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# Review
# The internal friction of glasses

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Basic fundamentals of the elastic behaviour of a standard linear solid and the internal friction technique based on this model are briefly described. The internal friction ($Q^{-1}$) caused by various thermally activated processes in vitreous solids are reviewed for several glass compositions in relation to ionic mobility and other relevant properties. Similar relaxation mechanisms characterize many vitreous solids. The relaxation of alkali ions is essentially independent of the glass network former and has an activation energy of 15 to 25 kcal mol$^{-1}$. Other processes like the interaction of oxygen ions and protons, alkali ions and protons, mixed-alkali ion interaction and the motion of single bonded oxygen ions have an activation energy of 30 to 40 kcal mol$^{-1}$. The activation energy for relaxation of the glass network is 100 to 120 kcal mol$^{-1}$.

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## 1. Introduction

The theoretical and experimental study of anelasticity in solids was originally confined to metals. With the development and utilization of many inorganic vitreous solids a need arose for understanding the anelastic behaviour of solids in general and its relation to atomic structure. There have been advances in the structural theory of various relaxation processes, but a unified theory successfully describing all relevant glass properties simultaneously, has not been achieved. Fortunately, different relaxation phenomena have essentially identical macroscopic mathematical description. This offers a basis for solving many practical problems such as selecting appropriate glass compositions and annealing parameters for applications where control of thermal stresses is important (glass strengthening by tempering, glass to glass and glass to metal seals), choice of glass working temperature, control of optical properties (index of refraction and bi-refringence), maintenance of volume stability, control of phase separation kinetics, production of glasses with low mechanical, optical and dielectric losses, etc.

This paper reviews investigations of internal friction (mechanical damping) which have provided information for the atomic arrangement and various processes occurring in glasses with reference to their individual oxide components.

## 2. Fundamentals of anelasticity

If a solid in thermodynamic equilibrium is suddenly subjected to a change in external conditions, it must achieve a new state of equilibrium consistent with the new conditions. This readjustment process, or relaxation, commonly occurs in nature. In the following discussion only recoverable anelastic effects that originate from rearrangement of the atomic configuration under the influence of an applied stress will be considered, although diffusional, thermal, dielectric and magnetic relaxations are analogous phenomena.

Recoverable anelasticity implies that, when a stress is applied to a solid, the free energy increases

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due to slight displacements of atoms from their equilibrium positions. When an energy barrier must be overcome, a certain time is required for the completion of the process so the maximum strain is delayed with respect to the maximum applied stress. When the stress is removed, the deformation is fully recovered by thermal motion.

A mechanical model [1–4], termed standard linear solid, consisting of two perfectly elastic springs (stiffness constants $C_1$ and $C_2$) and a dashpot (inertia member with a viscous flow constant $1/\eta$) satisfactorily describes the anelastic behaviour of many solids. The linear differential equation [5] describing this model is:

$$F\left(\frac{1}{C_1}+\frac{1}{C_2}\right)+\frac{\tau}{C_1}\frac{\mathrm{d}F}{\mathrm{d}t} = x+\tau\frac{\mathrm{d}x}{\mathrm{d}t} \qquad (1)$$

where $F$ is the applied force (stress) and $x$ is the total displacement (strain). When a relaxation time $\tau$ is defined as $\eta \equiv \tau \cdot C_2$, and $C_1$ and $C_2$ are replaced by unrelaxed and relaxed compliances $S_u = 1/C_1$ and $S_r = 1/C_1 + 1/C_2$, respectively, Equation 1 becomes:

$$S_rF+\tau S_u\frac{\mathrm{d}F}{\mathrm{d}t} = x+\tau\frac{\mathrm{d}x}{\mathrm{d}t} \qquad (2)$$

When the stress ($F$) and strain ($x$) vary periodically, the following expression [3, 5] for the loss tangent is obtained from Equation 2.

