

## Internal friction behaviour of mixed alkali glasses

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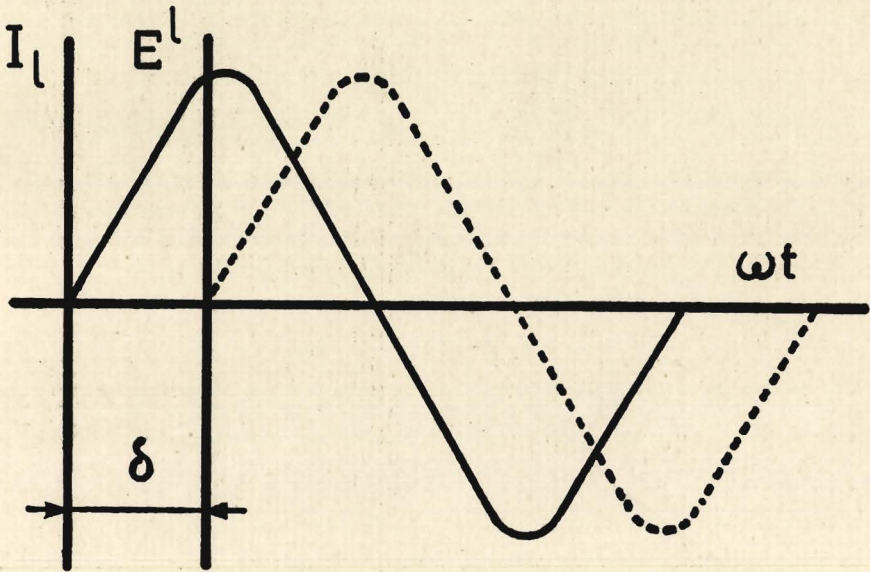
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# INTERNAL FRICTION BEHAVIOUR OF MIXED ALKALI GLASSES



H. M. J. M. VAN ASS

# INTERNAL FRICTION BEHAVIOUR OF MIXED ALKALI GLASSES

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR  
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## ABSTRACT

### Internal friction behaviour of mixed alkali glasses

Glasses, containing only one kind of alkali ions exhibit a relaxation peak slightly below room temperature when measured at a frequency of 1 Hz. This peak is called the single alkali peak.

Previous work has shown that this relaxation correlates closely with the electrical conductivity of the glasses and with the mobility of the alkali ions. These observations have led to the generally accepted viewpoint that alkali diffusion and electrical conduction in single alkali glasses are caused by the same basic mechanism which is also responsible for the mechanical and dielectric losses: viz. the jumping of alkali ions from interstice to interstice.

Some glasses, e.g. alkali silicate and alkali phosphate glasses exhibit a second relaxation peak at intermediate temperatures. This peak has been previously attributed to the stress induced motion of non-bridging oxygen ions. However, more recent work has cast serious doubts on this hypothesis and provides strong indications that this intermediate temperature peak is related to the presence of water in the glass.

Glasses containing more than one kind of alkali ions have been investigated as well. Such mixed alkali glasses exhibit large departures from ideal mixing behaviour in many of their physical properties.

One of these non-linear effects is the occurrence of an additional mechanical relaxation peak at high temperature. This peak is called the mixed alkali peak and is the subject of the present investigation. As mixed alkali silicate glasses have already been investigated in the past, this investigation was directed to metaphosphate glasses and borate glasses.

The internal friction and dielectric losses are measured of series of mixed alkali metaphosphate and borate glasses, containing  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$  ions. In addition, the influence of non-alkali monovalent cations like  $\text{Ag}^+$ ,  $\text{H}^+$  and  $\text{D}^+$  is investigated, as well as some series of mixed alkaline-earth — alkali metaphosphate glasses.

The internal friction measurements are made with a torsion pendulum at approximately 0.5 Hz between  $-100^\circ\text{C}$  and the annealing range. Some of the glasses are also measured at approximately 2 kHz, using a resonance technique in flexure.

The dielectric losses are measured at frequencies between 300 and 30,000 Hz, at temperatures up from  $40^\circ\text{C}$ .

It is found that the properties of mixed alkali metaphosphate glasses and borate glasses are very similar to those of the corresponding silicates. The magnitude of the mixed alkali peak depends on the difference in size of the alkali ions. The relation between peak magnitude and size difference is completely analogous in the three types of vitreous systems mentioned. Non-alkali monovalent cations behave similarly to alkali ions with respect to the mixed alkali effect.

The intermediate temperature peak in the metaphosphate glasses is interpreted

as the proton-alkali peak. A comparison of the influence of protons and deuterium ions on the properties of metaphosphate glasses shows that large changes in the ion mass have negligible effects on the mixed alkali behaviour. This observation gives further support to the hypothesis that the mixed alkali effect is governed by size differences of the ions.

An explanation for the mixed alkali peak is given: This relaxation is caused by the presence of dissimilar charge carriers in the non-conducting matrix of the network. Electrical forces, set up by the stress induced diffusion of one of the charge carriers, will cause a coupling with the other. The introduction of divalent cations gives rise to a mixed peak as predicted by this model.



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Reprint 'Relaxation processes in mixed alkali Na-K-metaphosphate glasses'  
J. Non-Crystalline Solids 14 (1974) 131.

Reprint 'Internal friction of mixed alkali metaphosphate glasses. I. Results'  
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metaphosphate glasses containing 1 % potassium metaphosphate'  
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Reprint 'The influence of dissolved heavy water on the internal friction of  
lithium metaphosphate glasses containing 1 % potassium metaphosphate'  
J. Non-Crystalline Solids 16 (1974) 161.

Reprint 'Internal friction and dielectric losses of mixed alkali borate glasses'  
J. Non-Crystalline Solids 16 (1974) 281.

Reprint 'Internal friction and dielectric losses of mixed alkaline-earth — alkali  
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The investigation into mechanical relaxation processes in glass was started in July 1971 in the Department of Inorganic Chemistry of the Eindhoven University of Technology. At that time, a number of basic instruments were available for this investigation, like an Elastomat \* console and several sets of transducers. In addition to that, the main structural elements of a torsion pendulum \*\* were present as a gift to the Department from the 'Technisch Physische Dienst TNO-TH, Delft.

The Elastomat consists of a frequency generator and a measuring unit. A glass specimen is suspended from two loops of fused silica fiber strands inside the controlled zone of an electric furnace. Each strand is attached to a piezoelectric transducer.

The specimen, which is a rectangular bar, is supported by these loops at approximately  $\frac{1}{4}$  length distance from each end of the bar, very close to the nodal planes of the transversal first harmonic. Through one of the fused silica loops the signal of a transducer is applied. The response of the specimen is read out through the second loop. The generator is tuned to the  $T_1$  mode of the bar specimen and the half width of the resonance peak is determined at various temperatures. The dimensions of the specimens are such that the resonance frequency is approximately 2 kHz.

The measurements with the torsion pendulum are conducted at the much lower frequency of approximately 0.5 Hz.

An inertia member is attached to a glass fiber which is positioned inside the controlled zone of an electric furnace. The system is set in torsional vibration by means of a pair of electromagnets, located close to the steel ends of the inertia member. The oscillation of the system is followed by means of an optical electronic detector which determines essentially the angular velocity of the pendulum when it passes through its rest position. The whole system is contained in a vacuum enclosure and is provided with a double-walled glass bell jar, to be used for liquid nitrogen cooling.

The dielectric losses are determined on disc-shaped specimens, coated with a platinum electrode paste. The used equipment consisted of a Rhode & Schwarz R.C. generator, a dielectric testbridge and a tunable indicator amplifier.

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\* Elastomat, type 1.015, Institut Dr. Förster, Reutlingen, Germany.

\*\* H. de Waal, Thesis, Delft, Netherlands, 1967.

Oxide glasses consist of one or more oxides, cooled from their melts without the occurrence of crystallization. Generally speaking, the constituent oxides can be divided into two groups: viz. the network forming oxides and the network modifying oxides.

The network forming ions have large field strength and their best known representatives are the  $\text{Si}^{4+}$ ,  $\text{B}^{3+}$  and  $\text{P}^{5+}$  ions. They build rigid structures in which the network forming ions mainly occur in tetrahedral or triangular coordination. By sharing one or more corners, these tetrahedra and triangles can build linear or three dimensional networks, depending on the chemical composition of the glass.

The network modifying ions, like alkali ions, are ions with a relatively low field strength and they form the weaker links in the network structure. Increasing the concentration of network modifiers will make the glass less rigid and consequently, more workable at lower temperatures\*.

This can be visualized best by considering the modifying oxides to depolymerize the network; they act as the terminal groups of the polymer structures.

Not all of the constituents of known glasses can be classified in terms of network formers and network modifiers; there is a group of oxides which take intermediate positions, e.g.  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$ . The influence of these oxides on the structure of the glass network is more complicated and cannot be described easily in general terms.

Whether a crystalline solid or a glassy material will form on cooling from a particular melt is a matter of crystallization kinetics and cooling rate. Typical glass forming melts have a high viscosity at their freezing point and the structure cannot adapt itself fast enough to the changes in temperature. In this way, a structure of low ordering is 'frozen-in' which shows many features of the liquid structure. X-ray diffraction analyses has shown that glasses lack the presence of long range ordering. Similar to liquids, when a glass network is viewed on a short range basis, one can observe a high degree of ordering.

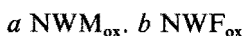
Owing to the fact that the liquid-solid transition, as prescribed by thermodynamics, has not occurred during the cooling of the glass melt, the resulting glass is thermodynamically not in equilibrium and it will convert in due time to a crystalline material. In commercial glasses, which are used far below their melting point, the viscosity is that high that the rate of this conversion becomes negligible and it will take centuries before the continuously progressing crystallization becomes noticeable by X-ray diffraction techniques.

Due to the specific applications of vitreous materials and to their manufacturing techniques, physical properties like e.g. resistivity, viscosity, expansivity and refractivity are very important for glasses. Therefore, it has been a goal for many

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\* The present discussion is limited to the more common glasses. Other types of glasses can be obtained by adding very large amounts of network modifying oxides. The network is then depolymerized and 'cut' in relatively short chains. The glasses of this type are called 'invert glasses' and their coherence arises mainly from electrostatic interactions.

investigators to find relations for the dependence of these properties on the chemical composition. Many of such relations are available to the glass technologists in order to design glasses with required properties. As a result of the almost unlimited number of possible glass compositions, this field of investigation is very broad. In the present discussion we will confine our attention to the mixing behaviour of binary glasses of the type:



These glasses consist of a combination of *a* gram molecules of network modifying alkali oxide and *b* gram molecules of network forming oxide. Most commercial glasses contain more than two components. In the present investigation these complicated compositions are omitted.

It is known for a long time that mixtures of alkali silicate glasses have some remarkable aspects: some physical properties show extremely large deviations from linearity, while others do not. Mixed alkali systems have already been investigated systematically by Wiebe in 1884. Wiebe showed that mixed alkali glasses give rise to freezing point depressions which are about ten times larger than those given by single alkali glasses. The freezing point depression in the 0 °C-point drift of a thermometer after immersion in boiling water. Wiebe's work led to the development of Jena 16<sup>III</sup>normal thermometer glass in 1885, containing only soda and having a freezing point depression of only 0.05 °C. Mixed alkali glasses, which were used previously because of their better working properties, had values up to 0.65 °C.

The physical property which shows the largest departure from linearity is the electric conductivity. When one alkali is progressively substituted for another, the variation of conductivity with the amount substituted often deviates from linearity to such an extent that the initial trend is later reserved, giving rise to an extremum. This extreme departure from linearity is called the 'mixed alkali effect'. In Russian literature, this is sometimes referred to as the 'neutralisation effect' or the 'poly-alkali effect'.

Glasses, having very low conductivities, belong to the group of materials referred to as insulators. The electric conduction of glasses is due to alkali ion migration \* and is a measure of the alkali ion mobility. It has been recognized early that the gradual substitution of one alkali for another decreases the alkali mobility drastically and a minimum in the conductivity is found at a composition which contains about equal amounts of both alkalis.

The conductivity at this minimum is often over 1000 times lower than for single alkali glasses.

The magnitude of the mixed alkali effect on a property must be gauged in relation to the sensitivity of the property to compositional changes in general. A useful comparison is the effect of varying the total alkali concentration. By doing so, it is seen that the conductivity is lowered **considerably more** by replacing

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\* This does not apply to all known glass systems; electronic conducting glasses can be manufactured by incorporating plurivalent ions.

half the amount of initially present alkali by a second alkali than by simply removing half the alkali.

Another measure of the extremely large mixed alkali effect is that, if the total alkali content of a sodium silicate glass is increased by substituting some potassium oxide for silicon oxide, the conductivity is **lowered**, whereas in single alkali glasses an increase of alkali content always leads to an increase in the conductivity.

The viscosity also shows a negative departure from linearity in a mixed alkali series. Thus, for sodium-potassium silicate glasses the viscosity at the minimum is between one and two orders of magnitude lower than in the corresponding single alkali glasses. In a single alkali glass such an effect would require a large increase in alkali content.

The expansivity of glasses does show a much smaller effect upon mixing the alkalis. In general, it is found that the expansion coefficient shows a small positive departure from linearity, which is equivalent to an increase in the total alkali concentration of a few percent. Other investigations however, reported a linear variation of expansion coefficient. The shape of the expansion curves for mixed alkali glasses differs from those for single alkali glasses. Whereas single alkali glasses show a slight linear increase of expansion coefficient with temperature between 0 °C and the transformation range, mixed alkali glasses show a steeper non-linear increase at temperatures below about 200 °C, and a linear rise between 200 °C and the transformation range. This particular behaviour of mixed alkali glasses has been attributed to a transformation range phenomenon at these low temperatures. The refractive index of such glasses shows a dependence on 'thermal history' when heat treatments are applied in this temperature range.

The anelastic effect associated with this low temperature transformation range phenomenon is also responsible for the extremely large freezing point depressions of mixed alkali glasses.

Additional information about this anelastic effect can be obtained from internal friction measurements.

If an ideal elastic material is subjected to a stress, an immediate strain response will occur, being proportional to the applied stress. In general, materials are not ideal, and in glasses the resulting strain lags behind with respect to the stress. Therefore if a glass specimen is subjected to a periodic stress, elastic energy will be dissipated. The energy loss per cycle will be proportional to the phase lag between stress and strain. As a result of this, the amplitude of oscillation of a freely resonating specimen will decrease logarithmically with time and the rate of this decay is a measure for the phase lag  $\delta$ .

Internal friction or mechanical damping curves may be obtained by plotting the tangent of the phase lag angle  $\delta$  versus the temperature, at a specific frequency of oscillation. The internal friction curves of single alkali glasses at 1 Hz show a maximum below room temperature. This peak temperature is frequency dependent and the internal friction can be described by a relaxation time  $\tau$ , according to the equations:

$$\tan \delta = C \frac{\omega\tau}{1 + \omega^2\tau^2} \text{ and } \tau = \tau_0 \exp (E_a/RT)$$

The magnitude of an internal friction peak at its maximum is basically frequency independent.

There is general agreement that the internal friction peak below room temperature at 1 Hz in single alkali glasses is caused by the stress induced diffusion of alkali ions. The basis for this hypothesis is formed by the following observations.

- (i) The magnitude of the internal friction peak is proportional to the total alkali content of the glass.
- (ii) The magnitude of this peak correlates well with the conductivity data and the coefficient for alkali self diffusion.
- (iii) The average activation energy, calculated for this peak, is basically equal to the activation energy for ionic conduction and for alkali self diffusion.

The mechanical losses of single alkali glasses amount to  $\tan \delta = 5 \times 10^{-3}$  approximately at the peak maximum. Mixed alkali glasses show a much larger loss peak, at a higher temperature. A peak magnitude of  $\tan \delta = 68 \times 10^{-3}$  has been reported for a sodium-potassium phosphate glass.

Initially, it was assumed by some authors that the large peak in mixed alkali glasses had the same origin as the small peak in single alkali glasses. In 1967 it was found that this large peak is a different phenomenon, since at very low concentrations of the second alkali two peaks occur. The alkali ion peak moves to higher temperatures as the second alkali is added, but it is quickly 'swallowed up' by the large peak, which develops simultaneously at higher temperatures.

The alkali ion peak, located below room temperature at 1 Hz, is called the **single alkali peak**, while the very large loss peak at high temperature is called the **mixed alkali peak**.

This mixed alkali peak is a manifestation of the same phenomenon which is observed in the expansivity and the freezing point depression of mixed alkali glasses.

The relation of this peak to a simple ionic rearrangement is less clear than for the single alkali peak. In general, the trends for the mixed alkali peak are opposite to those for the ionic mobility.

Relaxation phenomena in glass cannot be explained by a single relaxation time. Both the single and the mixed alkali peak are a factor three to four wider than what should be expected if a single relaxation time were present. In addition to this, the relaxation peaks are asymmetric in that they exhibit a long tail at the low temperature side.

The single and the mixed alkali peaks are 'secondary relaxations', they appear as superpositions on the curve for the primary relaxation, which occurs in the transformation range of the glass. The losses associated with these structural rearrangements are very small at low temperatures but increase progressively with higher temperatures. In the literature, they are referred to as the 'background losses' or the 'network damping'.

Not all of the properties of mixed alkali glasses show departures from ideal mixing behaviour. Density and atomic volume appear not to be affected. Several investigators report linear relations, while others report positive and negative deviations which are rather insignificant compared to the changes brought about by a variation of the total alkali content.

### 3. PRESENT STATUS OF MIXED ALKALI RELAXATION

The internal friction is maximum whenever the product of the angular frequency  $\omega$  of the periodic stress and the average relaxation time  $\tau$  reaches the value of 1.

Variations in the entropy of activation will affect the relaxation time by means of its influence on the preexponential factor  $\tau_0$ .

However,  $\tau_0$  appears to be fairly constant for all mechanical loss phenomena. Major changes in the relaxation time are therefore always associated with a change in the activation energy. Investigations have shown that the temperatures at which internal friction peaks occur at some constant frequency, are direct measures for the activation energy of the loss causing process.

The following systematic changes have been observed upon introduction of a second alkali.

- (i) The magnitude of the single alkali peak decreases rapidly and the peak itself is shifted to higher temperatures. This observation is in good agreement with the experimental fact that the introduction of a dissimilar alkali will reduce the ion mobility and increases the activation energy for alkali self diffusion and conduction.
- (ii) A new peak emerges from the background at considerably higher temperatures, corresponding to a considerably higher activation energy. This peak shifts to lower temperatures as it develops.
- (iii) Upon further substitution of the initially present alkali for a dissimilar one, the relaxation times of the two processes approach each other: the peaks merge and from this moment onwards only the mixed alkali peak is visible, as it is very large compared to the remnant of the single alkali peak.
- (iv) The magnitude of the mixed alkali peak reaches a maximum and its activation energy reaches a minimum in a composition which contains approximately equal amounts of both alkalis. Continued alkali substitution will reverse this trend: the mixed peak becomes smaller and finally disappears into the high temperature background, while simultaneously a single alkali peak breaks away from the low temperature side of the mixed alkali peak and shifts to lower temperatures upon development. This single alkali peak, however, corresponds to the stress induced motion of the 'second' alkali ions, which have become now the predominating species.

The magnitude of the mixed alkali peak is not only affected by the mixing ratio, but also by the nature of the specific alkali ions which are being mixed. The combination of sodium and potassium in a glass will result in the occurrence of a mixed peak which is over three times larger than the peak which will result from the combination of lithium and cesium ions in a comparable glass. A systematic investigation of this effect has shown that the magnitude of this peak correlates well with the difference in size of the alkali ions. The mixed alkali peak increases with the difference between the alkali ion radii.

However, beyond a radius ratio of 1.4 this trend is reversed, possibly because

very large size differences lower the probability of the relaxation process. The optimum ion radius ratio of 1.4 is reached by combining sodium and potassium.

The occurrence of the mixed alkali peak is by no means confined to simple silicate glasses. Peaks of this type have been observed in aluminosilicate glasses, borosilicate glasses, borate glasses, germanate glasses and phosphate glasses and for all kinds of alkali ions. These various types of glasses show mixed alkali peaks of different magnitude. The size of this peak is also related to the total alkali concentration. Glasses which contain larger amounts of alkali oxide will show larger mixed alkali peaks, located at lower temperatures. At very low alkali concentration the mixed peak will disappear into the high temperatures background. In this respect, the mixed alkali peak behaves analogously to the single alkali peak.

Ions of non-alkali monovalent elements, like  $\text{Ag}^+$ ,  $\text{Cu}^+$  and  $\text{Tl}^+$  can also be used as network modifying ions. There is experimental evidence that these oxides do not behave differently from common alkali oxides with respect to mixed alkali relaxation. They can cause a similar large internal friction peak, which shows the same dependence on composition.

Ion exchange experiments have revealed that it is not essential whether the various components are molten together at high temperatures or not.

The introduction of a dissimilar ion at considerably lower temperatures, at which the glass network is rigid and able to conserve its original structural configuration, leads to the same relaxation behaviour.

Combined alkali diffusion and internal friction studies have shown that the magnitude of the mixed alkali peak correlates with the **diffusion coefficient of the slowest moving ion**. The alkali diffusion coefficient is largely affected by compositional changes.

It has been observed that a dissimilar alkali, present in small amounts, unvariably has a lower diffusivity than the alkali which is the most abundant. This is also observed when the second alkali has a considerably smaller ionic radius. Thus, in a mixed alkali series, there is a composition at which the diffusion coefficient of the two alkali types are equal and this composition has been shown to have the largest mixed alkali peak.

Another general observation is the fact that the introduction of dissimilar alkali ions is the more effective in causing a mixed peak the smaller they are. As a result of this, the composition which shows the largest mixed alkali peak generally contains the larger ions in a small excess.

The relaxation phenomenon associated with the single alkali peak can also be studied electrically. If a periodic electric field is applied an analogous periodic diffusion process will result.

The mixed alkali relaxation differs in this respect. **No electric analogue has been found for the large mixed alkali peak. As a matter of fact, the dielectric losses are even a minimum in the composition which shows the largest mechanical losses.**

It has been proposed to attribute the mixed alkali peak to 'elastic dipoles' which can be orientated by mechanical stresses without affecting the distribution of electric charge. The exchange of position of dissimilar ions has been offered as an alternative explanation.



The problem to be solved is to find an acceptable mechanism for the mixed alkali peak. This mechanism should be compatible with all experimental facts mentioned in the previous paragraphs.

The fact that the mixed alkali peak reflects so well the changes in the diffusivity of the less mobile alkali ions, together with the circumstance that this peak correlates to the size difference of the alkali ions, makes it very likely that the mixed alkali peak is caused by some reorientation involving alkali ions.

The observation that this process is electrically inactive forms a complicating factor. A simple exchange of position of two dissimilar alkali ions is compatible with electric neutrality. However, for such a mechanism to occur, it is necessary for at least one of the ions to migrate against the force field which results from the mechanical stress. One does encounter serious problems in explaining this in terms of mechanical forces.

It has been tried to avoid the problem by using the concept that dissimilar alkali ions form 'elastic dipoles' which are electrically neutral and which are capable of reorientation under the influences of mechanical stresses. It is the author's opinion that this formulation does not explain a great deal more than the former explanation. It still fails to explain why some of the alkali ions would migrate in a direction opposite to the mechanical force field.

A third mechanism to be discussed here has been recently proposed by Hendrickson and Bray. It suggests an electrodynamic interaction to arise from the difference in resonance frequency of dissimilar alkali ions and causing these dissimilar ions to associate.

The mixed alkali peak is explained by this theory to arise from the stress induced motion of the associated ions. The proposed electrodynamic interaction suggests a relation between the mixed alkali effect and the difference in mass of the involved ions. As this is not in agreement with the experimental observations, this theory is doubtful.

The author believes that a discussion of relaxation phenomena in which ions are involved should not be limited to considerations of mechanical forces only. The jump of an ion also affects the electric charge distribution and the proper way to discuss internal friction of oxide glasses is to consider both mechanical and electrical force balances.

The coupling between mechanical and electrical forces in such materials is caused by the simple fact that the mobile particles possess both a volume and a charge. This is the strongest coupling one can think of, and one is bound to expect 'cross-effects'.

**Single alkali glasses** are characterized by a rigid negatively charged oxide network in which mobile positive ions are distributed in such a way that the material is electrically neutral.

Deformations of the glass which will cause a stress gradient, will exert mechanical forces on the mobile ions. These forces are equal to the product of the stress gradient and the ion volume.

The ions will migrate under the influence of this mechanical force field, provided the duration of the applied deformation is sufficiently long compared to the relaxation time for the jumps of the ions.

The migration of ions will disturb the electric neutrality and an electric field will be set up in such a way that its direction opposes the direction of the mechanical field. The electrical forces are equal to the product of the electric counterfield and the ion charge. The counterfield strength will be proportional to the number of ions which have left their original sites.

This induced electric field will reduce the stress induced diffusion. Soon the condition is reached that the mechanical forces are fully compensated for by the electric forces. Under these conditions, the jump probability of the ions has spherical symmetry, like in the unstrained material, and an additional jump of an ion in the direction of the mechanical field will no longer cause energy losses as this energy is fully stored in the electric counterfield and reconverted to mechanical energy as soon as the strain is relieved.

**Mixed alkali glasses** reveal different features when discussed on this basis. These glasses can also be visualized as rigid structures which are negatively charged and which contain mobile ions. However, one group of ions is very mobile compared to the other.

At low temperatures, the most mobile ion species have a relaxation time which matches the inverse of the angular frequency of the constraint and the situation is basically identical to the one outlined above.

At high temperatures these mobile ions have such short relaxation times that they can respond almost instantaneously to the applied stress, so that they do not cause measurable energy losses. At these high temperatures the relaxation times of the less mobile particles approach the inverse of the angular frequency, and a new relaxation process is started. In contrast with the fast moving ions, the latter ones are not situated in a non-conducting environment but in a **conducting** one.

The presence of a relatively large number of charge carriers with a considerably larger mobility will prevent an electric counterfield from being build up. In other words, the mechano-electric cross-effect which imposes a barrier on the stress induced diffusion in single alkali glasses, is short-circuited here and the energy losses can reach very large values.

In this way it can be understood that mixed alkali glasses show a very large relaxation peak which is electrically inactive and which correlates with the mobility of the slowest moving alkali.

The energy losses to be expected for this combined process are proportional to:

$$\lambda (v_1 \nabla \sigma - q_1 \nabla U) - \lambda (v_2 \nabla \sigma - q_2 \nabla U) = \lambda (v_1 - v_2) \nabla \sigma$$

where:  $v_1, v_2$  = volumes of the alkali ions,  
 $\sigma$  = mechanical stress,  
 $q_1 = q_2$  = charges of the ions,  
 $U$  = electric potential,  
 $\lambda$  = jump distance

It can easily be seen from this simple approximation that the energy losses associated with the mixed alkali peak are proportional to the volume difference of the involved ions.

It is not essential for this mechanism that the relaxation times of the two ion species be different. Even when the relaxation times are equal, the larger ion will still be more susceptible to mechanical forces and jump preferentially in the direction of the mechanical field, while the smaller ions will jump in the opposite directions as they are more susceptible to the electric counterfield.

A mechanism of this type is very general and in no way specific for alkali ions. It is applicable to all materials which are composed of an insulating matrix containing mobile dissimilar charge carriers. Charge carriers are termed dissimilar here, if they possess dissimilar charge to volume ratios.

## 5. EXPERIMENTAL WORK

### 5. 1) Relaxation processes in mixed alkali Na-K metaphosphate glasses.

J. Non-Crystalline Solids 14 (1974) 131.

Over the past years, the mechanical and dielectric properties of silicate glasses have been investigated thoroughly. The borate glasses received considerably less attention in this respect. However, from the available data on these glasses it became evident that there was a large similarity between silicate and borate glasses. Both types of glasses show the mixed alkali effect and a mixed alkali peak.

In literature, very little data can be found about the properties of phosphate glasses. The present investigation was undertaken to study the mixed alkali effect in phosphate glasses and to determine if the pronounced analogy between silicate and borate glasses with respect to mixed alkali behaviour, is valid for phosphates as well.

As a first approach the sodium-potassium metaphosphate system was chosen as the raw materials for these glasses were commercially available. The metaphosphate composition had also the advantage that its structure is well defined and very stable. The results of this study were presented at the third Rolla Ceramic Materials Conference in Baden-Baden, Germany.

It was found that the Na-K metaphosphate glasses exhibit two internal friction peaks. The peak below room temperature at 0.5 Hz is the single alkali peak and is caused by the stress induced diffusion of alkali ions.

The height and the activation energy of this peak correlate well with that of the dielectric loss properties. The second peak which occurs at approximately 100 °C at 0.5 Hz has a pronounced dependence on the concentration of the second alkali. This is the mixed alkali peak.

The mixed alkali peak is electrically inactive and is extremely large in these glasses. It reaches a height above background of  $68 \times 10^{-3}$  at the composition  $0.5\text{Na}_2\text{O} \cdot 0.5\text{K}_2\text{O} \cdot \text{P}_2\text{O}_5$ . This is the largest value which has been reported to date for a mixed alkali peak.

In general, it was found that the behaviour of Na-K metaphosphate glasses is analogous to the behaviour of comparable silicate glasses. However, some distinct differences could be noted. Unlike silicate and borate glasses, the temperature at which the mixed alkali peak reaches its extreme height at a given frequency, does not show a pronounced minimum.

It was also noted that water, dissolved in the glass or adsorbed on the surface of the samples, had a very large influence on the properties of metaphosphate glasses. It was noted that especially the magnitude of the mixed alkali peak was sensitive to variations in water content.

## 5. 2) Internal friction of mixed alkali metaphosphate glasses.

I. Results. *J. Non-Crystalline Solids* 15 (1974) 215.

II. Discussion. *J. Non-Crystalline Solids* 16 (1974) 27.

These papers comprise a systematic investigation of the properties of mixed alkali metaphosphate glasses. Earlier work on silicate glasses by other investigators has shown that the size of the mixed alkali peak could be correlated to the size difference of the alkali ions. The largest mixed alkali peak in silicate glasses was obtained by combining sodium ions with potassium ions. It was also shown that the mixed peak temperatures are related to these size differences.

The metaphosphate glasses give further support to the existence of such relation. In the present work it is shown that the behaviour of mixed alkali silicate and metaphosphate glasses is analogous.

In general, these types of glasses show three distinct relaxation peaks at 0.5 Hz between  $-100^{\circ}\text{C}$  and the annealing range:

- (i) The low temperature single alkali peak.
- (ii) An intermediate temperature peak which is also present in single alkali glasses.
- (iii) The mixed alkali peak at high temperatures. This peak is not observed in single alkali glasses.

The exact temperature of the mixed alkali peak depends on the size of the second alkali. The peak occurs at lower temperatures if the radius of the second alkali is smaller. In this way it is possible that the mixed peak occurs at a lower temperature than the intermediate peak.

In some compositions, e.g. in the Na-K glasses, the intermediate temperature peak and the mixed alkali peak occur so close to each other that only one relaxation peak is observed.

It has been shown in silicate glasses that the introduction of non-alkali monovalent cations like  $\text{Ag}^+$ ,  $\text{Tl}^+$  and  $\text{Cu}^+$ , can also cause a 'mixed alkali' effect. In the present work the silver metaphosphates are included and it is verified that the extension of the mixed alkali effect to include silver ions is also permissible in phosphate glasses.

In view of the general nature of the mixed alkali peak, its electric neutrality and its relation to the mobility of the slowest moving ions, the mixed alkali peak is attributed to a coupled diffusion process of dissimilar alkali ions. The coupling of the two individual diffusion processes is explained by considering the combined electric and mechanical forces associated with stress induced diffusion of ions in a non-conducting matrix. It is predicted that any insulating material, containing dissimilar charge carriers should reveal such a mixed peak.

5. 3) **The influence of dissolved water on the internal friction of lithium metaphosphate glasses containing 1 % potassium metaphosphate.**  
J. Non-Crystalline Solids 13 (1973/74) 304.

In the course of the investigation of metaphosphate glasses it was noted very soon that small amounts of dissolved water had a large influence on their properties. During the period this paper was written, Day et al. came to the conclusion that protons in metaphosphate glasses behave similarly to alkali ions and that the intermediate temperature peak is caused by an interaction of alkali ions with protons. This is not so surprising, considering the fact that  $\text{Ag}^+$ ,  $\text{Tl}^+$  and  $\text{Cu}^+$  behave similarly.

The present study was made in a glass composition which shows the intermediate temperature peak well resolved from the single alkali peak and the mixed alkali peak. It could be verified that the intermediate peak correlated very well to the amount of dissolved water. This peak depends on the water concentration in a way identical to the dependence of the mixed alkali peak on the concentration of the second alkali.

The study of the dielectric losses showed that the introduction of protons reduces the alkali mobility and that the intermediate temperature peak is electrically inactive. It is concluded that protons in a glass can 'act' like alkali ions and that the mechanism for the proton-alkali peak is identical to the one proposed for the mixed alkali peak: viz. stress induced diffusion processes of dissimilar cations, according to the crosseffect described already.

It was also noted that the introduction of small amounts of water interferes with the mixed alkali peak.

5. 4) **The influence of dissolved heavy water on the internal friction of lithium metaphosphate glasses containing 1 % potassium metaphosphate.**  
J. Non-Crystalline Solids 16 (1974) 161.

The various studies of mixed alkali glasses provide indications that the effects observed upon introduction of a dissimilar alkali are related to the difference in size of the ions.

Recently a theory has been proposed which attributes the mixed alkali effect to electrodynamic interactions of dissimilar ions. It was postulated that these interactions arise from the difference in resonance frequency of the dissimilar ions. The latter suggests a quantitative relation between the mixed alkali effect and the difference in mass of the involved alkali ions.

The distinction between ion size differences and ion mass differences as the primary cause of a phenomenon is a difficult matter. It is not possible to vary the size of alkali ions while keeping their mass constant. In most investigation both parameters are varied simultaneously.

The use of alkali isotopes is not very promising either; the relative mass differences are rather small.

The recognition that protons in a glass act similarly to alkali ions opens much better perspectives. By comparing the influence of protons with the influence of deuterium ions one should be able to decide between size and mass differences.

For the ease of this comparison the present study was made in the same base glass as the one which had been used for the investigation of the effect of dissolved water. It was found that the mechanical and dielectric properties of metaphosphate glasses are influenced in exactly the same way by dissolved  $D_2O$  as they are by dissolved  $H_2O$ . This experimental fact is in agreement with the hypothesis that the mixed alkali effect is controlled by the difference in size and not in the masses of the alkali ions.

5. 5) Internal friction and dielectric losses of mixed alkali borate glasses \*  
J. Non-Crystalline Solids 16 (1974) 281.

