomaly. Coenen reported the occurrence of a second internal friction peak, situated at higher temperatures. He related this peak to the high-temperature peak in soda silicate glasses (cf. Chapter III). Karsch and Jenckel, however, were not able to confirm the existence of this peak.

In 1961 A.E. Owen¹⁴ put forward a new aspect to the study of the boric-oxide anomaly by introducing alumina as a constituent of borate glasses. He studied the ternary system $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$, called the Cabal system.

Although these glass compositions do not contain alkali ions a boric-oxide anomaly occurs in the presence of the divalent calcium ions. In Fig. IV-4 the glass-forming region of this system is shown with the two series studied by Owen. Among the various properties investigated were the dc conductivity, the dielectric loss and the thermal expansivity. He concluded that the destruction region of this system could be represented by the shaded area in Fig. IV-4. He was able to bring this into agreement with the theory of Abe, accepting a fourfold coordination for the aluminium ions. Besides, Owen had to assume that the AlO_4 groups, unlike the BO_4 groups, did not require screening by BO_3 groups. This is a rather remarkable result, in view of the net negative charge of AlO_4 groups.

In respect of the coordination number of aluminium in glass, E.D. Lacy¹⁵ suggested three possible ways in which aluminium ions may be taken up into the network. Normally aluminium is four-coordinated in glasses. Lacy shows that aluminium is unlikely to occur as a truly interstitial cation.

In glasses having a high proportion of basic oxides there seems to be no stoichiometric or geometrical obstacle to the formation of AlO_6 groups, but sharing of three or more oxygens between an AlO_6 cluster and other network groups must then be introduced. In principle such a

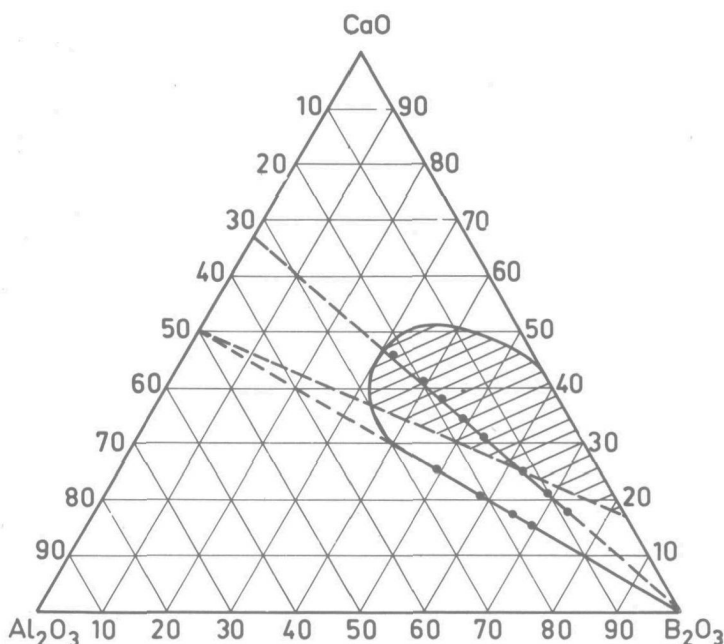


Fig.IV-4. System $\text{CaO-B}_2\text{O}_3\text{-Al}_2\text{O}_3$ on molar basis with the two series of "Cabal" glasses, studied by Owen¹⁴.
 ● = compositions by chemical analysis.

structural unit would have to consist of an aluminium ion surrounded by three bridging oxygens, one nonbridging oxygen and two oxygens, each shared by two tetrahedra (so-called "tripod" oxygens). Logically this can be described as network-forming behaviour only. Since the occurrence of these structural units requires the presence of an appreciable amount of nonbridging oxygen ions their existence in borate glasses must be considered very unlikely.

In silicate compositions with molar excess of alumina over basic oxides triclusters may be formed in which an oxygen is shared between three tetrahedral groups. A tricluster consists of an aluminium ion surrounded by three bridging ions and one tripod ion.

According to Lacy the occurrence of triclusters is stimulated in glasses with a low number of nonbridging oxygen ions. This means that in aluminoborate glasses these structural units may well occur. Since tripod oxygen ions give rise to a denser packing of the network the number of these ions is limited. Too many tripod oxygen ions will give rise to crystallization.

From NMR measurements on glasses in the Cabal system published

recently by S.G. Bishop and P.J. Bray¹⁶ it appears that in these glasses no saturation of BO_4 groups occurs at 16 mol.% CaO. Their results indicate that this ternary glass system may be treated as a binary system with CaO as the network modifier and B_2O_3 and Al_2O_3 serving jointly as the network former. For a given CaO concentration the fraction of four-coordinated boron decreased with increasing Al_2O_3 content, as if the aluminium ions also assumed a tetrahedral configuration, thereby depriving some of the boron of the oxygen necessary for its four-coordination. Of course, it would be expected then that the number of BO_4 groups fell to zero in glasses whose compositions fall on the line $\text{CaO}/\text{Al}_2\text{O}_3 = 1$. This, however, is not confirmed by the experiments of Bishop and Bray. They find in all the glasses investigated, containing a one-to-one ratio of CaO and Al_2O_3 , that about 10% of the boron ions are in fourfold coordination. This clearly indicates that not all the aluminium ions in these glasses are fourfold coordinated with bridging oxygen ions.

Beekenkamp¹⁷ suggests that this is the consequence of the formation of triclusters, as proposed by Lacy. If some of the oxygen ions, surrounding the aluminium ions, are tripod oxygens the total number of oxygen ions available for the boron ions increases, giving rise to the formation of BO_4 groups.

Beekenkamp performed NMR measurements on glasses in the $\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ system (the Kalbal glasses) and measured the dc conductivity and the viscosity of a number of glasses in this system. He found some evidence on the existence of triclusters in these glasses, especially from the viscosity measurements. The number of triclusters was thought to be increasing with increasing Al_2O_3 content.

We investigated glasses in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$, called the Nabal glasses. Since we measured the thermal expansivity of these glasses we may expect to find evidence on the occurrence of the boric-oxide anomaly and it will be interesting to determine the position of the boundary between the destruction region and the accumulation region in these glasses, in comparison with the results of Owen on the Cabal glasses.

Our internal friction measurements may provide further evidence on the structure of borate glasses with substitution of alumina for boric oxide, especially on the environmental conditions of the alkali ions in the glass.

IV.2. Experimental results

IV.2.1. The Nabal System

Four series of borate glasses were prepared and investigated. The

results of the chemical analyses were given in Table II-2.

The glasses in series 1 did not contain any alumina and may be represented on a molar basis as $x \text{Na}_2\text{O} \cdot (1-x) \text{B}_2\text{O}_3$. The 7 glasses that were investigated in this series were numbered 1 to 7.

In series 2 10 mol.% Al_2O_3 was substituted for the B_2O_3 . The 5 glasses in this series had the general composition $x \text{Na}_2\text{O} \cdot (0.9-x) \text{B}_2\text{O}_3 \cdot 0.1 \text{Al}_2\text{O}_3$ and were numbered 8 to 12.

In series 3 the Na_2O content remained constant as alumina was substituted for boric oxide according to the formula: $0.17 \text{Na}_2\text{O} \cdot (0.83-y) \text{B}_2\text{O}_3 \cdot y \text{Al}_2\text{O}_3$. Six glasses, numbered 13 to 18, were investigated in this series.

The glasses in series 4 had a Na/Al ratio of 1. The general composition of the 6 glasses, investigated in this series, was: $x \text{Na}_2\text{O} \cdot (1-2x) \text{B}_2\text{O}_3 \cdot x \text{Al}_2\text{O}_3$. The glasses in series 4 were numbered 18 to 23.

The series are shown in the diagram of Fig. IV-5. The glasses on the intersection points of the composition lines belong to more than one

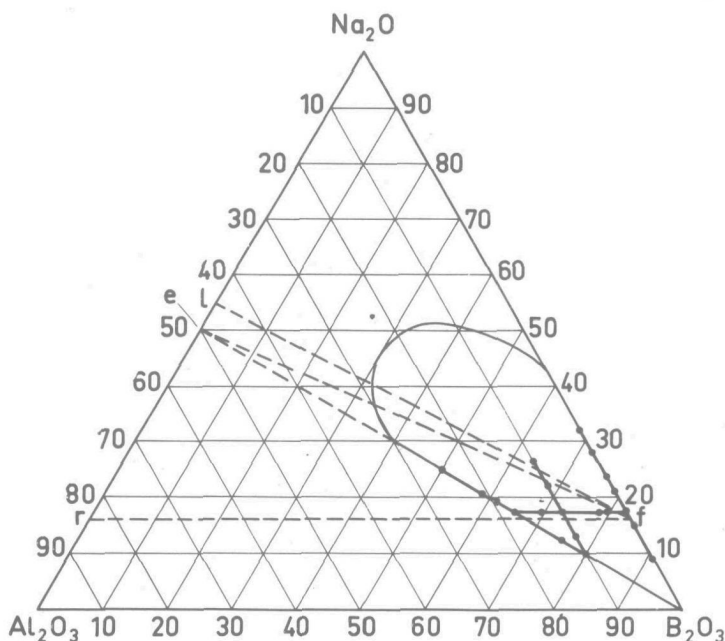


Fig.IV-5. System $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ on molar basis with the four series of "Nabal" glasses that were studied.

● = compositions by chemical analysis.

series. Yet, for clearness's sake, in each series these glasses were given an appropriate number. Glass no.3 equals glass no.13 and the glasses no. 8, 10 and 18 are respectively identical to the glasses no.19, 16 and 21, as can also be seen in Table II-2.

The results of the experiments on the series will be presented separately in the following sections.

IV.2.2. Glasses in series $1:x\text{Na}_2\text{O}\cdot(1-x)\text{B}_2\text{O}_3$

The results of the measurements on the glasses of series 1 are summarized in Table IV-1. In Fig. IV-6 the measured properties are represented as a function of the Na_2O concentration.

The curve of the thermal expansion coefficient exhibits a minimum at about 16 mol.% Na_2O , which is in agreement with the results of other investigators⁴.

The data on the internal friction measurements do not exhibit a minimum or a maximum as a function of the Na_2O content. The curves representing the temperature of the internal friction peak and the mean activation energy ΔH of this peak versus the Na_2O concentration have a similar trend. At high Na_2O concentrations both curves are relatively flat, whereas down from 20 mol.% Na_2O both the peak temperature and the activation energy increase rapidly. The peak temperature soon becomes so high that the peak can no longer be detected. In glass composition no.1 the internal friction peak has disappeared. This may be due to the decreasing peak height (also shown in Fig. IV-6) and to the increasing background absorption in the temperature range above 250°C .

The internal friction curves as a function of temperature of some of the glasses in this series are shown in Fig. IV-7. Compared with the internal friction peaks in soda silicate glasses (cf. Chapter III) the peaks are small. In contradiction to the results of Coenen¹² no "high-temperature peak" could be detected in these glasses.

Another distinction from the results of Coenen can be found by comparing his results on glasses in series 1 - shown in Fig. IV-3 - with our results on the peak temperatures. Whereas Coenen finds a linearly decreasing peak temperature at increasing Na_2O concentration our curves are obviously flattened at high concentrations of sodium oxide. There is, however, little doubt as to the reliability of our results, since they are in complete agreement with the measurements of Karsch and Jenckel¹³, also represented in Fig. IV-3.

The activation energies of the internal friction peaks in sodium borate

Table IV-1. Results on the glasses in the nabal system

No.	Composition	Temp.of int. fr.peak (°C)	Activ.energy of int.fr.peak (kcal/mol)	Height above background of int.fr.peak	Thermal expansion coefficient $\times 10^7$
Series 1: $x \text{ Na}_2\text{O} \cdot (1-x) \text{ B}_2\text{O}_3$.					
1	$x = 0.090$	-	-	-	110.5
2	0.150	210	32	1.6	101
3	0.169	156	22	2.0	101
4	0.208	98	19	2.4	105.5
5	0.236	75	17.5	2.6	111
6	0.280	50	17	2.8	120
7	0.323	35	16.5	3.2	
Series 2: $x \text{ Na}_2\text{O} \cdot (0.9-x) \text{ B}_2\text{O}_3 \cdot 0.1 \text{ Al}_2\text{O}_3$.					
8	0.100	240	36	1.3	103
9	0.125	195	29	1.5	99
10	0.172	125	19.5	1.9	107
11	0.220	72	17	2.5	112
12	0.260	53	16.2	3.2	117
Series 3: $0.17 \text{ Na}_2\text{O} \cdot (0.83-y) \text{ B}_2\text{O}_3 \cdot y \text{ Al}_2\text{O}_3$.					
13 (=3)	$y = 0.000$	156	22	2.0	101
14	0.025	144	21	2.0	102.5
15	0.043	134	20.5	1.9	108
16 (=10)	0.100	125	19.5	1.9	107
17	0.131	118	19.0	2.0	103
18	0.167	109	18.5	2.0	104
Series 4: $x \text{ Na}_2\text{O} \cdot (1-2x) \text{ B}_2\text{O}_3 \cdot x \text{ Al}_2\text{O}_3$.					
19 (=8)	$x = 0.100$	240	36	1.3	103
20	0.125	188	28	1.5	99
21 (=18)	0.169	109	18.5	2.0	104
22	0.193	85	17	2.7	105.5
23	0.209	76	16.5	2.8	106.5
24	0.249	60	16	3.6	113.5

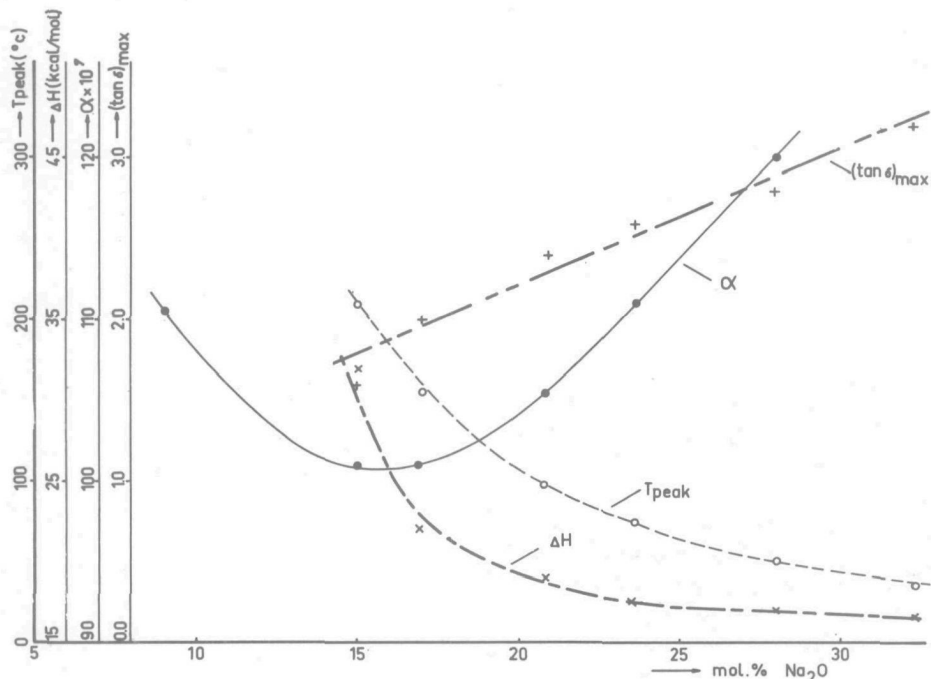


Fig.IV-6. Results on the glasses in series 1: $x \text{ Na}_2\text{O} \cdot (1-x) \text{ B}_2\text{O}_3$ as a function of the Na_2O concentration.

α = thermal expansion coefficient.

T_{peak} = temperature of the internal friction peak.

ΔH = activation energy of the internal friction peak.

$(\tan \delta)_{\text{max}}$ = maximum height of the internal friction peak above background.