$$\tan\delta = \frac{(S_r-S_u)\,\omega\tau}{S_r+S_u\omega^2\tau^2} \qquad (3)$$

where $\omega$ is the angular frequency. In many solids the relaxation ratio (relaxation strength) $\Delta = (S_r-S_u)/S_u$ is often $\ll 1$ so Equation 3 commonly reduces to:

$$\tan\delta \simeq \delta = \Delta\frac{\omega\tau}{1+\omega^2\tau^2} \qquad (4)$$

Tan $\delta$ is a symmetrical function of $\omega\tau$ (or $\log\omega\tau$), with $\delta_{\mathrm{max}} = \Delta/2$ centred at $\omega\tau = 1$. Tan $\delta$ asymptotically approaches 0 as $\omega\tau \rightarrow 0$, since atomic motion keeps strain and stress in phase (relaxed, isothermal condition). As $\omega\tau \rightarrow \infty$, atom motion is unable to relax the anelastic strain and, thus, $\delta \rightarrow 0$ (unrelaxed, adiabatic condition). The width of the tan $\delta$ peak at half maximum is ideally $(\log\omega\tau)_2 - (\log\omega\tau)_1 = 1.414$, but the actual peak width observed in many solids is often much larger (2 to 3 times for glasses). For large relaxation strengths ($>$ 10%) a change in peak shape will occur and one has to account for the modulus variation due to the relaxation [6].

For a thermally activated process the relaxation time, $\tau$, varies as:

$$\tau = \tau_0 \exp(u/RT) \qquad (5)$$

where $R$ and $T$ have their usual meaning and $U$ is an activation energy. By measuring the peak temperature (i.e., where $\omega\tau = 1$) for several frequencies, $U$ can be calculated from

$$U = R\frac{\ln\omega_1-\ln\omega_2}{1/T_2-1/T_1} \qquad (6)$$

Tan $\delta$, commonly called internal friction or mechanical damping, is also referred to as $Q^{-1}$ because of its electrical analogue. Physically, it is a measure of the absorption of vibrational energy in a solid and is related, therefore to the vibrational (acoustic) [7], optical, dielectric and magnetic spectrum. Experimentally $Q^{-1}$ can be determined from the logarithmic decrement $\lambda$ of a freely vibrating solid using the expression

$$Q^{-1} = \tan\delta = \frac{2.303\lambda}{\eta\pi} \qquad (7)$$

where $\lambda = \ln A_0/A_n$; $A_0$ is the initial amplitude and $A_n$ is the amplitude after $n$ cycles.

Although some solids are described well by the standard linear model, most solids, and glasses in particular, are better represented by several such models connected in series, each with a different $\tau$. Equation 3 must then be summed over the various values of $\tau$ in order to account for the experimentally observed broadening in tan $\delta$ peaks. This distribution in $\tau$, which can result from a distribution in the activation energy (barrier heights), is often satisfactorily represented by a Gaussian function, and related to the disorder in vitreous solids.

In vitreous solids the primary atomic processes producing characteristic tan $\delta$ peaks are: the stress-induced motion of cations, interactions between different cations and between cations and protons, the motion of single-bonded oxygen ions and the viscoelastic character of the network. The latter mechanism has activation energy of 100 to 150 kcal mol$^{-1}$.

Tan $\delta$ increases in going from crystalline solids, to glasses and to polymers. The internal friction is $10^{-6}$ for quartz, $10^{-5}$ to $10^{-3}$ for metals, $10^{-2}$ for most glasses and $10^{-2}$ to 10 for high polymers

[8, 9]. Values for commercial ceramics are variable [10].

## 3. Techniques for measuring relaxation spectra

Suitable methods depend upon the magnitude of the internal friction, the shape and size of the specimens available and the desired mode of vibration. In broad terms, the range 0.1 to 250 Hz can be measured by torsional oscillations of a fibre, 1 to 50 kHz by flexural vibrations of a bar, 10 to 110 kHz by longitudinal vibrations and $>0.5$ MHz by measurements of the attenuation of ultrasonic stress waves.