The borates take a special place among the glass forming systems in that they show the so called 'boric oxide anomaly'. In the alkali silicate systems, an increase in the alkali content results in a decrease in viscosity and an increase in thermal expansion coefficient, effects which can be simply explained in terms of the Warren-Zachariasen model for the structure of these glasses. The structure is weakened by the increasing number of non-bridging oxygens. However, in the alkali borate glasses the opposite effects are observed. This anomalous behaviour is only observed in the region of low alkali contents and reverses to normal behaviour at higher alkali concentrations. It is explained by a change in coordination number of all of the boron atoms from three to four in the low alkali range. This particular feature of borate glasses makes a systematic investigation of the mixed alkali borate glasses highly desirable.

Alkali borate glasses show another remarkable difference when compared with silicate and phosphate glasses: The intermediate temperature peak, caused by the interactions of protons and alkali ions, is absent. However, borate glasses, prepared in the conventional way, definitely contain small amounts of dissolved water.

In spite of the exceptional nature of borate glasses, their mixed alkali behaviour appears to be governed by the very same principles as in silicate and phosphate glasses. The introduction of dissimilar alkali ions causes a large reduction of the mobility of the initially present alkali ions and simultaneously the occurrence of a mixed alkali peak. The magnitude and the activation energy of this peak is related to the difference in size of the alkali ions, completely analogous to what is observed in other glass systems.

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\* Some of the experimental work described in this paper was carried out by Mr. W. J. T. van Gemert.

The influence of varying the total alkali content is also studied in this work. The mixed alkali effect fades out when the total alkali content is reduced. It is found that the alkali mobility in glasses containing less than 10 mole % of alkali oxide does not show noticeable deviations from linearity.

It is possible that the existence of a threshold alkali concentration for the mixed alkali effect is peculiar to borate glasses. As mentioned before, the first amount of alkali oxide is used for the increase of the boron coordination number. The alkali ions associated with these oxygens, may very well be more firmly bonded and unable to migrate under the influences of mechanical stresses. Moreover, it is also observed in common glass systems that the alkali mobility decreases sharply when the total alkali content is reduced.

#### 5. 6) **Internal friction and dielectric losses of mixed alkaline-earth — alkali metaphosphate glasses.** *J. Non-Crystalline Solids* **16** (1974) 267.

The explanation given for the mixed alkali peak in the second paper attributes this peak to coupled stress induced diffusion of dissimilar alkalis. It was predicted at that time that this type of relaxation should be a very general phenomenon.

Earlier work had already shown that the introduction of alkaline-earth ions in simple alkali silicate glasses causes a new relaxation peak at elevated temperatures. At that time this new relaxation was attributed to a cluster network interaction, in which the energy absorption was caused by the phase lag of the cluster vibrations.

The present work provides evidence that divalent ions also cause a new relaxation peak in metaphosphate glasses. The dependence of the magnitude and activation energy of this peak on the composition is in good agreement with the expectations for the mixed alkaline-earth — alkali peak, as predicted by the 'cross-effect' theory in the second paper.

It is also noted that the activation energy of the losses in simple alkaline-earth glasses is much lower than what should be expected if those losses were caused by the migration of alkaline-earth ions. The data are in better agreement with the assumption that these losses are caused by monovalent cations, e.g. protons.

The observations of a minimum in the dielectric losses upon substitution of alkali ions for alkaline-earth ions, gives further support to this hypothesis.

## SAMENVATTING

Glazen die slechts een soort alkali ionen bevatten vertonen een relaxatie piek beneden kamertemperatuur indien de meetfrequentie 1 Hz bedraagt. Deze relaxatie piek wordt de **single alkali peak** genoemd. Het is reeds geruime tijd bekend dat deze relaxatie goed correleert met de elektrische geleidbaarheid van de glazen en met de beweeglijkheid van de alkali ionen.

Deze experimentele feiten hebben tot de algemeen aanvaarde opvatting geleid dat alkali diffusie en elektrische geleiding in glazen van het genoemde type berusten op het zelfde mechanisme dat ook verantwoordelijk is voor hun mechanische en diëlectrische verliezen, namelijk het springen van alkali ionen van netwerkholtte naar netwerkholtte.

Sommige van deze glazen, bijvoorbeeld de alkali silikaat- en de alkali fosfaat glazen vertonen nog een relaxatie piek bij ongeveer 100 °C. Deze piek, die de **intermediate temperature peak** genoemd wordt, heeft men in het verleden toegeschreven aan verplaatsingen, onder invloed van mechanische spanningen, van zwevende zuurstof ionen.

Meer recent onderzoek heeft echter ernstige twijfels doen rijzen tegen deze opvatting en er zijn tegenwoordig duidelijke aanwijzingen dat deze **intermediate temperature peak** in verband staat met de aanwezigheid van water in het glas.

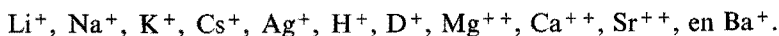
In het verleden heeft men ook glazen onderzocht die meerdere soorten alkali ionen bevatten. Dergelijke „mixed alkali” glazen vertonen in een aantal van hun fysische eigenschappen een sterke afwijking van het ideale menggedrag. Een van deze niet-lineaire effecten is het optreden van een nieuwe relaxatie piek bij hoge temperatuur. Deze piek wordt de **mixed alkali peak** genoemd en vormt het onderwerp van dit proefschrift.

Omdat in het verleden reeds ruim aandacht geschonken is aan de eigenschappen van mixed alkali **silikaat** glazen, is het hier beschreven onderzoek hoofdzakelijk gericht op de overeenkomstige **fosfaat** en **boraat** glazen.

In dit proefschrift zijn metingen ter bepaling van de inwendige wrijving van „mixed alkali” metafosfaat en boraat glazen beschreven. De metingen werden verricht met behulp van een torsie slinger, bij een frequentie van 0,5 Hz en bij temperaturen tussen —100 °C en de ontspannings temperatuur van het glas.

Een gedeelte van de metingen is herhaald bij 2 kHz. Voor dit frequentiegebied werd gebruik gemaakt van de door Dr. Förster beschreven resonantie methode. Naast de voorgenoemde mechanische verlies metingen werd ook aandacht geschonken aan de diëlectrische verliezen, die in deze glazen optreden in het frequentiegebied van 300 tot 30.000 Hz bij temperaturen vanaf 40 °C.

Het onderzoek omvat verder een serie metingen aan glazen die aardalkali ionen bevatten. Het onderzoek heeft betrekking op glazen die ionen of combinaties van ionen uit de volgende groep bevatten:



De mechanische en diëlectrische eigenschappen van mixed alkali metafosfaat en boraat glazen vertonen een grote gelijkenis met de overeenkomstige eigenschappen



van vergelijkbare silikaat glazen. De grootte van de zogenaamde „mixed alkali peak” blijkt in al deze glazen in een duidelijk verband tot de afmeting der ionen te staan. Eén-waardige ionen, die niet tot de reeks der alkali ionen behoren, zoals  $H^+$ ,  $D^+$  en  $Ag^+$ , blijken in dit verband dezelfde eigenschappen te bezitten als de alkali ionen.

Op deze manier kan de **intermediate temperature peak** worden toegeschreven aan een interactie tussen alkali ionen en protonen.

De geringe invloed van onderlinge verschillen in de massa's van de ionen wordt duidelijk geïllustreerd door de vergelijking van het gedrag van protonen en deuterium ionen in glazen: Het gedrag van deze ionen is, binnen de nauwkeurigheidsgrenzen van de experimenten, identiek.

In dit proefschrift wordt ook een verklaring gegeven voor de **mixed alkali peak**. Deze relaxatie wordt toegeschreven aan de aanwezigheid van ongelijksoortige ladingsdragers in het glasnetwerk: Wanneer ladingsdragers van de ene soort onder invloed van mechanische spanningen verplaatst worden, wordt de elektrische neutraliteit van het materiaal verstoord. Hierdoor ontstaat in het materiaal een elektrisch spanningsveld, dat tegengesteld gericht is aan het geïntroduceerde mechanische spanningsveld.

Onder deze omstandigheden zullen de ladingsdragers met het grootste volume toegeven aan de mechanische krachten en die met de grootste relatieve lading aan de elektrische krachten. Op deze wijze vindt er een relaxatie plaats van de mechanische spanningen, zonder dat er een effectieve elektrische ladingsverplaatsing optreedt. Het hierboven beschreven model impliceert dat twee-waardige ionen op volkomen analoge wijze een dergelijke relaxatie kunnen veroorzaken. Dit laatste aspect kon experimenteel geverifieerd worden.

## LEVENSBERICHT

Har van Ass werd op 16 december 1945 te Heel (L) geboren. Na het beëindigen van de Lindanus school (U.L.O.) te Roermond in 1961 volgde zijn eerste kennis-making met de scheikunde als laborant bij het chemisch laboratorium van de Zuid Nederlandsche Zuivelbond te Roermond. In september 1962 werd hij ingeschreven aan de Hogere Technische School te Heerlen, waar hij in juli 1966 afstudeerde in de afdeling Chemische Techniek.

In augustus van het zelfde jaar trad hij in dienst van de Suriname Aluminium Company te Paramaribo, Suriname, als process engineer. In 1969 keerde hij naar Nederland terug, waar hij in september werd ingeschreven als student aan de Technische Hogeschool te Eindhoven.

In mei 1972 legde hij het ingenieurs examen met lof af in de afdeling der Scheikundige Technologie. Met ingang van die datum trad hij in dienst van de Nederlandse Organisatie voor Zuiver-Wetenschappelijk Onderzoek, waar hij in het kader van de S.O.N. werkgroep onder leiding van prof. dr. J. M. Stevels aan de T.H. Eindhoven werkte aan het onderzoek dat in dit proefschrift is beschreven.

In januari 1974 trad hij in dienst van de N.V. Philips als medewerker van het Natuurkundig Laboratorium.

## RELAXATION PROCESSES IN MIXED ALKALI Na–K METAPHOSPHATE GLASSES

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The internal friction and the dielectric losses of Na–K metaphosphate glasses have been investigated. A single alkali and a mixed alkali internal friction peak were observed. The single alkali peak shifted to higher temperatures with increasing concentration of the second alkali and eventually disappeared. The activation energy of this peak increased with the alkali mixing ratio. As in silicate and borate glasses, the single alkali peak correlates closely with the dielectric loss. The mixed peak showed a dramatic increase in size with the addition of the second alkali, but the activation energy was practically independent of the alkali mixing ratio. The large reduction in height of the mixed peak, observed on annealing, is discussed together with the influence of water.

### 1. Introduction

The internal friction versus temperature curves for sodium phosphate glasses [1] are similar to those for sodium silicate glasses in that two peaks are observed between  $-100^{\circ}\text{C}$  and the annealing range at 1 Hz. There is considerable evidence for silicate [2–4] glasses that the low temperature peak, located between  $-40$  and  $0^{\circ}\text{C}$  at 1 Hz, is due to the stress-induced movement of alkali ions. The second peak has been attributed to other mechanisms, e.g. to the movement of non-bridging oxygen ions [5–7], non-bridging oxygen ions associated with protons and alkali ions [8, 9] and to the movement of hydrogen ions [10]. Recently, this peak has been attributed to the cooperative motion of alkali ions and protons [11, 12], according to a mechanism similar to that responsible for the mixed alkali peak in silicate glasses.

A silicate or borate glass containing a mixture of dissimilar alkali ions, exhibits an unusually large internal friction maximum as first reported by Rötger [5] and Jagdt [2]. They suggested that mixing the alkalis causes the original peak to be enlarged and to move to higher temperatures. Steinkamp et al. [13] found this large peak was actually a new peak. Since this peak was observed only in mixed alkali glasses, it was referred to as the mixed alkali peak. More recently this peak was also observed in glasses containing silver [14–16] and copper [17] as a second 'alkali'.

The present investigation was undertaken to study the mixed alkali effect in phosphates and to determine if the pronounced analogy between silicate and borate glasses, with respect to mixed alkali behaviour, is valid for phosphate glasses as well. The metaphosphate composition was chosen because of its good glass forming properties and well-known structure.

X-ray diffraction analysis of vitreous sodium metaphosphate [18, 19] has shown that the structure consists of infinitely long chains of  $\text{PO}_4$  tetrahedra which are essentially cross-linked by sodium ions. Each  $\text{PO}_4$  group ideally contains two non-bridging oxygen ions. As preliminary work on meta-phosphate glasses [11] had shown the pronounced sensitivity of the internal friction peaks to the amount of dissolved water, the melting conditions were closely controlled for all glasses.

## 2. Experimental procedure

### 2.1. Sample preparation

The metaphosphate glasses were prepared by placing about 100 g of reagent grade  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KH}_2\text{PO}_4$  in a platinum dish in an electric furnace at  $700^\circ\text{C}$ . The orthophosphate decomposed rapidly and the furnace temperature was raised over a 30 min period to  $900^\circ\text{C}$ . After steam evolution had ceased, a platinum tube was lowered into the glass melt, through a small hole in the top lid of the furnace. The glass melt was bubbled with oxygen, which had been dried over soda-asbestos and 'drierite' for an additional 60 min. The furnace temperature was held between  $900$  and  $950^\circ\text{C}$ ; the oxygen flow-rate was estimated to be  $2 \text{ cm}^3/\text{sec}$ .

After bubbling, the platinum tube was removed and the melt was allowed to cool outside the furnace. Fibers, approximately 0.5 mm in diameter, were drawn from the melt with a platinum wire. Under these circumstances, one can obtain several meters of usable fiber before the melt freezes. The fibers were handled with oil-coated fingers and stored immediately in oil-filled tubes containing drierite. The glasses containing less than 12 mole %  $\text{K}_2\text{O}$  (of the total alkali), did not show any significant crystallization tendency. Glass P15, containing equal amounts of sodium and potassium, had to be treated in a slightly different way to prevent crystallization. A small drop of glass was taken from the melt with a cold platinum wire and a fiber was drawn from this drop.

Immediately after fiber pulling the dish was returned to the furnace and reheated. A few minutes later the dish was removed again and cooled in the laboratory atmosphere to  $\pm 400^\circ\text{C}$ . Rectangular bars,  $106 \times 9 \times 9 \text{ mm}$ , for density and internal friction measurement were cast in preheated ( $\pm 200^\circ\text{C}$ ) stainless steel molds.

Glasses with an enhanced crystallization tendency were cast at slightly higher temperatures, using graphite oil (Caramba 3) as a mold lubricant. Glass P15 was cast at much higher temperatures, in a mold containing a lining of aluminum foil.

After reheating the melt to  $900^\circ\text{C}$ , disc specimens were made, 25 mm in diameter and 2 mm thick, for the dielectric loss measurements. The discs were cast in graphite molds, preheated to  $\pm 200^\circ\text{C}$ . The bars and discs were annealed for 30 min at the temperatures listed in table 1 and slowly cooled to room temperature. All specimens were stored in oil-filled tubes containing drierite.

## 2.2. Determination of water content

The water content was determined by infrared absorption measurements\* on discs having thicknesses between 200 and 60  $\mu\text{m}$ . During grinding, the discs were continually protected with dry oil to prevent attack by atmospheric moisture.

Absorption at 3400, 2910 and 2355  $\text{cm}^{-1}$  were observed. The intensity of the OH absorption at approximately 2910  $\text{cm}^{-1}$  was used to determine the relative water content. This absorption was used in the present investigation, since it has been used previously to determine the water content of phosphate glasses [20] and has been related to internal friction data [11]. The absorption at 3400  $\text{cm}^{-1}$  was generally poorly resolved as a shoulder on the 2910  $\text{cm}^{-1}$  absorption and was very sensitive to exposure of the specimens to the atmosphere. The error in the calculated extinction at 2910  $\text{cm}^{-1}$  is based on a  $\pm 10 \mu\text{m}$  uncertainty in the specimen thickness.

## 2.3. Internal friction measurements

All measurements were made, using two different techniques, on specimens annealed for 30 min at the temperatures listed in table 1. The fiber specimens were annealed and measured in a torsion pendulum, at 0.3 to 1.7 Hz and at a pressure below 0.05 torr. This apparatus\*\* is very similar to the one described by de Waal [21], except for the specimen suspension and the optical-electronic part of the detection system. The internal friction of the bar specimens was measured after the bars had been ground on a carborundum wheel to  $103 \times 6 \times 5 \text{ mm}$ . During grinding the bars were covered with dry oil to prevent attack by atmospheric water. The bar specimens were measured\*\*\* in air using a resonance technique [22], in the flexural mode at about 2 kHz. The activation energy,  $E_a$ , for the internal friction peaks was calculated from the temperature shift of the peak maximum at different frequencies, using the equation

$$E_a = \frac{R(\ln f_1 - \ln f_2)}{1/T_2 - 1/T_1}, \quad (1)$$

where:  $f_1$  and  $f_2$  = frequency at peak maximum (Hz),  
 $T_1$  and  $T_2$  = temperature of peak maximum ( $^{\circ}\text{K}$ ),  
 $E_a$  = apparent activation energy (kcal/mole).

Internal friction maxima exceeding  $30 \times 10^{-3}$  could not be measured accurately using the resonance technique and in those glasses the activation energy was calculated from the temperature shift of a point, located on the low-temperature side of the peak at  $\tan \delta = 30 \times 10^{-3}$ .

\* Grubb Parsons, MK III Spectromaster.

\*\* This apparatus was a gift from Technisch Physische Dienst. TNO-TH, Delft to our Laboratory; the authors wish to express their feelings of gratitude to this Institution.

\*\*\* Elastomat, type 1.015, Institut Dr. Forster, Reutlingen, Germany.

Table 1  
Numerical data on Na-K metaphosphate glasses.

Batch No.	$X^a$	Annealing temp.		Single alk. peaks		H.a.B.	Mixed alk. peaks		
		bars, discs	fiber	temp.	freq.		temp.	freq.	H.a.B.
Do	0.000	—	—	—8	1.68	12.4	127	1.60	4.2
				55	2085	10.8	220	1910	1.2
P4	0.005	265	275	—15	0.67	7.3	108	0.63	7.1
				65	1853	6.0	223	1715	2.3
P3	0.010	265	280	—9	0.84	5.2	108	0.81	7.6
				66	2181	8.2	214	2040	4.9
P5	0.020	265	270	—11	0.61	2.9	118	0.57	10.2
				65	1660	5.4	218	1533	6.8
P12	0.030	275	269	—4	0.77	5.8	118	0.71	19.9
				75	2015	3.4	225	1835	8.1
P7	0.040	255	269	6	1.08	4.0	123	0.98	22.5
				88	2240	2.2	235	2030	18.0
P13	0.055	275	251	9	0.45	2.5	119	0.41	25.0
				100	2192	2.7	232	2000	18.3
P8	0.070	255	254	13	0.49	1.8	121	0.45	24.8
				105	2112	2.9	245	1915	24.0
P14	0.085	275	254	19	0.80	1.6	125	0.73	30.7
				—	—	—	—	—	—
P2	0.100	265	246	27	1.06	1.3	130	0.97	26.2
				98	1579	1.3	—	—	—
P9	0.160	275	242	31	0.55	1.4	129	0.49	43.4
				—	—	—	—	—	—
P10	0.240	245	242	—	—	—	136	0.50	52.6
				—	—	—	—	—	—
P6	0.300	245	217	—	—	—	133	0.40	65.0
				—	—	—	—	—	—
P15	0.500	275	213	—	—	—	138	0.34	68.0
				—	—	—	—	—	—

a)  $X = K/(K + Na)$ ; all temperatures in °C, frequencies in Hz, height above background (H.a.B.) and dielectric loss in units of  $\tan \delta \times 10^{-3}$  and activation energy in kcal/mole.

#### 2.4. Determination of density and molar volume of oxygen

The density of the glasses was determined at room temperature, using a pycnometer adapted to the size of the bars. Paraffin oil,  $D_4^{23} = 0.8671$ , was used as a reference liquid. The density,  $D_4^{23}$ , was calculated from the equation

Table 1  
(continued)

Density	Molar volume of oxygen	Water content (wt%)	Dielectric loss at 80°C; 3kHz	$E_a$ (single peak)	$E_a$ (mixed peak)	$E_a$ (conduction losses)
2.463	27.60	0.120	1,800	16.0	27.0	17.3
2.490	27.32	0.170	930	17.1	25.9	16.3
2.503	27.20	0.197	570	18.6	33.1	17.1
2.487	27.42	0.127	510	18.0	30.3	18.4
2.460	27.76	0.137	450	18.5	28.4	20.6
2.477	27.61	0.123	320	18.7	27.2	19.1
2.462	27.85	0.141	205	19.5	29.7	21.8
2.473	27.79	0.180	160	19.6	27.7	21.5
2.489	27.68	0.104	115	—	—	22.7
2.496	27.66	0.209	108	22.7	27.9	22.9
2.466	28.27	0.133	45	—	24.9	22.7
2.461	28.67	0.152	20	—	26.6	23.4
2.465	28.88	0.240	13	—	28.7	27.7
2.467	29.73	—	7	—	31.0	30.1

$$D_4^{23} = \frac{W_b}{V^{23} - \left( \frac{W_p - W_b - W_e}{0.8671} \right)} \quad (2)$$

where:  $W_b$  = weight of the specimen (g),  
 $V^{23}$  = volume of the pycnometer ( $\text{cm}^3$ ) at 23°C,  
 $W_p$  = total weight of the pycnometer and bar, balanced with oil (g),  
 $W_e$  = empty weight of the pycnometer (g).

The accuracy is estimated to be  $\pm 0.1\%$ . The Molar Volume of Oxygen, MVO, was calculated from the density according to the following equation:

$$\text{MVO} = \frac{xM_{\text{R}_2\text{O}} + (1-x)M_{\text{R}'_2\text{O}} + yM_{\text{OX}}}{D_4^{23}(0.5 + yz)}, \quad (3)$$

where the glass composition is represented by  $x\text{R}_2\text{O} \cdot (1-x)\text{R}'_2\text{O} \cdot y\text{OX}$ ,  $M_{\text{R}_2\text{O}}$ ,  $M_{\text{R}'_2\text{O}}$  and  $M_{\text{OX}}$  are the molar weights of the oxides, and  $2z$  = the number of oxygen atoms per mole of network-forming oxide (OX).

### 2.5. Dielectric loss measurements

The dielectric losses were measured\* at 300, 3 000 and 30 000 Hz at temperatures from 40 to 160°C, using an ac bridge connected according to the 'Schering-principle'. Prior to measurement, the disc specimens were ground to a thickness of 1 mm and both planar sides were coated with electrode paste\*\*. The cylindrical side of the specimens and the outside rims (2 mm wide) on both planar sides were uncoated.

The measuring cell consisted of a set of solid silver electrodes, mounted in a fused silica support and enclosed in a large copper tube, connected to earth.

The average activation energy,  $E_a$ , of the observed losses was calculated from the equations:

$$\tan \delta = C \frac{\omega\tau}{1 + \omega^2\tau^2}; \quad \tau = \tau_0 \exp(E_a/RT), \quad (4)$$

where:  $\omega$  = the angular frequency of the alternating current ( $\text{sec}^{-1}$ ),

$\tau$  = the relaxation time (sec),

$C$  = a constant.

The error is estimated to be  $\pm 1$  kcal/mole.

## 3. Results and discussion

Measurements of the internal friction of annealed fibers and bars revealed an extremely large mixed alkali peak and a single alkali peak of 'normal' size, figs. 1 and 2 and table 1. The magnitude of the mixed peak can be understood if one considers the large amounts of alkali oxide in the metaphosphate glasses, compared to more common glasses.

As the concentration of potassium increased, the single peak became smaller and

\* Rhode and Schwarz R.C. generator, type SRM BN 4085, dielectric test bridge, type VRB BN 3520 and tunable indicator amplifier, type VBM BN 12 121/2.

\*\* Leitplatin 308 A, DEGUSSA, Frankfurt a.M., Germany.



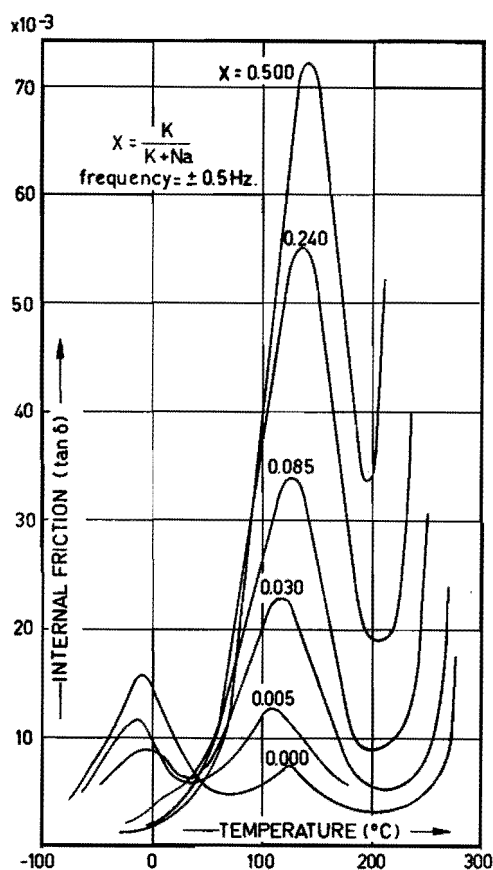


Fig. 1. Internal friction of Na–K metaphosphate glasses versus temperature. Intermediate compositions have been omitted for clarity. The curves were measured with a torsion pendulum at 0.2 to 1.7 Hz.

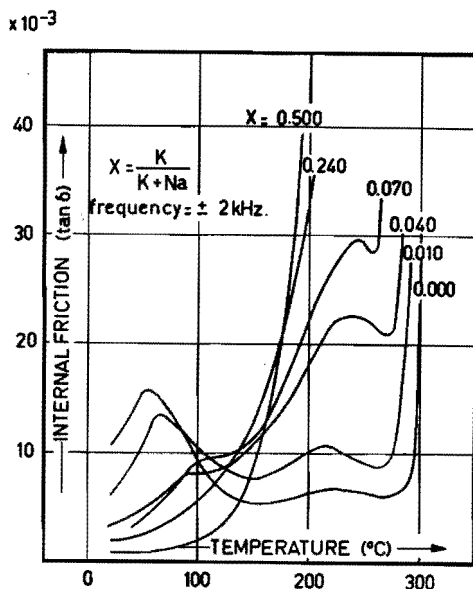


Fig. 2. Internal friction of Na–K metaphosphate glasses versus temperature. Intermediate compositions have been omitted for clarity. The curves were measured with an 'elastomat', in flexure vibration, at about 2 kHz.

shifted to higher temperatures, quite similar to the behaviour of the single alkali peak in borate [14, 23, 24] and silicate [2–4] glasses. At the same time the mixed alkali peak developed at a considerably higher temperature, but did not shift to lower temperatures with increasing magnitude. Careful examination even shows an increase in peak temperature. The second peak in the pure sodium metaphosphate glass should be ignored in this respect, as it arises from alkali-proton interactions [11]. The mixed peak eventually reaches a height above background of  $\tan \delta = 68 \times 10^{-3}$  (fig. 6, table 1). The addition of potassium also has a relatively large influence on the network damping by shifting the background to lower temperatures. In the Na–K metaphosphate system, the annealing temperature of the completely mixed glass was more than  $60^\circ\text{C}$  lower than the annealing temperature of the single alkali glass, fig. 3.

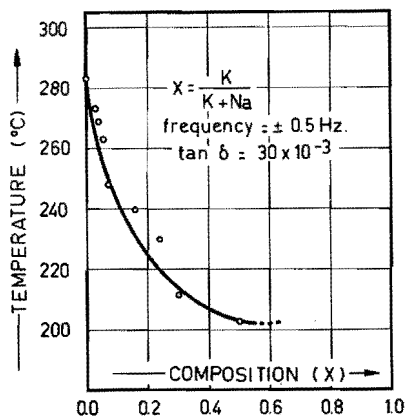


Fig. 3. Isofriction curve for the network-damping of Na-K metaphosphate glasses at 0.5 Hz. The temperatures at which the background reaches a height of  $30 \times 10^{-3}$  is plotted versus composition. The transformation temperature as a function of composition, will be very similar.

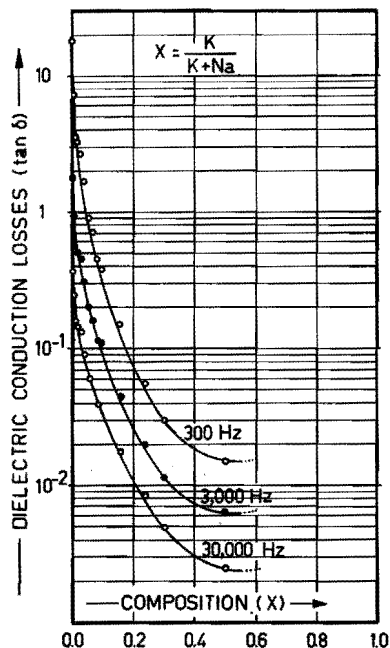


Fig. 4 Dielectric losses at 80°C of Na-K metaphosphate glasses as a function of composition, at 300, 3 000 and 30 000 Hz. The losses are mainly due to the conductivity of the glasses.

The activation energy of the single alkali peak increased as the second alkali was added (fig. 5). Similar to borate and silicate glasses, the agreement between the single alkali peak and dielectric (conduction) losses is good for both the magnitude and the activation energy, figs. 4 and 5. The mixed alkali peak appears to be electrically inactive; i.e. no dielectric loss peak was found that correlated with the large mechanical mixed peak.

The activation energy of the mixed peak remained constant, within experimental error (fig. 5 and table 1) throughout the compositional range examined, consistent with the previously mentioned absence of a change in peak temperature. The activation energy of the mixed peak approaches the value of the activation energy of the single alkali peak for  $x = 0.5$ , an observation which is very common for mixed alkali metaphosphate glasses [16] in general. At  $x = 0.5$ , the single alkali peak completely merges into the mixed peak (fig. 1) and it is assumed that the relaxation times of the mixed and the single alkali process are equal, or at least very close to each other.

The density and the Molar Volume of Oxygen, as computed from the density and the composition, showed a linear dependence on composition (fig. 7). In general, a rather large data scatter was observed in these glasses. Although this scatter did not correlate with the water content as determined from the OH infrared absorption of disc specimens, it is felt that its main cause is differences in water content, partic-

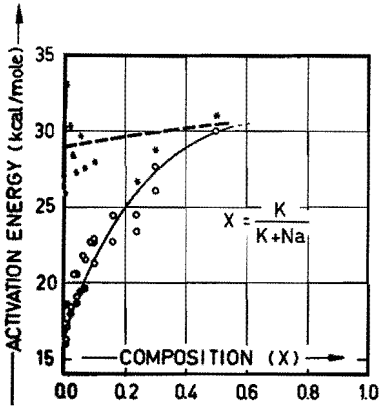


Fig. 5. Activation energy of relaxation processes in Na-K metaphosphate glasses. The open circles refer to the dielectric losses, the solid circles to the single alkali peaks; and the asterisks refer to the mixed alkali peaks.

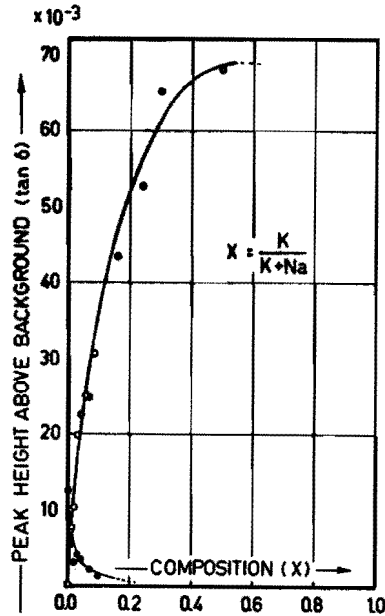


Fig. 6. Height (above background) of the mechanical loss peaks in Na-K metaphosphate glasses as a function of composition. The open circles refer to mixed alkali peaks, the closed circles refer to single alkali peaks.

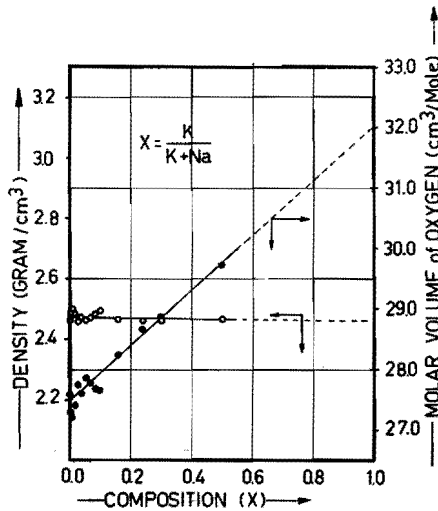


Fig. 7. Density and Molar Volume of Oxygen of Na-K metaphosphate glasses. The open circles refer to the density measurements, the solid ones to the Molar Volume of Oxygen.

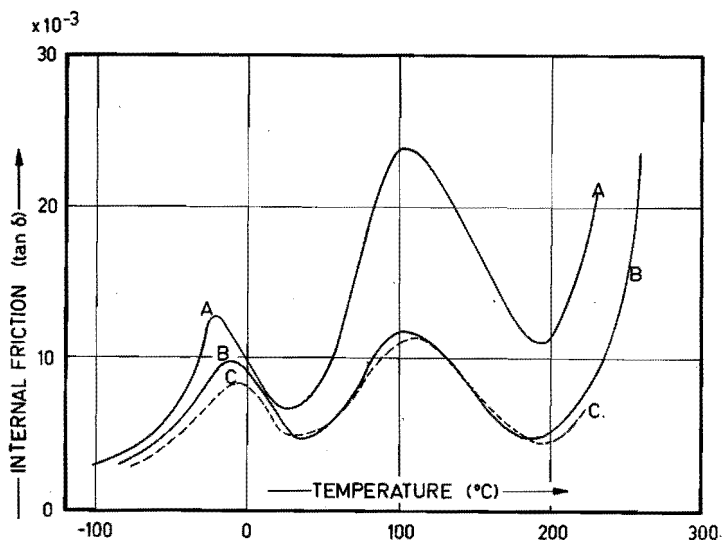


Fig. 8. Influence of annealing in vacuum on the internal friction of glass P3. Frequency is 0.8 Hz and the pressure is 0.03 torr. Curve A: Unannealed fiber. Curve B: Same fiber, but annealed for 30 min at 280°C. Curve C: Same fiber, after additional annealing for 90 min.

ularly on the surface layers of the specimens.

Because of the hygroscopic nature of the glasses, the water content of the surface layers will be mainly determined by the time of exposure and relative humidity of the atmosphere. This viewpoint is substantiated by the observed large influence of annealing a fiber in vacuum, fig. 8. The magnitude of the mixed peak is reduced several times as compared to the unannealed fiber, as by this treatment water is removed from the surface layers of the specimen.