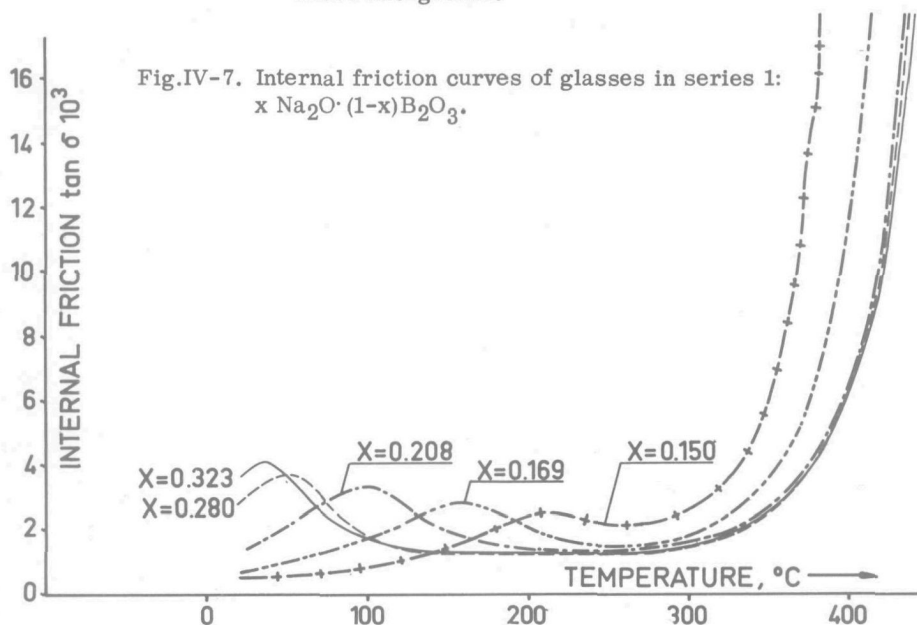


Fig.IV-7. Internal friction curves of glasses in series 1: $x \text{ Na}_2\text{O} \cdot (1-x) \text{ B}_2\text{O}_3$.

glasses have not yet been measured by other investigators. Karsch¹⁸ suggests on theoretical grounds, after a questionable discussion, a value of 440 cal/mol for this quantity. He admits that some preliminary measurements did not confirm this value. Our experiments give rise to much higher values of the activation energy, more in agreement with results on the dc conductivity, for instance¹⁷. Although the accuracy of the determinations of the activation energies is not very high (deviations as large as 3 kcal/mol may be possible in some cases) we can accept the general trend of the curve showing the activation energy as a function of the sodium content, since a shift to higher temperatures is usually due to an increasing activation energy.

The maximum height of the internal friction peak linearly increases with the soda content in the composition range studied in this series. Strictly speaking it is not correct to define the magnitude of the peak by its height. It would be more to the point to use the area under the peak as a measure of the relative strength of the relaxation effect (cf. Sec.II-1.3.). Since, however, the width of the peak was found to be very little dependent on the composition in sodium aluminoborate glasses, and since the peaks were too small to determine the area under the peak with sufficient accuracy, we found it more convenient to use the height of the peak above the background absorption as an indication of the relaxation strength.

IV.2.3. Glasses in series $2:x\text{Na}_2\text{O} \cdot (0.9-x)\text{B}_2\text{O}_3 \cdot 0.1 \text{ Al}_2\text{O}_3$

The results on the glasses in series 2 are not very different from those on the glasses of series 1. It does not seem to make much difference whether the sodium borate glasses contain Al_2O_3 or not, as can be seen in Table IV-1 and Fig. IV-8.

The thermal expansivity still exhibits a minimum as a function of the sodium concentration. The minimum seems to have shifted to a somewhat lower Na_2O concentration. The minimum in this series is situated at about 12 mol.% Na_2O , which means a shift of 4 mol.%.

There is one result that may not be overlooked. We are quite certain that at low Na_2O concentrations the temperature of the internal friction peak has decreased after the addition of alumina. In glass no.8, containing 10 mol.% Al_2O_3 and 10 mol.% Na_2O , we can still discover an internal friction peak, although very reduced in height. There is no doubt that the activation energy of the peak in this concentration range is lower than in glasses that do not contain Al_2O_3 .

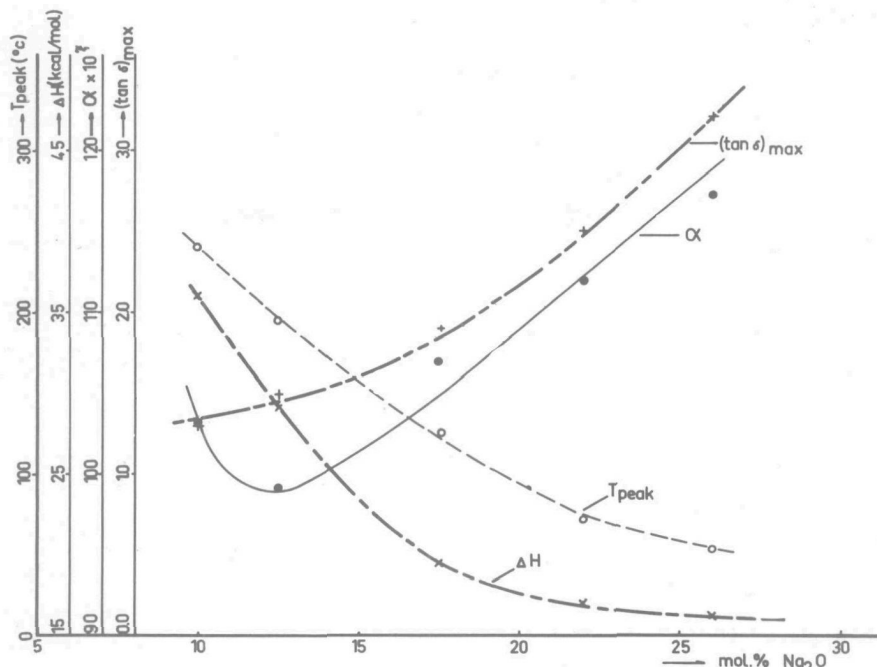


Fig. IV-8. Results on the glasses in series 2: $x \text{ Na}_2\text{O} \cdot (0.9-x) \text{ B}_2\text{O}_3 \cdot 0.1 \text{ Al}_2\text{O}_3$ as a function of the Na_2O concentration.

α = thermal expansion coefficient.

T_{peak} = temperature of the internal friction peak.

ΔH = activation energy of the internal friction peak.

$(\tan \delta)_{\text{max}}$ = maximum height of the internal friction peak above background.

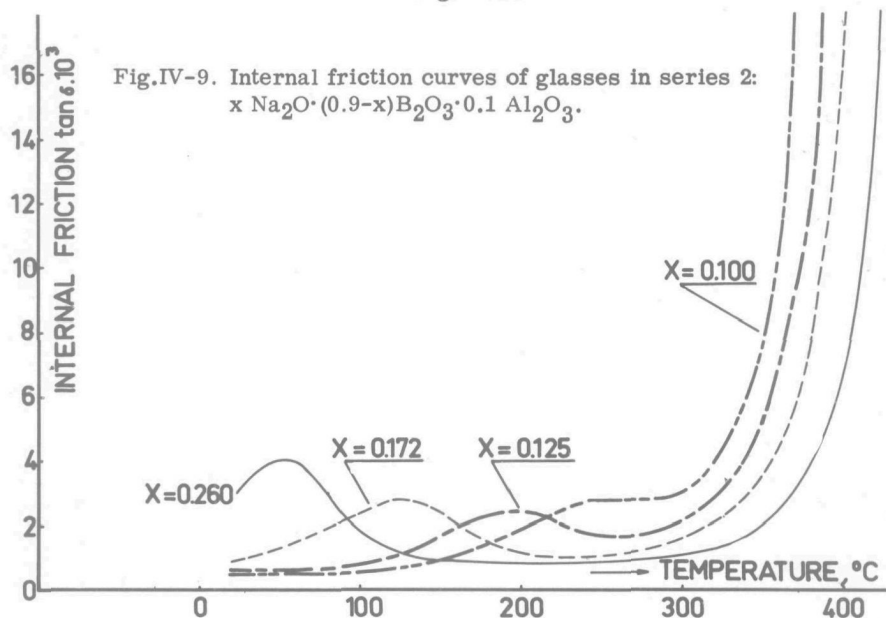


Fig. IV-9. Internal friction curves of glasses in series 2: $x \text{ Na}_2\text{O} \cdot (0.9-x) \text{ B}_2\text{O}_3 \cdot 0.1 \text{ Al}_2\text{O}_3$.

At high concentrations of Na_2O we find less influence of the alumina substitution. Here the peak temperature and the activation energy are not essentially different from the values plotted in Fig. IV-6.

The overall trends of the curves of the peak temperatures and the activation energies are not different from those found in the glasses of series 1. Both curves show a decrease of the values recorded at low concentrations and an approximately constant value at concentrations higher than 20 mol.% Na_2O .

In Fig IV-9 some of the internal friction curves recorded of the fibers of series 2 are represented. It can be seen that also in these curves no more than one internal friction peak can be detected.

IV.2.4. Glasses in series 3: $0.17 \text{ Na}_2\text{O} \cdot (0.83-y) \text{B}_2\text{O}_3 \cdot y \text{Al}_2\text{O}_3$

As can be seen in Fig. IV-10 and Table IV-1 the results of the measurements on the glasses in series 3 differ considerably from those on the glasses in the series 1 and 2, discussed in the preceding sections. In these glasses, with a constant concentration of 17 mol.% Na_2O , no minimum is found in the thermal expansivity as a function of the Al_2O_3 content. The thermal expansion coefficient is slightly increasing at low concentrations and decreases after the addition of more than 6 mol.% Al_2O_3 .

The curves representing the temperature of the internal friction peak and the activation energy versus the Al_2O_3 concentration show only a slight decrease with increasing Al_2O_3 content. These changes are approximately linear and no sign of any anomaly can be detected. This is an important result, since it rules out a number of possible explanations for the boric-oxide anomaly, as we shall see in Section IV.3.

The internal friction curves of the fibers in the composition range of series 3 are shown in Fig. IV-11. It can be seen that the peak height is not affected by the Al_2O_3 substitution, nor is the width of the peak. There are no signs of the occurrence of a high-temperature peak in these glasses.

IV.2.5. Glasses in series 4: $x \text{Na}_2\text{O} \cdot (1-2x) \text{B}_2\text{O}_3 \cdot x \text{Al}_2\text{O}_3$

The results of the determinations on the glasses of the series 4 are shown in Fig. IV-12 and in Table IV-1. It is clear that the glasses in this series behave more or less as the glasses of the series 1 and 2. The thermal expansion coefficient has a minimum at about 13 mol.%

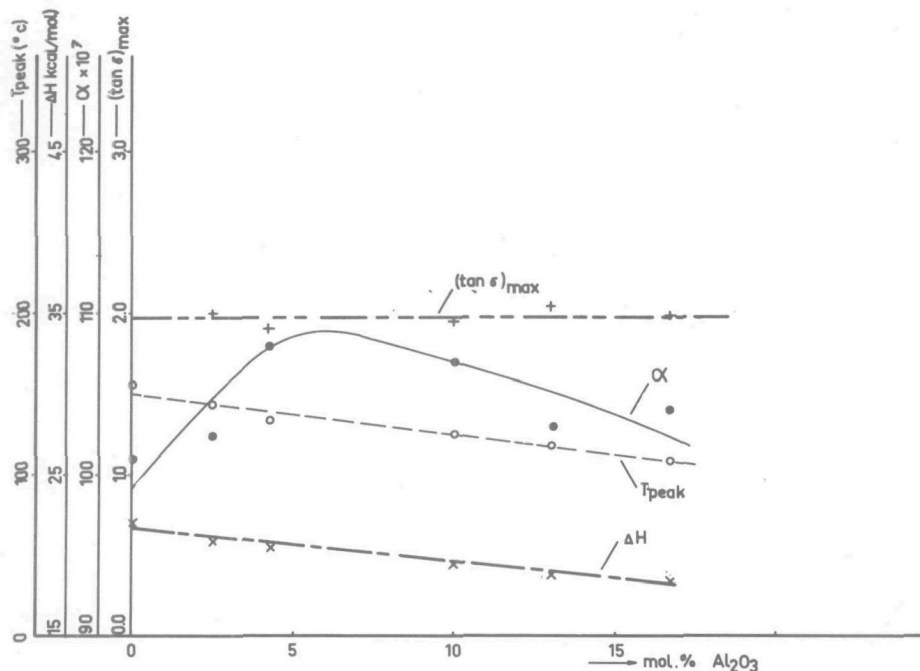


Fig. IV-10. Results on the glasses in series 3: $0.17 \text{Na}_2\text{O} \cdot (0.83-y) \text{B}_2\text{O}_3 \cdot y \text{Al}_2\text{O}_3$ as a function of the Al_2O_3 concentration.

α = thermal expansion coefficient.

T_{peak} = temperature of the internal friction peak.

ΔH = activation energy of the internal friction peak.

$(\tan \delta)_{\text{max}}$ = maximum height of the internal friction peak above background.

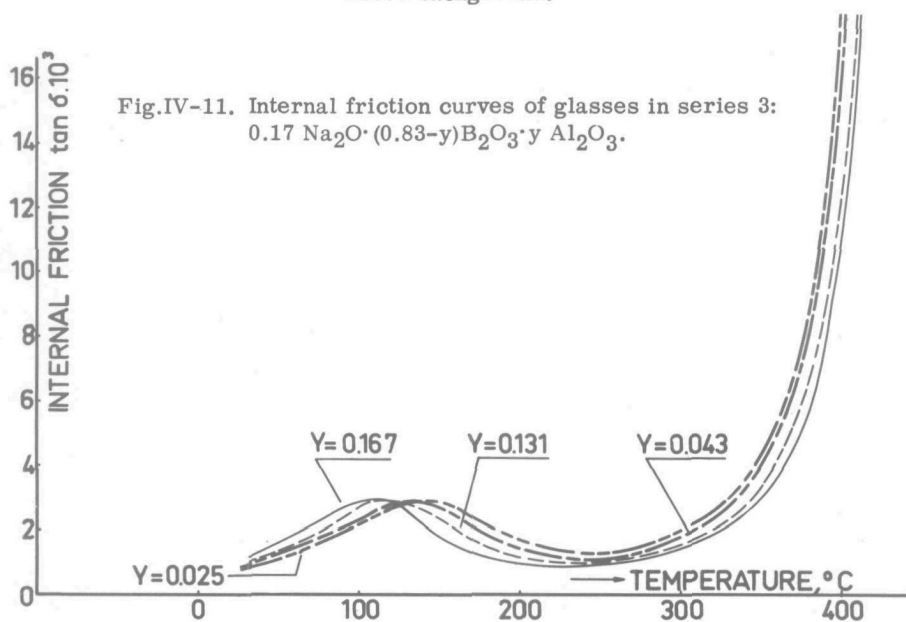


Fig. IV-11. Internal friction curves of glasses in series 3: $0.17 \text{Na}_2\text{O} \cdot (0.83-y) \text{B}_2\text{O}_3 \cdot y \text{Al}_2\text{O}_3$.

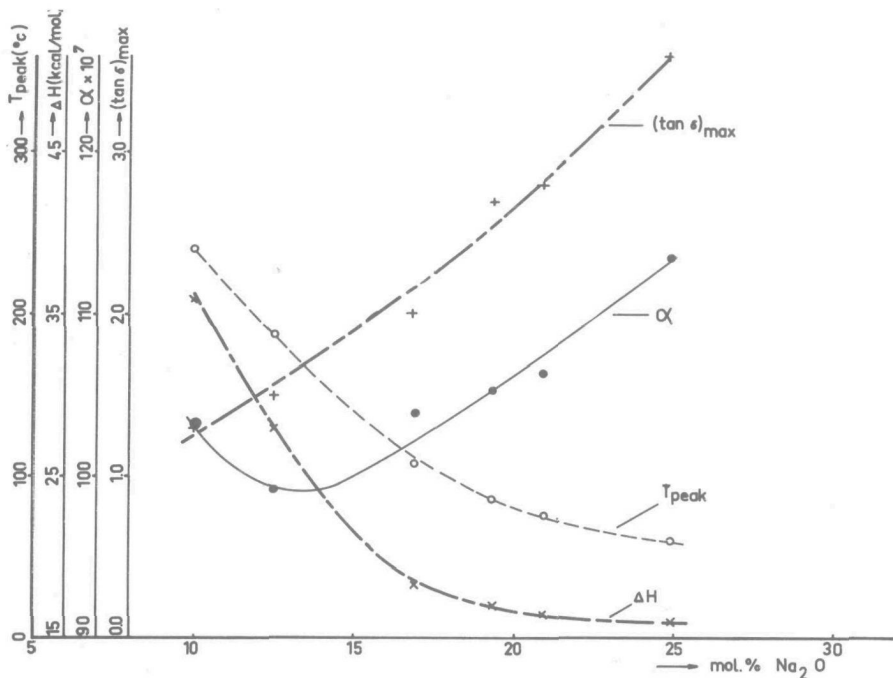


Fig. IV-12. Results on the glasses in series 4: $x \text{ Na}_2\text{O} \cdot (1-2x) \text{ B}_2\text{O}_3 \cdot x \text{ Al}_2\text{O}_3$ as a function of the Na_2O (or Al_2O_3) concentration.
 α = thermal expansion coefficient.
 T_{peak} = temperature of the internal friction peak.
 ΔH = activation energy of the internal friction peak.
 $(\tan \delta)_{\text{max}}$ = maximum height of the internal friction peak above background.