#### 4. Summary and conclusions

Mixed alkali Na-K metaphosphate glasses exhibit two internal friction peaks. The peak below room temperature at 1 Hz is attributed to the stress induced motion of sodium ions as in borate and silicate glasses. The second peak above 100°C at 1 Hz has a pronounced dependence on the amount of second alkali (K) present and is very large compared to the second peak in silicate glasses.

The second peak is electrically inactive and is attributed to a cooperative motion of sodium and potassium ions, similar to that proposed for the mixed alkali peak in silicate and borate glasses. The dielectric losses decrease rapidly as the second alkali is introduced. In this respect metaphosphate glasses behave analogously to the silicate glasses and exhibit the 'mixed alkali effect'.

Unlike silicate and borate glasses, the activation energy of the mixed peak does

not show a pronounced minimum at a composition where both alkalis are present in about equimolar concentrations. At this composition the activation energies of the single alkali peak and the mixed alkali peak are equal, within experimental error, and it is believed that the relaxation times of both processes are equal also. The transformation temperature decreases appreciably as the alkalis are mixed.

Surface water has a large influence on the internal friction of Na-K metaphosphate glasses, especially on the magnitude of the mixed alkali peak.

### Acknowledgement

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# INTERNAL FRICTION OF MIXED ALKALI METAPHOSPHATE GLASSES

## (I). Results

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The internal friction of Li–Na, Li–K, Li–Cs, Li–Ag, Na–Cs and Na–Ag metaphosphate glasses was measured at 0.5 Hz and 2 kHz. The dielectric losses were also measured from 40 to 160°C, at frequencies of 300, 3 000 and 30 000 Hz. The densities of the glasses were determined and the molar volume of oxygen was calculated. In general, the mixed alkali behaviour of metaphosphate glasses is very similar to the mixed alkali behaviour of silicate glasses. Silver behaves in this respect like an alkali ion with approximately the same size as a sodium ion.

### 1. Introduction

The internal friction versus temperature curves for sodium phosphate glasses [1] are similar to those for sodium silicate glasses, in that two peaks are observed at 0.5 Hz between –100°C and the annealing range. There is considerable evidence for the silicate [2–4] glasses that the low-temperature peak, located between –40 and 0°C at 0.5 Hz, is due to the stress-induced movement of the sodium ions. The second peak has received much attention in many previous investigations, as can be illustrated by the number of possible explanations that have been offered, e.g. the movement of non-bridging oxygen ions [5–7], non-bridging oxygen ions associated with protons and alkali ions [8, 9], the movement of hydrogen ions [10], and more recently, the cooperative motion of alkali ions and protons [11, 12]. The introduction of a second type of alkali in a glass gives rise to an unusually large internal friction maximum, as first reported by Rötger [5] and Jagdt [2]. Steinkamp et al. [13] found that this large peak did not originate from the low-temperature peak, but was actually a new peak. As this peak only occurred in a mixed alkali glass, it was referred to as the mixed alkali peak.

From the numerous studies on silicate [17, 18] and other [18–21] glasses, it is known that the dielectric behaviour of the alkali ions correlates very well with the dc conductivity [19], diffusion of alkali [22, 23] and the low-temperature internal friction peak [4, 24], as these properties are all related to the same basic mechanism:

the jump of an alkali ion from one interstice to another [24, 26, 27]. The low-temperature internal friction peak is called the single alkali peak. With the introduction of a second alkali, the dielectric losses of a glass are significantly reduced, sometimes by several powers of ten. This phenomenon is known in the literature as the mixed alkali effect [14–16].

No dielectric analogy, corresponding to the large mechanical losses associated with the mixed peak [25], has been found in the silicate and borate glasses, and it has been concluded that the mechanism responsible for the mixed alkali peak is electrically inactive. It has been proposed that the two dissimilar alkali ions form an elastic dipole [24] and that the energy dissipation is caused by an exchange of position of both ions [28]. Since this exchange mechanism involves no net charge transport, there will be no contribution to the dielectric losses, consistent with the observations for mixed alkali glasses. The phosphate glasses have received considerably less attention in the past. The present investigation was undertaken to extend our knowledge concerning the properties of mixed alkali glasses to the metaphosphate compositions and to determine to what extent the predictions, based on our knowledge of other glasses, would apply to the metaphosphates.

The metaphosphate composition was chosen because of its good glass-forming properties and its well-known structure. X-ray diffraction analysis of vitreous sodium metaphosphate [29, 30] has shown that the structure consists of infinitely long chains of  $\text{PO}_4$  tetrahedra which are essentially crosslinked by sodium ions. Each  $\text{PO}_4$  group ideally contains two non-bridging oxygen ions.

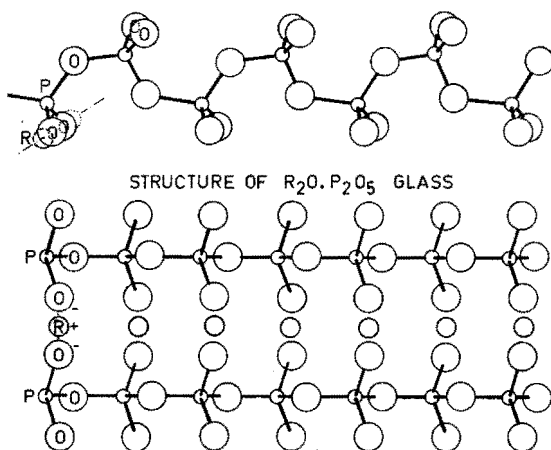


Fig. 1. Expanded schematic representation of linear structure of metaphosphate glasses.

## 2. Experimental procedure

### 2.1. Preparation of chemicals

The glasses were prepared from commercially available  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (Merck 6346) and  $\text{KH}_2\text{PO}_4$  (Merck 4873) and specially prepared  $\text{LiH}_2\text{PO}_4$ ,  $\text{CsH}_2\text{PO}_4$ , and  $\text{AgPO}_3$ .

$\text{LiH}_2\text{PO}_4$  was prepared from  $\text{H}_3\text{PO}_4$  87% (Merck 564) and  $\text{Li}_2\text{CO}_3$  (Merck 5671) by adding the carbonate, under slow and continuous stirring, to a beaker containing 110 to 120 % of the calculated amount of the orthophosphoric acid solution. After the  $\text{CO}_2$  evolution had ceased, the mixture was allowed to stand for half an hour and a small volume of water was added and removed again by boiling. Lithium-dihydrogen orthophosphate precipitated on cooling. The product was collected in a Büchner funnel and washed with a small volume of ice-water. Finally the  $\text{LiH}_2\text{PO}_4$  was dried at  $60^\circ\text{C}$  to constant weight and stored in a well-sealed container.  $\text{CsH}_2\text{PO}_4$  was prepared in an analogous way from  $\text{Cs}_2\text{CO}_3$  (Merck 2040).

Silver metaphosphate was prepared from the nitrate (Merck 1510) by adding a solution of sodium carbonate (Merck 6392) to a concentrated solution of  $\text{AgNO}_3$ . Upon complete precipitation of the silver carbonate the latter was collected by filtration in a Büchner funnel and washed very carefully with water to remove all the trapped sodium. The carbonate was dried and added to a beaker containing 105 to 110% of the calculated amount of a 87%  $\text{H}_3\text{PO}_4$  solution (Merck 564). When  $\text{CO}_2$  evolution ceased, the solution was heated to remove the excess water by boiling. Boiling was continued until the beaker contained a clear transparent viscous liquid, which would produce a white precipitate when water was added. If the addition of water produced a yellow precipitate, boiling was continued for a short time. The water additions had to be made very carefully as the temperature of the solutions was estimated to be about  $300^\circ\text{C}$ . As soon as the white precipitate formed, water additions were continued until the  $\text{AgPO}_3$  precipitation was completed, avoiding the use of any excess water. The liquor was removed as completely as possible by suction filtration. The white product was dried at 100 to  $120^\circ\text{C}$  and stored in a dark-brown and well-sealed container.

### 2.2. Melting procedure

The metaphosphate glasses were prepared by placing about 50 g of a mixture of the corresponding chemicals in a platinum crucible in an electric furnace at  $700^\circ\text{C}$ . The orthophosphates decomposed rapidly and the furnace temperature was raised to  $900^\circ\text{C}$  over a 30 min period. The silver-containing glasses were melted in a porcelain crucible (Weta 3271). The glass melts were bubbled with oxygen, which had been dried with soda-asbestos and 'drierite' for approximately 1 h at a temperature between 900 and  $950^\circ\text{C}$ . The oxygen flow rate was approximately  $2 \text{ cm}^3/\text{sec}$ .



### 2.3. Sample preparation

Three types of specimens were made from each melt.

(1) The crucible was removed from the furnace and fibers, approximately 0.5 mm in diameter, were drawn by inserting a platinum wire and withdrawing it slowly from the melt. The fibers were handled with oil-coated fingers and stored immediately in oil-filled tubes, containing drierite. The crucible was returned to the furnace and reheated to 950°C.

(2) A few minutes later the crucible was removed again and cooled in the laboratory atmosphere to 400°C. Rectangular bars, 106 × 9 × 9 mm<sup>3</sup> for density determination and internal friction measurements were cast in preheated (200°C) stainless steel molds. Glasses with a large crystallization tendency were cast at slightly higher temperatures, using graphite oil ('Caramba 3') as a mold lubricant. Immediately after casting, the bars were placed in an annealing furnace, preheated to the proper temperature.

(3) After reheating the glass melt, discs, 25 mm in diameter and 2 mm thick, were made for the dielectric loss measurement. The discs were cast in graphite molds, preheated to 200°C, and annealed together with the bars. All specimens were stored in oil, containing drierite.

### 2.4. Measuring techniques

#### 2.4.1. Internal friction measurements

All measurements were made using two different techniques on specimens annealed for 30 min, at temperatures listed in table 2. The fiber specimens were annealed and measured in a torsion pendulum, at frequencies between 0.2 and 2.0 Hz and at a pressure below  $50 \times 10^{-3}$  Torr. This apparatus\* is very similar to the one described by de Waal [28], except for the specimen suspension and the optical-electronic part of the detection system.

The internal friction was determined from the decay of velocity of the oscillating pendulum. The velocity was measured by a light beam reflected from a mirror on the oscillating pendulum and focussed on a pair of photo-diodes. An electronic timer (hp 5302A) measured the time required for the light beam to travel between the two photo-diodes, as well as the period of oscillation of the pendulum. Because the time necessary for the light beam to travel the fixed distance between the diodes is inversely proportional to the velocity, the internal friction was calculated using the equation:

$$\tan \delta = \frac{1}{n\pi} \ln (t_n/t_0), \quad (1)$$

where  $\tan \delta$  = the internal friction,  $n$  = the number of cycles,  $t_n$  = the time required

\* This apparatus was a gift from Technisch Fysische Dienst T.N.O.-T.H. at Delft.

for the light beam to pass between the diodes on the  $n$ th cycle (sec) and  $t_0$  = the time required for the light beam to pass between the diodes on the zeroth cycle (sec).

The internal friction of the bar specimens was measured after the bars had been ground on a carborundum wheel to  $103 \times 6 \times 5 \text{ mm}^3$ . During grinding the bars were kept covered with dry oil to prevent attack by atmospheric moisture. The bar specimens were measured \* in air using a resonance technique [32], in flexural mode at frequencies of approximately 2 kHz. The internal friction was calculated from the equation:

$$\tan \delta = \frac{1}{\pi\sqrt{3}} \frac{\Delta f}{f_p}, \quad (2)$$

where  $\tan \delta$  = the internal friction,  $\Delta f$  = the width of the resonance peak at half-height (Hz) and  $f_p$  = the resonance frequency of the specimen (Hz).

The apparent activation energy,  $E_a$ , for the internal friction peaks was calculated from the temperature shift of the peak maximum at different frequencies, using the equation:

$$E_a = \frac{R(1 \ln f_1 - 1 \ln f_2)}{1/T_2 - 1/T_1}, \quad (3)$$

where  $f_1$  and  $f_2$  = the frequencies at peak maximum (Hz),  $T_1$  and  $T_2$  = the temperatures of the peak maximum (K) and  $E_a$  = the activation energy (kcal/mol). Internal friction maxima where  $\tan \delta > 30 \times 10^{-3}$  could not be measured accurately with the resonance technique and in those cases the activation energy was calculated from the temperature shift of a point, located on the low-temperature side of the peak at  $\tan \delta = 30 \times 10^{-3}$ , using equation (3).

#### 2.4.2. Determination of density and molar volume of oxygen

The density of each glass was determined at room temperature, using an immersion method. Paraffin oil,  $D_4^{23} = 0.8671$ , was used as a reference liquid.

The molar volume of oxygen, MVO, was calculated from the density according to the equation:

$$\text{MVO} = \frac{xM_{\text{R}_2\text{O}} + (1-x)M_{\text{R}_2^*\text{O}} + yM_{\text{nwf oxide}}}{D(0.5 + yz)}, \quad (4)$$

where the glass composition is represented by:  $x\text{R}_2\text{O} \cdot (1-x)\text{R}_2^*\text{O} \cdot y \text{ nwf oxide}$ ,  $M_{\text{R}_2\text{O}}$ ,  $M_{\text{R}_2^*\text{O}}$  and  $M_{\text{nwf oxide}}$  = the molar weight of the oxides (g/mol),  $2z$  = the number of oxygen atoms per mole of network-forming oxide OX. For phosphate glasses  $z = 2.5$ ,  $D$  = the density of the glass ( $\text{g/cm}^3$ ).

\* Elastomat, type 1.015, Institut Dr. Forster, Reutlingen, Germany.

Table 1

Internal friction data on mixed alkali metaphosphate glasses. For most glasses, the high-frequency data are not listed.

Batch No.	$x$	Frequency (Hz)	Single alkali peaks			Proton-alkali peaks			Mixed alkali peaks		
			Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)
$x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
Do	0.00	1.60	-8	12.4	16.0	127	4.2	27.0	-	-	-
		1910	55	10.8		220	1.2		-	-	-
PL8	0.05	0.33	-	-	-	-	-	-	98	29.8	-
PL4	0.10	0.45	-	-	-	-	-	-	104	39.4	28.7
		1900	-	-	-	-	-	-	209	-	-
PL6	0.30	0.38	-	-	-	-	-	-	104	53.2	28.6
PL10	0.40	0.61	-	-	-	-	-	-	105	55.7	28.7
PL1	0.50	0.44	-	-	-	-	-	-	108	61.5	27.1
PL9	0.60	0.42	-	-	-	-	-	-	99	57.5	28.0
PL5	0.70	0.48	-	-	-	-	-	-	97	53.2	25.3
PL3	0.90	0.60	-	-	-	-	-	-	96	40.1	23.4
PL7	0.95	0.50	-	-	-	-	-	-	90	32.5	-
		0.88	-26	8.4		79	12.2		-	-	-
PL2	1.00	1995	50	9.8	18.0	181	7.3	24.0	-	-	-
$x\text{K}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
L1	0.00	0.44	-33	10.0	16.4	74	9.9	23.4	-	-	-
		2338	47	10.9		192	6.9		-	-	-
LK3	0.01	0.52	-38	9.9	14.2	75	10.0	22.3	200	10.3	-
		2040	50	9.3		192	6.7		-	-	-
LK4	0.05	0.51	20	6.0	15.2	94	7.2	23.1	182	17.2	-
		2346	78	-		227	-		-	-	-

Table 1 (continued)

Batch No.	$x$	Frequency (Hz)	Single alkali peaks			Proton-alkali peaks			Mixed alkali peaks		
			Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)
LK5	0.25	0.54 2186	49 155	3.5 —	21.5	— —	— —	— —	165 —	23.0 —	$\approx$ 29
LK2	0.50	0.40	—	—	—	—	—	—	147	29.0	$\approx$ 30
LK6	0.60	0.32	—	—	—	—	—	—	148	30.5	$\approx$ 29
LK7	0.70	0.29	—	—	—	—	—	—	150	30.5	$\approx$ 31
$x\text{Cs}_2 \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
LC3	0.10	0.31 2787	—7 92	6.5 5.0	17.8	83 206	5.9 2.8	25.1	— —	— —	—
LC5	0.20	0.34 2422	36 146	5.0 5.0	20.8	107 241	4.7 4.0	25.7	— —	— —	—
LC4	0.30	0.40 1365	— —	— —	—	105 200	5.0 5.1	30.5	215 —	11.0 —	—
LC6	0.40	0.44	—	—	—	—	—	—	186	15.8	$\approx$ 30
LC2	0.50	0.34	—	—	—	—	—	—	165	21.0	$\approx$ 31
LC7	0.60	0.34	—	—	—	—	—	—	167	22.0	$\approx$ 30
LC8	0.70	0.24	—	—	—	—	—	—	150	—	$\approx$ 34
$x\text{Ag}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
AL10	0.01	0.43 2125	—26 64	5.9 6.0	15.7	— —	— —	—	88 200	23.0 14.5	25.8
AL9	0.05	0.57	—20	2.1	—	—	—	—	97	31.4	22.3
AL3	0.10	0.31	—	—	—	—	—	—	85	38.5	24.5
AL5	0.20	0.48	—	—	—	—	—	—	87	44.8	25.8
AL7	0.30	0.27	—	—	—	—	—	—	75	48.1	26.8

Table 1 (continued)

Batch No.	$x$	Frequency (Hz)	Single alkali peaks			Proton-alkali peaks			Mixed alkali peaks		
			Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H.a.B. ( $10^{-3}$ )	$E_a$ (kcal/mol)
AL2	0.50	0.31	—	—	—	—	—	—	72	53.0	24.1
AL8	0.70	0.22	—	—	—	—	—	—	65	54.4	22.1
AL6	0.80	0.36	—	—	—	—	—	—	69	52.7	—
AL4	0.90	0.25	—	—	—	—	—	—	59	48.3	20.3
AL11	0.99	0.34	-92	—	—	—	—	—	60	26.7	—
A1	1.00	0.29	-93	4.9	—	49	12.9	—	—	—	—
		1266	—	—	$\approx 12$	146	5.6	19.9	—	—	—
$x\text{Cs}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
CN3	0.01	0.51	-21	13.5	—	113	5.0	—	215	8.5	—
CN4	0.05	0.42	-15	9.0	—	122	3.0	—	208	18.0	—
CN6	0.125	0.28	10	4.7	—	—	—	—	199	19.0	—
CN5	0.20	0.29	24	3.7	—	—	—	—	183	—	—
CN7	0.30	0.32	66	3.0	—	—	—	—	173	—	—
CN2	0.50	0.26	—	—	—	—	—	—	147	—	—
$x\text{Ag}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$ glasses											
AN10	0.01	0.44	-16	11.8	—	127	12.8	—	—	—	—
		2162	72	10.2	16.6	250	6.0	28.7	—	—	—
AN9	0.05	0.26	0	—	—	115	14.4	—	27	—	—
AN3	0.10	0.40	—	—	—	120	12.5	—	36	19.0	—
		1937	—	—	—	—	—	—	126	13.3	23.0
AN5	0.20	0.31	—	—	—	116	8.0	—	38	27.0	—
		2099	—	—	—	—	—	—	135	22.7	23.0

Table 1 (continued)

Batch No.	$x$	Frequency (Hz)	Single alkali peaks			Proton-alkali peaks			Mixed alkali peaks		
			Temp. (°C)	H. a. B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H. a. B. ( $10^{-3}$ )	$E_a$ (kcal/mol)	Temp. (°C)	H. a. B. ( $10^{-3}$ )	$E_a$ (kcal/mol)
AN7	0.30	0.22	--	--	--	96	6.0	--	37	29.3	22.6
		2040	--	--	--	--	--	--	140	25.5	
AN2	0.50	0.38	--	--	--	--	--	--	43	32.4	22.8
		0.43	--	--	--	--	--	--	36	30.0	
AN8	0.70	1815	--	--	--	--	--	--	136	25.0	20.9
		0.36	--	--	--	--	--	--	30	28.0	
AN6	0.80	1850	--	--	--	--	--	--	132	21.1	20.4
		0.33	--	--	--	--	--	--	49	23.6	
AN4	0.90	1652	--	--	--	--	--	--	138	18.1	23.9
			--	--	--	--	--	--			

Table 2

Dielectric losses, densities and molar volume of oxygen for mixed alkali metaphosphate glasses.

Batch No.	x	Annealing temperature (°C)	Dielectric loss at 3 kHz ( $\times 10^{-3}$ )	$E_a$ (kcal/mol)	Density ( $\text{g}/\text{cm}^3$ )	Molar volume of oxygen ( $\text{cm}^3/\text{mol}$ )
$x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$						
DO	0.00	—	15 000	17.3	2.463	27.60
PL8	0.05	258	1 400	20.5	2.490	27.08
PL4	0.10	243	470	22.1	2.491	26.86
PL6	0.30	232	100	27.3	2.458	26.35
PL10	0.40	241	72	27.1	2.447	26.03
PL1	0.50	230	82	28.3	2.447	25.59
PL9	0.60	240	85	28.3	2.409	25.55
PL5	0.70	241	125	26.3	2.395	25.26
PL3*	0.90	274	1 180	24.8	2.362	24.70
PL7	0.95	290	3 200	21.0	2.247	24.63
PL2	1.00	310	25 000	16.6	2.352	24.35
$x\text{K}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$						
L1	0.00	315	3 100	16.4	2.344	24.43
LK3	0.01	308	2 050	16.5	2.345	24.51
LK4	0.05	294	510	18.2	2.351	24.81
LK5	0.25	249	25	23.2	2.374	26.38
LK2	0.50	233	4.9	27.0	2.397	28.36
LK6	0.60	223	4.4	26.2	2.405	29.15
LK	0.70	197	5.8	23.5	2.401	30.10
$x\text{Cs}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$						
LC3	0.10	294	320	18.9	2.528	25.98
LC5	0.20	281	54	21.6	2.692	27.51
LC4	0.30	274	13	23.9	2.840	29.03
LC6	0.40	263	5.3	24.6	2.973	30.56
LC2	0.50	252	3.9	24.4	3.088	32.14
LC7	0.60	225	4.6	24.0	3.199	33.65
LC8	0.70	187	6.3	23.9	3.300	35.16
LC9*	0.80	—	11	20.5	3.393	36.68
$x\text{Ag}_2\text{O} \cdot (1-x)\text{Li}_2\text{O} \cdot \text{P}_2\text{O}_5$						
AL10	0.01	312	114	19.3	2.358	24.58
AL9	0.05	303	57	21.1	2.451	24.74
AL3	0.10	284	25	22.9	2.587	24.74
AL5	0.20	257	13.7	23.7	2.807	25.20
AL7	0.30	233	10.2	25.5	3.036	25.52
AL2	0.50	197	22	21.7	3.481	26.12
AL8	0.70	185	122	20.0	3.926	26.59

Table 2 (continued)

Batch No.	x	Annealing (°C)	Dielectric loss at 3 kHz ( $\times 10^{-3}$ )	$E_a$ (kcal/mol)	Density (g/cm <sup>3</sup> )	Molar volume of oxygen (cm <sup>3</sup> /mol)
AL6	0.80	184	270	16.9	4.129	26.91
AL4	0.90	176	820	15.6	4.362	27.01
AL11	0.99	198	4 500	13.2	—	—
A1	1.00	185	8 500	12.4	4.558	27.33
$x\text{Cs}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$						
CN3	0.01	279	670	17.0	2.516	27.30
CN4	0.05	264	270	18.4	2.579	27.78
CN6	0.125	241	77	20.6	2.685	28.73
CN5	0.20	220	25	21.8	2.782	29.70
CN7	0.30	214	10.0	24.1	2.902	30.99
CN2	0.50	176	3.4	28.0	—	—
CN8*	0.70	—	4.9	29.4	—	—
$x\text{Ag}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{P}_2\text{O}_5$						
AN10	0.01	280	175	18.0	2.502	27.40
AN9	0.05	274	130	19.3	2.585	27.39
AN3	0.10	271	110	19.9	2.733	26.94
AN5	0.20	262	102	20.8	2.919	27.16
AN7	0.30	245	110	21.3	3.096	27.44
AN2	0.50	224	310	18.7	3.550	27.12
AN8	0.70	215	1 100	16.9	3.912	27.50
AN6	0.80	206	2 500	15.2	4.146	27.32
AN4	0.90	200	5 000	14.3	4.382	27.14
AN11	0.95	—	17 000	12.7	4.558	27.33

#### 2.4.3. Dielectric loss measurements

The dielectric losses were measured\* at 300, 3 000 and 30 000 Hz at temperatures ranging from 40 to 160°C, using an AC-bridge connected according to the 'Schering principle'. Prior to measurement the disc specimens were ground to a thickness of 1 mm and both planar surfaces were coated with an electrode paste\*\*. The cylindrical side of the specimens and the outside rims (2 mm wide) on both planar surfaces were not coated. The measuring cell consisted of a set of solid electrodes, mounted in a vitreous silica support and enclosed in a grounded large copper tube. The average activation energy,  $E_a$ , of the observed losses was calculated from the equations:

\* Rhode and Schwarz R.C. generator, type SRM BN 4085; Dielectric test bridge, type VRB BN 3520 and Tunable indicator amplifier, type VBM BN 12 121/2.

\*\*Leitplatin 308A, Degussa, Frankfurt a.M., Germany.



$$\tan \delta = C \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (5)$$

$$\tau = \tau_0 \exp(E_a/RT) \quad (6)$$

where:  $\omega$  = the angular frequency of the AC field ( $\text{sec}^{-1}$ ),  $\tau$  = the relaxation time (sec) and  $C$  = a constant. The error is estimated to be 1 kcal/mol.

### 3. Results

#### 3.1 General

Lithium and sodium metaphosphate form good glasses readily but potassium, rubidium and cesium metaphosphate could not be obtained in the vitreous state. The metaphosphate glasses are hygroscopic, especially the sodium glass, which is attacked readily by atmospheric moisture and develops a sticky surface. Lithium metaphosphate glass is considerably less hygroscopic, it could be exposed to the laboratory atmosphere for several months without any visible change in appearance. The solubility of the lithium glass in water is consequently smaller than that for the sodium glass.

Silver metaphosphate glass also has good glass-forming properties. The melt (800 to 900°C) exhibited a brilliant dark-red colour and on very rapid cooling it solidified to a dark-yellow transparent glass. When the glass was cooled slowly and properly annealed, it was colourless to faint-yellow. Melting was done in an oxidizing atmosphere. Upon exposure of the glass to the laboratory atmosphere, a thin film of metallic silver formed on the surface. This reduction of the surface layers was also observed on the bar specimens, which were annealed in a neutral to slightly reducing

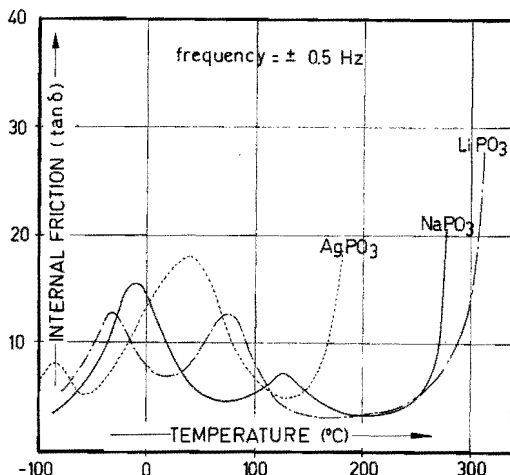


Fig. 2. Internal friction versus temperature curves for single alkali metaphosphate glasses at 0.5 Hz.

atmosphere. After annealing, the silver-rich bars had a metallic appearance. This reduction of silver was neglected as the total amount of silver on the surface was small (the silver coating was still partially transparent) and the outside layers of the bars were removed by grinding, prior to measurements.

### 3.2. Internal friction

The numerical data on the internal friction are given in table 1. Fig. 2 shows the

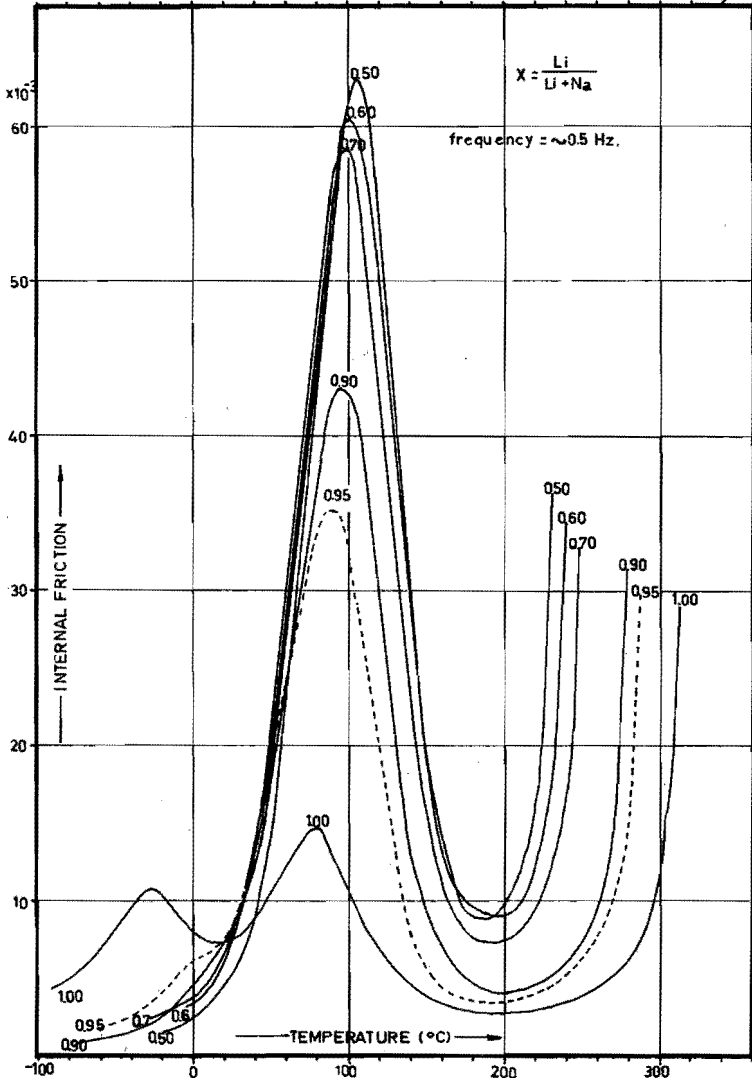


Fig. 3. Internal friction at 0.5 Hz of Li-Na metaphosphate glasses for high  $\text{Li}_2\text{O}$  contents.

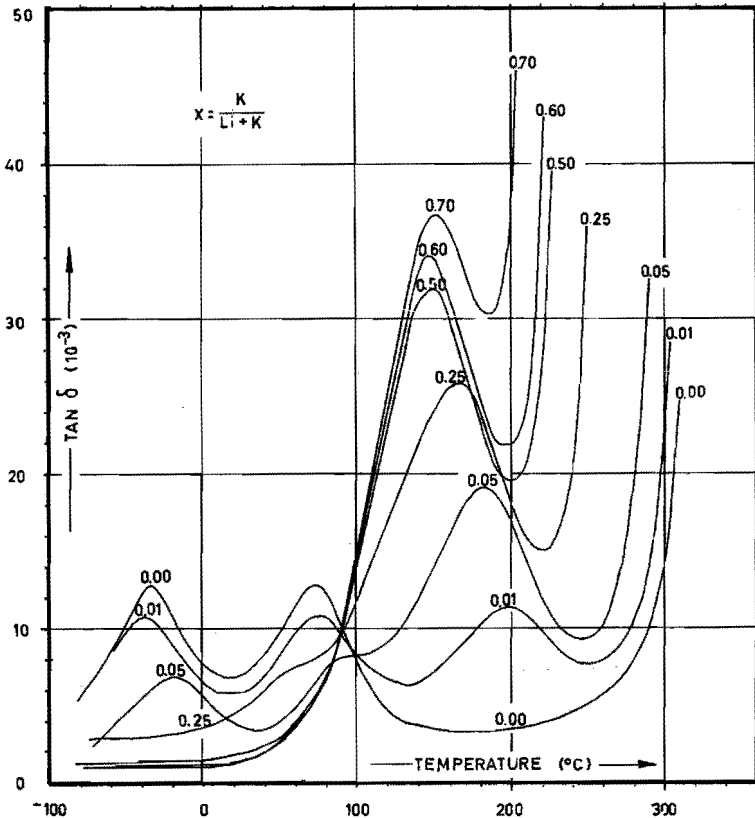


Fig. 4. Internal friction at 0.5 Hz of Li-K metaphosphate glasses for high Li<sub>2</sub>O contents.

internal friction versus temperature curves at 0.5 Hz for lithium, sodium and silver metaphosphate glasses. Figs. 3 to 9 show the internal friction curves for the various mixed alkali series.

The single alkali glasses all exhibit a single alkali peak at low temperatures and a proton-alkali peak at intermediate temperatures. Replacing the alkali ions originally present with dissimilar alkali ions causes the single alkali peak to become smaller and to shift to higher temperatures. At the same time a new relaxation peak emerges from the background at temperatures ranging from 80 to 250°C. This mixed alkali peak reaches its maximum height at a composition containing approximately equal amounts of both alkalis.

The maximum height also depends on the type of alkali ions present in the glass, e.g. the lithium-sodium mixed peak is much larger than the lithium-caesium mixed peak. In some of the glasses, the mixed alkali peak occurs at about the same temperature as the proton-alkali peak and in these cases the mixed alkali peak does not shift to lower temperatures with increasing amounts of the second alkali. Whenever the

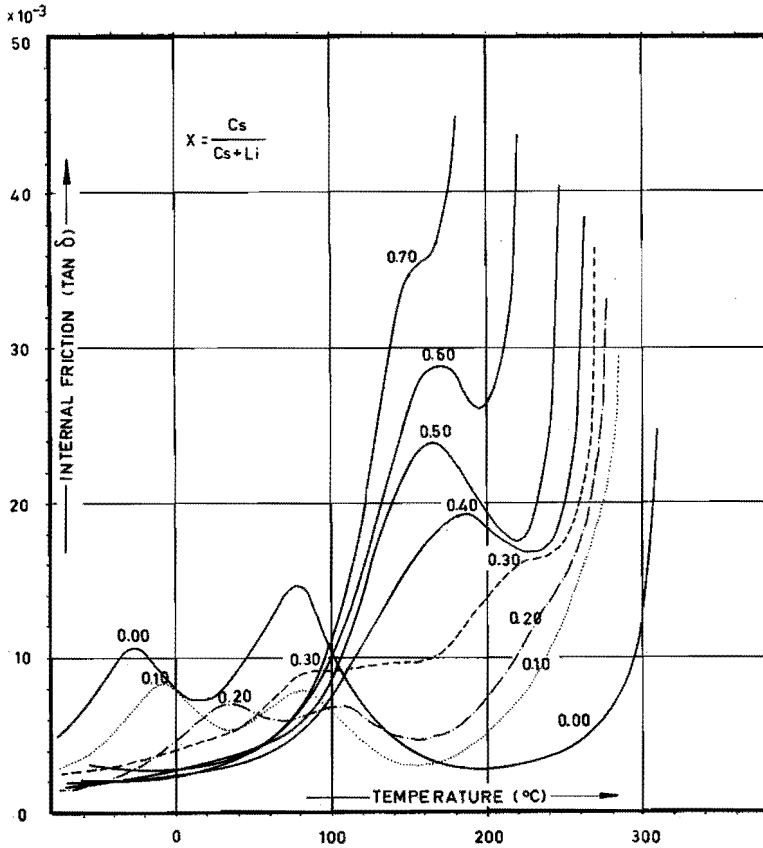


Fig. 5. Internal friction at 0.5 Hz of Li–Cs metaphosphate glasses for high Li<sub>2</sub>O contents.

mixed peak occurs at higher temperatures than the proton-alkali peak, the normal behaviour is found, in that the mixed peak temperature passes through a pronounced minimum as the amount of second alkali is varied.