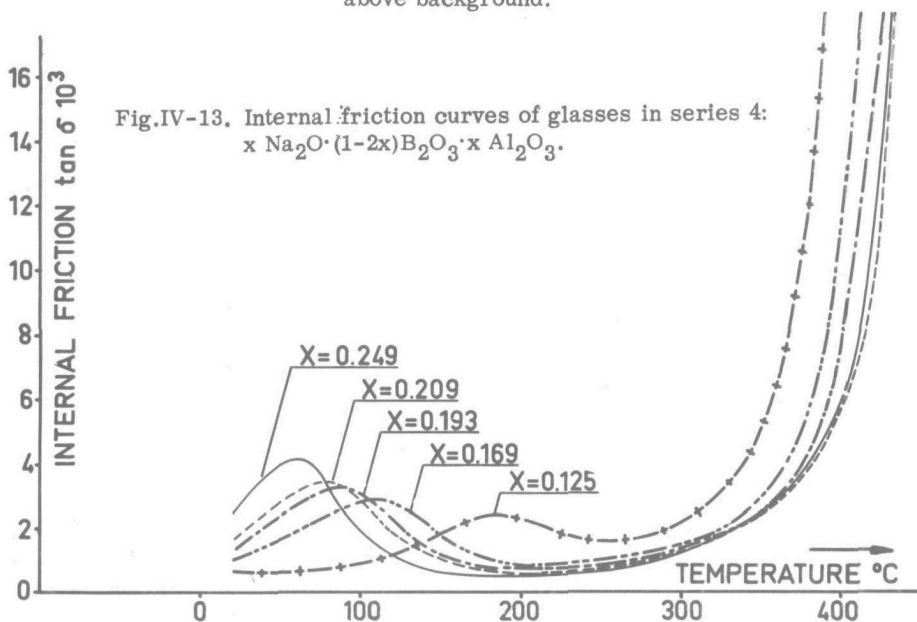


Fig. IV-13. Internal friction curves of glasses in series 4: $x \text{ Na}_2\text{O} \cdot (1-2x) \text{ B}_2\text{O}_3 \cdot x \text{ Al}_2\text{O}_3$.

Na_2O . The activation energy and the temperature of the internal friction peak decrease as the Na_2O concentration increases from 10 to 20 mol.%. At higher Na_2O concentrations these curves still exhibit a decreasing value, but the rate of decrease has diminished considerably. The height of the internal friction peak increases almost linearly with increasing Na_2O content. This can also be read from the internal friction curves, which have been plotted in Fig. IV-13 for this series.

IV.2.6. Internal friction measurements on some Babal and Cabal glasses

We investigated the internal friction of some barium aluminoborate glasses and a calcium aluminoborate glass.

No internal friction peaks were discovered in the compositions:

0.25 $\text{BaO} \cdot 0.75 \text{B}_2\text{O}_3$,

0.20 $\text{BaO} \cdot 0.75 \text{B}_2\text{O}_3 \cdot 0.05 \text{Al}_2\text{O}_3$,

0.25 $\text{BaO} \cdot 0.65 \text{B}_2\text{O}_3 \cdot 0.10 \text{Al}_2\text{O}_3$,

0.25 $\text{BaO} \cdot 0.55 \text{B}_2\text{O}_3 \cdot 0.20 \text{Al}_2\text{O}_3$,

and 0.20 $\text{CaO} \cdot 0.60 \text{B}_2\text{O}_3 \cdot 0.20 \text{Al}_2\text{O}_3$.

An example of the internal friction curves of these glasses is shown in Fig. IV-14 for a fiber with the composition 0.25 $\text{BaO} \cdot 0.55 \text{B}_2\text{O}_3 \cdot 0.20 \text{Al}_2\text{O}_3$. Only a contribution of the background absorption is found.

IV.3. Discussion of the results

IV.3.1. Thermal expansion measurements

Investigations on the thermal expansivity of glasses can only be discussed qualitatively, since no useful quantitative theory of the thermal expansivity has been developed as yet. In spite of this lack of quantitative knowledge the results of the measurements of the thermal expansivity of borate glasses are among the most important arguments used in theories concerning the boric-oxide anomaly. The existing theories all aim to explain the minimum that occurs in this property at a concentration of about 16 mol.% Na_2O in sodium borate glasses. The idea behind all these theories was a saturation in the formation of the BO_4 groups at a concentration of about 16 mol.% Na_2O . From the NMR measurements performed since 1958^{6,7,8} it appeared that this idea could not be sustained. Beekenkamp⁹ suggests that the

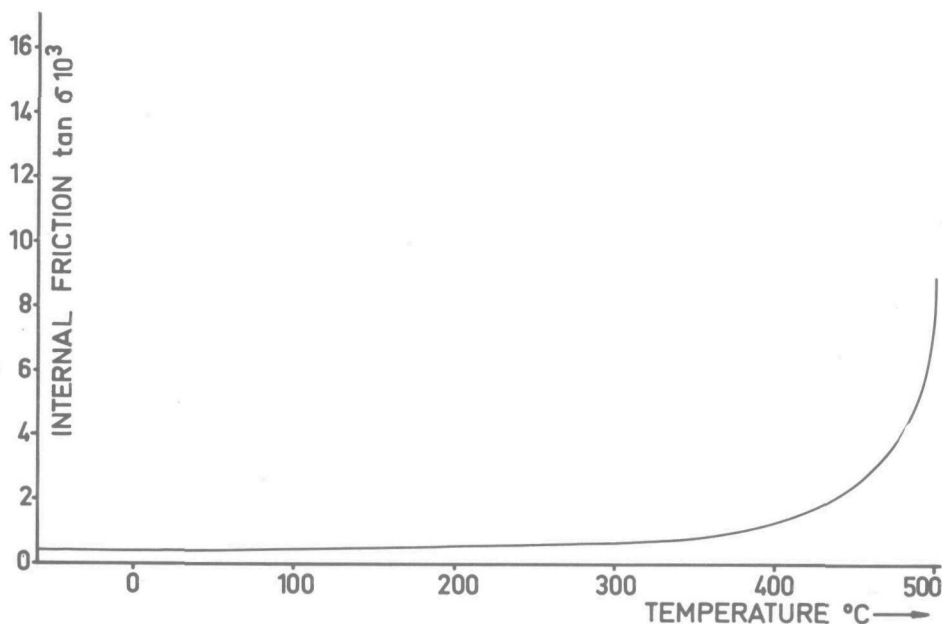


Fig.IV-14. Internal friction curve of the glass:
 $0.25 \text{ BaO} \cdot 0.55 \text{ B}_2\text{O}_3 \cdot 0.20 \text{ Al}_2\text{O}_3$.

decisive factor is not the formation of BO_4 groups, but the occurrence of nonbridging oxygen ions. On theoretical and experimental grounds it may be assumed that at concentrations higher than 15 mol.% alkali oxide no longer all the oxygen ions introduced with the alkali ions are used for the formation of BO_4 groups. At this concentration the first B-O-B linkages seem to be broken with the formation of nonbridging oxygen ions. The increasing coherence of the network, due to the increasing number of BO_4 groups, will then soon be outweighed by the destructive influence of the nonbridging oxygens. So the thermal expansion coefficient, first decreasing because of the increasing coherence, will soon be increasing after the appearance of the nonbridging oxygen ions.

Meanwhile Owen published his experiments on the Cabal glasses, from which he deduced that for these glasses the theory of Abe could be used. In view of the results of Bray and Beekenkamp this must be considered very unlikely.

It was shown in the preceding section that aluminoborate glasses containing only divalent modifying ions like barium or calcium do not exhibit internal friction peaks in the temperature range between -100°C and $+500^\circ\text{C}$. This is due to the stronger binding forces

between these ions and the surrounding oxygen ions, because of their higher field strength.

The Nabal glasses are in many aspects comparable with the Cabal glasses, but the occurrence of the monovalent sodium ions instead of the divalent calcium ions makes a study of the internal friction more interesting. Therefore we preferred to perform the experiments on glasses in the Nabal system.

Owen used the screening theory of Abe to explain his results. This theory was originally developed for alkali borate glasses. It will therefore be necessary to extend this theory (cf. Section IV.1) to glasses containing alumina.

Substitution of Al_2O_3 for B_2O_3 means the substitution of ions that cannot accept a threefold coordination. Assuming a fourfold coordination for the aluminium ions Abe's theory offers three possible ways in which a critical concentration can be attained, which we will discuss in some detail.

In the first place we may assume that the negatively charged AlO_4 groups need screening by BO_3 groups. The AlO_4 groups then would take up fully equivalent places as the BO_4 groups and the critical concentration of Na_2O would not change after the addition of Al_2O_3 . The boundary between the destruction region and the accumulation region in the ternary system would then be represented by the line rf in Fig. IV-5.

If we assume that the AlO_4 groups do not require screening we can calculate the critical concentration of Na_2O as follows: calling the molar fraction of Na_2O in the glass x and the fraction of Al_2O_3 y , the critical number of BO_4 groups will be reached at a molar fraction of $5(x-y)\text{B}_2\text{O}_3$. Hence, it follows that: $x + y + 5(x-y) = 1$, or: $6x - 4y = 1$. The boundary between the two regions can then be represented by the line ef in Fig. IV-5. In the area under the line ef (i.e. at low concentrations of Na_2O) no broken B-O-B linkages will occur, whereas after a crossing of this boundary no BO_4 groups will be formed, according to Abe.

In the third place we may assume that the AlO_4 tetrahedra are able to serve as screening units for the BO_4 groups. This, however, is very unlikely since both types are negatively charged. The critical concentration of B_2O_3 would amount to $5(x-y)-y$ in this case, which gives rise to a boundary represented by the line lf in Fig. IV-5.

Owen explained his results on the Cabal glasses by supposing that the AlO_4 groups did not require screening. If, however, we take a closer look at the two series he studied (Fig. IV-4) it appears that neither of these series crosses the line rf in Fig. IV-5, representing the boundary for the more probable supposition that the AlO_4 groups do require

screening by BO_3 groups.

The results of our determinations on the thermal expansion coefficient of Nabal glasses indicate that in these glasses the boundary between the destruction region and the accumulation region can approximately be represented by the line rf. This is in agreement with the results of the NMR measurements of Bishop and Bray¹⁶, discussed in Section IV.1. They state that, to a first approximation, the ternary Cabal system may be treated as a binary system, with B_2O_3 and Al_2O_3 serving jointly as the network former.

Since the NMR measurements show that the amount of BO_4 groups keeps increasing after the crossing of the critical Na_2O concentration we can not follow the theory of Abe in detail. It seems, however, that the considerations of Beekenkamp, discussed in Section IV.1, concerning the occurrence of nonbridging oxygen ions are also valid for the Nabal glasses.

Our experiments on the thermal expansivity suggest that the number of nonbridging oxygen ions starts to increase at a somewhat lower concentration of alkali ions after the addition of alumina. The minimum in the curves of the thermal expansion coefficient versus the Na_2O concentration in the series 2 and 4 seems to be situated at a somewhat lower concentration of sodium ions than in series 1. This may be due to the formation of the triclusters, proposed by Lacy¹⁵ as discussed in Section IV.1. Triclusters require less oxygen ions than do aluminium ions surrounded by four bridging oxygen ions, so there may be more oxygen ions available in the structure for the formation of nonbridging oxygen ions.

Beekenkamp¹⁷ pointed out that in the structure of $\text{K}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3$ glasses there are some indications of the occurrence of triclusters, so this explanation for our results seems not unreasonable.

The idea of the occurrence of triclusters is further supported by the trend of the thermal expansion coefficient in the glasses of series 3. These glasses contain a constant amount of sodium ions. The first addition of Al_2O_3 causes the thermal expansion coefficient to increase. This may be due to the fact that a part of the BO_4 units is replaced by AlO_4 groups, which might well result in a more loosely bound network (the AlO_4 groups can be considered as centre of asymmetry). The addition of more than 5 mol.% Al_2O_3 causes the thermal expansion coefficient to decrease again. This may be due to the formation of triclusters, resulting in a denser structure with a higher degree of coherence.

IV.3.2. Internal friction measurements

Unlike the thermal expansivity the position and the magnitude of the

internal friction peak in Nabal glasses is mainly defined by the behaviour of the sodium ions positioned in the holes of the aluminoborate network. This can be concluded from the effect of the Na_2O concentration on the results of the internal friction measurements.

The activation energy required for the jumping of an ion depends on the binding forces between this ion and the surrounding oxygen ions. These binding forces are related to the degree of coherence of the network itself. In general the sodium ions will tend to surround themselves with unsaturated oxygen ions. Since a BO_4 group contains four (partly) unsaturated oxygen ions we can accept the idea that the sodium ions will be stronger bound to their surroundings in the presence of BO_4 groups than if only BO_3 groups were present. The occurrence of nonbridging oxygen ions considerably disturbs the symmetry of the network. Two types of oxygen ions are created then, most of which are saturated and only a few - the nonbridging oxygens - are unsaturated. It can be understood that this provides less suitable surrounding conditions for the sodium ions.

This may explain why the internal friction peak does not appear in glasses with a low Na_2O concentration. In these glasses no nonbridging oxygen ions are believed to be present. In this respect our measurements confirm the conclusions of Beekenkamp¹⁹ in that the amount of nonbridging oxygen ions attains a detectable value at about 15 mol.% Na_2O . At a concentration of 15 mol.% Na_2O the internal friction peak appears to be situated in a very high temperature range, whereas the activation energy amounts to 32 kcal/mol (series 1).

The addition of more Na_2O gives rise to a higher number of nonbridging oxygen ions and soon the activation energy decreases to about 16 kcal/mol. Simultaneously the peak size increases.

Ryder and Rindone¹⁹ suggest that an increase in peak height can be due to two factors: a change in the distribution of relaxation times and an increase in the concentration of relaxing units. If the increase in the height of the peak is accompanied by a decrease in the width of the peak, in such a way that the area under the peak remains constant, the effect is due to a change in the distribution of relaxation times. If the increase in height is not accompanied by a diminishing of the width, such that the general shape of the peak is not affected, the effect is suggested to be due to an increase in the concentration of relaxing units.

In our experiments there can be no doubt that the changes in peak height are not accompanied by changes in the width of the peak. This would lead us to believe that the increasing size of the peak is simply due to the increasing Na_2O concentration.

There is, however, a third reason for an increase in peak height that may not be neglected. We want to put forward that in a fully symmetri-

cal network the sodium ions are not able to produce an internal friction peak. Not only the concentration of sodium ions is important, but also the degree of symmetry of the network surrounding these ions. As will be discussed in Chapter V no internal friction peak is produced, when an ion jumps from one site to another, unless these sites are different from each other - different with respect to the direction of the macroscopic stress. If a sodium ion can only "choose" between two positions that are completely equal and remain equal after the application of a macroscopic stress or strain nothing is gained when a jump occurs. Even if the two sites were energetically unlike (from the view-point of the sodium ion), but were modified to the same extent by the application of a stress, no internal friction peak would occur. It is absolute necessary that the sites are unevenly modified by a macroscopic stress or strain. This will be possible only if the distribution of the binding forces between a sodium ion and the surrounding oxygen ions is asymmetrical, the direction of this asymmetry varying from site to site.

From these considerations it is obvious that the formation of BO_4 groups (where all the oxygen ions are of the same type) is unfavourable for the occurrence of internal friction. The presence of nonbridging oxygen ions, on the contrary, introduces a great asymmetry in the network. The production of two different types of oxygen ions introduces a certain asymmetry in the distribution of the binding forces between a sodium ion and the surrounding oxygen ions and this is in favour of the occurrence of an internal friction peak. It must be noted that this has nothing to do with the value of the activation energy, but only with the "relaxation strength"; not with the position of the internal friction peak, but only with its magnitude.

The height of the peak does not always increase linearly with increasing Na_2O concentration, as can be seen in Fig. IV-8. This result is confirmed by the results of Goenen, represented in Fig. IV-3. A linear increase can hardly be expected, in view of the complicated relationship between peak size and soda content.

The addition of alumina has a small, but detectable, effect on the internal friction curves. From the glasses in series 3 it can be seen that the peak temperature and the activation energy of the peak are lowered with the addition of Al_2O_3 , in these glasses. The effect cannot be compared, however, with the large changes accompanying an addition of Na_2O . This effect may be due to the increasing asymmetry in the network that accompanies the substitution of Al_2O_3 for B_2O_3 , brought about by the different field strengths of the ions involved, or to an increasing number of nonbridging oxygen ions in the glass. The formation of triclusters would certainly stimulate the production of nonbridging oxygen ions.

In Section IV.2.3. we pointed out that in the glasses of series 2, containing 10 mol.% Al_2O_3 , the internal friction peak appears at a lower Na_2O concentration than in the glasses of series 1, containing no Al_2O_3 . In the alumina-containing glasses the peak can even be detected at a concentration of 10 mol.% Na_2O . This is certainly not possible without the presence of alumina. We consider this to be another indication of a lowering of the Na_2O concentration, where the first nonbridging oxygen ions begin to appear if Al_2O_3 is present.

From our study on the Nabal glasses we may conclude that it is very improbable that the interpretation Owen gave for his results on the Cabal glasses is correct. In fact his results may well be interpreted in a way that is in accordance with our measurements. This is due to the fact that all the glass compositions in his investigation contained more than 15 mol.% CaO .

Our results confirm the statement of Bishop and Bray that in a first approximation the ternary aluminoborate glasses can be treated as a binary system. Only in a more refined approximation differences can be found for the substitution of Al_2O_3 for B_2O_3 .

We suggest that with the addition of Na_2O two competing processes are introduced, giving rise to an increasing and a decreasing network coherence respectively.

The first addition of Na_2O makes all boron-oxygen forces more uniform. This behaviour may be described by pointing out that the B^{3+} ion expands its coordination from 3 to 4. It is, however, not necessary to place much emphasis upon a possible change in the coordination number of the boron ions and it seems more reasonable to emphasize the symmetry of the binding forces instead.

Weyl and Marboe²⁰ pointed out that the description of a structural unit by a number becomes misleading when this unit is not a regular polyhedron with the cation in the geometrical centre. The X-ray diffraction patterns and the NMR absorption spectra of alkali borate glasses may well be interpreted by assuming that in vitreous B_2O_3 the boron ions are surrounded by four oxygen ions, with three well defined B-O distances and one larger but poorly defined B-O distance. With the addition of Na_2O the latter distance might change to approximately the value of the former ones, thus increasing the symmetry of the binding forces. This leads to a compaction and an increasing coherence of the network.

Some of the excess oxygen ions involved in the addition of Na_2O are used for the formation of nonbridging oxygen ions. This gives rise to a disproportionation of the binding forces, which decreases the coherence of the network. We do not believe that the formation of nonbridging oxygen ions is coupled with a specified alkali concen-

tration, as is predicted by Abe's theory. The number of nonbridging oxygen ions in sodium borate glasses seems to be continuously increasing with the concentration of alkali ions, as if governed by some equilibrium equation of the type given by Beekenkamp⁹ (cf. Sec.IV.1.). This statement is especially supported by the results of our internal friction measurements. Both the temperature and the activation energy of the peak are continuously decreasing (without "marked changes") with increasing soda content. Both properties seem to be mainly determined by the degree of coherence of the B-O network and we believe that the observed trend of the curves can be related to the decreasing coherence of the network, due to the increasing number of nonbridging oxygen ions.

The introduction of Al_2O_3 in the glass seems to increase the number of nonbridging oxygen ions, which is especially noticeable at low Na_2O concentrations. It may be possible that not all the aluminium ions are surrounded by four bridging oxygen ions. There are indications of the occurrence of aluminium ions surrounded by three bridging oxygens and one tripod oxygen, thus increasing the total number of nonbridging oxygen ions in the glass.

References

1. J.Biscoe, B.E.Warren, J.Am.Ceram.Soc., 21, 287 (1938).
2. G.W.Morey, "The Properties of Glass", Reinhold, New York, 1954.
3. J.M.Stevens, "Progress in the Theory of physical Properties of Glass", Elsevier, Holland, 1948.
4. E.J.Gooding, W.E.S.Turner, J.Soc.Glass Technol., 36, 5T (1934).
5. T.Abe, J.Am.Ceram.Soc., 35, 284 (1952).
6. P.J.Bray, A.H.Silver, "Modern Aspects of the vitreous State", ed. J.D.Mackenzie, Butterworths, London, 1960, Vol.I.
7. P.J.Bray, J.G.O'Keefe, Phys.Chem.Glasses, 4, 37 (1963).
8. S.E.Svanson, E.Forslind, J.Krogh-Moe, J.phys.Chem., 66, 174 (1962).
9. P.Beekenkamp, "Physics of non-Crystalline Solids", Proc.Int. Conf.Delft, 1964, Ed.J.A.Prins, North-Holland Publ. Comp., Amsterdam, 1965.
10. B.D.McSwain, N.F.Borelli, Gouq-Jen Su, Phys.Chem. Glasses, 4, 1 (1963).
11. P.Beekenkamp, "Colour Centres in Borate, Phosphate and Borophosphate Glasses", Thesis, Eindhoven, 1965.
12. M.Coenen, Z.für Elektrochemie, 65, 903 (1961).
13. K.H.Karsch, E.Jenckel, Glastechn.Ber., 34, 397 (1961).
14. A.E.Owen, Phys.Chem Glasses, 2, 87 (1961).
15. E.D.Lacy, Phys.Chem Glasses, 4, 234 (1963).
16. S.G.Bishop, P.J.Bray, Phys.Chem.Glasses, 7, 73 (1966).
17. P.Beekenkamp, to be published.
18. K.H.Karsch, "Über das mechanische und thermische Verhalten der Alkaliboratgläser", Thesis, Aachen, 1959.
19. R.J.Ryder, G.E.Rindone, J.Am.Ceram.Soc., 44, 532 (1961).
20. W.A.Weyl, E.C.Marboe, "The Constitution of Glasses", Vol.II, Part I, John Wiley and Sons, New York, 1964.

CHAPTER V

ON THE MECHANISM OF THE INTERNAL FRICTION IN GLASSES CONTAINING MONOVALENT IONS

V.1. Introduction

The internal friction curves of alkali-containing silicate glasses exhibit a maximum near room temperature, when measured at a frequency of about 1 cps. In Chapter III we called this peak the low-temperature peak, in distinction of the peak occurring at higher temperatures. In borate glasses (Chapter IV) only one internal friction peak could be detected, occurring at somewhat higher temperatures than the low-temperature peak in silicate glasses. We related these maxima to the presence of the monovalent metal ions in the glass, while the results on the borate glasses seemed to indicate that in these glasses the peak occurred only in the presence of nonbridging oxygen ions. It is not self-explaining why the alkali ions are able to bring about an internal friction peak. In this chapter we will discuss the conditions that must be fulfilled to allow the occurrence of this internal friction peak. We will propose a mechanism that may be responsible for the occurrence of the maximum, and we will also go into a mechanism that might give rise to the intermediate-temperature peak, occurring when two types of metal ions are present in the glass (cf. Chapter III). Although the number of publications dealing with this subject is small, the existing literature is interesting enough to be discussed in a separate section.

As is customarily in the literature we will take advantage of two-dimensional representations to discuss the glass structure, in which the ions involved are represented by rigid spheres. Especially for the more easily polarizable ions, like oxygens and the larger alkali ions, this is not fully correct. As long as we realize the shortcomings of these illustrations, they can be of great use.

Discussing the energy of the system another type of model has proved to be very helpful, i.e. the so-called two-dimensional potential diagrams. In these models the change of energy⁺) is considered that is experienced by one ion (e.g. a Na^+ ion) when it moves through the

+) Strictly speaking the use of the indication "energy" is not correct, since both the free energy and the thermodynamic potential are involved. We will, however, continue to use the word "energy", thinking in terms of "activation energies".

network along such a path that this energy is always a relative minimum. The change of energy is then plotted against a spatial coordinate, representing the path of the ion.

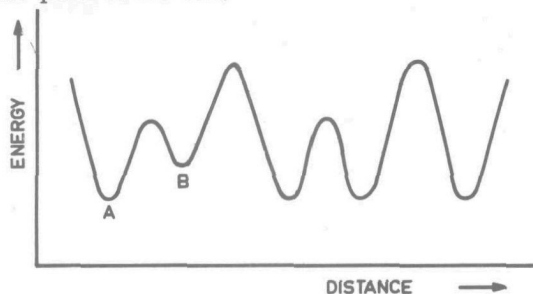


Fig. V-1. Potential diagram that may occur in a random ionic structure. Energy changes, experienced by an alkali ion, plotted against a two-dimensional representation of the path through the glass structure, followed by the ion.

An example of this type of model is given in Fig. V-1 for a random structure. The equilibrium positions of the metal ions are the wells between the energy barriers. The height of the barrier separating two adjacent potential wells represents the activation energy involved in the jumping of the ion from one well to the other. It can be seen that in the case of the potential wells A and B in Fig. V-1 this activation energy is higher for a jump from A to B than from B to A. Of course it must be kept in mind that this is no more than a two-dimensional picture. In fact the ion is surrounded by a three-dimensional structure, and the influence of the neighbouring ions results in the apparent barrier being more in the nature of a col or a saddle. The neighbouring ions will exercise an important effect on the height of the pass (i.e. the original barrier). Besides, the ion in the potential well will have more than one possibility to leave the well considered. This restricts the influence of an incidentally occurring high potential barrier, since it may be avoided.

It must be pointed out that it is too simple to use a picture in which the ion considered is positioned in one potential well. If there is an adjacent "empty" well there will always be a certain transition probability, depending upon the temperature, since the distribution of the ions will be governed by the Boltzmann equation. It is more convenient to speak in terms of an occupation number, denoting the relative amount of time the ion spends in one of the potential wells. In all theories concerning the jumping of ions this must necessarily be the basis of the discussion.

V.2. Literature

Dealing with theories about relaxation mechanisms and the jumping of metal ions, we must distinguish between papers concerned with measurements on the dc conductivity in glasses, papers in which the results of dielectric loss measurements are dealt with, and others in which the mechanisms behind the mechanical losses are discussed.

Although some connections exist between the models used for conductivity and dielectric losses in glass and for the internal friction, it must be remembered that essential differences exist between the electrical and the mechanical behaviour of a glass. A common misconception is to imagine that the application of a macroscopic stress to a material results in a biased potential diagram (the "wells" on a "hillside" picture). This is not the case. In the case of a mechanical stress the desired picture of an unsymmetrically biased potential diagram cannot be used (neither for a tensile stress nor for a shear stress).

In contrast to this is the directed migration of alkali ions, which is the mechanism of the ionic-conduction process in glass¹. The electric field possesses a sense (due to the polarity characteristic) in addition to its direction and thus gives rise to an unsymmetrically biased potential diagram directly applicable to the spatial movement of a single ion within the relatively stationary lattice.

To explain the results of dielectric measurements the same picture can be used, although in these cases a continuously varying field is present. Here polarization effects and electrical dipoles, orienting to the applied field, come into the picture.

R.J.Charles² proposed a theory to explain the orientation polarization, the dc and ac conductivity, as well as the alkali-ion self-diffusion. In his model it was necessary to postulate that a number of equivalent positions of stability exist for the alkali ions around each nonbridging oxygen ion. Because of the intervening glass structure and the electrostatic binding conditions these equivalent positions are separated by energy barriers. Charles suggests that there are far more sites than alkali ions, but that in equilibrium no more than one of the equivalent positions around a nonbridging oxygen ion will be occupied. Conduction and polarization events take place by the formation of defects, he believes to exist of doubly occupied equivalent sites. In Fig. V-2 it is shown that this results in some oxygen ions having none of their equivalent sites occupied and others having two of their equivalent sites occupied. Migration of the doubly occupied equivalent sites allows an effective rotation at each step, for it is clear that when two equivalent sites of one oxygen ion are occupied,

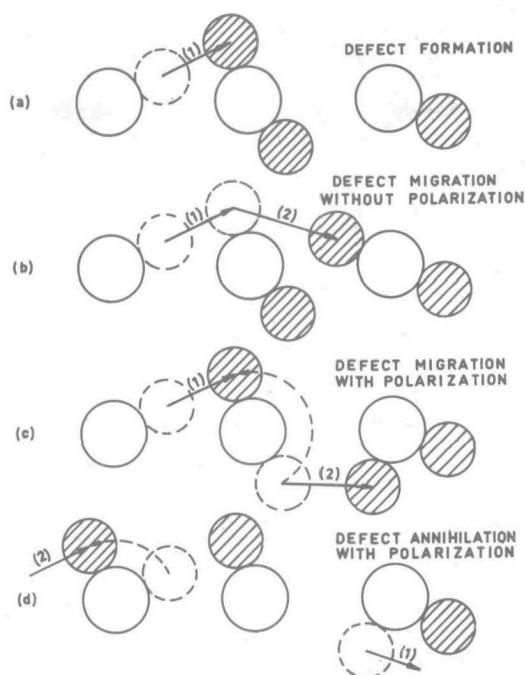


Fig. V-2. Hypothetical defect formation, conduction, and polarization events in an alkali silicate glass, after Charles².

○ = nonbridging oxygen ions.

● = alkali ions.

Dashed circles represent former positions of ions; arrows show the jumps that took place, and dashed arrows represent the apparent changes of position.

In the situation without defects each alkali ion is associated with one nonbridging oxygen ion.

one cannot distinguish between the alkali ion which will continue migration and that which will remain.

Charles derives that the energy of defect formation amounts to about 0.9 eV, whereas the energy barrier to migration amounts to 0.1 - 0.4 eV. To obtain these values Charles assumes that the equivalent sites correspond with the three saddle-point positions between neighbouring oxygen ions of the silica tetrahedra.

Y. Haven and B. Verkerk³ proposed a different model to explain diffusion of, and electrical conduction by, alkali ions in alkali silicate glasses. In their investigation the correlation factor plays an important role. This factor appears, when the results of measurements on the dc conductivity and the diffusion (both due to the migration of Na^+ ions) are compared. They could not agree with the model

proposed by Charles and pointed out that the assumption of equivalent positions of stability for an alkali ion around each nonbridging oxygen ion is equivalent to the adoption of a large concentration of vacancies. This would imply that the correlation factor, due to some non-random distribution of the directions of successive jumps of a particle, had to approach unity and this could not explain their results. Haven and Verkerk measured the diffusion of sodium ions in some sodium silicate glasses and compared the results with data on the electrical conductivity. They found that the two could be related to each other by the Nernst-Einstein equation only if a correlation factor $f = 0.4 - 0.5$ was introduced. Only two mechanisms of transport, namely the vacancy mechanism and the indirect interstitial mechanism (also called the interstitialcy mechanism), can account for correlation factors as small as this.

In their model Haven and Verkerk suppose that each nonbridging oxygen ion is surrounded by two or three sodium ions, so that on the average each sodium ion will be surrounded by two or three nonbridging oxygen ions. They distinguish between two types of sites for the sodium ions. The sites which are usually occupied by sodium ions are called sodium sites or simply sites. A sodium site that is unoccupied is called a vacancy. The sites corresponding to energy levels of sodium ions higher than the levels of the bulk of the sodium sites are called interstitial sites. Sodium ions occupying sites of this type are called interstitial ions.