The silver-containing glasses behave analogously to the alkali glasses, in that a single silver peak, a silver-proton peak and a mixed silver-alkali peak are observed. The compositional dependence of these three relaxations is identical to that observed in regular mixed alkali glasses.

The activation energies of the mixed alkali peaks are given in the figs. 10 and 11 and one can see that the activation energy increases with increasing size of the second alkali. In mixed alkali silicate glasses [25] the activation energy for the mixed alkali peak reaches a minimum for compositions in which both alkali ions are about equally abundant. However, this minimum has not been observed in the phosphate glasses where the mixed peak occurs at a temperature close to the temperature of the proton-alkali peak. In all other compositional systems the phosphate and silicate glasses are

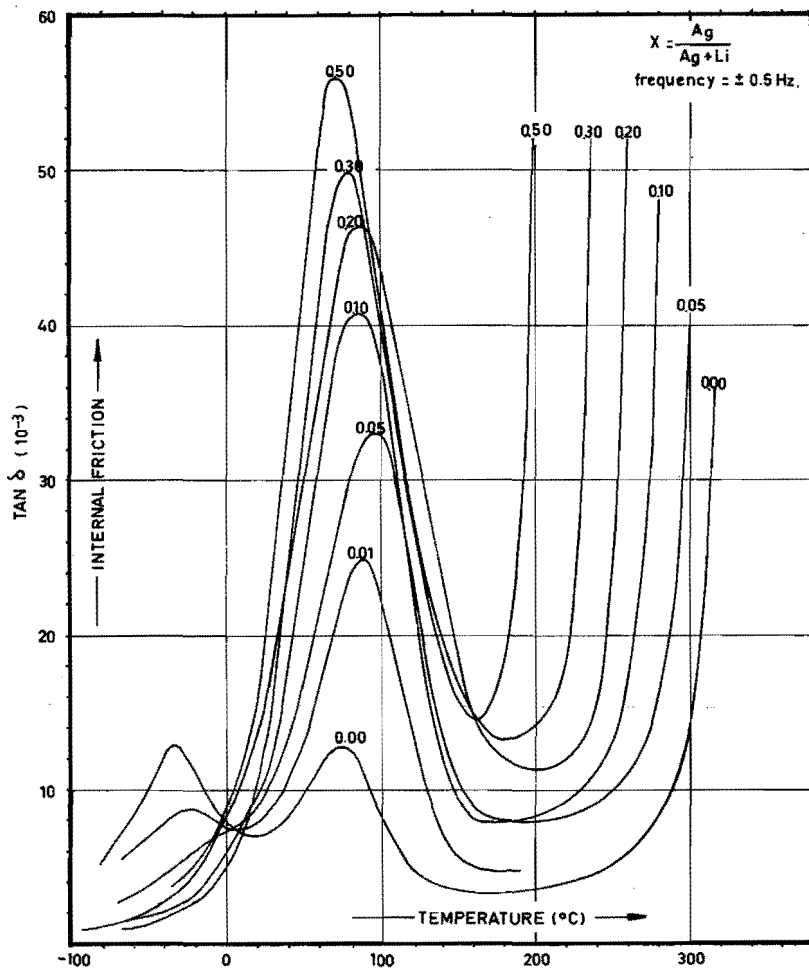


Fig. 6. Internal friction at 0.5 Hz of Li-Ag metaphosphate glasses for high Li<sub>2</sub>O contents.

analogous. In fig. 11 a curve for the Na-K glasses is given. This curve was obtained from earlier work, where numerous details are given for the sodium-potassium metaphosphate system [31].

### 3.3. Density and molar volume of oxygen

The density and the molar volume of oxygen are shown as functions of the alkali content in figs. 12 to 15. Both quantities are almost linearly related to the composition and also depend on the mass and size of the alkali ions respectively, in that the glasses with the larger alkali ion mass have the larger density, and those with the

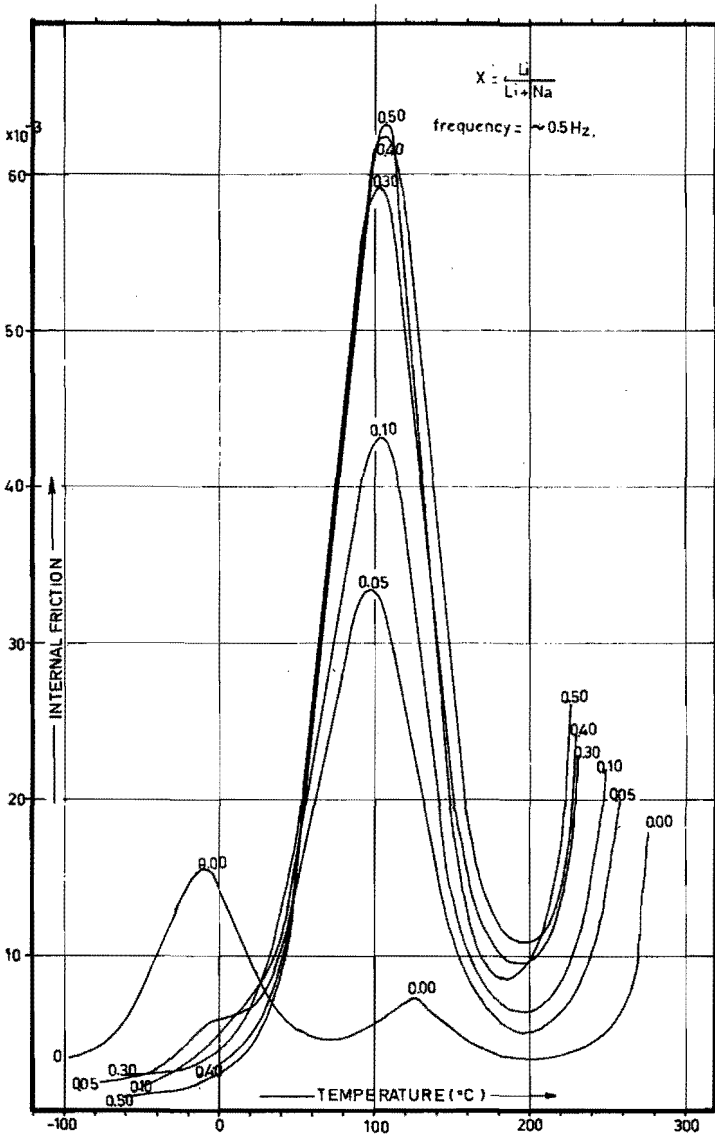


Fig. 7. Internal friction at 0.5 Hz of Na–Li metaphosphate glasses for high Na<sub>2</sub>O contents.

larger alkali ions radius have the larger apparent volume of oxygen. The silver metaphosphate glass deviates from the other glasses, in that its structure is relatively more compact. The molar volume of oxygen in silver metaphosphate glasses is about equal to the molar volume of oxygen in sodium metaphosphate glasses,

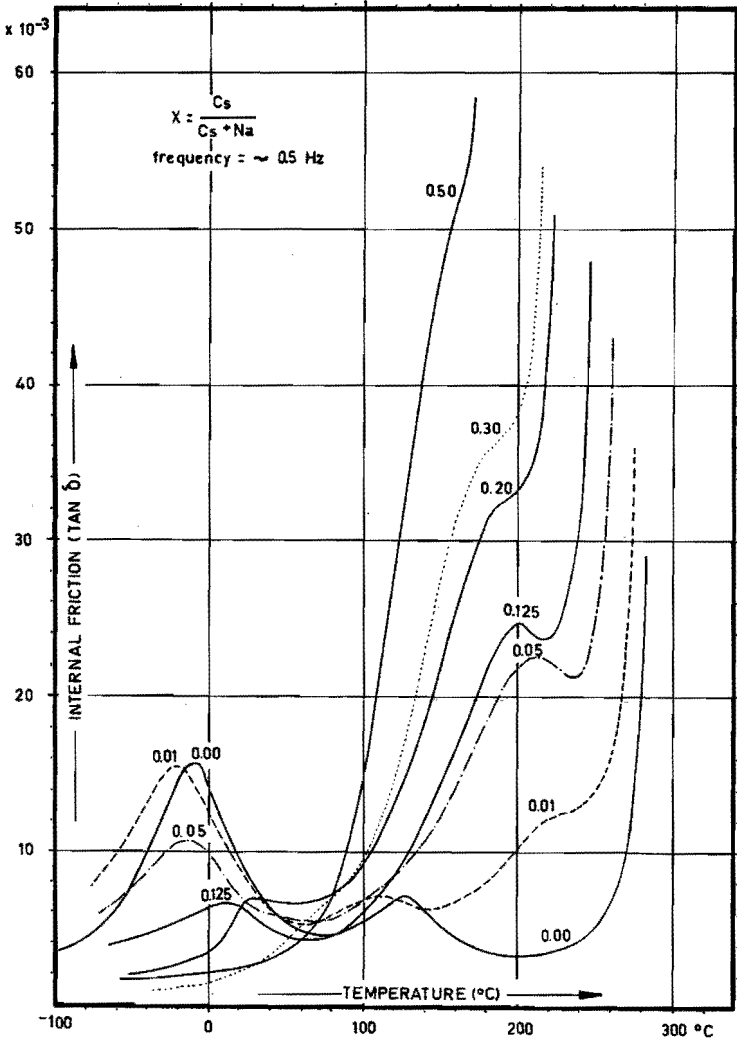


Fig. 8. Internal friction at 0.5 Hz of Na-Ce metaphosphate glasses for high  $Na_2O$  contents.

although the densities of these glasses differ considerably. Fig. 16 shows that the molar volume of oxygen in metaphosphate glasses is, a first approximation, a linear function of the cation volume. In this respect silver behaves like an alkali ion of about the size of a sodium ion.

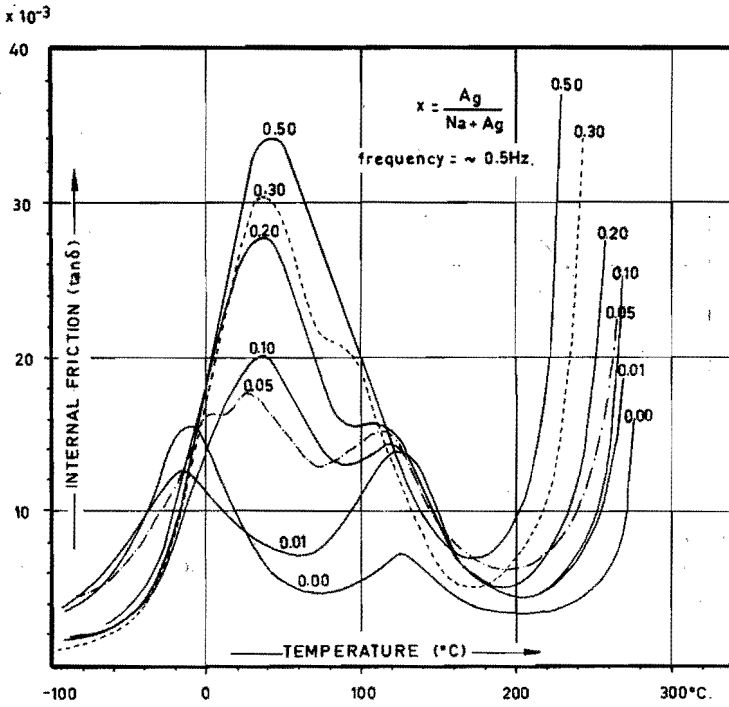


Fig. 9. Internal friction at 0.5 Hz of Na-Ag metaphosphate glasses for high Na<sub>2</sub>O contents.

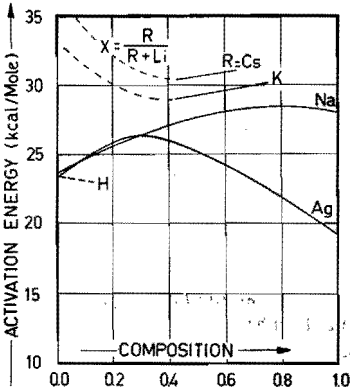


Fig. 10. Activation energies for the mixed peaks in Li metaphosphate glasses as functions of the composition. The dashed curves are estimated from the peak temperatures at 0.5 Hz.

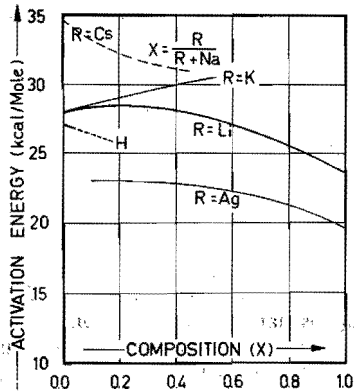


Fig. 11. Activation energies for the mixed peaks in Na metaphosphate glasses as functions of the composition. The dashed curves are estimated from the peak temperatures at 0.5 Hz.



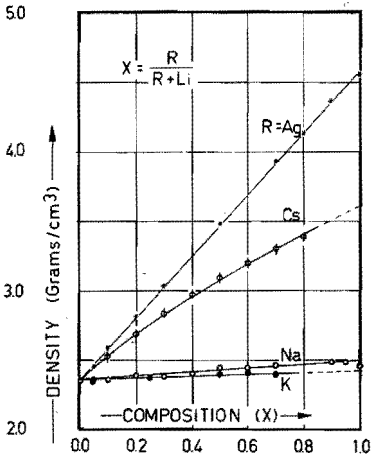


Fig. 12. Densities of lithium metaphosphate glasses as functions of the composition.

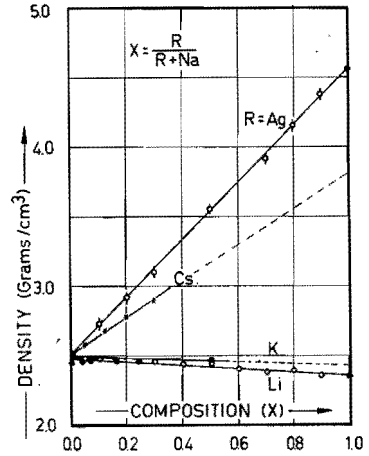


Fig. 13. Densities of sodium metaphosphate glasses as functions of the composition.

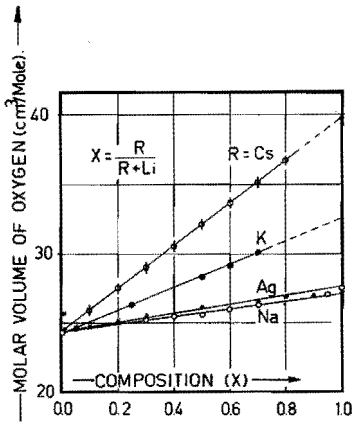


Fig. 14. Molar volume of oxygen of lithium metaphosphate glasses as functions of the composition. In this paper the molar volume of oxygen is defined as the volume of an amount of glass, which contains 32.0 g of oxygen.

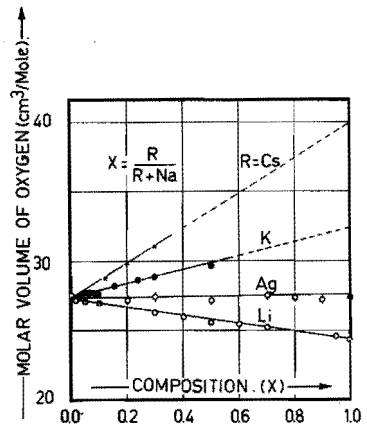


Fig. 15. Molar volume oxygen of sodium metaphosphate glasses as functions of the composition.

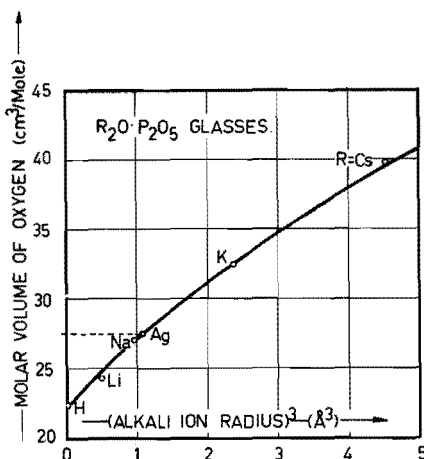


Fig. 16. Molar volume of oxygen of metaphosphate glasses as a function of the third power of the cation radii.

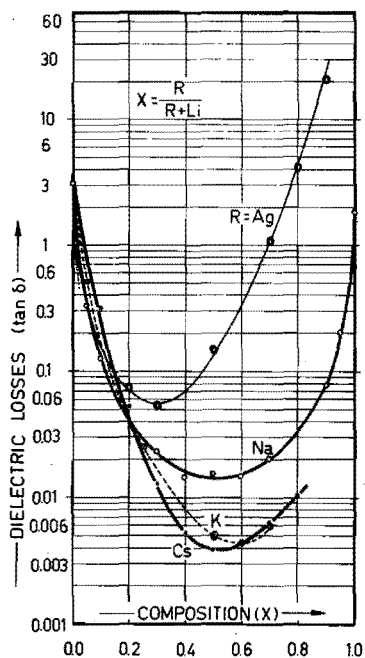


Fig. 17. Dielectric losses at 80°C and 3 kHz of lithium containing mixed alkali metaphosphate glasses.

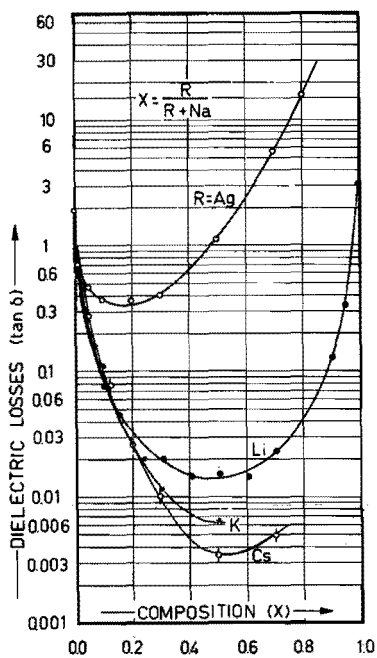


Fig. 18. Dielectric losses at 80°C and 3 kHz of sodium containing mixed alkali metaphosphate glasses.

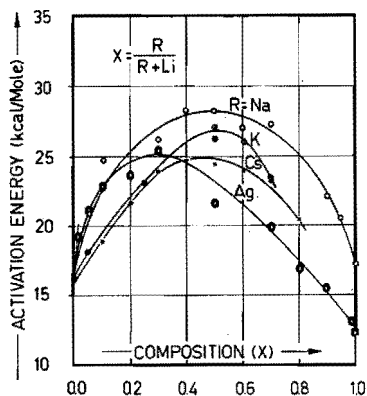


Fig. 19. Activation energies for the dielectric losses of lithium containing metaphosphate glasses.

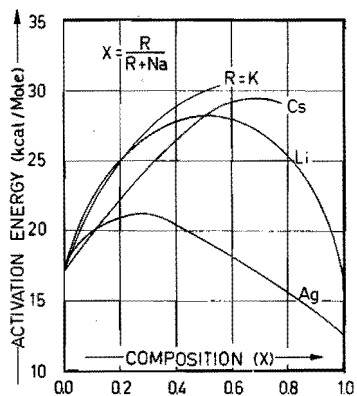


Fig. 20. Activation energies for the dielectric losses of sodium containing metaphosphate glasses.

### 3.4. Dielectric losses

Figs. 17 and 18 show the dielectric loss at 80°C and at a frequency of 3 kHz as a function of the composition. Under these circumstances the dielectric losses are governed by the conductivity of the specimens and may reach very high values. Partial replacement of the alkali with dissimilar alkali ions reduces the losses dramatically and a deep minimum can be observed in the losses as a function of composition. The activation energy of the dielectric losses is increased by the introduction of a second alkali (figs. 19 and 20). In general, a maximum in the activation energy for the dielectric loss is observed in glasses containing about equal amounts of both alkalis; very close to the composition having the smallest losses.

## 4. Summary

The mechanical and dielectric loss properties of mixed alkali metaphosphate glasses are very analogous to the corresponding properties in borate and silicate glasses, with respect to the following:

(a) The single alkali peak is reduced in magnitude and is shifted to higher temperatures by the introduction of a second alkali. The activation energy also increases and is a maximum in the composition containing about equal amounts of both alkalis.

(b) The introduction of a second alkali causes a mixed alkali peak to occur at higher temperatures. This mixed peak is very large compared with the single alkali peak and reaches its maximum height in a composition in which both alkali ions are about equally abundant.

(c) The dielectric losses are reduced by the introduction of a second alkali, and

reach a minimum at some particular composition. The activation energy for the losses is a maximum at approximately the same composition.

In some of the glasses, a third relaxation peak can be observed at intermediate temperatures. This is the proton-alkali peak, which has also been observed in single alkali silicate glasses [8] and phosphate glasses [11, 12].

Silver ions in a glass behave like alkali ions in that they cause a single silver peak, a silver proton peak and a mixed silver-alkali peak. The dielectric properties of silver-containing glasses are also analogous to the dielectric properties of alkali glasses. From the value of the molar volume of oxygen, it follows that silver behaves like a 'alkali ion' with a radius slightly larger than that of the sodium ions.

### Acknowledgements

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## INTERNAL FRICTION OF MIXED ALKALI METAPHOSPHATE GLASSES

### (II). Discussion

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The internal friction and dielectric losses of mixed Li–Na, Li–K, Li–Cs, Li–Ag, Na–K, Na–Cs and Na–Ag metaphosphate glasses are interpreted on the basis of explanations proposed for the mixed alkali effect. It was found that the magnitude of the mixed peak correlates better with size differences than with mass differences. The intermediate temperature peak is treated as a mixed proton-alkali peak. The large mechanical loss peak, appearing when the alkalis are mixed, was attributed to a coupled movement of dissimilar alkali ions and an explanation of the nature of this coupling is proposed. From this model it is predicted that mixed peaks can occur in any electrically insulating material containing dissimilar charge carriers.

### 1. Introduction

Numerous studies [1–4] on the internal friction of glasses have shown that three different relaxation peaks can be distinguished between  $-100^{\circ}\text{C}$  and the annealing range of the glass at 0.5 Hz; viz. a low-temperature peak at about  $-40^{\circ}\text{C}$ , an intermediate-temperature peak between 50 and  $100^{\circ}\text{C}$  and a high-temperature peak at temperatures ranging from approximately  $100^{\circ}\text{C}$  up to the annealing range. These three internal friction peaks are caused by secondary relaxations and appear as superpositions on the very large internal friction peak of the primary relaxation which occurs in the glass transition range.

Glasses that contain only one kind of alkali usually exhibit a low-temperature and an intermediate-temperature peak [5–8]. The high-temperature peak occurs upon the introduction of a second, dissimilar alkali in the glass [9]. If the initially present alkali is gradually replaced with a dissimilar alkali the following changes can be observed:

(1) The low-temperature peak is reduced in magnitude rapidly, and shifted to higher temperatures. This temperature shift is an indication of an increase in the activation energy of the relaxation process.

(2) The high-temperature peak increases and is shifted to lower temperatures. The magnitude of this peak reaches a maximum in a composition that contains approxi-

mately equal amounts of both alkalis. This composition depends on the type of alkali ions present and this glass generally contains the larger alkali ions in a small excess.

(3) The high-temperature background is shifted to lower temperatures. This can be seen as an indication for a decrease in the viscosity and a shift of the primary relaxation peak to lower temperatures. Previous work has shown that the low-temperature peak correlates with the dielectric losses, the conductivity and the diffusion coefficients of the alkali ions, both for magnitude and for activation energy [10–12]. It has been concluded that all of these phenomena are related to the same basic process: the jumping of alkali ions from one interstice to another, and the low-temperature peak has been called the single alkali peak.

From the changes that occur in the single alkali peak when the alkalis are mixed, one can see that the mobility of the alkali ions is greatly decreased by mixing and that the activation energy for alkali migration is increased. The high-temperature internal friction peak, which occurs when at least two dissimilar alkalis are present, has been called the mixed alkali peak and has been attributed to the stress-induced reorientation of elastic dipoles, formed by the dissimilar alkali ions [1–3].

In the literature a so-called mixed alkali effect has been described many times. The occurrence of the mixed alkali effect does not depend on the network forming component in the glass: it consists in a considerable decrease of the electrical conductivity by mixing the alkali ions and it has been observed in silicate [11, 13], borate [14], borosilicate [13], germanate [15] and phosphate [4] glasses. In some cases a dependence on the total alkali content was found: e.g. in germanate and borate glasses the mixed alkali effect was not observed in glasses containing less than 10 mol % total alkali oxide.

The composition that shows the lowest conductivity and dielectric losses is generally not the same composition that exhibits the largest mixed alkali peak. McVay and Day have shown that the mixed alkali peak is controlled by the slowest moving alkali species: they observed that the maximum in the mixed peak occurred in a composition in which the diffusion coefficients for both alkalis were equal [16]. The maximum height the mixed peak can attain depends strongly on the type of alkali ions that are present. The combination of sodium and potassium causes a mixed peak which is more than three times larger than the lithium–cesium mixed peak [1, 4].

The occurrence of a mixed peak is not restricted to alkali glasses. It has been shown that silver ions and copper ions can cause a mixed peak in borate [17] and aluminosilicate [18] glasses. Recent work on sodium [19] and lithium [20] metaphosphate glasses has shown that water can cause a similar effect and a mixed proton-alkali peak was observed at intermediate temperatures. There is strong experimental evidence that the intermediate-temperature peak, observed in most single glasses and also in some mixed alkali glasses, is actually a mixed peak caused by a coupled diffusion process of alkali ions and protons. In the past this intermediate-temperature peak has been attributed to several mechanisms [21–24], including the movement of non-bridging oxygen ions. Shelby and Day have studied the mechanical relaxations

of mixed alkali silicate glasses and have found that the magnitude of the mixed alkali peak is related to differences in the size of the alkali ions, rather than to differences in masses of the ions [1]. They propose an interaction between dissimilar alkali ions such that an electrically inactive 'elastic dipole' is formed and assume a linear relation between the absorption strength of these dipoles and the alkali ion radius ratio. More recently Hendrickson and Bray have proposed a theory for the mixed alkali effect in glass, based on a short-range electrodynamic interaction, arising from the differences in resonance frequencies between dissimilar alkali ions [25]. The latter theory predicts a relation between the magnitude of the interaction and the mass differences of the involved ions. They assume a mobility reducing 'association' between dissimilar alkali ions, located within an 'interaction range' of approximately 6 Å. This model is very successful in describing transport phenomena as each dissimilar ion can have interactions with more than one alkali ion of the initially present type.

In the present work, relaxation peaks of ions with extreme mass and size ratios (like silver-alkali and proton-alkali) are included and an explanation of the experimental observations, in terms of mass and size differences, is attempted.

## 2. The interpretation of internal friction measurements

If the standard anelastic solid is represented by a three-parameter Maxwell model, in which the stress per unit strain goes from the instantaneous value  $M_u$  to a final value  $M_r$ , the response can be described by the differential equation:

$$\sigma + \tau \frac{d\sigma}{dt} = M_r \epsilon + M_u \tau \frac{d\epsilon}{dt}, \quad (1)$$

where  $\sigma$  is the stress (N/m<sup>2</sup>),  $\epsilon$  is the strain and  $M$  is the elastic modulus (N/m<sup>2</sup>). The dynamic  $M_1$  and  $M_2$  functions, corresponding to a given periodic strain, can be obtained by substituting  $\epsilon = \epsilon_0 \exp(i\omega t)$  and  $\sigma = (\sigma_1 + i\sigma_2) \exp(i\omega t)$  in eq. (1), and the well-known Debye functions are obtained:

$$M_1(\omega) = M_u - \frac{\delta M}{1 + \omega^2 \tau^2}, \quad (2)$$

$$M_2(\omega) = \frac{\delta M \omega \tau}{1 + \omega^2 \tau^2}, \quad (3)$$

where  $M_1(\omega)$  and  $M_2(\omega)$  are the real and imaginary part of the frequency-dependent complex modulus:  $M(\omega) = M_1(\omega) + iM_2(\omega)$  and  $\delta M$  is the difference between the unrelaxed and relaxed modulus,  $\omega$  is the angular frequency of the periodic strain field (sec<sup>-1</sup>) and  $\tau$  is the relaxation time (sec). The  $M_2$  function is symmetrical about  $\omega\tau = 1$  and the width of the peak at half maximum is given by



$$\Delta(\log_{10} \omega\tau) = 1.144, \quad (4)$$

for a single relaxation time. In the case of a distribution of relaxation times, the peak becomes broader. Disregarding the losses of the primary relaxation at  $T_g$  (background losses) the frequency dependence of the mechanical losses for a single relaxation time is given by:

$$\tan \delta = \frac{M_2(\omega)}{M_1(\omega)} = \frac{\Delta}{(1+\Delta)^{1/2}} \frac{\omega\tau}{1+\omega^2\tau^2}$$

or

$$\tan \delta = \frac{\Delta\omega\tau}{1+\omega^2\tau^2} \text{ in the case } \Delta \ll 1, \quad (5)$$

where  $\tan \delta$  is the internal friction and  $\Delta = \delta M/M_1$ . By using an Arrhenius equation for the relaxation time

$$\tau = \tau_0 \exp(E_a/RT), \quad (6)$$

where  $E_a$  is the activation energy (kcal/mol) and  $\tau_0$  is the pre-exponential factor in the relaxation time (sec), it can be shown that there is a linear relation between  $\ln \omega\tau$  and the reciprocal absolute temperature at constant measuring frequency and the frequency-dependent expressions can readily be converted into temperature-dependent ones. If  $\tau_0$  is treated as a constant, then

$$E_a = R \frac{\partial \ln \tau}{\partial (1/T)} \quad \text{and} \quad E_a = R \ln \left( \frac{\tau_m}{\tau_0} \right) T_m, \quad (7)$$

where  $T_m$  is the temperature of the peak maximum (K) and  $\tau_m$  is the reciprocal value of the angular frequency of the measurement (sec). In this case, the activation energy plotted *versus* the absolute peak temperature should give a straight line through the origin and the slope of this line would be equal to  $R \ln \tau_m/\tau_0$ . If a distribution of relaxation times is involved one can use the same reasoning for the *average* activation energy and the peak temperature. The existence of such a linear relationship is demonstrated by fig. 2. The relaxation ratio  $\Delta$ , or the magnitude of the internal friction peak  $(\tan \delta)_{\max}$ , is given by:

$$\frac{1}{2} \Delta \approx (\tan \delta)_{\max} = aCW, \quad (8)$$

where  $W$  is the energy absorption per relaxing unit (J),  $C$  is the concentration of relaxing units ( $m^{-3}$ ) and  $a$  is a proportionality constant ( $m^3/J$ ).  $W$ , the absorption strength, is supposed to be constant for each particular combination of two dissimilar alkali ions and does not depend on the mixing ratio of the alkali ions. The concentration factor  $C$  can vary with the mixing ratio and the type of alkali ions.

### 3. The distribution of relaxation times

The observed internal friction peaks are much broader than the peaks calculated for a single relaxation time. For a thermally activated process having a single relaxation time, the width at half-height on a temperature scale should be

$$\Delta \left( \frac{1}{T} \right) = \frac{R}{E_a} \ln \left( \frac{2 + \sqrt{3}}{2 - \sqrt{3}} \right) \approx 2.635 \frac{R}{E_a}, \quad (9)$$

where  $\Delta(1/T)$  is the width at half-height ( $K^{-1}$ ),  $R$  is the gas constant ( $kcal/mol \cdot K$ ) and  $E_a$  is the activation energy ( $kcal/mol$ ). Previous work [27] has shown that the distribution of relaxation times for the single and the mixed alkali peaks in aluminosilicate glasses is asymmetric: a 'long drawn-out tail' at high  $\omega\tau$  values (low-temperature side of the peak) was observed. In the present work this asymmetry was noted as well. However, as it has been shown [27] that a log-normal distribution function can include 95% of the experimental data, the low-temperature tail of the peaks is neglected here and the log-normal distribution function  $\psi(z)$  is used as an approximation:

$$\psi(z) dz = (1/\beta\sqrt{\pi}) \exp[-(z/\beta)^2] dz, \quad (10)$$

where  $z$  is given by:  $z = \ln(\tau/\tau_m)$  and  $\tau_m$  is the mean relaxation time (sec). The parameter  $\beta$  in this equation is related to the relative width of the peaks in a unique way.  $\beta = 0$  represents a single relaxation time. When the relaxation peak becomes broader,  $\beta$  increases and the height of the peak is reduced. Therefore, a quantitative study of relaxation peaks should also include the changes in the distribution function. In the present work, the value of the  $\beta$  parameter was determined by comparing the experimentally observed width of the peak with the theoretical width, calculated from eq. (9), and by using table 4-2 from ref. [26], which contains numerical computations for the dependence of the relative peak width on the distribution parameter  $\beta$ , for log-normal distributions with  $\beta$  values between 0.00 and 5.00. It was found that  $\beta$  did not vary systematically with the type of relaxation (single, mixed or proton peak) or with the type of cations in the glass. An average value of approximately 4 was found for all peaks, except for some peaks, which occurred in the same temperature range as the proton-alkali peak. In these cases, the observed peak actually is the sum of two peaks, each with a  $\beta$  value of about 4. The present data are in good agreement with the results of Moore and Day, who obtained  $\beta$  values between 3.6 and 4.3 for internal friction peaks in aluminosilicate glasses.