Haven and Verkerk illustrate their point of view with the two-dimensional crystal models of the Figs. V-3 and V-4. They believe the indirect interstitial transport mechanism to be more probable than the vacancy mechanism, but are not able to make a final choice between the two possibilities. Making use of data from Forry⁴ and Mohyuddin and Douglas⁵ on mechanical relaxation they derive a fraction of defects of the order of 0.1 - 1% at 123°C in sodium silicate glasses, which can be related to an energy of formation of a vacancy-interstitial pair of about 0.2 eV. To obtain these quantities Haven and Verkerk attribute the relaxation phenomenon to a rearrangement of the vacancies or the interstitials over the available sites when a mechanical force is applied. They assume that in the case of shear deformation the possible sites for an interstitial or a vacancy can be divided into three classes: the energy level becomes higher or lower or remains unchanged by the deformation. They call these sites X, Y, and Z sites respectively and assume that half the neighbours of Z sites are X sites and half of them are Y sites, etc. (this model being inspired by the situation of the C ions in Fe, causing the Snoek internal friction peak¹⁰).

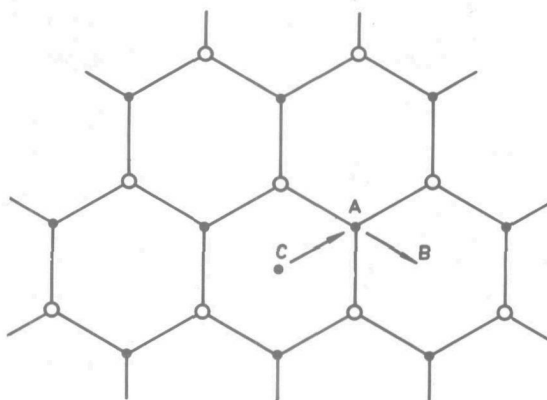


Fig. V-3. Two-dimensional lattice with 3-3 coordination after Haven and Verkerk³.

● = sodium site, O = oxygen site, C = interstitial sodium ion. In the case of a vacancy transport mechanism for sodium a vacancy moves to any of the six nearest sodium neighbours. In the case of an indirect interstitial transport, C moves to A, A to B. Ion A moves to any of three interstitial sites, the interstitial moves to any of six interstitial sites.

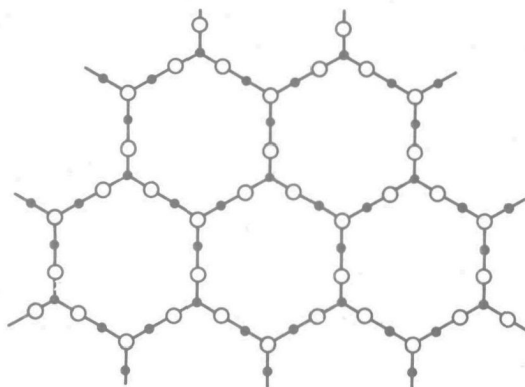


Fig. V-4. Two-dimensional lattice with mixed 3-3 and 2-2 coordination after Haven and Verkerk³.

● = sodium site, O = oxygen site; the centres of the hexagons are considered as the interstitial sites. A vacancy moves to any of the three nearest sodium neighbours. In the case of indirect interstitial transport, ions move either to three interstitial sites or to two interstitial sites. The interstitial moves to any of six interstitial sites.

We do not believe that this approach applies to a glassy structure. It does not even apply to the models of the figures V-3 and 4. In the case of a homogeneous shear (or tensile) stress the energy levels of the vacancies as well as those of the interstitials in the model of Fig. V-3 are changed to the same extent when the stress is applied, since all the sites have equivalent surroundings. This also applies to the interstitial positions in the model of Fig. V-4. Only the energy levels of the vacancies in Fig. V-4 are unevenly changed when a mechanical force is applied, but certainly not in a way as simple as proposed by Haven and Verkerk. Probably they had in mind the inhomogeneous character of the shear stress in a torsion experiment, assuming that the relaxation must be attributed to the structural deformation increasing in a radial direction in the fiber.

Since A.E.Badger and W.B.Silverman⁶ showed that relaxation occurs also in a tensile stress experiment, we do not believe that this explanation can be accepted. The inhomogeneity of the stress is only a secondary effect in comparison to the deformation brought about by the stress itself.

Karsch⁷ used an approach similar to the one followed by Haven and Verkerk in his discussion of the results on the internal friction in alkali borate glasses. He assumed that the inhomogeneity of the shear stress in a torsion experiment causes a biased potential diagram in such a way that the sodium ions are forced to diffuse to the centre of the fiber, thus giving rise to an internal friction peak. Based on this assumption Karsch derives a value for the activation energy of the internal friction peak in the borate glasses that is wrong by a factor of 50 (cf. Section IV.2.2.).

We believe that the mechanical relaxation phenomena, observed in glasses, cannot be explained on the basis of a biased potential diagram, caused by an inhomogeneous deformation. As will be discussed in the following sections the environmental conditions must be taken into account to explain the phenomena recorded.

G.A.Korn⁸ developed a theory on the low-frequency sound absorption in solids, with application to soda silicate glasses. He assumes that in glass there exist a number n_1 of sodium ions at an energy level H_1 and a number n_2 at an energy level H_2 . The energy levels H_1 and H_2 are believed to be separated by an energy barrier H_a , which Korn thinks to be an activated state for the sodium ions, associated with an occupation number n_a .

The transition probabilities of the transitions 1 to 2 (via a) and 2 to 1 (via a) are assumed to be finite and respectively governed by the quantities

$$\exp\left\{-\frac{H_a - H_1}{kT}\right\} \quad \text{and} \quad \exp\left\{-\frac{H_a - H_2}{kT}\right\}.$$

Korn suggests that the effect of the relatively small stress changes, produced by acoustical disturbances, will be to change the equilibrium values of n_1 , n_2 and n_a by only small amounts, and proposes a linear relationship between the changes Δn_{1a} and $\Delta(H_1 - H_a)$, between Δn_{2a} and $\Delta(H_2 - H_a)$, and between $(\Delta n_1 + \Delta n_2)$ and $\Delta(H_2 - H_1)$. He thus suggests that the excess pressure, brought about by a sinusoidal sound wave, produces a change in the occupation numbers n_1 , n_2 and n_a . In his opinion the transitions 1-2 and 1-a are respectively associated with volume changes (per mole) δV_{12} and δV_a . This, of course, would result in a relaxation phenomenon, since the changes δV_{12} and δV_a are associated with a certain relaxation time, which is governed by the transition probabilities.

From this Korn derives a value for the logarithmic decrement of the absorption phenomena λ that is given by:

$$\lambda = \frac{\pi}{(\partial p / \partial V)_{n_a}} \cdot \frac{n_1}{n_a} \cdot \frac{\delta V_{12}}{(\delta V_a)^3} \cdot \frac{(H_1 - H_2)}{4} \cdot \frac{\omega \tau}{(1 + \omega^2 \tau^2)}.$$

This result suggests the logarithmic decrement to be proportional to the volume change per mole for the transition 1-2. This might be expected. It is less easy to understand why λ is inversely proportional to $(\delta V_a)^3$, but a real weakness in this theory is that λ appears to be linearly dependent on the quantity $(H_1 - H_2)$. In the following sections it will be shown that in glasses it is not necessary to assume $H_1 \neq H_2$ to explain the relaxation phenomena.

The theory of Korn gives the relaxation that might occur in solids under a hydrostatic pressure. Since sound waves, just like mechanical stress waves, do not produce a three-dimensional compression in solids, it is not necessary to make such a restriction, neither in the case of sound absorption, nor in the case of torsional, transverse or longitudinal oscillations. Nevertheless, the way in which Korn approached the problem is in the main correct. In the following sections we will propose a mechanism that shows some resemblance with the theory of Korn.

V.3. Energetic conditions for the occurrence of internal friction in glasses

In Section II.1.1. it has been pointed out that internal friction may be defined as the dissipation of energy. It has been shown that the decay of the amplitude in a free torsional oscillation experiment is only

one of the various ways in which this effect can be observed. The anelastic strain that occurs in addition to the instantaneous (elastic) deformation after the application of a certain tensile stress has been put forward as an example of another way to observe the effect. We are thus permitted to discuss the internal friction phenomena in (sometimes more convenient) terms of a " $\Delta\epsilon$ effect", where $\Delta\epsilon$ stands for the anelastic increase of the instantaneous strain ϵ , due to the relaxation mechanism. It suffices to find an explanation for the occurrence of an anelastic strain, approaching a final value some time after the application of a constant tensile stress. We can describe this varying stress-strain relationship by introducing an unrelaxed and a relaxed elastic modulus, as pointed out in Section II.1.1. With the help of Eq. II-7 we can relate these quantities to $\tan\delta$, being a measure for the internal friction.

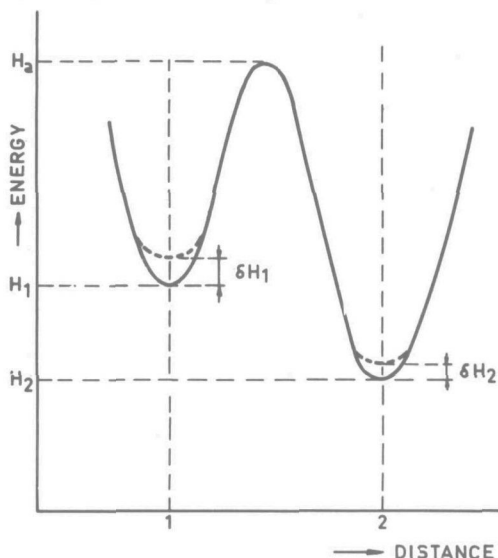


Fig. V-5. Energetic representation of two sodium sites with energy levels H_1 and H_2 respectively, separated by an energy barrier H_a . δH_1 and δH_2 represent the changes in the energy levels of the sites, brought about by an applied tensile stress.

Suppose that somewhere in the structure a vacancy exists. An adjacent sodium ion then has two sites at its disposal. We can represent this in an energy scale with the help of the potential diagram of Fig. V-5 (discussed in Sec.V.1). The energy of the sodium ion in position 1 amounts to H_1 , the energy of the ion in site 2 amounts to H_2 .

The height of the separating energy barrier will be called H_a , which means that the activation energy associated with a transition from site 1 to site 2 amounts to $(H_a - H_1)$. The probabilities for the transitions from 1 to 2 and from 2 to 1 are finite, and depend on the thermal energy kT of the ion considered, according to the Arrhenius equation. It is certainly not correct to state that under equilibrium conditions the sodium ion will be positioned in site 2, simply because $H_2 < H_1$. We can only say that when $H_2 < H_1$ the sodium ion will spend more time in site 2 than in site 1. Only when $H_1 = H_2$ the probability of finding the ion in site 1 will equal the probability of finding the ion in site 2.

In general the application of a macroscopic tensile stress will accomplish changes in the values of the energy levels H_1 and H_2 . The value of H_a may also change, but since $H_a \gg H_1$ and H_2 we may neglect this effect. Besides, the effect of a change in the value of H_a on $(H_a - H_1)$ is not different from the effect on $(H_a - H_2)$, and therefore, as we shall see, this does not lead to a relaxation effect, but only to a small change in the activation energy. We will call the increases in the values of H_1 and H_2 , brought about by the tensile stress, δH_1 and δH_2 respectively.

The occupation of site 1 will give rise to a microscopic strain of the surrounding structure ϵ_1 , and the occupation of site 2 will give rise to a microscopic strain ϵ_2 , both measured in the direction of the applied stress. We must assume that $\epsilon_1 \neq \epsilon_2$, which is not unreasonable since the two sites are not fully alike. (Once more we want to point out that to achieve this it is not necessary to postulate that $H_1 \neq H_2$, but that $\delta H_1 \neq \delta H_2$ suffices).

Without going into detail we can accept the assumption $\epsilon_1 \neq \epsilon_2$ by realizing that the amount of an energy level is related to the binding forces between the sodium ion and its surroundings. These binding forces of course influence the coherence of the surrounding structure, and this coherence determines the amount of strain brought about by the stress. We will discuss this further in the following section. In itself the inequality of ϵ_1 and ϵ_2 does not lead to a macroscopic " $\Delta\epsilon$ -effect", unless the distribution of vacancies over the available sites of the types 1 and 2 is changed by the application of the stress. If the relative occupation numbers of the sites 1 and 2 do not change by the application of the stress we may not expect to find any relaxation phenomenon. The application of the stress must, one way or another, produce preferential sites. This can only be accomplished when $\delta H_1 \neq \delta H_2$. It has nothing to do with the equality or inequality of H_1 and H_2 . It does not matter whether there are sites in the structure that may be considered preferential before the application of the stress,

or not. The only condition is that the stress must produce a separation between the available sites in such a way that some of these sites become preferential. This is a general principle. In the following section it will be applied to a certain model to account for relaxation by alkali ions. It should be noted, however, that application of this principle to other models or mechanisms will give analogous results, because the formalism to derive the final equations will hardly be different.

Thermodynamically speaking it is quite clear that any change in the occupation numbers, due to the application of a macroscopic stress, must be accompanied by a relaxation effect. The principle of Le Chatelier says: "If the external conditions of a thermodynamical system are altered, the equilibrium of the system will tend to move in such a direction as to oppose the change in the external conditions." This principle enables us to determine, without calculations, the direction in which a change in the external conditions tends to shift the equilibrium of a thermodynamical system. So if - one way or another - the application of a macroscopic stress gives rise to an inequality of the δH values, there can be no doubt that the microscopic strains ϵ will also be different, and that the ions will tend to occupy the sites with the larger values of ϵ , because this leads to an extra strain (macroscopically) and a relaxation of the applied stress.

V.4. Discussion of a mechanism accounting for the "low-temperature peak" in alkali-containing glasses

In the preceding section we established the energetic conditions to be met for the occurrence of relaxation in glass. We are now concerned with the description of a structural equivalent. The question is, if it is possible to meet the requirement $\delta H_1 \neq \delta H_2$ in a glassy structure, with or without the equality of H_1 and H_2 .

In Chapter I we saw that a sodium silicate glass can be considered as a network of quadrivalent silicon ions, tetrahedrally surrounded by bivalent oxygen ions. Most of these oxygen ions form bridges between two Si^{4+} neighbours. Between this network the modifying ions, in this case the sodium ions, are distributed, and a corresponding number of oxygen ions becomes nonbridging, i.e. bonded to only one silicon ion. The number of nonbridging oxygen ions is equal to the number of sodium ions.

The sodium ions are surrounded by oxygen ions, the mean coordination number being about six. They tend to surround themselves

with the unsaturated nonbridging oxygen ions and it seems reasonable to suppose that two or three of the oxygen ions surrounding a sodium ion are nonbridging³.

The nonbridging oxygen ions produce an appreciable degree of asymmetry in the structure, as has been pointed out by Weyl and Marboe⁹. The binding forces between a sodium ion and a neighbouring nonbridging oxygen ion exceed those between a sodium ion and a bridging oxygen ion, because of the unsaturated character of the former. This causes an asymmetry in the way in which a sodium ion is bonded to its site. In a three-dimensional structure two or three nonbridging oxygen ions are not able to accomplish a spherically symmetrical environment for a sodium ion. It will always be possible to define a line or a plane through the centres of the nonbridging oxygen ions belonging to one site. Performing this for a number of sites it must be noted that the resulting lines or planes will not be parallel to each other, which is due to the lack of long-range order in glass. With the application of a unilateral tensile stress it will be possible to define an angle Θ between the direction of the stress and the plane or line connecting the nonbridging oxygen ions of one site. In principle this angle Θ will vary from site to site, which gives rise to the appearance of preferential sites after the stress has been applied.

Before the application of the tensile stress the value of the angle Θ is immaterial. In spite of the varying values of Θ the energy levels of the sites may be fully alike. There is no relation between Θ and the energy level of a site. After the application of the stress, however, this is no longer the case. The energy level of a site, for which $\Theta = 0$, will respond differently from the energy level of a site, for which $\Theta = \pi/2$, for instance. This can be understood as follows: the elastic deformation, brought about by the one-dimensional stress, will give rise to a change in the interionic distances in the network structure. The distance between two ions, whose binding forces are directed parallel to the direction of the stress, will be enlarged. The distance between two ions, the connecting line of which is positioned perpendicular to the direction of the stress, on the contrary, will be somewhat reduced. This implies that the change in the distance between a sodium ion and its neighbouring nonbridging oxygen ions will depend on the value of the angle Θ between the direction of the stress and the plane or line connecting the centres of the nonbridging oxygen ions concerned. Simultaneously the binding forces between the sodium ion and its surroundings will be altered, because the amount of the electrostatic attraction depends on the distance between the ions. This gives rise to a change δH in the energy level of the site, depending upon the angle Θ .

Since the angle Θ may differ from site to site this mechanism satisfies the requirement $\delta H_1 \neq \delta H_2$, and it appears to be immaterial whether $H_1 = H_2$ or not (although a dissimilarity between H_1 and H_2 may well occur in a glassy structure).

The inequality of the values of δH for neighbouring sites in itself is not sufficient to provide relaxation. When all the sites are occupied, the dissimilarity between the δH values is immaterial, since transitions are impossible. Even if the sodium ions interchanged their positions no relaxation would occur, since one cannot distinguish between the sodium ion leaving and the one entering a site, so that the net effect of such an interchange would be zero. It seems necessary therefore to assume that there are a number of unoccupied sites or vacancies in the structure. This might be done in the way proposed by Charles², postulating that a number of equivalent sites for an alkali ion is present around a given nonbridging oxygen ion. This, however, does not correspond with the correlation factors for diffusion, measured by Haven and Verkerk³, as has been explained in Section V.2.

It seems more plausible to assume the occurrence of a small number of vacant sodium sites, as defined by Haven and Verkerk. A vacancy mechanism applies to diffusion in metals and alkali halides. In simple salts each cation vacancy is balanced by an anion vacancy to maintain electrical neutrality (Schottky defects). However, the formation of such a defect in a glass would require either that a single sodium ion can be removed from the glass, leaving a net negative charge on its associated oxygen atom, or the removal of an electron or oxygen ion along with the sodium ion. The latter process destroys the site, so it does not seem possible to form a Schottky defect of the usual type in a silicate glass.

The above argument is not valid for another type of defects, called the Frenkel defects. Frenkel defects exist of an interstitial-vacancy pair. For each vacant sodium site there must also occur an interstitial sodium ion in the structure. In this way the electrical neutrality can be maintained. In this respect interstitial sites must be considered as corresponding to energy levels of sites for sodium ions, higher than the levels of the bulk of the sodium sites (cf. Haven and Verkerk³).

We will accept the occurrence of Frenkel-type defects in the glass. The fraction of interstitial ions and vacancies will probably be governed by some energy of activation, so that the concentration n' of defects can be written as:

$$(V-1) \quad n' = n \exp \left(-\frac{\Delta H_f}{2 kT} \right),$$

where ΔH_f is the energy of formation of an interstitial-vacancy pair and n the concentration of sodium ions in the glass.

We will further assume a vacancy transport mechanism, which means that sodium ions are able to jump into the vacant sites. Of course this mechanism may also be described as if the vacancies jump from site to site instead of the sodium ions.

Haven and Verkerk were not able to distinguish between a vacancy mechanism and an interstitialcy transport mechanism (cf. Figs.V-3 and 4) in their glasses. We will continue our discussion in terms of a vacancy transport mechanism, but want to point out that the conclusions are also applicable to an interstitialcy transport mechanism, if it is assumed that each interstitial sodium ion is surrounded by a number of nonbridging oxygen ions, giving rise to an asymmetrical distribution of the binding forces between an interstitial sodium ion and its surroundings.

Suppose that at a certain temperature there is a number n_v of vacant sodium sites per cm^3 of glass. These vacancies move at random through the structure. If all sodium sites have the same energy level a vacancy will spend an equal amount of time in each site that comes into its way. We can express this behaviour with the help of a transition probability $W_0 dt$. For a transition from a certain site to a neighbouring site this probability is determined by:

$$(V-2) \quad W_0 = \nu A \exp \left\{ - (H_a - H)/kT \right\},$$

where ν is the oscillation frequency (frequency of escape attempts), A is a constant, H_a is the energy level of the barrier between the sites, and H is the energy level of the sites.

After the application of a tensile stress the values H of the energy levels of the sites are no longer equal, since they are modified by a quantity δH , being a function of the angle θ between the direction of the stress and the plane or line connecting the nonbridging oxygen ions, associated with the site.

Since it has been experimentally confirmed that in glasses the internal friction is not stress-dependent we may assume a linear relationship between δH and the value of the stress σ . To include the dependence of δH on the angle θ it seems reasonable to propose the following relationship:

$$(V-3) \quad \delta H(\theta) = p\sigma (a + \cos^2 \theta),$$

where a and p are constants and δH refers to an increase of H .

Now suppose that at the moment of application of the stress a vacancy

is situated in a site with $\Theta = \alpha$, whereas the angle Θ of an adjacent occupied site amounts to β . Calling these sites 1 and 2 respectively, it is clear that the difference ΔH between the energy levels of these sites, after the stress has been applied, amounts to:

$$(V-4) \quad \Delta H = \delta H_1 - \delta H_2 = p\sigma(\cos^2\alpha - \cos^2\beta)$$

Since $H_a - H \gg \delta H$, we may deal with this, as if the energy levels of the sites 1 and 2 were changed by an amount $\Delta H/2$ and $-\Delta H/2$ respectively, without loosing information. If we choose $\alpha < \beta$, we can consider the energy level of site 1 to be raised with $\Delta H/2$, whereas the energy level of site 2 has been lowered with the same amount. This leads to a change in the transition probabilities for a jump from site 1 to site 2 equal to $W_{12}dt$, and for a jump from site 2 to site 1 equal to $W_{21}dt$, respectively determined by:

$$W_{12} = \nu A \exp \left\{ - \frac{(H_a - H - \frac{1}{2} \Delta H)}{kT} \right\}$$

and

$$W_{21} = \nu A \exp \left\{ - \frac{(H_a - H + \frac{1}{2} \Delta H)}{kT} \right\}$$

Making use of Eq. (V-2), and since $\Delta H \ll kT$, this may be written as:

$$(V-5) \quad \left\{ \begin{array}{l} W_{12} = W_0 \left(1 + \frac{\Delta H}{2kT} \right) \\ \text{and} \quad W_{21} = W_0 \left(1 - \frac{\Delta H}{2kT} \right) \end{array} \right.$$

This gives rise to a change in the occupation numbers of site 1 and 2. The vacancy will spend more time in site 1 than in site 2. (The jump probabilities are related to the sodium ion and not to the vacancy, since the values of the energy levels are given in terms of the forces binding the sodium ion to the site).

The question that remains to be answered is how a change in the occupation numbers can account for relaxation phenomena. We will discuss this in terms of the " $\Delta \epsilon$ effect", put forward in the preceding section.

When a sodium site is empty its oxygen ions will repel each other because of the electrostatic forces. The repulsive forces of the unsa-

turated, negatively charged, nonbridging oxygen ions will exceed those of the bridging oxygen ions. So, in occurrence of nonbridging oxygens, there will be an asymmetrical expansion of the site, since the 2 or 3 nonbridging oxygens, associated with a site, are not able to produce a three-dimensional screening. The maximum expansion is found in the direction of the line or the plane through the centres of the nonbridging oxygen ions, associated with the site.

Since these directions vary from site to site, the effect will not be noticed macroscopically as long as no directed force is applied. We can discuss this asymmetrical expansion in terms of a strain in the direction of the stress. Assuming that this strain may be represented by $\epsilon = b + q \cos^2 \theta$, where b and q are constants, we can illustrate the mechanism by pointing out that the "extra" strain, brought about by a jump of the vacancy from a site with $\theta = \alpha$ to a site with $\theta = \beta$, can be written as:

$$\Delta \epsilon = q (\cos^2 \alpha - \cos^2 \beta).$$

Since, before the application of a tensile stress, all jumps are equally probable, the $\Delta \epsilon$ effects, occurring on a microscopic scale, cancel out in the sum taken over all the vacancies available. Once the stress has been applied, all jumps are no longer equally probable, as we have seen. The vacancies tend to jump to sites with small values of θ . If, for the two sites discussed above, called 1 and 2 with $\theta = \alpha$ and $\theta = \beta$ respectively, we write $\epsilon_1 = b + q \cos^2 \alpha$ and $\epsilon_2 = b + q \cos^2 \beta$, we can find the $\Delta \epsilon$ effect with the help of the transition probabilities $W_{12}dt$ and $W_{21}dt$:

$$\Delta \epsilon = \frac{\epsilon_1 W_0 \left(1 + \frac{\Delta H}{2kT}\right) + \epsilon_2 W_0 \left(1 - \frac{\Delta H}{2kT}\right)}{W_0 \left(1 + \frac{\Delta H}{2kT}\right) + W_0 \left(1 - \frac{\Delta H}{2kT}\right)} - \frac{\epsilon_1 + \epsilon_2}{2},$$

$$\text{or: } \Delta \epsilon = (\epsilon_1 - \epsilon_2) \frac{\Delta H}{4kT}.$$

Substituting the values for ϵ_1 , ϵ_2 , and ΔH gives:

$$(V-6) \quad \Delta \epsilon = \frac{pq\sigma}{4kT} (\cos^2 \alpha - \cos^2 \beta)^2.$$

For each combination of a vacancy plus an adjacent ion α and β will have different values. The mean value of the microscopically occurring $\Delta \epsilon$ effect per vacancy will thus be:

$$(V-7) \quad \overline{\Delta \epsilon} = \frac{pq\sigma}{4kT} \overline{(\cos^2 \alpha - \cos^2 \beta)^2}, \text{ with } 0 \leq \alpha \leq \frac{\pi}{2}$$

$$\text{and } 0 \leq \beta \leq \frac{\pi}{2}.$$

The quantity $\overline{(\cos^2 \alpha - \cos^2 \beta)^2}$, which we shall further denote as B, can be obtained numerically from the relation:

$$B = \frac{\int_{\alpha=0}^{\pi/2} \int_{\beta=0}^{\pi/2} (\cos^2 \alpha - \cos^2 \beta)^2 \sin \alpha \sin \beta \, d\alpha \, d\beta}{\int_{\alpha=0}^{\pi/2} \int_{\beta=0}^{\pi/2} \sin \alpha \sin \beta \, d\alpha \, d\beta},$$

which is, however, in principle only valid for the case that Θ represents the angle between two lines. When three nonbridging oxygen ions are involved Θ represents the angle between a line and a plane. In that case the relation reads:

$$B = \frac{\int_{\alpha=0}^{\pi/2} \int_{\beta=0}^{\pi/2} (\cos^2 \alpha - \cos^2 \beta)^2 \sin (\pi/2 - \alpha) \sin (\pi/2 - \beta) \, d\alpha \, d\beta}{\int_{\alpha=0}^{\pi/2} \int_{\beta=0}^{\pi/2} \sin (\pi/2 - \alpha) \sin (\pi/2 - \beta) \, d\alpha \, d\beta},$$

which can easily be understood by considering the angle between the line (i.e. the direction of the stress) and the normal on the plane through the three nonbridging oxygen ions.

Because of their symmetrical character both relations yield the same numerical value for B:

$$B = 8/45 \approx 0.18.$$

To describe the macroscopic $\Delta \epsilon$ effect, occurring after the application of a tensile stress, we must multiply the quantity $\overline{\Delta \epsilon}$ by the concentration of vacancies, i.e. by n_v/n , where n_v is the number of vacancies and n the number of sodium sites per unit of volume. (To understand why n_v/n and not n_v is determining, it must be kept in mind that only a fraction n_v of the sites contributes to the anelastic strain, whereas all sites contribute to the elastic strain). Hence:

$$(V-8) \quad (\Delta \epsilon)_{\text{tot}} = 0.18 \frac{pq\sigma}{4kT} \cdot \frac{n_v}{n}.$$

Since the elastic strain ϵ_{el} can be represented by $\epsilon_{el} = \sigma/E_U$, where

E_U is the unrelaxed elastic modulus, we can rewrite Eq. (V-8):

$$(V-9) \quad \frac{\Delta \epsilon}{\epsilon_{el}} = 0.18 \frac{pqE_U}{4kT} \cdot \frac{n_V}{n}.$$

To translate this result into the language of internal friction Eq. (II-7) can be used. From this equation we can derive:

$$\tan \delta = \frac{\Delta \epsilon}{\epsilon_{el}} \cdot \frac{\omega \tau}{1 + (\omega \tau)^2},$$

so that:

$$(V-10) \quad \tan \delta = 0.18 \frac{pqE_U}{4kT} \cdot \frac{n_V}{n} \cdot \frac{\omega \tau}{1 + (\omega \tau)^2}$$

and

$$(V-11) \quad (\tan \delta)_{\max} = 0.18 \frac{pqE_U}{8kT} \cdot \frac{n_V}{n}.$$

Unfortunately, it is impossible at present to check this result directly because of lack of knowledge of the quantities p , q , and n_V/n . Haven and Verkerk derived an approximate value for n_V/n of the order of 0.1 - 1% for sodium silicate glasses at 123°C. Examination discloses that the experimentally observed values of $\tan \delta$ are yielded by quite reasonable values of p and q when a fraction of defects of this order of magnitude is accepted.

V.5. Discussion of a mechanism accounting for the

"intermediate-temperature peak" in mixed-alkali silicate glasses

From our experiments on mixed-alkali silicate glasses, discussed in Chapter III of this thesis, we know that the trend of the internal friction curves of these glasses differs considerably from the one of simple alkali silicate glasses. The so-called low-temperature peak, the mechanism of which has been discussed in the preceding section, diminishes in height and shifts to higher temperatures. The substitution of about 5 mol.% Li_2O for a part of the soda in a sodium disilicate glass appears to be sufficient to accomplish the occurrence of a new high peak at intermediate temperatures which covers the reduced low-temperature peak completely. From the literature, available on this subject, we know that at the same time the ionic conductivity

is considerably reduced. In our opinion the ionic conductivity and the low-temperature peak in the internal friction curve are both directly related to the concentration of Frenkel-type defects in the glass (cf. Section V.4). The reduction of the height of the low-temperature peak and of the ionic conductivity in mixed-alkali glasses can be understood as due to a diminished fraction of defects in these glasses.

Evidence to support this statement is found in the experiments on ion-exchanged fibers, also discussed in Chapter III. We have seen that the internal friction curve of a sodium disilicate fiber, where the Na^+ ions are partly exchanged by Li^+ or Ag^+ ions, hardly changes before the fiber is heat treated at 275°C . To be exact: before reheating the ion-exchanged layer contributes to the low-temperature peak found in the original fiber. After reheating to 275°C the layer no longer contributes to this peak (e.g. Fig. III-11). This behaviour can easily be understood when it is accepted that it is the concentration of vacancies (or Frenkel defects) that is responsible for the occurrence of the low-temperature peak.

The ion-exchange treatment in itself does not need to interfere with the number of vacancies. Sodium ions are exchanged for lithium or silver ions, but this does not necessarily produce a change in the fraction of empty sites. So in a first approximation we may assume an unaltered concentration of vacancies. This means that the reduction of the peak height would be very small, even though the concentration of sodium ions has been reduced. As has already been pointed out in Chapter III we attribute the measured effect of the reheating treatment to a modification of the glass structure. We are now able to refine this statement. Although the structural modifications tend to produce better suitable places for the foreign ions, this seems to imply a reduction of the number of vacant sites. The energy of formation of defects seems to increase rapidly, which is equivalent to saying that the ions are more firmly bound to their sites, or that the energy levels of the interstitial positions are raised. It must be noted that the modifications do not necessarily result in an overall compaction of the structure. The total amount of "free volume" may remain unchanged or may even increase. It is sufficient when the distribution of "free volume" changes in such a way that the interstitial sites become less occupied. This does not require large-scale reorganizations of the structure. It will be sufficient when some of the SiO_4 tetrahedra or some of the bridging oxygen ions accept slightly different positions.

We do not believe that the structural rearrangements give rise to the occurrence of two types of sites, one type that is best suited

for sodium ions and another type that contains only lithium (or silver) ions. In contradiction to the suggestions often found in the literature we are of opinion that in mixed-alkali glasses one type of metal sites is present, the features of which are somewhere between those of typical sodium sites and those of typical lithium (or silver) sites. We will call these sites "intermediate sites", although it must be remembered that the configurational details will depend not only on the characteristics of the ions involved, but also on their concentration ratio in the glass.

It may be assumed that the ion species are sufficiently similar to permit the positions of the ions to be interchanged. At high temperatures the mobility of the alkali ions is very high and it seems rather improbable that at temperatures in or above the annealing range the structure will be able to differentiate between the two ion species in such a way that the ions of one kind are not mixed up with ions of the other kind (phase separation tendencies excluded). It is more likely that the ions continuously interchange their positions, and the result of this behaviour will be that after cooling the glass contains no more than one type of sites, able to contain both ion species, but, of course, not especially suited for either of them.