## 4. Discussion

### 4.1. General

The introduction of a dissimilar alkali ion causes a new internal friction peak to

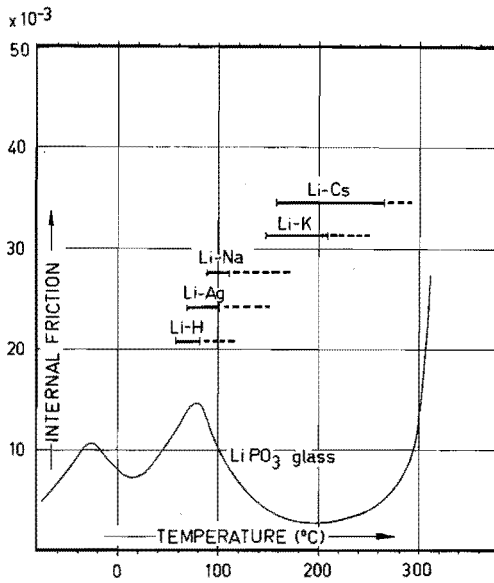


Fig. 1. Internal friction 'spectrum' for lithium metaphosphate glasses at 0.4 Hz. The bars indicate the temperature ranges where the various internal friction peak maxima are located. The dashed extensions of these bars represent thermal regions where the peaks are believed to occur as well. However, at these temperatures the various peaks were masked by other peaks or by the background relaxation.

occur at higher temperatures [9]. Each type of dissimilar alkali ion causes a separate mixed peak to occur, so that a glass which contains many sorts of alkalis will show a spectrum of mixed peaks [3]. This is illustrated by fig. 1 in which the temperature ranges are indicated for the various mixed peaks in lithium metaphosphate glass. Fig. 1 also demonstrates that the mixed peak is controlled by the less mobile alkali ion, in that the peaks are arranged along the temperature axis in the order of decreasing mobility of the second alkali. In general, these individual mixed peaks overlap in one glass, and cannot be observed separately. Only when the mobility of the involved ions differs sufficiently, do the peaks appear well resolved from each other in the damping spectrum, e.g. in a lithium metaphosphate glass containing small amounts of dissolved water and potassium or cesium ions, three internal friction peaks can be observed [20].

In fig. 2 the average activation energies of the various mixed alkali peaks, alkali-silver peaks, alkali-proton peaks and single alkali peaks are plotted *versus* the peak temperature at 0.5 Hz. One can see that there is no principal difference between the pre-exponential factor  $\tau_0$  of the various types of relaxations. The average value of  $\tau_0$ , calculated from the slope of this plot, is  $10^{-15.3}$  sec. These figures also show that

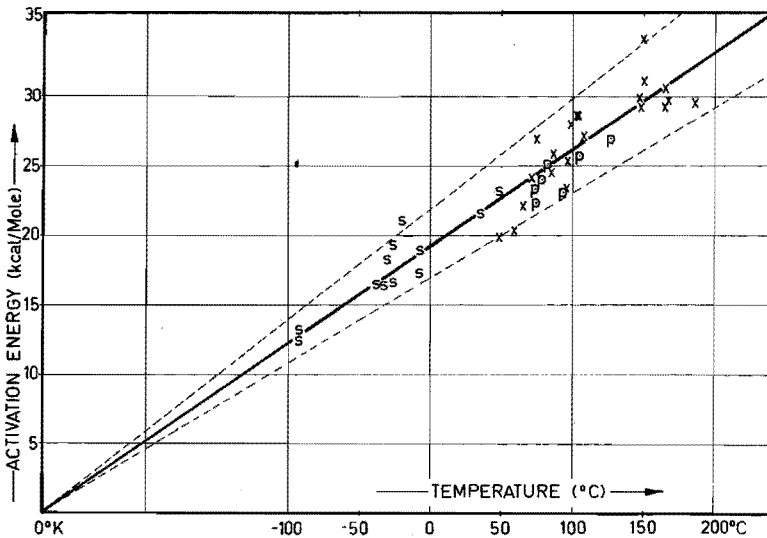


Fig. 2. Activation energies for the mechanical relaxation processes in lithium metaphosphate glasses, as a function of the peak temperatures at 0.5 Hz. The data points marked with S refer to single cation peaks, P refers to mixed proton-cation relaxations and X refers to the mixed cation peaks.

some spread in the pre-exponential factor does occur. The dashed lines in these figures correspond to  $\log \tau_0 = -15.3 \pm 0.7$  \*.

#### 4.2. The intermediate-temperature peak

In all of the single alkali glasses and in some of the mixed glasses, an intermediate-temperature peak could be observed. However, in some of the mixed alkali glasses, the intermediate peak may have been hidden since it occurred in the same temperature range as the mixed alkali peak, so that overlapping resulted. In these cases the peaks could not be observed separately and the collected data on peak magnitudes and peak temperatures are less accurate. In general, the intermediate-temperature peak is reduced in height and shifted to higher temperatures upon introduction of a second alkali, very similar to the changes that occur in the single alkali peak.

\* The rather low value for  $\tau_0$  is an indication of the fact that the relaxation process has an entropy of activation  $S_a$ . In the case in which no entropy is involved,  $\tau_0 = h/kT = 1.6 \times 10^{-13}$  sec or  $\log \tau_0 = -12.8$ . If there is entropy, it follows from the relation

$$\log \tau_0 = \log h/kT - S_a \ln 10/R$$

that  $S_a = 11.5 \pm 3.2$  cal/mol · K. The value for  $S_a$  is somewhat higher than found for various silicate glasses (4.4 to 7.7 cal/mol · K) [27].

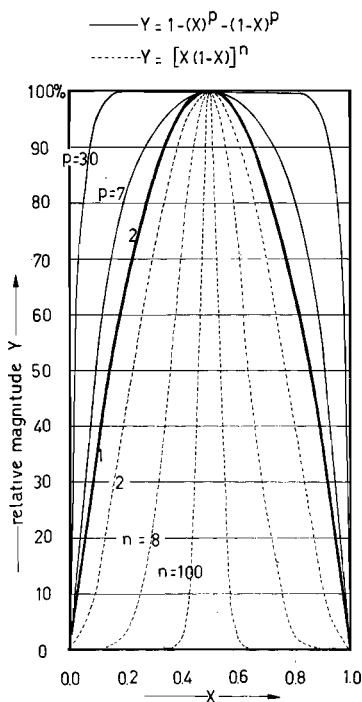


Fig. 3. Relative magnitude of the probability factors for various alkali ion configurations, as a function of the mixing ratio. The thick curve is a parabola and can be represented by either  $p = 2$  or  $n = 1$ .

From previous work on lithium [20] and sodium [19] metaphosphate glasses, it is known that this intermediate-temperature peak is actually a mixed peak caused by the interactions of protons and alkali ions, and that this peak would be absent in a water-free glass.

In this paper, the intermediate-temperature peak will not be treated differently from other mixed peaks, as it is felt that the proper mechanism for this relaxation process must be able to predict relations for the relaxation time and absorption strength, which are also applicable to non-alkali monovalent cations, such as  $H^+$  and  $Ag^+$ .

#### 4.3. The peak magnitude as a function of the mixing ratio of the alkalis

In a first approximation the dependence of the magnitude of the mixed peak on the composition can be represented by a parabola of the type  $c(x)(1-x)$ . The actual shape of the curve usually differs from this parabola in that the maximum is located slightly out of centre and that the top is flattened.

This parabola-like relationship strongly suggests that the mixed peak is caused by a process which requires the presence of both alkalis, e.g. if the mixed peak depended on the occurrence of pairs of dissimilar alkali ions or larger clusters of dissimilar alkali ions, the magnitude of the peak would be expected to vary as  $x(1-x)$  or  $\{x(1-x)\}^n$  respectively ( $n > 1$ ). However, these series of curves show much sharper maxima than are experimentally observed.

A broader maximum in the curve can be obtained by allowing  $n$  to have values between 1 and 0 and the experimental results can be represented adequately in this manner. The physical meaning of  $n$  values smaller than unity is that the requirements for the occurrence of the mixed alkali peak are reduced: dissimilar alkali ions *only have to be in each others vicinity or influence sphere*. In this case the number of 'influenced' ions can be expressed more easily by using different mathematics. Let  $n$  be the number of alkali ions in a volume of glass equivalent to the influence sphere of the alkali ions and  $x$  be the mole fraction of the dissimilar alkali ions. The probability,  $P$ , that the alkali ion in the centre of this sphere is not influenced by the presence of a dissimilar alkali, is equal to the probability that the central ion itself is non-dissimilar, multiplied by the probability that all ions inside this sphere are non-dissimilar. Thus

$$P = (1-x)(1-x)^{p-1} = (1-x)^p .$$

This is equal to the mole fraction of the uninfluenced ions of the first type. The fraction of the uninfluenced ions of the second type will be:  $(x)^p$ , so that the number of influenced ions will be:  $1-(x)^p - (1-x)^p$ . This mathematical representation is equivalent to the one used above; e.g.  $p = 2$  and  $n = 1$  both describe the possibility of the formation of dissimilar pairs.

Curves of this type are symmetric in  $x$  and  $1-x$  while the experimental data are not. One can introduce the desired asymmetry by assigning a different influence sphere to each alkali, so that the fraction of the influenced ions can be represented by  $1-(x)^p - (1-x)^{p'}$ . If a curve of this type is fitted to the experimental data on the magnitude of the mixed alkali peak as a function of the mixing ratio, typical values of 7 to 8 are obtained for  $p$ . This  $p$ -value can be converted to the average radius of the influence area. For metaphosphate glasses with a molar volume of oxygen of 27 cm<sup>3</sup>/mol the radius of the influence sphere has a typical value of 5 Å. The mathematical description used here is very similar to the one proposed by Hendrickson and Bray [25] and consequently leads to comparable results: Hendrickson and Bray calculated values of 5 to 6 Å for the interaction range of alkali ions in silicate glasses.

#### 4.4. *The peak magnitude as a function of the type of alkali*

The peak magnitude depends strongly on the type of alkali ions (figs. 4 and 5). The combination of Na and K ions causes a mixed peak which is more than three times larger than the Li-Cs mixed peak [4]. In addition to that the relaxation time  $\tau$  varies with the alkali type. The present data are in good agreement with the result

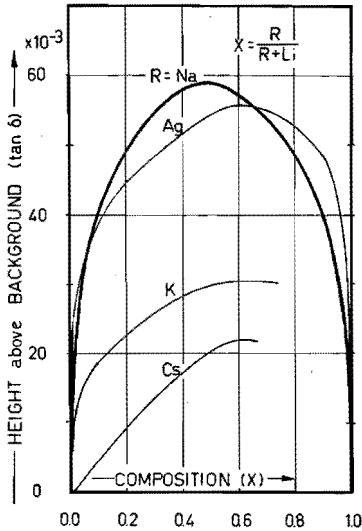


Fig. 4. Heights above background of the mixed cation peaks in lithium metaphosphate glasses as a function of the mixing ratio.

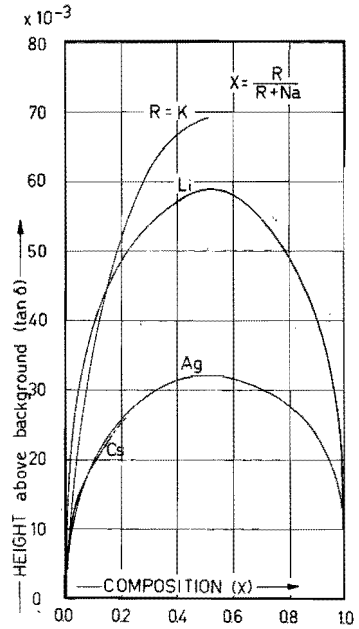


Fig. 5. Heights above background of the mixed cation peaks in sodium metaphosphate glasses as a function of the mixing ratio.

Shelby and Day obtained for silicate glasses [1]. In fig. 6 it can be seen that the magnitude of the mixed peak in metaphosphates depends on the size of the alkali ions in the same way as in silicate glasses. This can also be observed for the activation energy in fig. 7. In general the mixed peaks in metaphosphate glasses are about twice as large and the activation energy is slightly larger. The silver-containing glasses differ from the alkali glasses in that they do not fit so well on these curves. This discrepancy is attributed to inaccuracies in the data as well as to the fact that the ion radius ratio is not the exact quantity that determines the magnitude of the relaxation peak. It is believed that for a coupled reorientation under influence of a stress field, the difference in ionic volume, rather than the radius ratio, should determine the relaxation strength, and in the present work an attempt will be made to interpret the data on this basis. Hendrickson and Bray attribute the anelastic behaviour of the mixed alkali glasses to an association of dissimilar alkali ions, caused by a short-range electrodynamic interaction, arising from the difference in resonance frequency of the dissimilar alkali ions. This electrodynamic interaction will depend on the masses of the alkali ions and therefore suggests a relation between the difference of the reciprocal mass of the ions and the relaxation time of the mixed peak. This relation is not observed, nor does the reciprocal mass ratio correlate well with the magnitude of the peaks.

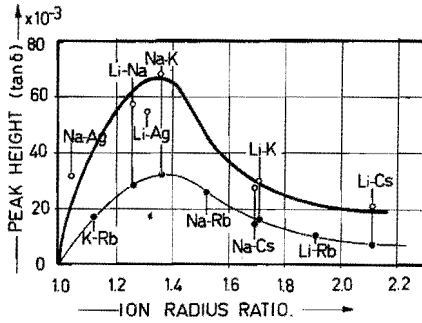


Fig. 6. Heights above background of the mixed cation peaks in metaphosphate and trisilicate glasses, as functions of the cation radius ratio. The solid circles refer to the trisilicate glasses and were obtained from ref. [1]. The open circles refer to the metaphosphate glasses.

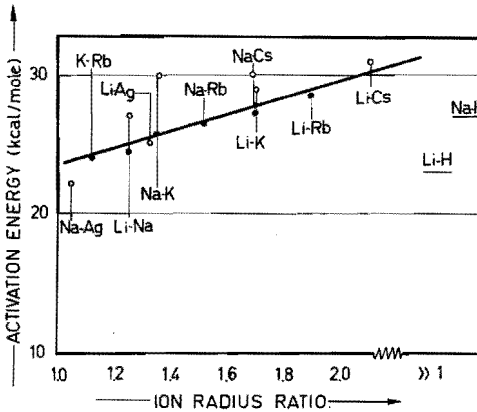


Fig. 7. Activation energies of the mixed cation peaks in metaphosphate and trisilicate glasses versus cation radius ratio. The solid circles refer to the trisilicate glasses and were obtained from ref. [1]. The open circles refer to the metaphosphate glasses.

If one assumes that the absorption strength,  $W$ , of the mixed relaxation is a linear function of the volume difference between the alkali ions involved, one can calculate the relative concentration of relaxing units from eq. (8):

$$W = \text{constant} (v_1 - v_2)$$

so that  $(\tan \delta)_{\max} = \text{constant} a (v_1 - v_2) C$  and  $C_{\text{rel}} = (\tan \delta)_{\max} / (v_1 - v_2)$ .

This relative concentration,  $C_{\text{rel}}$ , correlates with the mobility of the associated ions, in that mixed peaks observed at relatively high temperatures are related to glasses with a low concentration of relaxing units.

The peak temperature at constant frequency is a linear function of  $\log \tau$  and



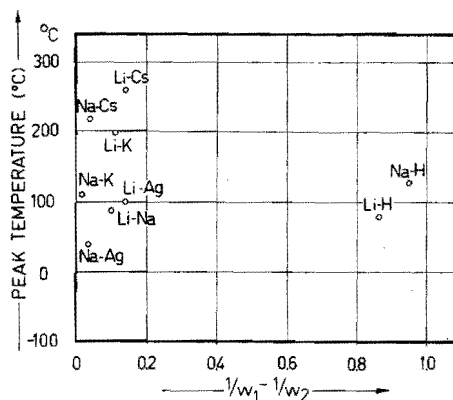


Fig. 8. Temperatures of the mixed cation internal friction maxima at 0.5 Hz in metaphosphate glasses *versus* the difference in reciprocal mass of the cations.

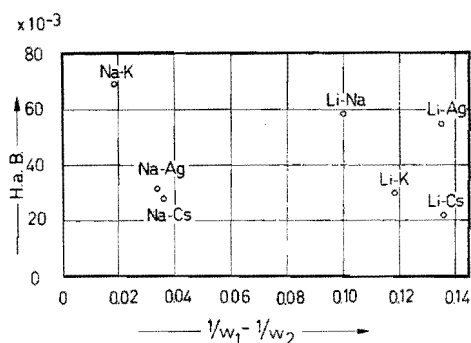


Fig. 9. Magnitudes of the mixed cation relaxations in metaphosphate glasses *versus* the difference in reciprocal mass of the cations.

therefore it is used here as a measure of the relaxation time. As a result of the fact that the pre-exponential factor in the relaxation time does not vary with the composition, an increase in the mean relaxation time will be observed as a shift of the peak maximum to higher temperatures, at constant measuring frequency. For similar reasons, the peak temperature also gives information about the mobility of the involved ions and the activation energy.

In metaphosphate glasses, the relaxation time of the mixed peak can be represented as a function of the volume difference of the alkali ions. This relationship does not only hold for ordinary mixed alkali glasses, but also includes the extreme cases in which protons and silver ions are substituted for alkali ions (fig. 11). The behaviour of mixed alkali glasses can be understood to a large extent, by assuming a short-range interaction between dissimilar alkali ions; this will reduce their mobility.

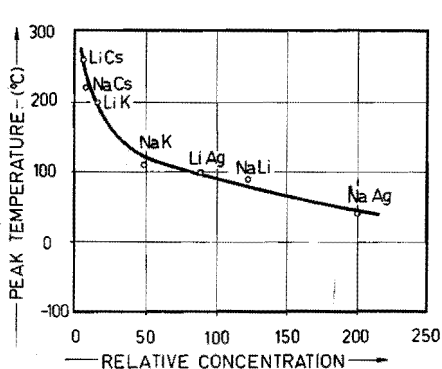


Fig. 10. Temperatures of the mixed cation internal friction maxima at 0.5 Hz in metaphosphate glasses, as a function of the relative concentration of relaxing units. The relative concentration has been computed by assuming that the absorption strength of the relaxing units is proportional to the volume difference of the cations.

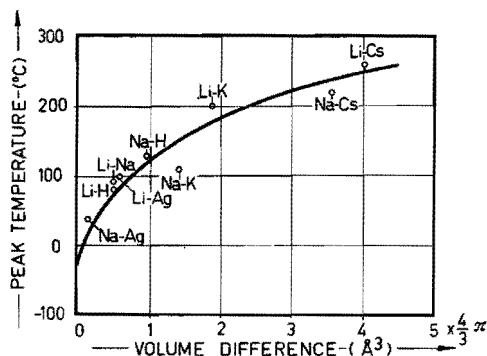


Fig. 11. Temperatures of the mixed cation internal friction maxima at 0.5 Hz in metaphosphate glasses as a function of the volume difference of the cations.

The assumption that this interaction is a result of different resonance frequencies of the alkali dipoles is not confirmed by the present work, as the dependence of this interaction on the masses of the ions is not observed. The exact nature of this interaction remains unknown.

#### 4.5. The density and molar volume of oxygen

Many physical properties show large deviations from linearity upon mixing the alkalis. The density and the molar volume of oxygen appear to be the least affected in this respect [28]. Both quantities vary almost linearly with the mixing ratio and the size of the alkali ions.

The silver-containing glasses differ from the alkali glasses in that they are relatively more compact: the molar volume of oxygen in silver metaphosphate glass is equal to the molar volume of oxygen in a hypothetical alkali metaphosphate glass, with an alkali ion radius of 1.02 Å, whereas the Goldschmidt radius for silver ions is 1.13 Å.

In this paper, the value of 1.02 Å is used for the radius of the silver ions.

#### 4.6. The dielectric losses

The dielectric losses of the various glasses were measured at 3 kHz at temperatures between 40 and 160°C. Under these conditions the losses are mainly caused by alkali ion migration. The introduction of a second alkali reduces the losses and increases the activation energy for alkali ion migration. In this respect the dielectric behaviour

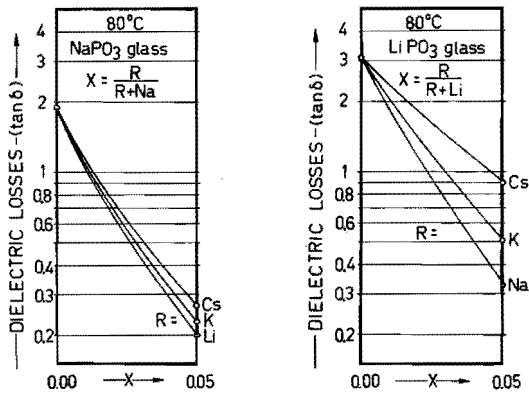


Fig. 12. Blocking effect of dissimilar alkali ions. The curves show the observed reduction in the dielectric losses at 3 kHz and 80°C upon replacement of 5 mol % of the originally present alkali ions with dissimilar alkali ions, in lithium and sodium metaphosphate glasses respectively.

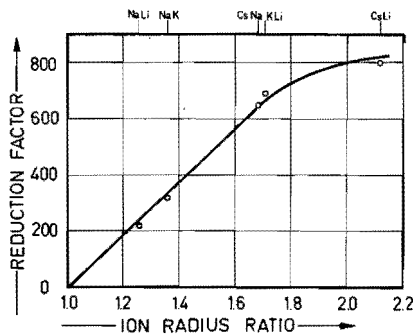


Fig. 13. Reduction factor for the dielectric losses at 3 kHz and 80°C, obtained by mixing the alkalis, for various alkali pairs.

is in good agreement with the diffusion data and the single alkali mechanical losses [10–12]. The reduction in the dielectric losses upon alkali substitution depends on the size of the second alkali ion. The smallest ions have the largest blocking effects, as can be seen from the initial slopes of the loss isotherms in fig. 12. The location of the minimum in the loss *versus* composition curve also depends on the type of alkali that is introduced, but here the largest ions cause the deepest minimum. The decrease of the dielectric losses by mixing the alkalis can be expressed in a reduction factor, being the ratio of the average of the dielectric losses of the two single alkali glasses and the losses in the mixed alkali glass with the lowest losses. A plot of this reduction factor *versus* ion radius ratio does not show a maximum for a IRR value of approximately 1.4 (corresponding to the Na–K ratio); the lowest dielectric losses were observed in the Li–Cs glass (fig. 13).

The maximum for the mechanical mixed peak does not coincide with the minimum for the electrical mixed alkali effect. Using the concept that some mobility-reducing interaction will occur between dissimilar ions which are separated by distances of 5 Å or less, it can be understood that the smallest dielectric losses will be observed in the glasses which will form associated ions of the lowest mobility: in a metaphosphate glass, containing equal amounts of two alkalis, about 98% of the alkali ions have a dissimilar alkali ion within a distance of 5 Å and are thus 'associated'. The minimum value of the losses therefore can be seen as a rough measure of the mobility of the associated species. This mobility is believed to decrease in the order Li–Ag, Li–Na, Li–K and Li–Cs. If the mixed alkali peaks are also caused by these associated ions, one would expect the relaxation times of the mixed peaks to display the same order. From the temperatures of the mixed peak maxima at 0.5 Hz we can indeed observe the same order of mobility (cf. fig. 1). Furthermore, the fact that the activation energy for the dielectric losses approaches the activation energy for the mechanical mixed peak in the completely mixed glasses (part I), can be seen as an additional indication that both phenomena are controlled by the same property: the mobility of the associated ions. The occurrence of a deep minimum in the dielectric losses of mixed alkali glasses, as a function of composition, is not restricted to the low-temperature range of the glasses; Kostanyan [29] even observed maxima in the resistivity of molten mixed alkali borate glasses up to temperatures of 800 and 1000°C.

Therefore the dielectric losses as a function of composition will also show a minimum if they are measured under the same temperature and frequency conditions as used for the mechanical mixed peak (150 to 350°C and 2 kHz). The mechanical losses show a maximum under these conditions and it can be concluded that the dielectric absorption strength of the associated ions is very small, or zero, compared to the mechanical absorption strength.

#### 4.7. *Relaxation mechanism*

The mixed alkali peak can be characterised by the following properties:

- (a) The magnitude of the peak is related to the concentration of both alkalis and the peak should be attributed to a mechanism in which both dissimilar alkali ions participate in an active way.
- (b) In a first approximation this mechanism should be symmetric, as the occurrence of a mixed alkali peak does not depend on which of the two alkalis is considered to be 'foreign'. This second alkali may be larger or smaller than the initially present alkali.
- (c) Combined diffusion and internal friction studies have shown that the magnitude of this relaxation is controlled by the diffusion coefficient of the slowest moving species.
- (d) The pre-exponential factors in the relaxation times of the single and the mixed alkali peaks, do not differ significantly. Neither do the widths of the distribution functions of the relaxation times. Therefore, it is very likely that both peaks are related to the same basic process: alkali diffusion.

(e) From the comparison of the magnitudes of the dielectric and mechanical losses one can conclude that the associated ions can move under the influence of a mechanical force in such a way that no electric charge transport results.

(f) The magnitude of this relaxation correlates better with size differences than with mass differences.

(g) The magnitude of this relaxation, as a function of composition can be explained by using a model, based on a short-range interaction between dissimilar alkali ions. The typical interaction range is approximately 5 Å. The nature of this interaction is unknown.

(h) If the mechanical absorption strength is assumed to be proportional to the volume difference of the alkali ions, the concentration of the relaxing units correlates well with the mobility of the associated ions.

The mixed alkali peak is believed to be caused by a coupled diffusion process of dissimilar alkali ions, located in each others vicinity at distances not exceeding 5 Å. The coupling of the diffusion processes is believed to be caused by electric forces: a jump of one ion in the direction of the mechanical stress field will disturb the electric neutrality of the initial configuration and set up an electric field which opposes the mechanical field. Nearby positioned ions of the same size are unable to contribute to this stress-induced diffusion process as the mechanical force  $v\nabla\sigma$  is equilibrated by the electric counterforce  $q\nabla U$  (the volume of the ion is indicated by  $v$ ,  $\nabla$  is the Nabla operator ( $\delta/\delta x$ ,  $\delta/\delta y$ ,  $\delta/\delta z$ ),  $\sigma$  is the mechanical stress,  $q$  is the electric charge of the ion and  $U$  is the electric potential of the counterfield).

If ions of different sizes are located in each others vicinity, the equilibrium between mechanical and electric forces cannot be obtained as the ion with the larger volume will always have a larger susceptibility to the mechanical field and the ion with the smallest volume (higher field strength) will be more susceptible to the electric counterfield, e.g. if  $v_1\nabla\sigma(r) = q\nabla U(r)$ , then  $v_2\nabla\sigma(r) \neq q\nabla U(r)$  because  $v_1 \neq v_2$ .

The assumption that  $\sigma(r)$  and  $U(r)$  are equal for both ions can be seen as a formulation of the requirement that the ions should be positioned very close to each other. It is assumed that this requirement is met if the ions are located within a distance of 5 Å from each other. Vicinal dissimilar ions will diffuse in opposite directions. The larger ion will diffuse in the direction of the mechanical field, and absorb an amount of mechanical energy proportional to  $(v_1\nabla\sigma)\lambda$ ; the smallest ion will jump in the direction of the electric counterfield, and restore an amount of mechanical energy proportional to  $(v_2\nabla\sigma)\lambda$ .  $\lambda$  is the jump distance of the ions.

The total effect of this process will be a mechanical relaxation proportional to the difference in volume of the participating ions ( $v_1 - v_2$ ) and an electric relaxation, equal to zero as both ions have equal electric charge. The relaxation time of this coupled process will be governed by the mobility of the slower moving ion. This model has the required symmetry, in that it is not essential whether the most mobile ion species have the larger or the smaller radius, the essential point is that the radii are different. It is not essential that the relaxation times of the two ion species are different. If  $\tau_1 \approx \tau_2$ , the larger ion will still be more susceptible to mechanical forces

than the smaller ion and a coupled diffusion in opposite directions will result. In this case the magnitude of the relaxation and the relaxation time will of course be sensitive to the mobilities of both ion species. In single alkali glasses the electric cross-effect will impose a barrier on the stress-induced diffusion and restrict the number of jumps that can be made, because the electric counterfield,  $\nabla U(r)$ , is proportional to the number of ions that have left their equilibrium sites. The observed single alkali relaxations are, in general, small compared to the mixed relaxations. The mixed relaxation process becomes possible at temperatures where both types of alkali ions can make stress-induced jumps. Under these conditions one of the alkalis (the smaller one) can always prevent the build-up of the electric counterfield, by jumping in the opposite direction and can act as a kind of 'short-circuit' for this cross-effect. The main result of this is that the number of jumps is no longer restricted by electrical forces and one can expect a much larger relaxation than in the case of single alkali diffusion. The principle difference between the single and the mixed relaxation can also be envisaged in the following way:

The single alkali peaks are caused by the stress-induced diffusion of particles with an electric charge in a *non-conducting* medium. The mixed alkali peaks are caused by the stress-induced diffusion of the less mobile alkali ions, but these ions diffuse in a *conducting* medium, as there are dissimilar alkali ions present, which have *shorter relaxation times*. From this it can readily be understood why the dielectric losses of glasses only correlate with the single alkali relaxation and why the mixed relaxation is not electrically observed. If one considers the stress-induced diffusion of the second (less mobile) alkali as the mechanism of the mixed peak, and the diffusion of the first alkalis in the opposite direction as a consequence of this, then of course the mixed alkali peak will be electrically active. However, the electric relaxation of the second alkali cannot be measured, as it will be wiped out faster (by the more rapid diffusing first alkalis), than it can build up. If one considers the cooperative diffusion of both types of alkali as the cause of the mixed peak, then the relaxation is truly electrically inactive, as no net electric charge is transported. Although the distinction between these two view points is merely a matter of formalism, the authors are in favour of the latter one: as the presence of both alkalis is essential for the occurrence of the mixed peak, the mechanism should include both alkali jumps, and is therefore electrically inactive. On the basis of this model, 'mixed peaks', which are electrically inactive, can be expected in any material containing at least two types of electric charge carriers with different charge to volume ratios. In case the mobility of the charge carriers differs substantially the relaxation time of the mixed process will be about equal to the relaxation time of the slower moving species. The magnitude of the relaxation will depend on the volume difference between the charge carriers.

In this respect, it is not surprising that protons and non-alkali monovalent cations like  $\text{Ag}^+$  and  $\text{Cu}^+$  can cause a 'mixed alkali' peak in glasses. The combination of divalent cations should give a similar mixed peak, but this peak will be located at higher temperatures, as the mobility of divalent ions is smaller. This proposed mech-

anism for the mixed alkali peak does not explain the reduction of the alkali mobility, observed upon the introduction of a second alkali; it merely explains how the mixed peak is related to the properties of the individual alkali ions.

## 5. Conclusions

The internal friction behaviour of mixed alkali metaphosphate glasses is similar to that of mixed alkali silicate glasses in that three relaxation peaks can be observed between  $-40^{\circ}\text{C}$  and the annealing range at 0.5 Hz. The low-temperature single alkali peak which has been attributed to the stress-induced movement of alkali ions, correlates with the dielectric losses, both for the magnitude and the activation energy. The intermediate-temperature peak, observed in the single alkali and in some of the mixed glasses, is recognized as a mixed proton-alkali peak and this relaxation can be described quantitatively in the same way as the high-temperature mixed peak. The high-temperature mixed peak is attributed to a stress-induced coupled movement of dissimilar alkali ions, in opposite directions, in such a way that no net electric charge transport will occur. The energy absorption of this mechanism is believed to be proportional to the volume difference of the ions. The coupling between the two diffusion processes is believed to be caused by an electric cross-effect and a mixed peak is predicted for any electrically insulating material containing dissimilar charge carriers.

The distribution of relaxation times and the pre-exponential factor in the relaxation time are basically the same for the single and mixed processes. Average values of  $\beta = 4$  and  $\tau_0 = 10^{-15.3}$  were obtained respectively.

The mobility reducing interactions between dissimilar alkali ions proposed by Hendrickson and Bray are useful for a more quantitative description of the mixed alkali effect. The interaction range in metaphosphate glasses is approximately 5 Å. However, the proposed nature of these interactions and their relation to the alkali ion mass differences, are in disagreement with the present results. The densities and the molar volumes of oxygen of the glasses are nearly linear functions of the compositions.

Silver ions in metaphosphate glasses act like alkali ions with a radius of 1.02 Å. The dielectric losses of the glasses show a deep minimum as a function of the alkali mixing ratio and are in this respect similar to the dielectric losses in silicate glasses.

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## THE INFLUENCE OF DISSOLVED WATER ON THE INTERNAL FRICTION OF LITHIUM METAPHOSPHATE GLASSES CONTAINING 1% POTASSIUM METAPHOSPHATE

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A series of lithium metaphosphate glasses, containing different amounts of water, was prepared. The water content was determined from the weight-loss of specimens during heating in vacuum.

It is found that dissolved water influences the internal friction and dielectric losses, in the same way as additions of dissimilar alkali ions do. With respect to the physical properties under discussion, one can consider water as an 'alkali-oxide'.

The intermediate temperature peak is increased in magnitude and shifted to lower temperatures with increasing water content. Extrapolation of the present results to the water-free composition shows that the intermediate temperature peak will be absent in the water-free glass.

### 1. Introduction

Recent investigations [1–6] have emphasized the influence of small amounts of dissolved water on the physical properties of glasses. Several studies have shown that the intermediate temperature peak in the internal friction versus temperature curves is governed by the water content and that its relation to the presence of non-bridging oxygen ions is less pronounced than was initially assumed.

The influence of water on the second peak in sodium metaphosphate glasses has been well studied by Day et al. The present study was undertaken on lithium metaphosphate glass containing 1% potassium metaphosphate, as preliminary work [5] had shown that in this glass the mixed alkali peak and intermediate temperature peak occur at temperatures which are more than 100°C apart from each other. In this way, interactions between these two relaxation phenomena can be studied.

### 2. Experimental procedure

All glasses were obtained from the same melt but at different heating times and

Table 1  
Melting conditions and resulting water contents of metaphosphate glasses.

Batch no.	Melting temp. (°C)	Melting time	Special treatment	Sample weight (g)	Weight-loss (mg) on thermo-balance in vacuum at 750°C	Water content (Mole %)
H1	800	15 min	none	2.5597	19.5	7.28
H2	850	15 min	none	2.1538	13.2	5.84
H3	900	30 min	none	2.2905	8.4	3.50
H4	950	45 min	none	2.3770	5.2	2.09
H5	950	1 h	dry O <sub>2</sub>	2.1976	3.1	1.33
H6	950	4 h	dry O <sub>2</sub>	3.1571	2.6	0.79

Table 2  
Numerical data on wet lithium-potassium metaphosphate glasses. All temperatures listed are in °C, frequencies in Hz, height above background of internal friction peaks and dielectric losses (tan δ), and activation energies in kcal/mole.