In a mixed-alkali glass prepared by an ion-exchange treatment the situation will be different. Here too only one type of sites occurs, but these sites are exactly suited for the original ions, whereas they are not suitable at all for the foreign ions. We believe that in our experiments reheating to 275°C leads to a transformation of the sites from typical sodium sites to the intermediate sites as defined above. This explains why the mobility of the sodium ions is involved in this process and not only the mobility of the foreign ions (and why the low-temperature peak shifts to higher temperatures after annealing of an ion-exchanged fiber): the modifications are not restricted to the surroundings of the foreign ions, but the surroundings of all the metal ions in the glass are affected.

The process is likely to be governed by some activation energy, involved in the translation or rotation of the structural units. It is not possible to estimate the value of this activation energy from our experiments, since the heating and cooling rates of the samples during the ion-exchange treatment itself and during the measurements are not known with sufficient accuracy. In principle, however, the activation energy of the process may be determined by measuring the reheating time, needed for the intermediate-temperature peak to reach its final height, as a function of temperature.

In our experiments on ion-exchanged fibers the intermediate-temperature peak has been found only after reheating to 275°C or higher.

The peak has no direct relation to the ionic conductivity and does not seem to have a counterpart in the dielectric properties. This means that no effective displacement of electrical charge carriers is involved and that the peak cannot be related to the occurrence of vacancies in the glass.

It is possible that the mechanism of an interchange of the positions of the two ion species is responsible for the appearance of this peak⁺). Of course an interchange of ion positions will give rise to an internal friction peak only when the application of a tensile stress produces some change in the transition probabilities determining the process (cf. Sec. V.3). Such a mechanism might very well originate from the angle θ between the direction of the stress and the line or plane through the nonbridging oxygen ions surrounding a metal ion. As discussed in the preceding section the value of θ may vary from site to site and this gives rise to changes in the energy levels of the sites. These changes will then be different for each site.

The extra strain (relaxation of the stress), resulting from this mechanism, may also originate from the fact that the angle θ varies from site to site. Since, according to Table III-3, the field strengths of the ion species involved are unlike we may expect the distance between the nonbridging oxygen ions, surrounding a site, to depend on the type of ion the site contains at a given moment.

To illustrate the point let us assume that the nonbridging oxygen ions be arranged in a cubic lattice with the metal ions positioned along the edges of the cube, as shown in Fig. V-6. Taking the edges of such a cube as the axes of a system of coordinates X, Y, and Z, it can be understood that the application of a tensile stress in the Z direction will promote a redistribution of the two types of metal ions in the three directions. The larger ions (with the lower field strength) will tend to occupy the edges parallel to the Z axis, and this will lead to an extra strain in the direction of the stress, because the nonbridging oxygen ions are less attracted to the larger ions.

The effect bears some resemblance to the elastic after-effect in alpha-iron containing carbon or nitrogen, as discussed by J.L.Snoek¹⁰ and others¹¹. Unfortunately the arrangement of the nonbridging oxygen ions can hardly be expected to be cubic. We can only say that each metal-ion site will be surrounded by a number of other metal-ion sites, each site responding differently to the applied stress.

+) The mechanism of an interchange of ion positions is not a familiar one. In the field of metals and ionic crystals it is not considered being a very probable process. Since, however, silicate glasses possess a rather open structure, such a mechanism may not be ruled out in these glasses.

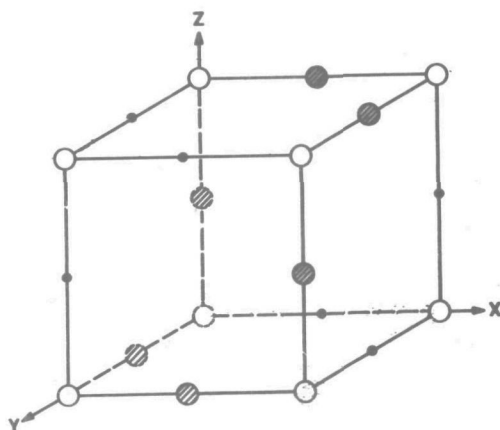


Fig. V-6. Model representation of a cubic arrangement of nonbridging oxygen ions with two types of metal ions positioned on the edges of the cube.

O = nonbridging oxygen ions.

● and ● = metal ions.

Our experiments on ion-exchanged fibers show that the intermediate-temperature peak does not occur until some structural modifications have taken place. We saw that these modifications can be considered as small rearrangements of the structure to meet the special demands of the foreign ions as far as possible at a given concentration ratio of the metal ions. This means that before reheating to 275°C only sodium sites are present in the structure, some of which are occupied by lithium (or silver) ions instead of sodium ions. In this situation no intermediate-temperature peak has been found experimentally. This behaviour can be explained in two different ways:

In the first place we may assume that in the unmodified structure the application of a stress does not lead to changes in the transition probabilities, involved in an interchange of ion positions. This may seem to contradict our concept of the occurrence of preferential sites, with an "attractive" Θ value after the application of a tensile stress. It might be assumed, however, that, although this mechanism is still active, it is not able to affect the transition probabilities, because the sites that become preferential for lithium ions also become preferential for sodium ions, and do so to the same extent.

In general the probability of an interchange of positions will be affected only when a certain site becomes more attractive to one kind of ions, without becoming more attractive to the other kind of ions involved, or at least not to the same extent.

It would be possible to explain the phenomena recorded by accepting the idea that only in a structure containing intermediate sites the changes effectuated in the energy levels lead to changes in the transition probabilities. It does not seem very likely, however, that in a structure containing sodium sites such changes would not be possible and that the transition probabilities would not be affected at all. We will therefore propose another explanation for this phenomenon; an explanation based on the fact that the absence of the peak in a certain temperature range does not necessarily mean that the mechanism is not active. It may well be that in the unmodified structure the internal friction mechanism is fully active, but that it does not contribute to the intermediate temperature peak of the modified structure, simply because the relaxation time of the process is much longer than in the modified structure. In fact this seems a reasonable assumption. The mobility of the sodium ions is high in the unmodified structure (higher than after modification), but no doubt the mobility of the foreign ions will be relatively low (cf. A.J.Burggraaf¹⁹), much lower than in the modified structure, and, since the probability of an interchange of positions will be determined mainly by the slowest ion, this will seriously increase the relaxation time.

A longer relaxation time means that the peak, caused by the interchange mechanism, is situated in a higher-temperature range, but since in this temperature range the structural modifications occur rather rapidly we are not able to detect this peak. It seems that the two processes are correlated. In the unmodified structure the ions do not easily interchange their positions (long relaxation time). The process may of course be activated by raising the temperature, but, as soon as the ions are able to interchange their positions in a "reasonable" period of time the network structure possesses enough flexibility to adjust to the changed composition and the sodium sites are transformed into intermediate sites in about the same period of time.

This statement may also be converted. The structural rearrangements in the ion-exchanged structure are completed in a period of time that is comparable to the relaxation time involved in the mechanism of interchange of ion positions in the unmodified structure. So we will never be able to find evidence of the internal friction peak due to the interchange of ion positions in an unmodified structure.

The mathematical treatment of the mechanism that causes the intermediate-temperature peak in mixed-alkali glasses is not essentially different from the one followed in the preceding section for the low-temperature peak. Assuming that both the sodium ions and the lithium ions are at an energy level H_1 , when positioned in the unstressed intermediate sites, we may introduce a change in the energy levels $\delta H(\theta)$, brought about by the applied stress. The resulting relation for $\tan \delta$ will then be of the type (V-10), with n_V/n replaced by $n_1/(n_1 + n_2)$, where n_1 and n_2 represent the concentrations of the metal ions (with $n_1 \leq n_2$):

$$\tan \delta = B' \frac{p' q' E_U}{4kT} \frac{n_1}{n_1 + n_2} \frac{\omega \tau}{1 + (\omega \tau)^2}$$

The value of the quantity B' depends - like in the case of the low-temperature peak - on the combination of θ values that occur in the structure. It does not seem very fruitful to try to evaluate B' , since this involves more knowledge of the glass structure than is available at the moment. We want to point out, however, that probably B' will depend strongly on the composition. At low lithium concentrations, for instance, a lithium ion will be able to interchange its position with several adjacent sodium ions. In that case the most favourable interchange is most likely to occur, resulting in a relatively high relaxation effect at extreme concentration ratios. This may explain why the amount of relaxation is not found to be

linearly rising with the concentration of lithium oxide up to a 1 : 1 ratio of sodium and lithium. Another reason for this behaviour may be that the configuration of the sites is most affected by the first addition of foreign ions.

V.6. Suggestions for the mechanisms accounting for the "high-temperature peak" and the "extra-high-temperature peak" in alkali silicate glasses

Our experiments on ion-exchanged fibers were not especially performed to solve the problem of the mechanism responsible for the high-temperature peak in sodium silicate glasses. Yet some interesting deductions can be made from our experiments.

In Chapter III we saw that the high-temperature peak is not noticeably influenced by an ion-exchange treatment, neither in height, nor in temperature. Especially in the experiments with silver-ion-exchanged fibers this is obvious (in the lithium-ion-exchanged fibers the intermediate-temperature peak partly overshadows the high-temperature peak). This means that the peak cannot be due to a cooperative migration of sodium ions, as was suggested by Forry⁴, nor to the migration of Na_2O groups, proposed by Rötger¹².

From our experiments it is not possible, however, to choose between the concepts of Rindone^{13,14} and Coenen¹⁵, which we shall discuss below. Rindone suggested the high-temperature peak to be due to a stress-induced movement of nonbridging oxygen ions. We found no evidence against this mechanism, although it must be admitted that we would expect the peak to shift in temperature after ion exchange. The replacement of sodium ions by lithium ions or silver ions certainly affects the binding forces between the nonbridging oxygen ions and the Si^{4+} cores. This effect may be too small, however, to effectuate a detectable temperature shift.

The mechanism has not been worked out in detail by Rindone. It may be that some of the nonbridging oxygen ions are thought to be able to occupy two equilibrium positions, and that the transition probabilities are affected by the application of a macroscopic stress. The mathematical treatment of this mechanism is essentially the one given in Sec V.4 for the mechanism we proposed for the low-temperature peak.

This mechanism would involve the existence of oxygen vacancies in the structure, which is not necessary for a slightly different mechanism that may also be considered, i.e. the interchange of positions of a bridging and a nonbridging ion (a nonbridging oxygen ion becomes bridging, whereas an adjacent bridging oxygen ion becomes non-

bridging). This mechanism can be treated in the way followed in Sec.V.5 for the intermediate-temperature peak in mixed-alkali glasses.

Coenen¹⁵ suggested a completely different mechanism to explain the occurrence of the high-temperature peak in alkali silicate glasses. He points out that a certain percentage of the hydrogen ions (protons), which are present in the glass structure, may be considered as being positioned in holes of the network, more or less in the way alkali ions are positioned.

H.Scholtze¹⁶ found that the percentage of these ions (sometimes called bridging protons) increases when a glass contains more nonbridging oxygen ions. Coenen assumes that the high-temperature peak is due to an interchange of the positions of bridging protons and alkali ions. This mechanism would thus be completely identical to the one we proposed for the intermediate-temperature peak in mixed-alkali glasses and may be treated in the same way.

In combination with our results on the mixed-alkali glasses the mechanism proposed by Coenen for the high-temperature peak seems very attractive, but as long as we do not have more information on the exact ways in which protons are built into the structure we must be careful in our conclusions. Weyl and Marboe⁹ pointed out that protons are able to penetrate into the electron clouds of oxygen ions and we may thus expect the behaviour of protons to be anomalous compared to alkali ions.

The absence of a high-temperature peak in alkali borate glasses (cf. Chapter IV) seems to be in favour of the mechanism proposed by Rindone, since these glasses possess very few quantities of non-bridging oxygen ions. According to Scholtze¹⁶, however, the number of bridging protons also seems to be very low in these glasses, so that no final decision can be made from the experiments on borate glasses.

In Chapter III we mentioned the appearance of an extra-high-temperature peak (at about 300°C) in sodium disilicate glass (cf. Fig. III-1). This peak could not be detected in sodium trisilicate glass (Fig. III-15). We do not have enough information on this peak to make a reliable suggestion for the mechanism accounting for this peak. Mackenzie¹⁷ stated that in glasses with a high concentration of alkali ions discrete ions such as $\text{Si}_3\text{O}_{20}^{8-}$ and rings such as $\text{Si}_3\text{O}_9^{6-}$ may be present. According to Huggins, Sun, and Silverman¹⁸ it is not unreasonable to accept the presence of small rings and chains in these glasses. The dimensions of none of these aggregates are believed to be in excess of about 20 Å and it is not impossible that at high temperatures these units are able to relax when a stress is applied, thus giving rise to an internal friction peak.

References

1. H.E.Taylor, J.Soc.Glass Technol., 43, 124 T (1959).
2. R.J.Charles, J.Appl.Phys., 32, 1115 (1961).
3. Y.Haven, B.Verkerk, Phys.Chem.Glasses, 6, 38 (1965).
4. K.E.Forry, J.Am.Ceram.Soc., 40, 90 (1957).
5. I.Mohyuddin, R.W.Douglas, Phys.Chem.Glasses, 1, 71 (1960).
6. A.E.Badger, W.B.Silverman, J.Am.Ceram.Soc., 18, 276 (1935).
7. K.H.Karsch, "Über das mechanische und thermische Verhalten der Alkaliboratgläser", Thesis Aachen, 1959.
8. G.A.Korn, J.Acoust.Soc.Am., 21, 547 (1949).
9. W.A.Weyl, E.G.Marboe, "The Constitution of Glasses", Vol.II, Part I, John Wiley and Sons, New York, 1964.
10. J.L.Snoek, Chemisch Weekblad, 39, 454 (1942).
11. D.Polder, Phil.Res.Rep., 1, 5 (1945).
12. H.Rötger, Glastechn.Ber., 31, 54 (1958).
13. R.J.Ryder, G.E.Rindone, J.Am.Ceram.Soc., 43, 662 (1960).
14. D.E.Day, G.E.Rindone, J.Am.Ceram.Soc., 45, 496 (1962).
15. M.Coenen, Z.für Elektrochemie, 65, 903, (1961).
16. H.Scholtze, Glastechn.Ber., 32, 81, 142, 278, 314 (1959).
17. J.D.Mackenzie in "Modern Aspects of the Vitreous State I".
Ed.J.D.Mackenzie, Butterworths, London, 1960.
18. M.L.Huggins, K.H.Sun, A.Silverman, J.Am.Ceram.Soc., 26, 393 (1943).
19. A.J.Burggraaf, "The mechanical strength of alkali aluminosilicate glasses after ion exchange", Thesis Eindhoven, 1965.

SUMMARY

This thesis covers the investigation of two phenomena that have presented quite some problems for several decennia. These phenomena are known as the "mixed-alkali effect" and the "boric-oxide anomaly". The mixed-alkali effect is discussed in Chapter III. The effect was originally observed in electrical experiments, when it was found that the electrical conductivity of alkali silicate glasses was considerably reduced if a part of the alkali ions was replaced by alkali ions of another type. The conductivity was found to be minimum at a concentration ratio of 1:1 of the alkali oxides. The dc conductivity of alkali silicate glasses is determined by the mobility of the alkali ions. Since it is generally accepted that the internal friction peak in alkali silicate glasses occurring in the region of room temperature can be related to the mobility of the alkali ions it may be expected that the internal friction curves of these glasses will also reveal some mixed-alkali effect.

We determined the internal friction of a number of mixed-sodium-lithium silicate glasses, containing a total concentration of alkali oxides of 33 mol.%. (The experimental details of these determinations are dealt with in Chapter II). It appears that even a small addition of Na_2O to a lithium silicate glass (or Li_2O to a sodium silicate glass) is sufficient to shift the internal friction peak to considerably higher temperatures. In common with the results on the ionic conductivity this indeed suggests that the mobility of the alkali ions is reduced. Simultaneously a new peak occurs in these glasses at about 120°C . This peak had been mentioned before in the literature. To study these phenomena in a different way we introduced the technique of ion exchange. By immersing a sodium silicate fiber in a salt melt for a certain period of time it was possible to replace part of the sodium ions in the surface layer of the fiber by lithium ions or silver ions. Performing this at a temperature at least 150°C below the transformation range, and restricting the treatment times to a few minutes, prevents the structure from being modified during the ion-exchange treatment.