Batch no.	x	annealing temp. (°C)	Single alkali peaks		Proton-alkali peaks			Mixed alkali peaks		Dielectric loss at 80°C, 3 kHz	
			temp. (°C)	H.a.B. (tan δ × 10 <sup>3</sup> )	temp. (°C)	freq. (Hz)	H.a.B. (tan δ × 10 <sup>3</sup> )	temp. (°C)	H.a.B. (tan δ × 10 <sup>3</sup> )	(tan δ × 10 <sup>3</sup> )	E <sub>a</sub> (kcal/mole)
H1	0.073	280	-16	3.0	60	0.64	21.0	204	6.0	480	19.50
H2	0.058	291	-20	4.0	59	0.51	19.1	204	8.2	600	18.40
H3	0.035	300	-24	6.5	62	0.48	16.8	198	10.0	1000	18.10
H4	0.021	305	-29	7.3	70	0.56	12.8	202	9.4	1500	17.30
H5	0.013	308	-40	9.9	78	0.50	10.0	197	10.3	1950	16.50
H6	0.008	315	-38	10.6	82	0.38	7.3	195	10.0	2300	16.60

temperatures. The glass melt was prepared by heating a quantity of about 100 g of lithium-dihydrogen orthophosphate, together with an addition of 1 mole % potassium-dihydrogen orthophosphate, in an electric furnace at 700°C. After the steam evolution has ceased, the temperature was raised to 800°C and the melt was allowed to stand for 15 min to promote fining. At that time the first sample (H1) was taken from the melt and the furnace temperature was raised to 850°C so as to obtain sample H2 and so on. The last sample, H6, was taken after the melt had been treated at 950°C for four hours with dried oxygen. The heat treatment figures and melting conditions of samples H1 to H6 are listed in table 1.

At each temperature, three samples were taken:

- (1) Fibers, about 0.5 mm in diameter, for the internal friction measurement at 0.5 Hz.
- (2) Discs, cast in preheated graphite molds and approximately 25 mm in diameter and 2 mm thick, for the dielectric loss measurements.
- (3) Samples of about 3 g each, for the determination of the water content.

All specimens were stored in water-free oil and annealed prior to measurement. The water content of the glasses was determined with a Mass Flow Vacuum and Gas Atmosphere Thermobalance, Model HF-H5, Stanton Instruments Ltd., at a temperature of 700°C and a pressure ranging from  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  Torr. In order to simplify the comparison of the present data with internal friction data of mixed alkali glasses, the water content is expressed in mole % of the total amount of monovalent cations in the glass and indicated by  $x$ :

$$x = \text{H}_2\text{O}/(\text{H}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O}) .$$

A detailed description of the measuring techniques is given in ref. [4].

### 3. Results and discussion

The internal friction of the fiber specimens was measured at 0.5 Hz with a torsion pendulum, working under vacuum of approximately  $20 \times 10^{-3}$  Torr. The results are shown in fig. 1 and table 2. One can clearly observe the presence of three distinct relaxation phenomena, between  $-100^\circ\text{C}$  and the annealing range. From earlier work on mixed alkali metaphosphate glasses [5], it is known that the peak located at  $-40^\circ\text{C}$  is the single alkali peak, attributed to the stress-induced motion of lithium ions. It is also known that the Li-K mixed alkali peak occurs at approximately  $200^\circ\text{C}$  at 0.5 Hz. This is the high-temperature peak in the glasses presently studied.

The pure lithium metaphosphate glass exhibits two internal friction peaks between  $-100^\circ\text{C}$  and the annealing range, viz.: the Li single alkali peak at low temperature and an intermediate temperature peak, attributed to an interaction of lithium ions and protons. This interaction peak with protons is located at approximately  $80^\circ\text{C}$  at 0.5 Hz. Glass H6 was prepared from a melt that had been bubbled with

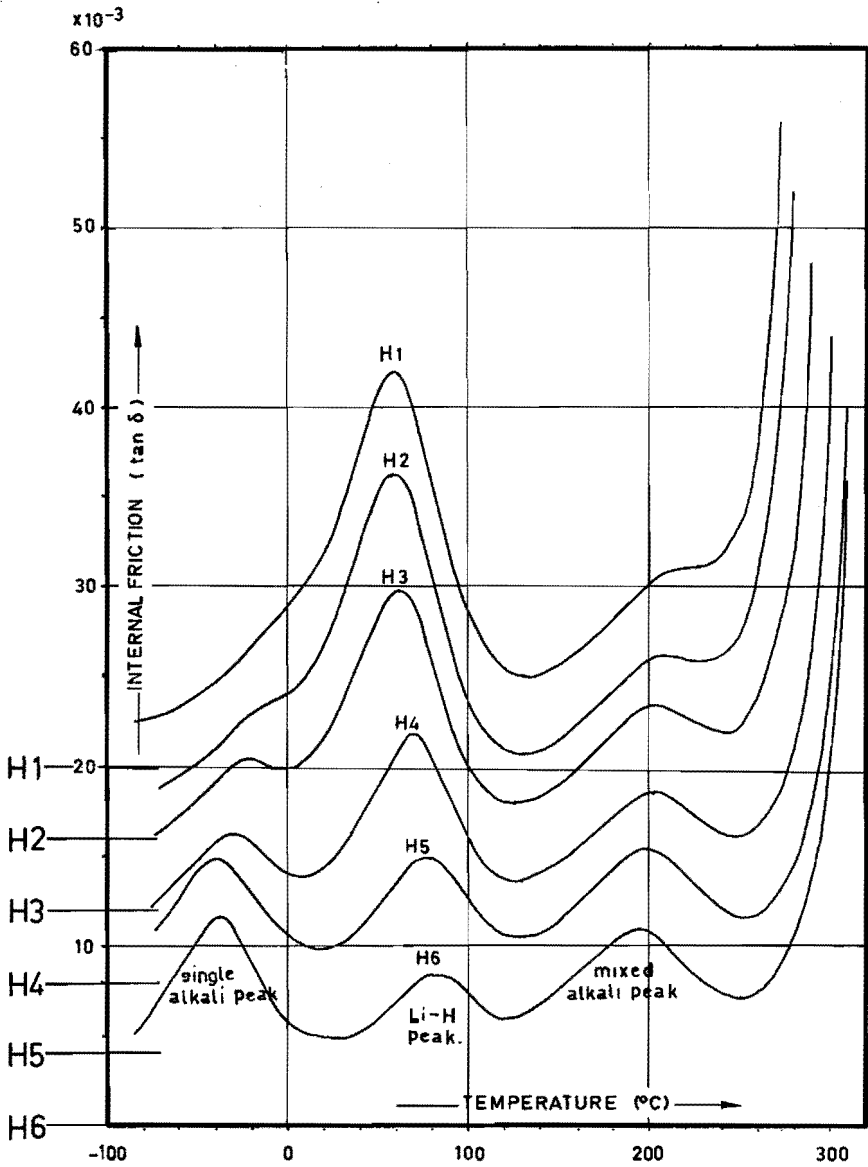


Fig. 1. Internal friction curves at 0.5 Hz for Li-K metaphosphate glasses, containing small amounts of dissolved water. Note that the curves are shifted upward along the vertical axis. The proper zero level for each curve is indicated at the left vertical axis.

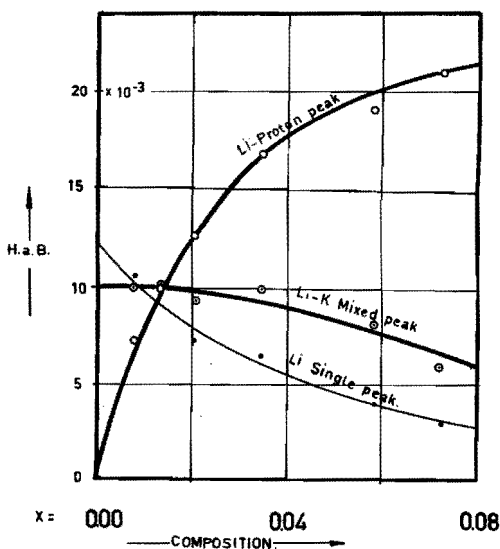


Fig. 2. Height above background of internal friction peaks at 0.5 Hz of Li-K metaphosphate glasses, as a function of composition.

dried oxygen gas for four hours at  $950^{\circ}\text{C}$  and which consequently contains very little water. The weight-loss of this glass, as determined with the thermobalance, corresponds to a water content of about 0.8 mole %. Glass H1 was prepared from a melt that contained much larger amounts of water and had the largest water content throughout these series: 7.2 mole %. The other glasses have intermediate water contents. Fig. 1 shows the large influence of this small amount of water on the internal friction: the single alkali peak is reduced in magnitude and shifted to higher temperatures. This shift is an indication of an increase in the activation energy for lithium diffusion and a decrease in the lithium mobility. At a water content of 6 mole % this peak is only visible as a shoulder on the low temperature side of the lithium-proton peak, and at even larger water content, the single alkali peak merges completely into the lithium-proton peak.

The initially small lithium-proton peak increases rapidly in magnitude on adding small amounts of water and finally dominates the general appearance of the internal friction curves. At the same time this peak shifts to lower temperatures, an indication of a decrease in the activation energy and an increase in the mobility of the rate-controlling species in this relaxation process. As this peak is believed to be caused by a coupled movement of protons and lithium ions, the rate-controlling factor would be the mobility of the protons.

Fig. 2 shows the height above background of the internal friction peaks at 0.5 Hz as a function of water content. Extrapolation to the completely dry glass, shows that in this glass the intermediate temperature peak (Li-H peak) will be completely

absent, or at least very small. The mixed alkali peak, located at 200°C at 0.5 Hz and attributed to a coupled movement, in opposite directions, of lithium ions and potassium ions ideally should not be influenced by small changes in the water content, as the concentration of both alkali ions remains unaffected. However, it appears that this mixed alkali peak is reduced in size and shifted to higher temperatures with increasing water content (figs. 1 and 4). Apparently, the activation energy of this peak is increased and the mobility of the rate-controlling potassium ions is decreased by the introduction of protons into the glass network.

The influence of the protons on the mobility of the potassium ions is in this respect identical to their influence on the mobility of the lithium ions, in that both species are blocked by the protons. The blocking effect of the protons on the lithium ions is not surprising, as this is very similar to the general observation that the introduction of a small amount of dissimilar alkali ions (which are immobile relative to the initially present alkali ions), will reduce the size of the single alkali peak and shift it to higher temperatures [9–12].

If one assumes that the alkali ions and protons are independently and randomly distributed through the glass network one can calculate from the chemical composition of the glasses that the average distance between protons and potassium ions is much larger than the distance between protons and lithium ions (about four times as large). Therefore one could expect that the blocking effect of the protons on the potassium ions would be negligible compared to the effect on the lithium ions. This conclusion is not correct as both blocking effects appear to have the same order of magnitude. From this it can be concluded that the distribution of protons is not independent of the alkali ion distribution. To some extent, the observed changes in the temperature and the magnitude of the Li–K mixed peak may be caused by the slight differences in measuring frequency and also by the relatively large shift of the background to lower temperatures.

The dielectric losses of the glasses were measured at 300, 3 000 and 30 000 Hz, at temperatures ranging from 40 to 160°C. Fig. 3 shows the loss isotherms (80°) and the calculated values of the activation energy for the losses. Under these conditions, the dielectric losses are mainly caused by the conduction of the specimens. One can observe that the introduction of water decreases the dielectric losses and increases the activation energy. The mechanical alkali-proton peak appears to be electrically inactive, as there is no simple relation between the magnitude of this peak and the dielectric losses. The activation energies of both processes also differ substantially.

From previous work it is known that the dielectric losses correlate well with the mechanical single alkali peak, both for magnitude and activation energy. This correlation can be verified once more from figs. 2, 3 and 4.

Fig. 4 shows the peak temperatures at a frequency of 0.5 Hz as a function of composition (water content) and can be interpreted so as to depict the changes in the activation energies of the mechanical relaxations. One can observe that the activation energies of both relaxation phenomena, controlled by alkali ions mobility

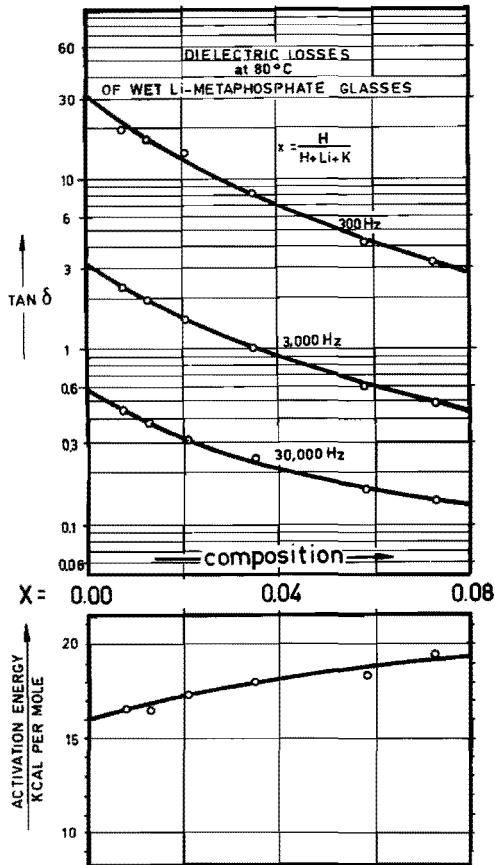


Fig. 3. Dielectric losses at 80°C and 300, 3 000 and 30 000 Hz as a function of the water content in Li-K metaphosphate glasses. The lower part shows the activation energy of the losses.

(single alkali and mixed alkali peak), respond in the same way to an increase in the water content, in that they are increased. In contrast with this, the activation energy of the relaxation controlled by the proton mobility, is reduced by dissolved water.

The top curve in fig. 4 is an isofriction curve for the network damping: the temperature at which the background reaches a value of  $\tan \delta = 30 \times 10^{-3}$  at 0.5 Hz, is plotted as a function of the water content and indicates the presence of a 'mixed alkali' effect in the viscous behaviour of the glasses. In general, the interaction of lithium-potassium metaphosphate glasses with 'water' exhibits all of the features of the well-known mixed alkali effect in that:

- (a) the magnitude of the single alkali peak is reduced.
- (b) the peak shifts to higher temperatures and eventually merges into the 'mixed-peak'.

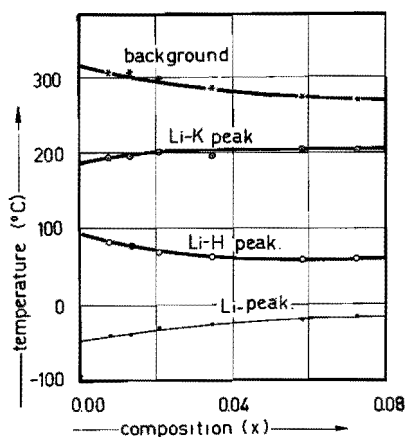


Fig. 4. Peak temperatures at 0.5 Hz as a function of the water content. The lower points refer to the single lithium peaks, the open circles to the lithium-proton peaks and the centred circles refer to the mixed Li-K peaks. The top curve is an isofriction curve for the background losses at  $\tan \delta = 30 \times 10^{-3}$ .

(c) a mixed peak is developed at higher temperatures, its size is much larger than the original single peak.

(d) the activation energy of this mixed peak is reduced.

(e) the dielectric losses are reduced.

(f) the activation energy of the dielectric losses is increased.

(g) the background shifts to lower temperatures.

In addition to that, the curvature of the plots of the above listed quantities versus composition is identical to the curvature of the corresponding curves in the mixed alkali metaphosphate glass systems [5]. This mixed alkali effect has also been observed upon the introduction of other monovalent cations, such as silver [5, 14] and copper [13], in an alkali glass and therefore it would be more proper to refer to it as 'mixed cation effect'.

#### 4. Summary and conclusions

Lithium metaphosphate glasses containing dissolved water, show an intermediate temperature peak in the internal friction curve at 0.5 Hz. The size of this peak depends on the amount of dissolved water in a similar way as the size of the mixed alkali peak depends on the concentration of a second alkali ion. From the extrapolation of the present results, to the water-free composition, it can be concluded that this peak would be absent in a really dry glass. The single alkali peak, the an-



nealing temperature and the dielectric losses of these glasses depend on the water concentration in the same way as on the concentration of a second alkali ion. Therefore, it is concluded that protons in a glass act like alkali ions and that the mechanism for the proton-alkali peak is identical to the one proposed for the mixed alkali internal friction peak: viz. a coupled movement of dissimilar cations in opposite directions, under the influence of the periodic stress on the network.

The introduction of small amounts of water also interferes with the mixed lithium-potassium peak, even at very low concentrations.

### Acknowledgement

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## THE INFLUENCE OF DISSOLVED HEAVY WATER ON THE INTERNAL FRICTION OF LITHIUM METAPHOSPHATE GLASSES CONTAINING 1% POTASSIUM METAPHOSPHATE

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A batch of very dry lithium metaphosphate glass, containing 1% potassium metaphosphate, was prepared and dissolved completely in nearly pure heavy water. From this solution, a series of glasses with varying deuterium oxide content was prepared. The internal friction and dielectric loss data were taken. The amount of dissolved deuterium oxide was determined from the weight-loss of specimens during heating in vacuum, and checked by means of tritium labeling. It is found that dissolved deuterium oxide influences the internal friction and dielectric losses, in the same way as additions of dissimilar alkali ions do (mixed alkali effect) so that one can say that deuterium behaves similarly to alkali ions.

A comparison of the present data with the results of a recent study on the influence of protons on the mechanical and electric properties in an identical host glass illustrates clearly that the mixed alkali effect is not governed by mass differences of the cations.

### 1. Introduction

The introduction of a dissimilar alkali ion in an alkali glass causes a new peak to appear in the internal friction versus temperature graph and reduces greatly the dielectric losses, conductivity and the coefficient for alkali self-diffusion [1–7]. The magnitudes and the activation energies of the observed losses reach extreme values in compositions in which both alkali ions are about equally abundant. In the literature, this particular behaviour is referred to as the “mixed alkali effect”. It has been shown that this phenomenon is very common: the mixed alkali effect has been observed in all kinds of glasses of different chemical nature and for all kinds of alkali combinations. It has also been found that typical mixed alkali behaviour can be induced by the introduction of non-alkali monovalent cations such as silver [8,9], copper [10] and protons [8, 11].

The magnitude of the mechanical relaxation which characterizes the mixed alkali glasses depends on the kinds of alkali ions, e.g. the combination of sodium and potassium ions causes a relaxation peak which is over three times as large as the peak which will occur in a comparable lithium–cesium glass [8].

Several explanations have been offered for this mixed alkali peak, e.g. (i) the exchange of position of two dissimilar alkali ions [13], (ii) reorientation of 'elastic dipoles' formed by adjacent dissimilar alkali ions [14], (iii) a combined diffusion process of dissimilar alkali ions, in which alkali ions with the larger radius jump in the direction of the applied stress field, while the smaller ions jump in the opposite direction to maintain electric neutrality [8], and (iv) the stress-induced migration of alkali ions, which are associated by electro-dynamical interactions, arising from the differences in resonance frequencies of the dissimilar alkali ions [15]. The first three listed explanations have in common that they suggest a dependence of the mixed peak magnitude on the difference in *size* of the dissimilar alkali ions. The latter suggests a quantitative relation between the mixed alkali effect and the difference in *mass* of the involved ions. In order to obtain an answer to the question whether the mixed alkali process is controlled by size or mass differences, the study of various mixed alkali systems can be helpful. However, one cannot study the effect of ion-mass differences and ion-size differences separately. The use of alkali isotopes does provide a method of measuring these effects independently, but the expected results from such minor changes render these experiments unattractive.

The recent recognition that protons in a glass do not act differently from alkali ions, offers a possibility of obtaining convincing results by comparing the mixed alkali effect caused by protons and alkali ions with the effect caused by deuterium ions and the same alkali ions.

## 2. Experimental procedure

### 2.1. Sample preparation

A mixture of 150 g of lithium-dihydrogen orthophosphate and 1.98 g of potassium-dihydrogen orthophosphate was placed in a platinum dish and heated in an electric furnace to 950°C. Oxygen gas, which had been dried over soda-asbestos and 'drierite', was bubbled through the glass melt for two hours at temperatures between 950 and 1000°C. The oxygen flow rate was approximately 2 cm<sup>3</sup>/sec. From previous work [8] it is known that this treatment will reduce the water content of the glass below 1 mol % (compared to the total alkali content). The melt was poured in small portions onto a stainless steel plate, flattened with an aluminum block and allowed to cool in a desiccator. The resulting glass was broken in small pieces (< 5 mm) and placed in a sealed flask, together with 100 g of heavy water (D<sub>2</sub>O Uvasol Merck 2919). The mixture was kept at a temperature of 35°C and stirred until the glass had dissolved completely (after 5 days). Then the solution was transferred to a large platinum dish and heated gently to boil off the excess deuterium oxide, until complete solidification would occur on cooling (formation of di-deutero orthophosphate). The dish was placed in an electric furnace and the temperature was raised to 800°C.

Table 1  
Melting conditions and resulting heavy water contents of Li-K metaphosphate glasses.

Batch No.	Melting temp (° C)	Melting time (min)	Special treatment	Sample weight (g)	Weight loss on thermobalance in vacuum at 750° C (mg)	Heavy water content (mol %)
D1	800	15	none	6.5040	41.0	5.42
D2	900	10	none	3.9991	24.2	5.20
D3	920	10	none	3.5173	17.6	4.30
D4	920	15	none	4.0347	19.1	4.06
D5	920	20	none	4.2456	14.0	2.83
D6	950	30	none	4.6639	12.0	2.21
D7	980	120	dry O <sub>2</sub>	4.1216	3.0	0.63
D8	900	15	none	3.6245	19.5	4.62

The first samples (D1) were taken after the melt had been allowed to stand for 15 min and the furnace temperature was raised to 900°C so as to obtain sample D2 and so on. The last sample (D7) was taken after the melt had been bubbled with dry oxygen for two hours at 980°C. The heat treatment figures and melting conditions of samples D1 to D7 are listed in table 1. Glass D8 was prepared by dissolving 30 g of lithium-potassium metaphosphate in 40 g D<sub>2</sub>O to which 100 μC of tritiated water (HTO) was added. The glass was prepared under conditions comparable to the melting conditions of glass D2 and the dielectric losses, weight-loss and radioactivity were determined. The radioactivity measurement will provide a check on whether the weight-loss data are in agreement with the actual amount of dissolved heavy water, and will also provide evidence to prove that the observed intermediate temperature peak is caused by the presence of heavy water and not by the small amount of common water, still present in the dried product.

Two types of specimens were made:

(1) Fibers, about 0.5 mm in diameter for the internal friction measurement at 0.4 Hz.

(2) Discs, cast in preheated graphite molds and approximately 25 mm in diameter and 2 mm thick, for the dielectric loss measurement and for the determination of the heavy water content. All specimens were stored in a desiccator over P<sub>2</sub>O<sub>5</sub> and annealed prior to measurement. To simplify the comparison of the present data with other internal friction data for mixed alkali systems, the heavy water content is expressed as the mole fraction of the total amount of monovalent cations and designated by  $x$ :

$$x = [D_2O] / ([D_2O] + [Li_2O] + [K_2O]).$$

Table 2  
Numerical data on Li-K metaphosphate glasses containing dissolved deuterium oxide.

Batch No.	$x$	Annealing temp (°C)	Frequency (Hz)	Single lithium peaks		Deuterium-lithium peaks		Potassium-lithium peaks		Dielectric losses at 80°C, 3 kHz	
				temp (°C)	H.a.B. ( $\tan \delta \times 10^3$ )	temp (°C)	H.a.B. ( $\tan \delta \times 10^3$ )	temp (°C)	H.a.B. ( $\tan \delta \times 10^3$ )	losses ( $\tan \delta \times 10^3$ )	$E_{act}$ (kcal/mol)
D1	0.054	280	0.380	-10	3.5	54	19.0	198	7.0	590	19.3
D2	0.052	285	0.370	-15	5.0	55	18.6	203	8.0	590	18.7
D3	0.043	288	0.380	-18	5.5	55	18.2	200	8.0	720	18.4
D4	0.041	297	0.364	-20	5.5	56	16.3	198	8.5	740	18.4
D5	0.028	297	0.337	-24	6.5	56	14.5	200	9.3	920	17.9
D6	0.022	302	0.341	-22	7.2	61	13.8	198	9.8	1260	17.9
D7	0.0085	316	0.541	-25	10.0	86	8.0	198	10.0	2200	17.5
D8	0.046	-	-	-	-	-	-	-	-	870	18.4

## 2.2. Measuring techniques

A detailed description of the internal friction and dielectric loss measurements is given in ref. [12]. The heavy water content of the glasses was determined with a 'Mass Flow and Gas Atmosphere Thermobalance', Model HF-H5, Stanton Instrument Ltd., at a temperature of 750°C and a pressure ranging from  $1 \times 10^{-5}$  to  $5 \times 10^{-5}$  torr. This method has been described by Day et al. [11].

The tritium activity of glass D8 was determined on three samples with a 'Liquid Scintillator Spectrometer', in Insta-gel and by using an internal standard method:

(1) A disc specimen of glass D8 was ground in the atmosphere (contact time two hours) and dissolved in common water. The  $D_2O$  content of the glass, determined in this way, appeared to be about 60% of the  $D_2O$  content as determined on the thermobalance.

(2) A disc specimen of glass D8 was dissolved in common water without grinding or exposure to the atmosphere. The  $D_2O$  content determined in this way appeared to be compatible with the  $D_2O$  content determined on the thermobalance.

(3) A specimen of glass D8 was dissolved in common water, after it had been heated in vacuum in the thermobalance. The residual activity of this sample was not significant as compared to the background radiation and less than 1% of the activity prior to the heating in vacuum.

## 3. Results and discussion

The internal friction of the fiber specimens was measured at 0.4 Hz with a torsion pendulum, working under a vacuum of approximately  $20 \times 10^{-3}$  torr. The results are shown in fig. 1 and table 2. One can observe three distinct relaxations between  $-100^\circ\text{C}$  and the annealing range. From earlier work on mixed alkali metaphosphate glasses, it is known that the low temperature peak at  $-20^\circ\text{C}$  is the single alkali peak, attributed to the stress induced motion of lithium ions. The size and the activation energy of this peak correlate well with the magnitude and the activation energy of the dielectric losses.

The high temperature peak, located at approximately  $200^\circ\text{C}$  in these glasses, is a mixed alkali peak caused by a coupled diffusion process of lithium and potassium ions, as discussed elsewhere [8].

The intermediate temperature peak, observed at approximately  $70^\circ\text{C}$ , depends on the amount of dissolved heavy water and exhibits typical 'mixed alkali features', in that the peak shifts to lower temperatures as larger amounts of heavy water are present, while the single alkali peak is reduced in size and shifted to higher temperatures. At even higher concentrations of heavy water the single alkali peak merges completely into the low temperature side of the 'deuterium peak'.

The large analogy in the properties of mixed alkali glasses and heavy water containing alkali metaphosphates can also be seen from the dielectric losses in fig. 4.

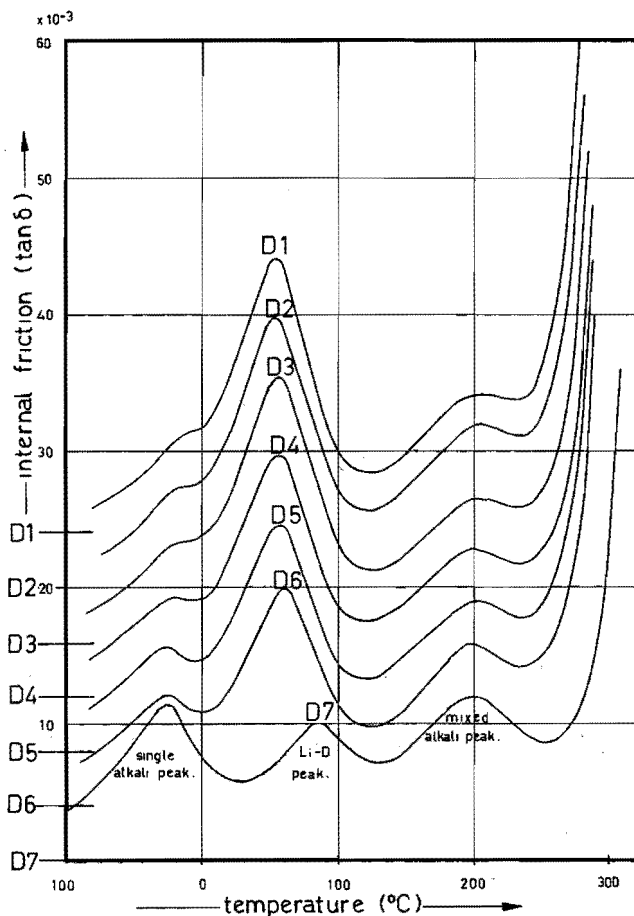


Fig. 1. Internal friction curves at 0.4 Hz for Ki-K metaphosphate glasses, containing small amounts of dissolved heavy water. Note that the curves are shifted along the vertical axis. The proper zero level for each curve is marked on the left vertical axis.

The introduction of heavy water causes the losses to be reduced considerably and the activation energy for alkali ion migration to be increased. It is also evident from this figure that the mechanical relaxation phenomenon associated with the intermediate temperature peak is electrically inactive, as the dielectric losses are minimal in the glass composition which has the largest lithium-deuterium mixed peak.

The intermediate temperature peak is assigned to a coupled motion of lithium and deuterium ions, identical to the mechanism which causes the regular mixed alkali internal friction peak. The rate controlling species in this coupled diffusion process are the deuterium ions.

From the experiments with the tritium labeled glass D8 the following conclusions can be drawn:

- (a) Tritium ions (and consequently deuterium ions and protons as well) are very

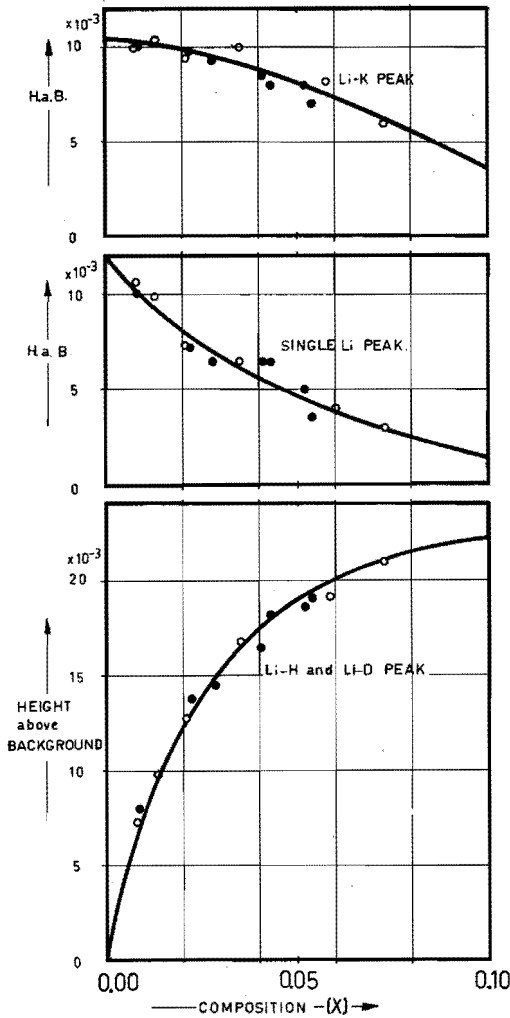


Fig. 2. Height above background of internal friction peaks at 0.4 Hz of Li-K metaphosphate glasses, as a function of composition. The composition is expressed as the molar ratio of the concentration of  $^2\text{H}$ -ions to the total concentration of monovalent cations in the glass. The open circles refer to proton containing glasses [8], the solid circles refer to the deuterium containing glasses from the present study.

mobile in lithium metaphosphate glasses at room temperature, as exchange with atmospheric water is achieved to an amount of 40% in a few hours.

(b) The weight-loss determined with the thermobalance is caused by the evaporation of heavy water. Heating the glass specimens for several hours at  $750^\circ\text{C}$  in a vacuum of approximately  $10^{-5}$  torr will remove the heavy water nearly completely.



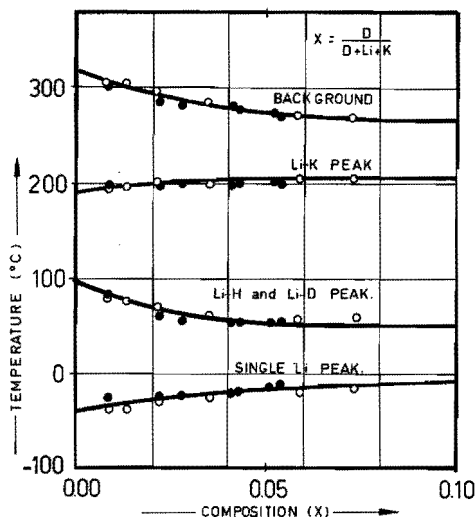


Fig. 3. Peak temperatures at 0.4 Hz as a function of the  $^n\text{H}_2\text{O}$  content. The open circles refer to the proton containing glasses from ref. [8] and the solid circles refer to the deuterium containing glasses of the present work. The top curve is an isofriction curve for the background losses at  $\tan \delta = 30 \times 10^{-3}$ .

(c) The glasses presently in study contain dissolved  $\text{D}_2\text{O}$ . The amount of dissolved  $\text{H}_2\text{O}$  is negligible.

#### 4. Comparison of deuterium-containing glasses with proton-containing glasses

Figs. 2 and 4 show the magnitudes of the internal friction peaks and the dielectric losses of deuterium- and proton-containing glasses. One can clearly observe that there is no systematic difference between both series of glasses. Apparently, *the magnitude of the mechanical relaxation and the dielectric losses is not governed by the difference in mass of the cations*. The activation energies of the mixed lithium-proton peak and the mixed lithium-deuterium peak are equal, and the peak temperatures at 0.4 Hz are also equal. Previous work has shown that the peak temperature is a direct measure for the activation energy of the process which causes the loss, and this rule has proved to hold well for the single alkali peak, single silver peak, mixed alkali peak, mixed alkali-silver peak and the mixed alkali-proton peak.

If one assumes that the resonance frequency of an alkali ion inside its negatively charged site is proportional to the square root of its reciprocal mass, in a first approximation, the resonance frequency difference between the lithium ions and protons would be more than twice as large as the resonance frequency difference between lithium and deuterium ions. These differences are large compared to those calculated for ordinary alkali pairs, such as Na-Li and Cs-Li. Using the concept that the mixed

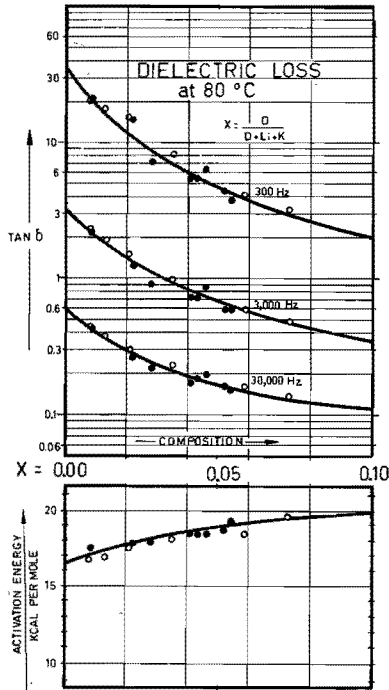


Fig. 4. Dielectric losses at 80°C and 300, 3 000 and 30 000 Hz as a function of the  $^1\text{H}$ -ion concentration. The lower part of the figure shows the activation energy of the losses. The open circles refer to the proton containing glasses of ref. [8] and the solid circles refer to the deuterium containing glasses of the present work.

alkali effect is caused by these differences, one would expect a very high activation energy for the mobility of protons and lithium ions in the  $\text{H}_2\text{O}$  containing glass and consequently a considerably lower activation energy for the cation migration in the glasses containing heavy water, both values being large compared to the activation energy for cation migration in ordinary mixed alkali glasses.

However, the activation energy for cation migration in  $\text{D}_2\text{O}$  and  $\text{H}_2\text{O}$  containing glasses is equal within experimental error, and of the same order of magnitude as in comparable Na-Li and Cs-Li metaphosphate glasses. These observations hardly seem compatible with the assumption that the difference in resonance frequency might be responsible for the mixed alkali effect.

### 5. Summary and conclusions

Lithium metaphosphate glasses containing dissolved heavy water show an intermediate temperature peak in the internal friction curve at 0.4 Hz. The magnitude of

this peak depends on the amount of dissolved heavy water in a similar manner as the mixed alkali peak depends on the concentration of a second alkali. From the extrapolation of the present results, to a composition free from heavy water, it can be concluded that this peak would be absent in a dry glass. The single alkali peak, the annealing temperature and the dielectric losses depend on the concentration of heavy water in a similar manner as they depend on the concentration of a second alkali oxide. It is concluded that deuterium ions in a glass can act like alkali ions and that the mechanism for the mixed deuterium-alkali peak is identical to the one proposed for the mixed alkali internal friction peak: viz. a coupled movement of dissimilar cations in opposite directions.

A comparison of deuterium-containing glasses with proton-containing glasses shows that the mechanical and dielectric behaviour of these glasses is quantitatively identical and this does not seem to be compatible with the theory that the mixed alkali effect is governed by differences in the resonance frequencies of the cations. One may draw the conclusions that the mixed alkali effect, in general, does not depend on the differences in mass of the ions in question, but that it is very probable that the difference in volume is a determining factor.

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## INTERNAL FRICTION AND DIELECTRIC LOSSES OF MIXED ALKALI BORATE GLASSES

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The internal friction and dielectric losses of Na–K, Li–Na, Li–Cs, Li–K, Na–Cs, K–Cs, Ag–Li, Ag–Na, Ag–K and Ag–Cs borate glasses were measured as functions of the temperature at various frequencies. In general, the behavior of mixed alkali borate glasses is very similar to the behavior of the comparable phosphate and silicate glasses. The magnitude of the mixed alkali peak was found to vary systematically with the size of the involved alkali ions. The silver-containing glasses also show the mixed alkali effect. The borate glasses are briefly compared with the silicate and the phosphate glasses and their behavior is found to be in agreement with the recent proposal that the mixed alkali peak is caused by an electro-mechanical cross effect.

### 1. Introduction

It has been known for a long time that many properties of glasses which contain two kinds of alkalis show large deviations from additivity, e.g. the alkali diffusion coefficient and the dielectric losses are reduced, whereas the resistivity is increased [1–8]. The study of the internal friction of such glasses has revealed a new relaxation peak, which is called the mixed alkali peak in the literature. The mixed alkali peak has been studied intensively during the past few years and it has been found that other monovalent cations can cause similar effects [9,10]. Systematic investigations of silicate glasses have shown that the mixed peak reaches its maximum height in a glass in which the diffusion coefficient of both alkalis is equal and that its magnitude is also related to the difference in size of the involved alkali ions [11,12]. Investigations on metaphosphate glasses have shown that even protons can cause a mixed alkali effect and that the relation between the size differences and the mixed peak magnitude is also applicable to phosphate glasses [13,14].

Several investigators agree upon the fact that the mixed alkali peak is caused by a cooperative motion of dissimilar alkali ions. However, the exact nature of this cooperation remains under discussion and various possible explanations have been offered [12,15,16].

A systematic investigation of the mixed alkali effect in borate glasses was still lacking so the present work to provide for this was started.

## 2. Experimental procedure

Series of mixed alkali borate glasses were prepared from reagent grade  $B_2O_3$  (Merck 163),  $Li_2CO_3$  (Merck 5671),  $K_2CO_3$  (Merck 4928),  $Cs_2CO_3$  (Merck 2040),  $Na_2CO_3$  (Merck 6392) and  $AgNO_3$  (Merck 1510). The glasses were melted in a platinum dish, placed in an electric furnace at temperatures between 950 and 1000°C. The melts were bubbled with dried oxygen for one hour to reduce the water content. The silver-containing glasses were prepared in porcelain crucibles (Weta 3271). Silver nitrate was used here instead of silver carbonate which would cause the formation of metallic silver. The oxidizing atmosphere created by the evolving nitric fumes, prevents the reduction of the silver oxide for a short while. The silver-containing melts were not treated with dried oxygen in order to keep the melting time as short as possible.

From each glass batch, three different sample types were made: (1) fibers, approximately 0.5 mm in diameter, (2) rectangular bars with the following dimensions: 5 × 6 × 103 mm, (3) discs, approximately 22 mm in diameter and 2 mm thick. All specimens were annealed prior to measurement and stored in water-free oil. The internal friction of the fiber specimens was measured with a torsion pendulum, using a vacuum of  $50 \times 10^{-3}$  torr, at 0.4 Hz. The internal friction of the bars was measured in air at approximately 2 kHz using a resonance technique in flexure. The dielectric losses were measured on disc specimens, which had a coating on both sides of silver electrode paste (Leitsilver, DEGUSSA), at temperatures ranging from room temperature to 300°C and at frequencies of 300, 3 000 and 30 000 Hz. More detailed information about the sample preparation and measuring techniques can be obtained from refs. [14,17].

## 3. Results and discussion

### 3.1. The sodium-potassium borate glasses

At room temperature sodium borate glass, containing 30 mol %  $Na_2O$ , shows a maximum in the internal friction versus temperature curve at 0.4 Hz. This relaxation peak is caused by the stress-induced movement of sodium ions and is called the single alkali peak. It has been shown that the position of the single alkali peak is correlated to the diffusion coefficient of the alkali ions and to the dielectric losses, while the activation energies calculated for these processes are basically the same.

The gradual substitution of sodium ions for potassium ions causes an additional internal friction peak to appear at higher temperatures. This mixed alkali peak has been observed whenever more than one alkali is present. Further substitution of the initially present alkali by a second one causes the mixed alkali peak to develop rapidly and to shift to lower temperatures. Simultaneously, the single alkali peak is reduced in size and shifted to higher temperatures. The single alkali peak finally

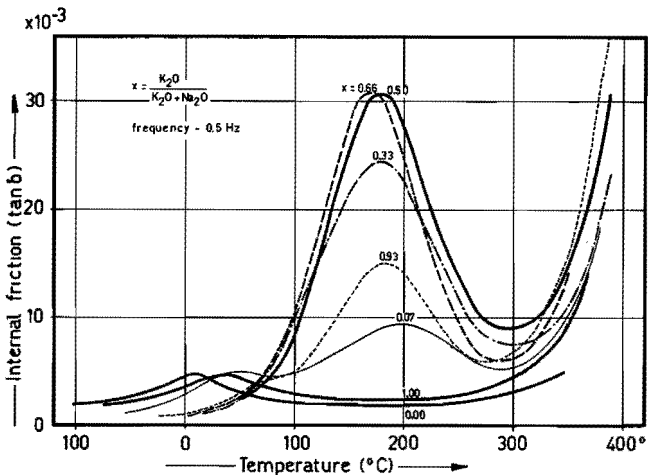


Fig. 1. Internal friction versus temperature curves of sodium-potassium borate glasses, containing 30 mol % total alkali oxide, at 0.5 Hz.

merges into the low-temperature side of the mixed alkali peak and cannot be observed anymore.

In a composition in which both alkalis are about equally abundant, the mixed peak reaches its maximum size and this maximum is usually very large compared to the size of the single alkali peak. Further addition of the second alkali causes the mixed peak to shrink down again and to shift to higher temperatures. When all of the initially present alkali is replaced by the second alkali, the mixed peak merges completely into the high-temperature background and a single alkali peak, associated with the second alkali, can be observed again at room temperature.

If the total amount of alkali oxide is varied without affecting the mixing ratio of the alkalis, changes in the internal friction can be observed like the ones shown in fig. 2. Reducing the total amount of alkali will result in a reduction of the mixed peak and a shift to higher temperatures.

Earlier work has shown that the peak temperature, at constant frequency, is a direct measure for the average activation energy of the loss process; therefore, the activation energy of the mixed alkali peak increases as the total amount of alkali is reduced. Karsch and Jenkel [18] have shown that this is also true for the single alkali peaks in borate glasses.

Figs. 3 and 4 show the dependence of the magnitude of the mixed alkali peak on the composition. It can be concluded that the occurrence of a mixed alkali peak is unaffected by the total amount of alkali and that the alkali mixing ratio which will cause the largest peak, remains basically unchanged. A variation of the total amount of alkali, at constant mixing ratio, causes a linear change in the magnitude of the mixed alkali peak. The compositional range, where the total alkali

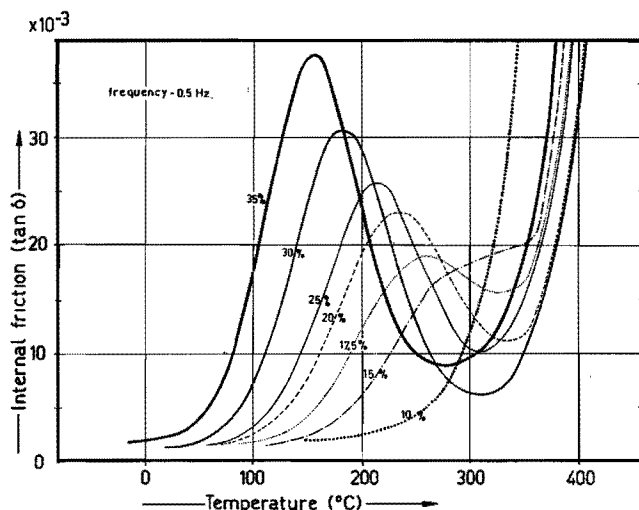


Fig. 2. Internal friction versus temperature curves of sodium-potassium borate glasses, containing equal amounts of both alkalis. The total alkali content is indicated above each curve. Frequency is approximately 0.5 Hz.

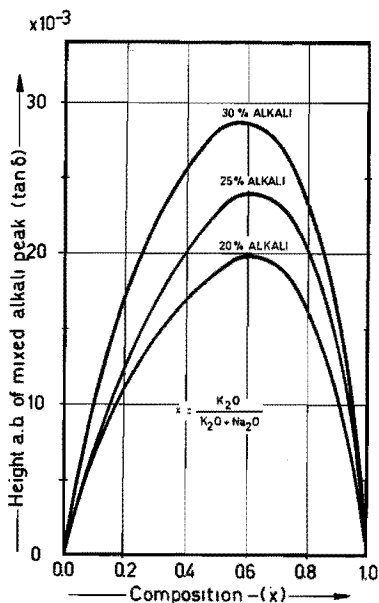


Fig. 3. Heights above background of the mixed alkali peaks in sodium-potassium borate glasses as functions of the alkali mixing ratio.

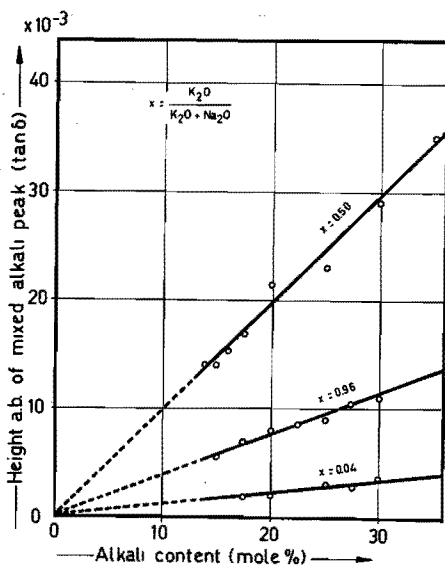


Fig. 4. Heights above background of the mixed alkali peaks in sodium-potassium borate glasses as functions of the total alkali content.

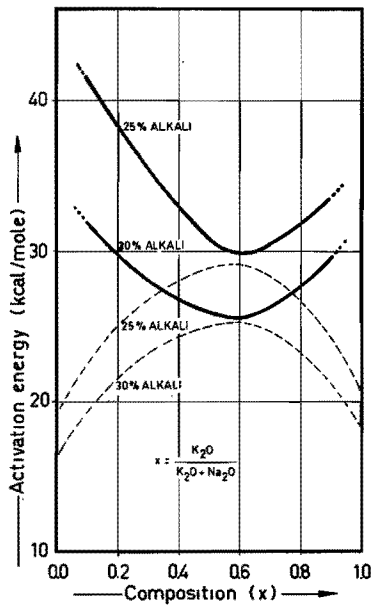


Fig. 5. Average energy of activation of the losses in sodium-potassium borate glasses as functions of the alkali mixing ratio. The solid lines refer to the mixed alkali peaks; the dotted lines to the single alkali peaks and the dielectric losses.

content is less than 15 mol %, could not be investigated as the increased activation energy of the relaxation will cause the peak to appear at a temperature which is too close to the transformation range of the glass so that the mixed peak can no longer be resolved from the background at 0.4 Hz.

Fig. 5 shows the activation energy of the mixed peak as a function of the mixing ratio. One can see that the activation energy reaches a minimum at approximately the same composition at which the largest mixed peak is found. Here again, the compositional range accessible to measurement is restricted by the resolution of the peak from the high-temperature background; the data on glasses containing less than 5 mol % of the second alkali oxide are lacking.

The dielectric losses of mixed Na-K borate glasses were measured between room temperature and 300°C at a frequency of 3kHz. Under these conditions the losses are mainly caused by the ionic conductivity and may reach very high values. The introduction of a second alkali causes a rapid decrease in the losses and an increase in the average activation energy. This particular behavior has been observed in many other glass-forming systems and for many other combinations of alkali ions, as well as for non-alkali monovalent cations.

In a composition which contains both alkalis in about equal amounts, the losses reach a minimum whereas their average energy of activation shows the opposite



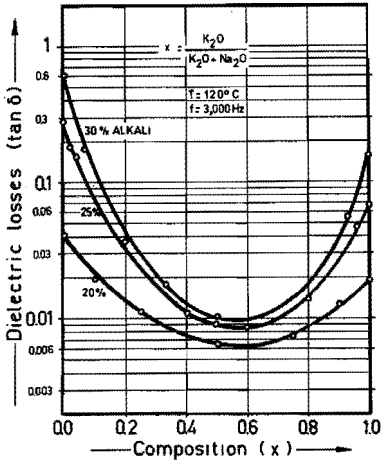


Fig. 6. Dielectric losses at 120°C and 3 kHz of sodium-potassium borate glasses, as functions of the alkali mixing ratio.

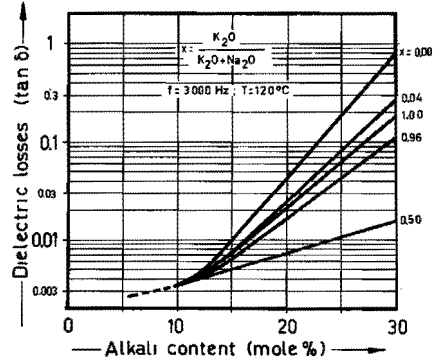


Fig. 7. Dielectric losses at 120°C and 3 kHz of sodium-potassium borate glasses, as functions of the total alkali content.

trend. The composition at which the latter extreme is found usually does not differ significantly from that which shows the largest mixed peak and contains as a rule the larger ion in a small excess.

Changing the total amount of alkali oxide, at a constant mixing ratio, produces a quite different effect: From fig. 7 it can be seen that the dielectric losses decrease rapidly with decreasing amounts of the total alkali. The lines for constant mixing ratio seem to converge at a composition between 10 and 15 mol % alkali, indicating that *below this concentration the dielectric losses of the glasses are no longer affected by the mixing ratio of the alkalis*. An obvious conclusion would be that there is a threshold concentration for the mixed alkali effect. However, this conclusion is premature if the mixed alkali effect is considered to be the reduction of the alkali mobility caused by the presence of dissimilar alkali ions. From the internal friction studies on borate glasses, it is known that at alkali concentrations below 15 mol % the relaxation peaks merge into the high-temperature background, indicating that the average energy of activation for alkali migration becomes very high and possibly approaches the activation energy for viscous flow. In these compositions it is doubtful if the dielectric losses at 120°C and 3 kHz are still dominated by ionic conduction, and the dielectric losses can no longer be regarded as a good measure for the mobility of the alkali ions.

Measurements at much higher temperatures, e.g. on molten borate glasses, could provide more reliable data. In this respect, one is referred to the conductivity measurements of Kostanyan [3] which have demonstrated that the mixed alkali effect is also shown by the glasses above  $T_g$  and that there is indeed a minimum alkali concentration below which the effect of mixing cannot be observed.

The existence of a threshold concentration is in agreement with a semi-quantitative model, recently proposed by Hendrickson et al. [16]. In this model an influence sphere is used. The radius of this sphere must be interpreted as the average value of the largest distance at which two alkali ions still interact. Alkali ions which are separated by a distance larger than this radius will no longer 'see' each other, so that it becomes unimportant whether an alkali ion is similar to the adjacent one or not and all non-additive mixing effects will vanish. As the average distance between the alkali ions in a glass matrix increases as the alkali concentration is reduced, this model predicts the existence of a threshold concentration for the mixed alkali effect.

The average activation energy for the dielectric losses is given in fig. 8 as a function of the total alkali content. Once more one can see that the alkali mobility is decreased by reducing the alkali concentration.

A comparison of fig. 3 with fig. 6 shows that the large mechanical losses, associated with the mixed alkali peak, lack an electric analogue; the dielectric losses are minimum in compositions which show a maximum mixed peak. A comparison of the average activation energies of the dielectric and mechanical losses also demonstrates that these two loss processes must have a different origin.

The electrically inactive mixed alkali peak is attributed to an electromechanical cross effect and is believed to be caused by a coupled diffusion process in which both kinds of alkali ions participate [14]: the alkali ions with the larger radius will migrate under the influence of the periodic stress on the network, and an electric field which opposes the mechanical field will be set up in this way. The alkali ions with the smaller radius, which are more susceptible to electrical forces, will jump in the direction of the electric counterfield and restore the electric neutrality. The net

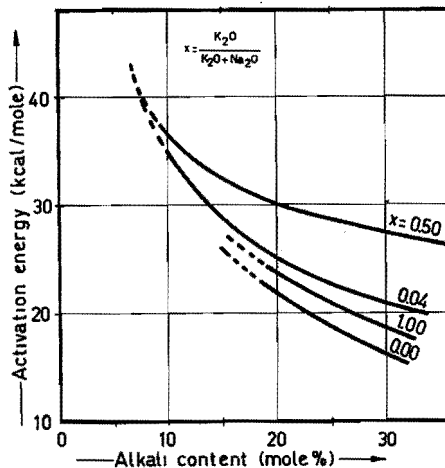


Fig. 8. Average energy of activation of the dielectric losses in sodium-potassium borate glasses, as functions of the total alkali content.

effect of this will be a mechanical relaxation which is electrically inactive and which is controlled by the alkali ions with the lowest mobility.

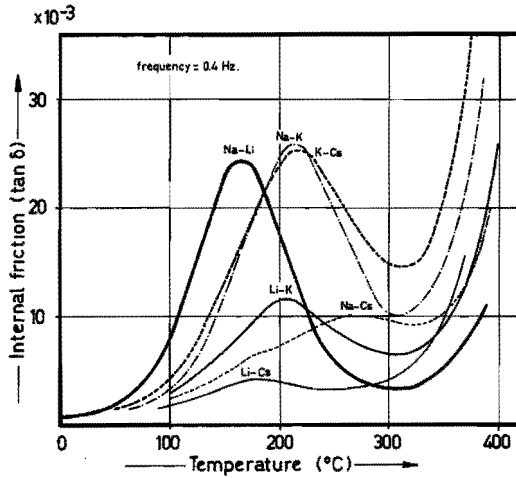


Fig. 9. Internal friction versus temperature curves at 0.4 Hz of mixed alkali borate glasses with the general composition  $R_2O \cdot R_2O \cdot 6B_2O_3$ .

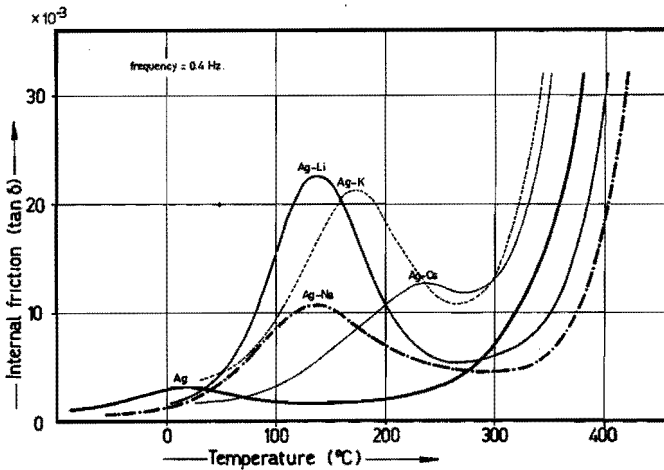


Fig. 10. Internal friction versus temperature curves at 0.4 Hz of mixed alkali-silver borate glasses with the general composition  $R_2O \cdot Ag_2O \cdot 6B_2O_3$ .

### 3.2. Other mixed alkali borate glasses

Other mixed alkali borate systems, in particular the Li–Na and the Li–Cs series, have also been investigated extensively. As the properties of these glasses appeared to be qualitatively comparable to the sodium–potassium glasses, further investigation was confined to compositions containing a total amount of 25 mol % alkali oxide and a mixing ratio of 1:1.

Figs. 9 and 10 show the internal friction curves of various mixed alkali borate glasses as functions of the temperature. The effects found in the silver-containing glasses show a large resemblance to those of the corresponding sodium glasses. Apparently, silver ions do not behave differently from alkali ions in this respect, except for the fact that the silver glasses have lower annealing temperatures. The relatively low annealing temperature gives an indication that the glass network is weakened, probably on account of the fact that the silver–oxygen bonds are considerably less ionic than the sodium–oxygen bonds. A weakened glass network will cause a reduction of activation energy for ion migration, higher dielectric losses, and lower internal friction peak temperatures.

The size and the temperature (activation energy) of the mixed peaks, as well as the annealing temperatures, depend to a large extent on the kind of alkali ions present. The largest mixed alkali peak is observed in the Na–K glass.

If one assumes that the mixed alkali relaxation is caused by a coupled diffusion process of dissimilar alkali ions in opposite directions, the magnitude of the peak should be proportional to the volume difference of the alkali ions and be given by:

$$\tan \delta_{\max} = k(v_1 - v_2)C,$$

where  $v_1 - v_2$  is the volume difference of the alkali ions ( $\text{m}^3$ );  $C$  is the concentration of relaxing units ( $\text{m}^{-3}$ );  $k$  is a proportionality constant.

Previous work on mixed alkali metaphosphate glasses [14] has shown that the relative concentration of relaxing units, calculated by this formula, depends on the alkalis which are present: this concentration diminishes as the difference in size of the ions becomes larger and the mixed peak is shifted to higher temperatures.

The dielectric losses and their average energy of activation bear a similar relation to the size difference of the ions. If the difference in the volumes of the alkali ions becomes larger, the dielectric losses at constant temperature are reduced and a slight increase in the activation energy can be observed. The numerical data are given in table 1. Note that the third power of the Goldschmidt ionic radius is used here so that the volume difference is expressed in units of  $\frac{4}{3}\pi \text{\AA}^3$ .

### 3.3. Comparison of the present results with the data on silicate and phosphate glasses

Shelby et al. [12] have studied the mixed alkali peak in glasses with the general formula  $(1-x)\text{R}_2\text{O} \cdot x\text{R}'_2\text{O} \cdot 3\text{SiO}_2$  and found that the magnitude of the mixed

Table 1

Numerical data on the mechanical and dielectric losses of mixed alkali borate glasses, containing 25 mol % alkali oxide in equimolar concentrations.

Alkali pair	$v_1 - v_2$ ( $\frac{4}{3}\pi\text{\AA}^3$ )	H.a.B. <sup>a)</sup> ( $\tan \delta$ )	$T_m$ ( $^{\circ}\text{C}$ )	Concentration of relaxing units (arbitrary units)	Dielectric losses at 3 kHz and 120 $^{\circ}\text{C}$ ( $\tan \delta$ )	Activation energy of the dielectric losses (kcal per mol)
Na-Ag						
Na-Ag	0.16	$10.0 \times 10^{-3}$	135	62.5	$31.5 \times 10^{-3}$	26
Li-Na	0.47	23.5	160	50.0	17.5	28
Li-Ag	0.62	21.0	135	33.9	39.0	27
K-Ag	1.26	20.1	175	15.9	17.0	28
Na-K	1.42	24.0	215	16.9	9.0	29
Li-K	1.88	10.0	208	5.3	7.2	30
K-Cs	2.15	23.3	220	10.8	5.2	30
Cs-Ag	3.41	9.0	235	2.6	6.2	29
Na-Cs	3.57	10.5	270	3.0	5.2	29
Li-Cs	4.03	3.1	-	0.8	6.8	30

a) Height above background.

alkali peak for glasses containing equal amounts of both alkalis is related to the size of the alkali ions. They assumed that the magnitude of the mixed alkali peak is a function of the ion radius ratio and obtained a curve as given in fig. 11.

Here again, one can see that the largest mixed alkali peak is obtained by combining sodium with potassium. This figure also shows the curves for the metaphosphate glasses [14] together with those for the borate glasses from the present study. For all three glass-formers the same basic relationship between peak height and ion size is observed. The silver-containing glasses do not fall into line with the alkali glasses, probably as a result of the different nature of the silver-oxygen bond. The large differences in the magnitudes of the mixed peaks in the three vitreous systems can be explained in terms of concentration and mobility effects. The alkali concentration (in mol  $\text{R}_2\text{O}$ /unit volume) is largest in the metaphosphates. Here four alkali ions are present for each six pairs of oxygen ions. The trisilicate glasses with four alkali ions per seven molecules of oxygen come next. The alkali concentration is lowest in the borate glasses; here four alkali ions are present per ten molecules of oxygen. The difference between the three systems is further influenced by the relative order of the diffusion coefficients of the alkalis. Metaphosphate glasses are relatively soft glasses with large alkali diffusivities; the borate glasses occupy an intermediate position and the silicate glasses are rigid and have relatively high softening points and low diffusivities.

The molar volume of oxygen (MVO), as calculated from the density, is a linear function of the alkali mixing ratio and increases with increasing alkali radius. The relation between the molar volume of oxygen and the third power of the alkali radius in borate glasses, is qualitatively identical to the corresponding relation in

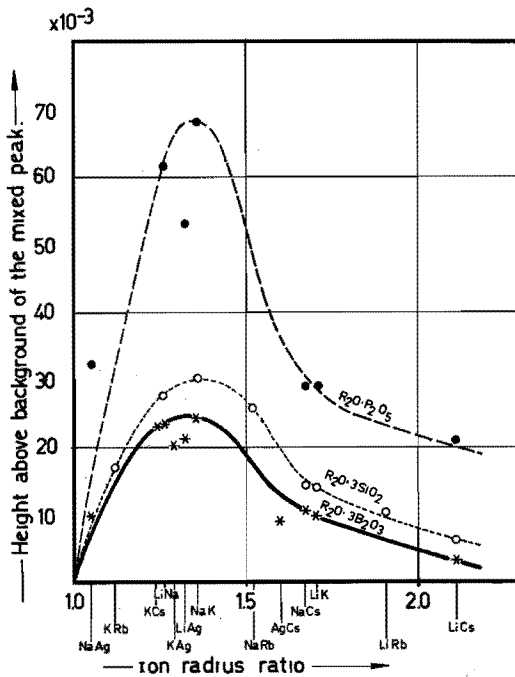


Fig. 11. The magnitude of the mixed alkali peak in various glasses as functions of the ion radius ratio. The solid circles refer to the metaphosphate glasses from ref. [14]; the open circles refer to the trisilicate glasses from ref. [12] and the asterisks represent the results of the present investigation.

Table 2

Densities and molar volumes of oxygen in alkali borate glasses containing 25 mol% total alkali content.

Composition	Density ( $\text{g}/\text{cm}^3$ )	Molar volume of oxygen ( $\text{cm}^3/\text{mol}$ )
$\text{Li}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	2.222	21.15
$\text{Na}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	2.325	23.30
$\text{Ag}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	3.512	24.10
$\text{K}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	2.216	27.35
$\text{Cs}_2\text{O} \cdot 3\text{B}_2\text{O}_3$	3.125	31.30

metaphosphate glasses [14]. The MVO data of the present glasses are given in table 2.

Silicate and phosphate glasses show a third internal friction peak at intermediate temperatures. This intermediate temperature peak has been attributed to the same

basic effect which causes the mixed alkali peak: in this particular case, protons act like alkali ions and the magnitude of this mixed alkali-proton peak depends on the amount of dissolved water in the same way as the mixed alkali peak depends on the concentration of a second alkali oxide.

In the presently investigated glasses, the mixed alkali-proton peak is absent. The reason for this is not fully understood yet. It is possibly due to a different bonding state of protons [19] in borate glasses or a result of the relatively low solubility of water in borate glasses.

#### 4. Summary and conclusions

The internal friction of mixed alkali borate glasses is characterized by the presence of a second relaxation peak, located at elevated temperatures. The introduction of dissimilar alkali ions causes the single alkali peak to be reduced in size and to shift to higher temperatures. The new peak, which merges from the background, attains its largest height at approximately equal concentrations of both alkalis.

The magnitude of this mixed alkali peak depends on the size of the alkali ions in a similar way as in silicate and phosphate glasses. The alkali-proton peak, which is commonly observed in silicate and phosphate glasses is absent in the presently studied borate glasses. To a first approximation, the magnitude of the mixed alkali peak is proportional to the total alkali content.

The dielectric losses of mixed alkali borate glasses are completely analogous to the dielectric losses of silicate and phosphate glasses. The logarithm of the dielectric losses varies about linearly with the total alkali content.

The present work provides an indication that mixed alkali glasses, containing less than 10 mol% of alkali oxide, will not show the mixed alkali effect.

In general, there is a striking similarity in the mechanical and dielectric behavior of mixed alkali silicate, borate and phosphate glasses. The magnitudes and the average activation energies of the single alkali peaks correlate well with the dielectric properties, giving further support to the assumption that these phenomena are associated with the migration of alkali ions. The data on the mixed alkali peaks are in agreement with the 'cross effect' theory which attributes the mixed alkali peak to stress induced diffusion processes of dissimilar alkali ions, coupled by electric forces. The size of the mixed peak seems to be controlled by the volume difference of the participating ions, their concentration and their diffusivity.

#### Acknowledgement

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## INTERNAL FRICTION AND DIELECTRIC LOSSES OF MIXED ALKALI–ALKALINE-EARTH METAPHOSPHATE GLASSES

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Several series of glasses with the general formula  $xR_2O \cdot (1-x)R'O \cdot P_2O_5$  were prepared and the dielectric loss and internal friction data were taken. The dielectric losses of alkali metaphosphate glasses are greatly reduced by the substitution of alkaline-earth oxide for alkali oxide. Some of the investigated series show a weak minimum in the dielectric loss.

The internal friction measurements reveal a high temperature peak, in addition to the single alkali peak and the intermediate temperature peak commonly observed in phosphate glasses. The origin of this high temperature peak is discussed.

### 1. Introduction

The internal friction and dielectric losses of single alkali and mixed alkali glasses have been studied intensively during the past few years and several new explanations have been proposed for the various relaxation peaks [1–10]. It has been shown that the intermediate temperature peak, which was originally attributed to the stress induced motion of the non-bridging oxygen ions, is controlled by the amount of dissolved water in the glass, and it has been proposed that this peak actually is a mixed alkali–proton peak [4, 7]. Among the recently proposed mechanisms for the mixed alkali peak is the one that explains the mixed alkali peak as a manifestation of an electro-mechanical cross effect. Such an effect should be very general and should not be restricted to mixed alkali glasses. It has been predicted [19] that any electrically insulating material containing mobile charge carriers with dissimilar charge to volume ratio should exhibit a large mixed peak, of which the relaxation time (or the peak temperature) is controlled by the less mobile particle. The magnitude of this relaxation should be determined by the volume difference of the charge carriers.

Previous work on silicate glasses [11, 12] has shown that the introduction of alkaline-earth ions in simple alkali glasses causes a new relaxation peak to appear at elevated temperatures, but at that time this new relaxation was attributed to a cluster–network interaction, in which the energy absorption was caused by the phase lag of the cluster vibrations.

The dielectric behaviour of mixed alkali glasses is characterized by the presence of a deep minimum in the losses, occurring at a composition which contains about equal amounts of both alkalis. This effect has been observed in all kinds of glasses and for all possible combinations of alkali ions. In addition to this it has been shown that other monovalent cations like protons [4, 7], silver ions [13, 19] and copper ions [14] can cause similar effects.

## 2. Experimental procedure

$\text{MgH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$  was prepared by adding reagent grade MgO (Merck 5866) in small portions to 10% excess of  $\text{H}_3\text{PO}_4$  (Merck 564). After the last addition of MgO, a small amount of water was added and the product was heated to obtain a clear solution which was viscous. Heating was continued until sufficient water was removed by boiling and the solution turned opalescent owing to crystallization. At that time, the solution was allowed to cool slowly over a period of 30 h and the resulting product was extracted and washed several times with ether. Finally, the product was dried at  $60^\circ\text{C}$ .

The water content of the compound was determined and the dehydrated product was identified as  $\text{Mg}(\text{PO}_3)_2$ , using X-ray diffraction.

$\text{CaH}_4(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ ,  $\text{SrH}_4(\text{PO}_4)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $\text{BaH}_4(\text{PO}_4)_2 \cdot \frac{1}{4}\text{H}_2\text{O}$  were prepared in a similar way from  $\text{Ca}(\text{OH})_2$  (Merck 2047),  $\text{SrCO}_3$  (Baker Chemical 0330) and BaO (Merck 1731). As the Ca, Sr and Ba phosphates would crystallize readily from their hot solutions, the extraction and washing process with ether was omitted and the product was collected by suction filtration and washed with a small amount of cold water. The compounds were analyzed for water content and the dehydrated products were investigated by means of X-ray diffraction. The Ca and Sr compounds could be identified as the corresponding metaphosphates; this was not possible for the Ba compound.  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (Merck 6346) and  $\text{LiH}_2\text{PO}_4$  [19] were used as the respective sodium and lithium sources.