One of the most outstanding results of these experiments is that the aforementioned changes in the internal friction curve also occur in the "mixed-alkali" glasses obtained by an ion-exchange treatment, but only after the fibers have been reheated to a temperature higher than 200°C . It is concluded that a small - but remaining - modification

of the network (to adjust to the changed composition) seems to be indispensable for the occurrence of the mixed-alkali effect in the internal friction curve.

Chapter IV is devoted entirely to the borate glasses and to the unexpected trend found in several properties of these glasses, when measured as a function of the alkali concentration. The thermal expansivity of sodium borate glasses, for instance, appears to reach a minimum value at about 16 mol.% Na_2O . The phenomenon used to be related to the shift in the coordination number of the boron ions from 3 to 4 that seems to occur as a result of the substitution of Na_2O for B_2O_3 . From X-ray experiments it was deduced that this shift occurred only as long as the concentration of Na_2O did not exceed 16 mol.%. Beyond that "critical" concentration the excess oxygen ions involved in a Na_2O substitution were supposed to become nonbridging. Since NMR measurements showed that such a critical concentration did not exist this explanation could no longer be accepted.

The introduction of Al_2O_3 to sodium borate glasses offers new possibilities for the study of the boric oxide anomaly, since aluminium ions may be considered to accept network-forming positions in fourfold coordination. We measured the internal friction and the linear thermal expansion coefficient of a number of glass compositions containing Na_2O , B_2O_3 and Al_2O_3 . The results of these determinations are represented and discussed in Chapter IV. It appears that the Na_2O concentration at which the expansivity reaches its minimum value is hardly affected by the Al_2O_3 content at all. To a first approximation the Al^{4+} ions seem to behave as boron ions in fourfold coordination. The results of the internal friction measurements confirm this statement.

The results of the experiments suggest that the boric-oxide anomaly is related to the number of nonbridging oxygen ions in the glass. Nonbridging oxygen ions can be considered as centre of asymmetry, reducing the coherence of the structure. Properties that are sensitive to the symmetry of the binding forces will reveal noticeable changes as soon as the number of nonbridging oxygen ions reaches a "detectable" value. The internal friction peak appears to be very sensitive to the occurrence of nonbridging oxygen ions.

In Chapter V a discussion is given of the mechanism responsible for the occurrence of the internal friction peak in alkali silicate glasses, that is usually related to the mobility of the alkali ions. The occurrence of defects and the asymmetry in the binding forces between a metal ion and its immediate environment (due to the occurrence of nonbridging oxygen ions) are considered to be indispensable.

The mechanism that gives rise to the internal friction phenomena in

mixed-alkali glasses has also been discussed in chapter V. In view of the results of chapter III the intermediate-temperature peak in these glasses would seem to be due to the interchanging of the positions of alkali ions of different types, promoted by an applied stress or strain.

The idea of the formation of "intermediate sites" has been put forward as an explanation for the phenomena recorded. It is suggested that in mixed-sodium-lithium glasses, for instance, only one kind of alkali-ion sites is present, the properties (energy level, geometry) of which are somewhere between the properties of typical sodium sites and those of typical lithium sites. If it is further assumed that in mixed-alkali glasses, prepared by an ion-exchange treatment, the formation of these intermediate sites involves a structural relaxation, it can be understood why the mixed-alkali effect in these glasses occurs only after reheating to higher temperatures.

The last section of chapter V has been devoted to a discussion of the high-temperature peak and the extra-high-temperature peak, found in glasses of the alkali disilicate composition. Some possible explanations for these phenomena are considered.

SAMENVATTING

In deze dissertatie komen twee onderwerpen ter sprake, die beide reeds enkele tientallen jaren bekend zijn, maar waarover de discussies nog altijd gaande zijn. Het betreft twee verschijnselen, die zodanig afwijken van het verwachte additieve gedragspatroon, dat ze in de literatuur een eigen benaming hebben gekregen, te weten het "mixed-alkali effect" en de "boric-oxide anomaly" (de boorzuuranomalie).

Het "mixed-alkali effect" wordt behandeld in Hoofdstuk III. Het verschijnsel, dat onder deze naam bekend staat, is oorspronkelijk geconstateerd in elektrische metingen, toen bleek dat het elektrisch geleidingsvermogen van binaire alkalisilicaatglazen sterk afnam wanneer een gedeelte van het aanwezige alkalioxide vervangen werd door een ander alkalioxide. Het geleidingsvermogen bleek minimaal te zijn wanneer de concentraties der beide alkalioxiden zich verhouden als 1:1. Nu wordt het elektrisch geleidingsvermogen in silicaatglazen bepaald door de beweeglijkheid van de alkaliïonen en er is daarom reden te veronderstellen dat ook in de inwendige demping het verschijnsel zal zijn terug te vinden. Algemeen wordt namelijk aangenomen, dat met name het maximum in de inwendige demping van alkalisilicaatglazen, dat meestal iets onder kamertemperatuur wordt aangetroffen, verband houdt met de mate van beweeglijkheid van de alkaliïonen in het glas. Wij maten de inwendige demping van een aantal silicaatglazen met een totale alkaliconcentratie van 33 mol.%, die zowel natrium- als lithiumoxide bevatten. De meetmethode, die daarbij werd toegepast, wordt besproken in Hoofdstuk II. Het blijkt, dat reeds een kleine toevoeging van Na_2O aan het lithiumsilicaatglas of omgekeerd voldoende is om het maximum naar hogere temperaturen te doen verschuiven. Dit kan wijzen op een verminderde beweeglijkheid van de ionen, zoals dat ook in metingen van de ionengeleiding wordt geconstateerd. Tegelijkertijd ontstond een nieuw maximum bij circa 120°C . Dit maximum werd reeds eerder in de literatuur gesignaleerd.

Teneinde deze verschijnselen op een andere wijze te kunnen bestuderen maakten wij gebruik van de techniek van ionenuitwisseling. Door een proefstaafje van een natriumsilicaatglas gedurende enige tijd in een gesmolten zoutbad te dompelen was het mogelijk om in de oppervlaktelaag een gedeelte van de natriumionen te vervangen door lithium- of zilverionen. Omdat dit plaats vond bij een temperatuur tenminste 150°C onder de verwekingstemperatuur en de behandelingstijden beperkt waren tot enkele minuten, kon aangenomen worden, dat de structuur van

de proefstaafjes tijdens dit proces geen veranderingen onderging. Het meest spectaculaire resultaat, dat bij deze proeven naar voren komt, is dat de hierboven beschreven wijzigingen in de inwendige demping ook optreden in de door ionenuitwisseling verkregen "mixed-alkali glasses", doch uitsluitend nadat de proefstaafjes een (korte) warmtebehandeling hadden ondergaan bij een temperatuur boven 200°C . Geconcludeerd wordt, dat een geringe blijvende aanpassing van de netwerkstructuur noodzakelijk is voor het optreden van een "mixed-alkali effect" bij metingen van de inwendige demping.

Hoofdstuk IV is geheel gewijd aan de boraatglazen en de daarin optredende boorzuuranomalië. Onder boorzuuranomalië wordt verstaan het "ongewone" verloop van diverse eigenschappen van de alkaliboraatglazen als functie van de alkaliconcentratie. Zo blijkt de uitzettingscoëfficiënt van natriumboraatglazen minimaal te zijn bij circa 16 mol.% Na_2O . Dit verschijnsel werd vroeger in verband gebracht met een verschuiving van het gemiddelde coördinatiegetal van de boorzurionen van 3 naar 4, die op zou treden wanneer alkalioxide wordt toegevoegd aan B_2O_3 . Dit mechanisme zou slechts werkzaam zijn zolang niet meer dan 16 mol.% alkalioxide aanwezig is. Experimenten met behulp van kernspinresonantie hebben echter sindsdien aangetoond, dat de verandering van het coördinatiegetal ook boven 16 mol.% alkalioxide plaats vindt. Daarmee is de genoemde verklaring van de verschijnselen niet langer houdbaar.

Het introduceren van Al_2O_3 in natriumboraatglazen schept nieuwe mogelijkheden voor de studie van de boorzuuranomalië, omdat aangenomen mag worden, dat de Al-ionen uitsluitend in 4-coördinatie in het netwerk worden ingevoegd. In Hoofdstuk IV zijn de resultaten weergegeven van metingen van de inwendige demping en van de lineaire uitzettingscoëfficiënt van een aantal glassamenstellingen, die zowel Na_2O , B_2O_3 als Al_2O_3 bevatten. Het blijkt, dat de Na_2O -concentratie, waarbij de uitzettingscoëfficiënt minimaal is, nauwelijks wordt beïnvloed door het gehalte aan Al_2O_3 . De Al-ionen blijken de plaats in te nemen van de B-ionen, voor zover deze in 4-coördinatie zijn. Ook onze resultaten van de metingen van de inwendige demping wijzen in deze richting. Op grond van de resultaten lijkt het waarschijnlijk, dat de boorzuuranomalië in verband moet worden gebracht met de concentratie aan zwevende zuurstofionen in het glas. Zwevende zuurstofionen kunnen beschouwd worden als centra van asymmetrie. Zij verlagen de algehele samenhang van het netwerk en veroorzaken een meer open structuur. Eigenschappen, die hiervoor gevoelig zijn, zullen een duidelijke verandering ondergaan zodra het gehalte aan zwevende zuurstofionen "van enige betekenis" wordt. Het blijkt, dat het maximum in de inwendige demping bijzonder gevoelig is voor de aanwezigheid van zwevende zuurstofionen.

In Hoofdstuk V wordt nader ingegaan op het mechanisme dat ten grondslag ligt aan het optreden van het maximum in de inwendige demping van alkalisilicaatglazen, dat doorgaans in verband wordt gebracht met de beweeglijkheid van de alkaliionen. Na een discussie van de bestaande literatuur wordt nagegaan aan welke voorwaarden een glasstructuur zal moeten voldoen, opdat de beweeglijkheid van de alkaliionen aanleiding zal kunnen geven tot een inwendige dempingspiek. Aan de hand van deze overwegingen wordt een eenvoudig model beschreven, waarmee het mogelijk is de relaxatieverschijnselen in silicaatglazen te verklaren en in formule te brengen. Hierbij wordt de nadruk gelegd op de aanwezigheid van op Frenkelfouten gelijkende dichtheidsfluctuaties van de alkaliionen in de structuur en op de door de zwevende zuurstofionen veroorzaakte asymmetrie in de wijze waarop de metaal- ionen aan hun plaats gebonden zijn.

Vervolgens wordt in dit hoofdstuk het mechanisme besproken, dat ten grondslag ligt aan de inwendige demping in silicaatglazen, die meerdere typen alkaliionen bevatten. Hierbij wordt gebruik gemaakt van de resultaten uit hoofdstuk III. Het wordt waarschijnlijk geacht, dat het onderling van plaats wisselen van de beide typen alkaliionen aanleiding geeft tot het ontstaan van de inwendige dempingspiek bij ca. 120°C in deze glazen.

Uitgaande van de gedachte, dat er bij hogere temperaturen geen sprake kan zijn van een onderscheid tussen de holtes, waarin de ene soort alkaliionen zich bevindt, en de holtes, waarin de andere soort zich bevindt, wordt het begrip "intermediate sites" ingevoerd, waarmee bedoeld wordt dat in "mixed-alkali glasses" de holtes niet geheel zijn aangepast aan de "wensen" van één van beide typen ionen, maar dat alle holtes in principe gelijk zullen zijn en van een soort gemiddelde gedaante (energetisch zowel als geometrisch).

Aangenomen wordt, dat in glazen, vervaardigd met behulp van ionen-uitwisseling, deze holtes gevormd worden door een structurele relaxatie, die pas kan optreden tijdens verhitting tot boven 200°C. Dit verklaart, waarom in deze glazen de relaxatieverschijnselen, behorend bij "mixed-alkali glasses", pas gevonden worden na verhitten tot boven deze temperatuur.

Tenslotte worden in hoofdstuk V nog enkele woorden gewijd aan de "high-temperature"- en de "extra-high-temperature" piek, die in alkalisilicaatglazen zijn waargenomen. Enkele mogelijkheden ter verklaring van deze effecten worden nagegaan, waarbij wordt aangegeven op welke wijze de wiskundige behandeling zou moeten verlopen.

STELLINGEN

1. De methode, die E.B.Shand toepast om op reproduceerbare wijze barsten aan te brengen in een glasoppervlak, geeft aanleiding tot het ontstaan van aanzienlijke spanningen rondom de gevormde barsten. Met de complicaties, die hiervan het gevolg zijn, is door Shand onvoldoende rekening gehouden.

E.B.Shand, J.Am.Ceram.Soc., 48, 43 (1965).

2. De conclusie van K.Peter, dat de barst, die bij het snijden van glas loodrecht op het oppervlak gevormd wordt, niet met de atmosfeer in verbinding zou staan, is onjuist.

K.Peter, Glastechn.Ber., 37, 333 (1964).

3. Bij de verklaring, die M.J.Kerper en T.G.Scuderi geven van hun metingen betreffende de elastische nawerking in door ionenuitwisseling versterkte glazen, is de invloed van het niet uitgewisselde deel van de monsters ten onrechte buiten beschouwing gelaten. Het valt daarom des te meer te betreuren, dat deze auteurs verzuimden de samenstelling van de basisglazen te vermelden.

M.J.Kerper, T.G.Scuderi, J.Am.Ceram.Soc., 49, 613 (1966).

4. De spanningsrelaxatie in door ionenuitwisseling versterkte glazen, die reeds bij temperaturen ver beneden het verwekingspunt optreedt, moet voor een groot deel worden toegeschreven aan structuurrelaxatie en zeker niet uitsluitend aan een vereffening van de concentratiegradiënt van de alkaliionen door diffusie. Een bespreking van dit verschijnsel aan de hand van een diffusiemodel, zoals toegepast door Garfinkel, is daarom weinig zinvol.

H.M.Garfinkel, "Symposium sur la Surface du Verre et ses Traitements Modernes", Luxemburg 1967.

5. De afwijkingen, die Guillemet et al. vonden tussen de experimentele en de theoretische waarden van de deformatiewarmte bij eenassige rek van glasstaven, zijn wellicht veroorzaakt door het feit, dat

de warmteuitwisseling met de omgeving tijdens het ijkken van de gebruikte calorimeter verschilde van die tijdens de metingen.

C.Guillemet, M.Houdion, P.Acloque, Phys.Chem.Glasses, 6, 1 (1965).

6. Het is in het algemeen af te raden om flessen, die voorzien zijn van een ingebrand etiket, veelvuldig in contact te laten komen met koperlegeringen. In het bijzonder de bronzen wormwielen, die bij vele vulmachines worden toegepast, kunnen een schadelijke invloed hebben op de kwaliteit van het etiket.

7. De door J.S.Cammerer et al. uitgevoerde berekeningen betreffende het damptransport in dakconstructies moeten met veel reserve worden beschouwd, omdat hierbij, ook wanneer het bouw materiaal betrof, waarin capillair vochttransport kan optreden, gebruik is gemaakt van de berekeningsmethode van H.Glaser.

J.S.Cammerer, W.Schüle, O.Krischer, Ber.Bauforschung, Heft 23 (1962).

H.Glaser, Kältetechnik, 11, 345 (1959).

8. Een afdeling voor kwaliteitscontrole kan in een bedrijf alleen dan doeltreffend functioneren, wanneer zij - uitgaande van in overleg vastgestelde kwaliteitseisen - geheel zelfstandig opereert en haar beslissingen kan nemen onafhankelijk van produktie- en verkoopafdelingen.

9. De wiskundige opleiding van natuurkundig ingenieurs zou meer gericht moeten zijn op het omzetten van fysische problemen in wiskundige taal dan op het oplossen van wiskundevraagstukken als zodanig.

10. Politieke discussies zouden aanzienlijk aan duidelijkheid winnen, indien de betrokkenen er van af wilden zien het eigen- of groepsbelang bij voorbaat gelijk te stellen aan het algemeen belang.

STELLINGEN BEHORENDE BIJ HET PROEFSCHRIFT VAN
H.DE WAAL.