The glasses were prepared by melting a mixture of approximately 40 g of the corresponding chemicals in a platinum dish, placed in an electric furnace. The melting temperatures are listed in table 1. Detailed information about the melting procedure, specimen preparation and measuring techniques can be obtained from refs. [15, 19].

## 3. Results

Alkaline-earth metaphosphate glasses possess good glass-forming properties. The resulting glasses appear to be mechanically strong and insoluble in water.

To facilitate the comparison of the present results with the data on mixed alkali systems, the composition of the glasses is expressed as the molar ratio of the alkali oxide to the total amount of metal oxides and designated with  $x$ , given by:

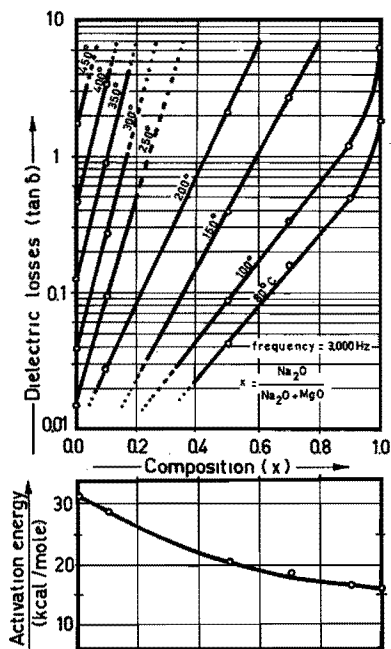


Fig. 1. Dielectric losses (at 3 kHz) and average activation energy of sodium-magnesium metaphosphate glasses as a function of composition.

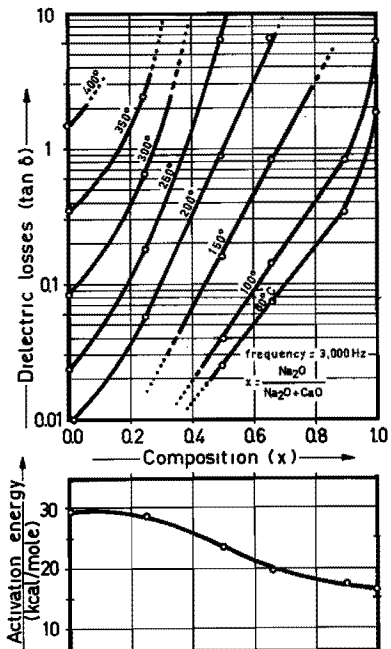


Fig. 2. Dielectric losses (at 3 kHz) and average activation energy of sodium-calcium metaphosphate glasses as a function of composition.

$$x = \frac{[R_2O]}{[R_2O] + [R'O]}$$

Note that in this investigation alkali oxide is replaced by alkaline-earth oxide on the basis of equivalence; e.g. two lithium ions are substituted for each calcium ion.

The dielectric losses of the glasses were measured at temperatures between room temperature and 450 °C, at frequencies of 300, 3000 and 30000 Hz and are shown in figs. 1 to 7. Under these temperature and frequency conditions, the losses are very high and are mainly caused by the ionic conductivity. The average energy of activation of the losses is also shown in these figures and has been calculated from the temperature dependence of the average relaxation time, using:

$$\tan \delta = C \frac{\omega\tau}{1 + \omega^2\tau^2}, \quad \tau = \tau_0 \exp(E_a/RT),$$

where  $\omega$  is the angular frequency of the AC field ( $\text{sec}^{-1}$ ),  $\tau$  is the average relaxation time (sec),  $C$  is a constant.

One can see that the dielectric losses are greatly reduced by the introduction of

Table 1  
Numerical data on mixed alkaline-earth-alkali metaphosphate glasses.

x	$T_{\text{melt}}$ (°C)	$T_{\text{anneal}}$ (°C)	Frequency (Hz)	Single alkali peak		Proton alkali peak		High temperature peak	
				Temp. (°C)	H.a.B. <sup>(c)</sup> ( $\times 10^3$ )	Temp. (°C)	H.a.B. <sup>(c)</sup> ( $\times 10^3$ )	Temp. (°C)	H.a.B. <sup>(c)</sup> ( $\times 10^3$ )
$x\text{Li}_2\text{O} \cdot (1-x)\text{MgO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.00	1300	510	0.56	225	2.0 <sup>a)</sup>	—	—	—	—
0.10	1200	437	0.28	125	3.0	200	3.0	350	12
0.50	1050	382	0.50	39	3.5	138	4.0	288	22
0.70	1000	364	0.47	5	5.0	120	4.0	263	24
0.90	1000	325	0.43	-37	9.0	88	8.0	250	18
1.00	950	310	0.88	-26	10.0	79	10.0	—	—
$x\text{Na}_2\text{O} \cdot (1-x)\text{MgO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.10	1100	457	0.36	—	—	190	7.5 <sup>b)</sup>	—	—
0.50	1000	375	0.31	32	3.0	139	3.4	not resolved	
0.70	1000	331	0.33	-5	6.4	106	4.2	”	”
0.90	950	296	0.38	-28	10.0	86	4.5	”	”
1.00	950	—	1.60	-8	12.4	127	4.2	—	—
$x\text{Li}_2\text{O} \cdot (1-x)\text{CaO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.00	1200	495	0.45	180	1.5 <sup>a)</sup>	—	—	—	—
0.10	1100	468	0.51	—	—	185	6.5 <sup>b)</sup>	380	11
0.25	1000	416	0.46	110	3.5	175	3.0	330	17
0.50	1000	363	0.43	45	4.0	145	3.5	290	24
0.66	1000	336	0.46	20	4.0	125	4.0	270	25
0.75	1000	322	0.28	-8	4.5	93	4.0	255	25
0.90	950	309	0.37	-22	6.6	83	6.0	260	22
0.95	950	301	0.28	-32	7.1	76	5.7	250	18

Table 1 (continued).

x	$T_{\text{melt}}$ (°C)	$T_{\text{anneal}}$ (°C)	Frequency (Hz)	Single alkali peak		Proton alkali peak		High temperature peak	
				Temp. (°C)	H.a.B. <sup>c)</sup> ( $\times 10^3$ )	Temp. (°C)	H.a.B. <sup>c)</sup> ( $\times 10^3$ )	Temp. (°C)	H.a.B. <sup>c)</sup> ( $\times 10^3$ )
$x\text{Na}_2\text{O} \cdot (1-x)\text{CaO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.25	1000	407	0.33	—	—	170	5.5 <sup>b)</sup>	320	20
0.50	1000	352	0.48	55	2.5	156	2.0	295	30
0.66	1000	311	0.33	9	3.0	141	2.0	269	32
0.90	950	282	0.45	-13	9.1	125	3.1	248	25
$x\text{Na}_2\text{O} \cdot (1-x)\text{SrO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.00	1150	463	0.46	138	2.0 <sup>a)</sup>	—	—	—	—
0.10	1050	415	0.30	125	2.5	175	3.0	—	—
0.50	1000	329	0.45	84	4.0	136	3.0	275	20
0.70	950	310	0.42	25	4.1	122	3.2	255	25
0.90	950	284	0.46	-12	8.2	100	4.0	238	15
$x\text{Li}_2\text{O} \cdot (1-x)\text{BaO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.00	1000	430	0.40	122	3.0 <sup>a)</sup>	—	—	—	—
0.50	950	337	0.39	60	4.5	120	3.0	not resolved	—
$x\text{Na}_2\text{O} \cdot (1-x)\text{BaO} \cdot \text{P}_2\text{O}_5$ glasses:									
0.70	950	294	0.42	19	4.0	100	2.5	not resolved	—

a) These peaks are believed to be caused by the migration of protons (single proton peaks).

b) In these compositions the mixed alkali-proton peak and the single alkali peak overlapped to such an extent that it was not possible to obtain individual values; this peak must be interpreted as the sum of both relaxations.

c) Height above background.

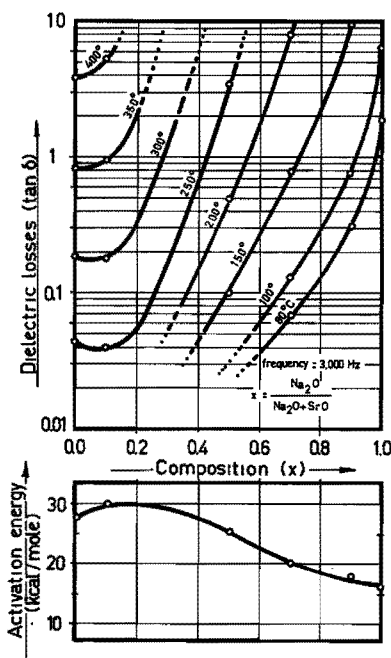


Fig. 3. Dielectric losses (at 3 kHz) and average activation energy of sodium-strontium metaphosphate glasses as a function of composition.

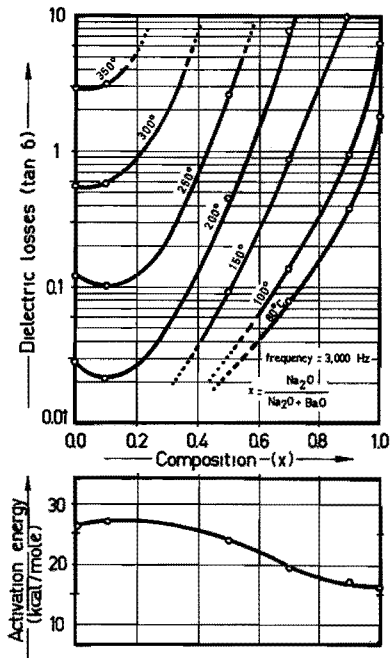


Fig. 4. Dielectric losses (at 3 kHz) and average activation energy of sodium-barium metaphosphate glasses as a function of composition.

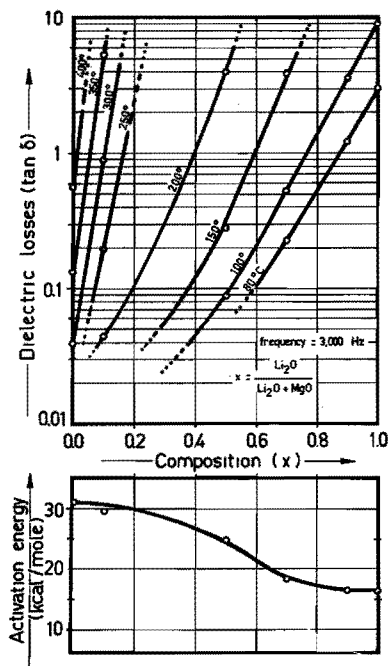


Fig. 5. Dielectric losses (at 3 kHz) and average activation energy of lithium-magnesium metaphosphate glasses as a function of composition.

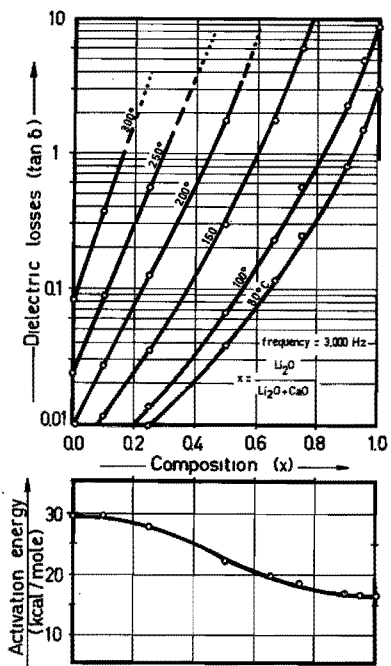


Fig. 6. Dielectric losses (at 3 kHz) and average activation energy of lithium-calcium metaphosphate glasses as a function of composition.

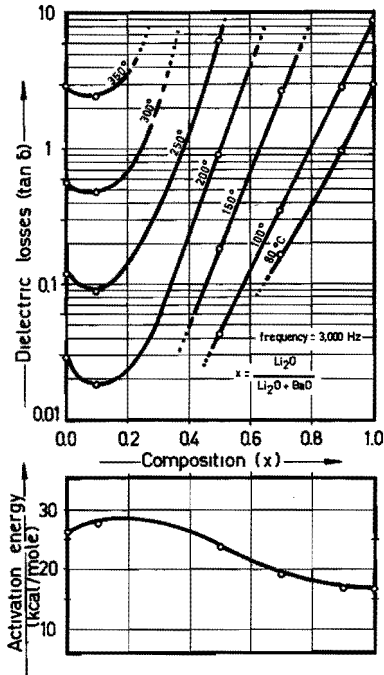


Fig. 7. Dielectric losses (at 3 kHz) and average activation energy of lithium-barium metaphosphate glasses as a function of composition.

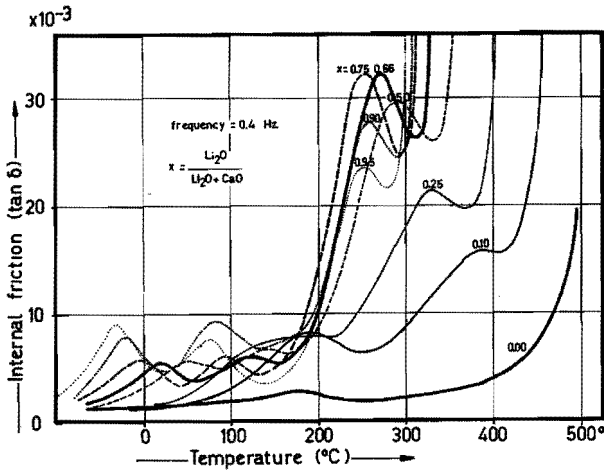


Fig. 8. Internal friction versus temperature graphs of lithium-calcium metaphosphate glasses at approximately 0.4 Hz.

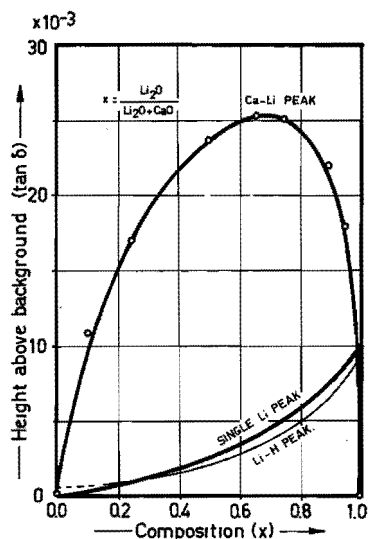


Fig. 9. Magnitudes of the relaxation peaks as a function of the composition in lithium-calcium metaphosphate glasses.

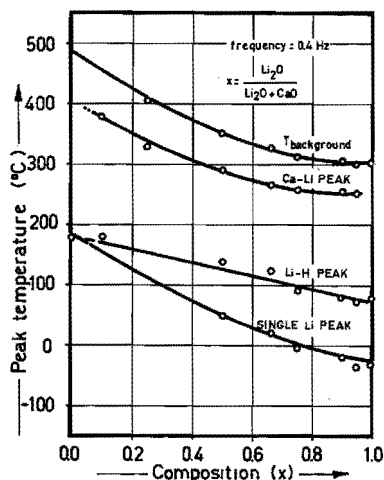


Fig. 10. Peak temperatures at 0.4 Hz of the mechanical relaxations in lithium-calcium metaphosphate glasses. The top curve is an isofriction curve for the background losses and is obtained by plotting the temperatures at which the background losses reach a value of  $30 \times 10^{-3}$ .

alkaline-earth ions and that the average energy of activation is increased. In contrast to what is observed with mixed alkali systems, a deep minimum in the losses and a pronounced maximum in the activation energy cannot be observed.

The dielectric losses of the alkaline-earth glasses are highest in the Ba glasses and decrease in the order: Ba, Sr, Ca, Mg. The average energy of activation of the loss causing process shows the reverse trend.

The internal friction was measured with a torsion pendulum, using a vacuum of  $50 \times 10^{-3}$  torr. The curves for the Ca-Li glasses are given in fig. 8. The internal friction of the other glasses is very similar to that in Ca-Li glasses; the peak temperatures and magnitudes are given in table 1. Mixed alkaline-earth-alkali glasses basically show three relaxation peaks between  $-100^\circ\text{C}$  and the annealing range at 0.4 Hz. The low temperature peak, at approximately  $0^\circ\text{C}$ , is the single alkali peak and has been attributed to the stress induced migration of the alkali ions. The activation energy and the magnitude of this peak have been shown to correlate well with the diffusion, dielectric loss and conductivity measurements [6, 9].

The gradual substitution of alkaline-earth oxide for alkali oxide results in a decrease of the single alkali peak. Simultaneously, a shift to higher temperatures can be observed, see fig. 8.

It can also be noted that the reduction in the magnitude of the single alkali peak, which occurs upon introduction of alkaline-earth oxide, is small compared to the



effect of introducing dissimilar alkali ions. The intermediate temperature peak, which occurs at approximately 100 °C, has also been studied in many other glasses. The exact nature of this relaxation is still under discussion. Replacing alkali oxide with alkaline-earth oxide causes this peak to decrease and to shift to higher temperatures. In this respect, the intermediate temperature peak behaves very similarly to the single alkali peak. Further replacement causes the two peaks to approach each other. Finally the two peaks overlap and only one broad absorption can be observed.

The high temperature peak, at approximately 300 °C, is a new internal friction peak, brought about by the presence of alkaline-earth ions. When a few percent of the originally present alkali oxide is replaced by alkaline-earth oxide, this peak emerges from the high temperature background. Continued substitution causes the peak to develop. The high temperature peak reaches its maximum height when about one third of the alkali oxide is replaced. Upon further replacement the peak decreases in height and finally merges again into the high temperature background.

The dependence of the height of the internal friction peaks and the peak temperatures on composition is given in figs. 9 and 10 respectively.

#### 4. Discussion

From figs. 1 to 7 it can be seen that the gradual substitution of alkaline-earth oxide for alkali oxide reduces the dielectric losses considerably. There is general agreement among the various investigators that the conduction losses in glasses are caused by the migration of mobile alkali ions. Alkaline-earth ions are considerably less mobile and consequently, the losses of the present glasses appear to be governed by the alkali content.

The losses that are observed in the *pure* alkaline-earth glasses cannot be explained so easily; their average energy of activation is much lower than one would expect for alkaline-earth ion migration. The actual diffusion data on alkaline-earth metaphosphate glasses are lacking, but Frischat [18] measured the diffusion constant and activation energy for comparable silicate glasses and obtained values between 50 and 60 kcal/mol for the activation energy of  $\text{Ca}^{++}$  in calcium silicate glasses at approximately 500 °C. The dielectric losses in these particular compositions are attributed to the presence of monovalent cations such as protons or possibly alkali impurities, and these monovalent impurities are also believed to be responsible for the weak extremes which are observed in the loss and activation energy curves of the Sr and Ba glasses (figs. 3, 4 and 7).

The introduction of alkaline-earth ions strengthens the glass network as is demonstrated by a substantial increase in the annealing temperatures. One can assume that the alkaline-earth metaphosphate glasses consist of long chains of  $\text{PO}_4$  tetrahedra, which are 'cross-linked' by the alkaline-earth ions. The rigidity of such a structure would depend on the P-O bond strength (along the chains) and on the strength of the alkaline-earth oxygen bonds (perpendicular to the chains). The determining

Table 2

Dielectric losses and activation energy of alkaline-earth metaphosphate glasses at 3 kHz and at temperatures of 200, 300 and 400 °C.

Composition	Dielectric losses at 3 kHz			Average activation energy (kcal/mol)
	400 °C	300 °C	200 °C	
Mg(PO <sub>3</sub> ) <sub>2</sub>	460 × 10 <sup>-3</sup>	39 × 10 <sup>-3</sup>	— × 10 <sup>-3</sup>	31.2
Ca(PO <sub>3</sub> ) <sub>2</sub>	1500	83	10	29.2
Sr(PO <sub>3</sub> ) <sub>2</sub>	3800	190	—	27.6
Ba(PO <sub>3</sub> ) <sub>2</sub>	—	569	29	26.1

factor would be the weaker of those two forces. The P—O bonds can be assumed to be strong bonds of covalent nature, while the cross-linking bonds are supposed to be considerably weaker and to a large extent of ionic nature.

The chainlike structure of alkali metaphosphate glasses has been verified by means of X-ray diffraction analysis [16, 17] and the hypothesis of the relative weakness of the electrostatic cross-links can be substantiated by the observation that the cross-links can be broken by hydrolysis without significant degradation of the PO<sub>4</sub> chains. Preliminary results of a Raman investigation on alkaline-earth and alkali metaphosphate glasses have shown that both glasses contain basically the same repeating structural units and, therefore, an extension of the structural data of alkali metaphosphate glasses to the alkaline-earth glasses seems obvious.

In view of this, one can expect a relation between the annealing temperatures of metaphosphate glasses and the field strength of the cations: the alkali glasses have relatively low annealing temperatures and these temperatures increase in the order Cs, K, Na, Li. The annealing temperatures of the alkaline-earth glasses are considerably higher and increase in the order of increasing field strength as well.

The same effect can be seen from the dielectric losses and their average energy of activation in table 2.

Fig. 8 shows typical internal friction curves for alkaline-earth-alkali metaphosphate glasses. The peak which occurs below room temperature at 0.4 Hz is the single alkali peak. There is general agreement that this peak is caused by the stress induced diffusion of alkali ions. As the alkali content of the glass is reduced, by substituting alkaline-earth oxide for alkali oxide, this peak becomes smaller and shifts to higher temperatures. The single alkali peak correlates well with the dielectric losses; both phenomena respond similarly to compositional changes.

The intermediate temperature peak, occurring at approximately 100 °C, shows a trend very similar to the one in the single alkali peak. The nature of the intermediate temperature peak is presently under discussion. This peak has been attributed in the past to non-bridging oxygen ions [6, 20, 21]. Other workers recognized the importance of protons [22–24]. More recent investigations provide evidence that this peak is *controlled* by the water content [4, 7, 25] and that it behaves in many respects like a *mixed alkali-proton peak*. A proposal has been made that attributes the

intermediate temperature peak to an alkali-proton interaction, similar to the one that causes the common mixed alkali peak.

It is difficult to draw conclusions about the influence of alkaline-earth oxide additions on the mobility of the protons from the present work, as the water content of the glasses is not known. At large alkaline-earth oxide concentrations ( $x = 0.25$ ) the single alkali peak and the proton-alkali peak merge together, indicating that the mobilities of alkali ions and protons are approaching each other. At higher alkaline-earth content the order of mobility may even reverse, so that the protons will dominate in the conduction losses or even cause a small *single* proton peak. The influence of dissolved water is expected to be largest in the Ba glasses. These glasses have been melted at lower temperatures and consequently, should contain larger amounts of dissolved water. In this respect, it is interesting to note from the dielectric-loss data that these glasses show a weak extreme at high alkaline-earth oxide content.

The large internal friction peak at approximately 300 °C is a new peak which is not observed in alkali metaphosphate glasses and which emerges from the background upon introduction of alkaline-earth oxides. Ryder et al. [11, 12] have reported a similar peak in silicate glasses. They attributed this peak to cluster-network interactions. It will be shown below that the presence of this peak is also in agreement with the cross effect theory [19].

As explained in ref. [19], the presence of mobile charge carriers with *different charge to volume ratio*, in a material which is basically an insulator, will cause a mixed internal friction peak to appear. The relaxation time (peak temperature) of this peak will be governed by the less mobile charge carriers, which are in this case the alkaline-earth ions. The particle with the larger volume-to-charge ratio will jump in the direction of the applied mechanical field and set up an electrical counterfield. The particle with the smaller volume-to-charge ratio will be more susceptible to electric forces and jump in a direction opposite to the mechanical field, to restore the electric neutrality. This theory predicts a mixed alkaline-earth-alkali peak to occur at a temperature at which  $\omega\tau = 1$  for the less mobile alkaline-earth ions. The activation energy of this process will be determined by the alkaline-earth ions and should be of the order of magnitude of 40 to 50 kcal/mol.

As previous work on metaphosphate glasses has shown that the peak temperature at constant frequency is a linear function of the activation energy, one can estimate that the mixed alkaline-earth-alkali peak must be expected between 300 and 400 °C at 0.4 Hz in metaphosphate glasses. The magnitude of the relaxation peak should be proportional to the volume difference of the involved particles. This volume difference should be calculated on the basis of equivalency, as the jump of each alkaline-earth ion is compensated by two jumps of an alkali ion. The magnitude of the peak should also depend on the concentration ratio of the constituent metal oxides. McVay et al. [1] have shown that in a mixed alkali system the mixed peak reaches its maximum height in the composition in which the diffusivities of both alkali ions are equal. For a relaxation peak which is caused by a coupled diffusion process, one must expect to find a maximum whenever the jump probability of the rate control-

ling species is largest. This jump probability is a complicated function of many variables, but in this discussion it suffices to recognize that it contains the concentration and the diffusivity.

In common mixed alkali systems the diffusivities are approximately symmetric and monotonic functions of the alkali concentration and the maximum in the mixed peak is defined by the equality of the product of concentration and diffusivity:  $C_1D_1 = C_2D_2$ . As this maximum is always found in a composition which contains approximately equal amounts of both alkalis ( $C_1 = C_2$ ), the condition to be met can also be formulated as:  $D_1 = D_2$  [1].

However, in mixed alkaline-earth-alkali metaphosphate glasses, the diffusion coefficients depend on the composition in a completely different way; e.g. the diffusivities of the constituent cations do not intersect and the alkaline-earth ions have the lower mobility throughout the whole system. This means that the alkaline-earth ions will control the rate of the coupled diffusion process throughout almost the whole system, except for compositions very close to the pure alkaline-earth glass. Here the product of the alkali concentration and the alkali diffusion coefficient becomes smaller than the corresponding value for the alkaline-earth ions.

The relative values of the diffusion coefficients, estimated from the peak temper-

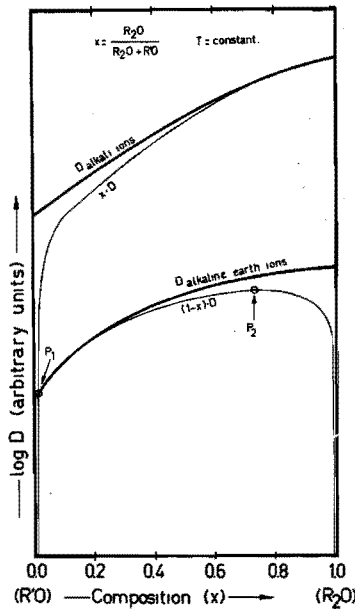


Fig. 11. Relative magnitudes of the diffusion coefficients for alkali ions and alkaline-earth ions as functions of the composition. The trends in this figure are estimated from the internal friction peak temperatures and serve only to demonstrate how the size of the mixed peak is related to concentrations and diffusivities.

atures at 0.4 Hz are sketched in fig. 11.  $P_1$  is the intersection of the line representing the product of the alkali diffusion coefficient and the alkali concentration, and the corresponding line for the alkaline-earth ions.

To the left of this point the coupled diffusion process is governed by the alkali ions, as their concentration is very low.

To the right of  $P_1$  the process is controlled by the slower diffusing alkaline-earth ions and the size of the mixed peak increases as the diffusivity becomes larger. Further to the right, at  $P_2$ , a maximum is reached and the size of the mixed peak drops back again, because the availability of the alkaline-earth ions becomes the limiting factor. Fig. 8 also demonstrates that the high temperature peak is not well resolved from the background. The values for the height above background of this peak, listed in table 1, are obtained by estimating the background contribution to the total losses. We realize that this method is arbitrary and that the actual peak height might differ considerably from our results. Nevertheless, the authors feel that their figures reflect the proper dependence on composition of the high temperature peak.

The lithium-beryllium metaphosphate system is also believed to yield useful information about this mixed peak, but, as the melting point expected for these glasses is not within reach of our equipment, this system has not been investigated.

Although the listed values of the peak heights should merely be regarded as estimates, the conclusion seems to be justified that the magnitude of the high temperature peak increases when the difference in volume (calculated on the basis of equivalence) of the involved ions becomes larger.

From figs. 1 to 7 it can be seen that the occurrence of the high temperature mechanical peak is not accompanied by similar dielectric losses. The activation energies of both processes also differ considerably and it can be concluded that this mechanical relaxation is electrically inactive.

## 5. Summary and conclusions

The internal friction curves of mixed alkaline-earth-alkali metaphosphate glasses show three relaxation peaks between  $-100^\circ\text{C}$  and the annealing range at 0.4 Hz. The low temperature peak is recognized as the single alkali peak, caused by the stress induced motion of the alkali ions. The intermediate temperature peak, at approximately  $100^\circ\text{C}$ , is attributed to an interaction of protons and alkali ions, similar to the one that is responsible for the common mixed alkali peak.

The high temperature peak, at about  $300^\circ\text{C}$ , is in agreement with the cross effect theory. This theory predicts a high temperature mechanical relaxation as a result of a coupled periodic diffusion process of alkaline-earth ions and alkali ions.

According to this model the coupling is caused by electric forces. The present work provides a possible explanation for the high-temperature internal peak in alkaline-earth ions containing glasses. However, the authors realize that additional and more conclusive evidence is needed for a definite assignment of this peak.

The small internal friction peak in the pure alkaline-earth glasses is attributed to the presence of small amounts of dissolved water. The dielectric losses are governed by the alkali content of the glasses. A deep minimum, similar to that found in mixed alkali series, is generally not observed. The dielectric losses of the pure alkaline-earth glasses are attributed to the presence of monovalent impurities, such as protons.

Some of the investigated systems show a weak minimum in the dielectric losses and a maximum in their activation energy. This also is an indication for the presence of dissolved water.

### Acknowledgements

The authors would like to thank Dr. D.L. Vogel and Mr. W.J.Th. van Gemert for helpful discussions. This investigation was supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands Organisation for the Advancement of Pure Research (Z.W.).

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## STELLINGEN

## I

Bij de verklaring van de mechanische relaxatie piek die in silikaatglazen, welke zowel aardalkali ionen als alkali ionen bevatten, waargenomen kan worden bij 300 °C en 1 Hz, is onvoldoende aandacht geschonken aan de mogelijkheid van het optreden van een gekoppeld diffusie proces van alkali ionen met aardalkali ionen.

R. J. Ryder and G. E. Rindone, *J. Am. Ceram. Soc.* 43 (1960) 662, 44 (1961) 532.

## II

Er zijn sterke aanwijzingen dat de elektrische geleidbaarheid van lood-silikaat glazen veroorzaakt wordt door mobile monovalente verontreinigingen.

G. C. Milnes and J. O. Isard, *Phys. Chem. Glasses* 3 (1962) 157.

S. W. Strauss et al., *J. Res. Nat. Bur. Stand.* 56 (1956) 135.

C. A. Elyard, P. L. Baynton and H. Rawson, *Glastechn. Ber.* 32 K V 39.

## III

De structurele verschillen tussen  $\text{CaPO}_3$ -glas en  $\text{MgPO}_3$ -glas, zoals ze door Kordes zijn voorgesteld, komen niet tot uiting in de mechanische en dielectrische eigenschappen. Voorts zijn zij strijdig met de Raman spectra van deze glazen.

E. Kordes, W. Vogel und R. Feterowsky, *Z. Elektrochem.* 57 (1953) 282.

## IV

Het grote belang dat men in het verleden aan „zwevende zuurstof ionen” als structuur element van oxidische glasnetwerken, heeft toegekend, is niet geheel gerechtvaardigd.

## V

In de „Encyclopedia of Physics” wordt ten onrechte de indruk gewekt dat  $\text{AlPO}_4$  glasvormende eigenschappen zou bezitten, analoog aan  $\text{SiO}_2$ .

*Encyclopedia of Physics*, Ed. J. M. Stevels, XIII sect. 10 p. 535.

## VI

De verklaring van de invloed van het watergehalte op de elektrische weerstand van natriumsilikaat glas, zoals gegeven door W. E. Martinsen et al. is aan ernstige twijfel onderhevig.

W. E. Martinsen and T. D. McGee, *J. Am. Ceram. Soc.* 54 (1971) 175.

## VII

De ontwikkeling van glazen voor optische communicatie is in sterke mate afhankelijk van de beschikbaarheid van analytische technieken met uiterst lage aantoonbaarheids grenzen voor lichte overgangsmetalen.



## VIII

Op grond van theoretische beschouwingen kan men verwachten dat ionomeren, waarin  $n$  ongelijksoortige ionen zijn ingebouwd,  $n$  secundaire mechanische relaxatie processen zullen vertonen. Men mag verwachten dat het proces met de kortste relaxatie tijd ook electrisch gemeten kan worden, terwijl de  $n-1$  andere relaxaties gekenmerkt zullen worden door een relatief grote absorptie sterkte, naast electrische inactiviteit.

## IX

De ontwikkeling van verschuimingsprocedé's voor moderne metaallegeringen en composietmaterialen, zou voor tal van toepassingen zeer aantrekkelijke mogelijkheden openen.

## X

Het veelvuldig gebruik van „bolletjes en staafjes” modellen voor het in beeld brengen van de atomaire rangschikking van de materie, heeft als nadeel dat men de bindingskrachten discretiseert.

## XI

Het feit dat in het „Handbook”, in de tabel „Fats and oils”, temidden van als zodanig bekendstaande grondstoffen voor de voedings- en genotsmiddelen industrie, ook mensenvet is opgenomen kan aanleiding geven tot ongegronde verdenkingen tegen margarine- en zeepfabrikanten.

Handbook of Chemistry and Physics, Ed. R. C. Weast, The Chemical Rubber Co., Cleveland, Ohio, 51st edition (1970) p. D-174.

## XII

De richtlijnen die de promotor de mogelijkheid bieden om te voorkomen dat bepaalde stellingen door de promovendus worden aangeboden, stellen de promotor in de gelegenheid zich te beschermen tegen kritiek van personen die doorgaans redelijk goed vertrouwd zijn met de problematiek van zijn vakgebied.

## XIII

Het is bevorderlijk voor de verkeersveiligheid om het „no-claim” kortings systeem dat tegenwoordig door veel autoverzekeraars gehanteerd wordt, te vervangen door een premie bepaling gebaseerd op voorwaardelijke kansberekening.

## XIV

Het verdient aanbeveling om investeringen in ontwikkelingslanden in eerste instantie af te stemmen op de economische benutting van de beschikbare **arbeidstijd** en de productie factor **grondstoffen** pas in een later stadium hierin te betrekken.

## XV

De chirurgische manipulaties die de achttiende eeuwse heelmeeester Petrus Camper propageerde om lieden van het steenlijden te verlossen, moeten in veel gevallen tot een resultaat geleid hebben dat aanzienlijk definitiever was dan het beoogde.

C. J. Doets, dissertatie, Leiden 1948.

H. M. J. M. van Ass  
25 febr. 1975