For glasses, measurement of the gradual decay in amplitude of free torsional oscillations at $\sim 1$ Hz is the most commonly used technique. A glass fibre suspended vertically with its lower end freely oscillating (torsion) constitutes the pendulum's anelastic member. The fibre can be surrounded by heating or cooling coils and the entire assembly placed in a vacuum chamber to eliminate air damping. The decay of the torsional oscillations is recorded in several ways, such as measuring the time a beam of light, reflected from a mirror attached to the bottom of the pendulum, passes between 2 photocells connected to an electronic timer. Various torsion pendulum designs [11–18] as well as the theoretical [19, 20] and experimental aspects of the procedures have been described [21–25].

## 4. Internal friction of glasses of various compositions

### 4.1. Glasses with low energy loss

Three-dimensional network glasses like vitreous $SiO_2$, $B_2O_3$, $As_2O_3$ or $GeO_2$ have very low energy losses. The limiting factor in measuring $Q^{-1}$ is often equipment sensitivity. In vitreous and crystalline $SiO_2$, Bömmel *et al.* [26] reported $Q^{-1} = 2 \times 10^{-6}$ and proposed a model of transverse vibration of the oxygen ions to explain the relaxation losses. Strakna and Savage [27], however, attributed the mechanical losses to longitudinal vibration of the oxygen ions. Traces of water in the glass structure may significantly increase the mechanical losses (Section 4.5) in these glasses. Feldspar glass ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) exhibits internal friction peaks due to alkali ion movement only. Barium silicate [28], Ti–Al–Mg-silicate [29] and chalcogenide glasses [30] also have losses $< 10^{-3}$.

### 4.2. Binary alkali–silicate glasses

Two-component glasses which have been studied extensively are: $Li_2O$–$SiO_2$ [31], $Na_2O$–$SiO_2$ [18, 22, 24, 31, 33–39], $K_2O$–$SiO_2$ [31], $Rb_2O$–$SiO_2$ [38]. These glasses when measured as a function of temperature at $\sim 1$ Hz show two peaks below the transformation temperature, Fig. 1. The first peak between $-40$ and $-25°$ C, is generally attributed to the stress-induced diffusion of alkali ions. This assignment of the low temperature peak is based on the close agreement between the activation energy for this peak [4, 22, 37] (15 to 20 kcal mol$^{-1}$) and that measured for the d.c. electrical conductivity (15 to 20 kcal mol$^{-1}$ for $R_2O{\cdot}3SiO_2$ glasses) [39–41]. The ionic conductivity of these glasses is well known to be due to alkali ion motion. This hypothesis is further supported by the correlation of this peak with the chemical durability of alkali glasses [42]. However, low temperature peaks, apparently similar to the alkali peak, have been observed in alkali-free glasses containing alkaline earth cations [31] (Section 4.4).

Typical internal friction curves characteristic of $Li_2O{\cdot}2SiO_2$ and $K_2O{\cdot}2SiO_2$ glasses are compared with fused $SiO_2$ and a mixed alkali glass in Fig. 1. The variation of the alkali peak height and temperature with $Na_2O$ content in silicate glasses is shown in Fig. 2.

As shown in Fig. 1, a second peak occurs in alkali silicate glasses between 100 and 300° C, depending on modifying cations, silica content and traces of dissolved $H_2O$. In $R_2O{\cdot}3SiO_2$ glasses this peak shifts to higher temperatures in the order: $Li < Na < K < Rb$ [31, 37], Table I. Its origin is not clear and several workers attribute it to the relaxation of the non-bridging oxygen ions [33] (i.e. oxygen ions bonded to only one silicon ion). Mohyuddin and Douglas initially reported [24] agreement between the activation energy for this peak and that for oxygen diffusion, but later found this agreement invalid [43]. Ryder and Rindone [31] favour the non-bridging oxygen hypothesis on the basis that the peak decreases and shifts to a higher temperature as a result of the immobilizing action of alkaline earth cations on the single bonded oxygen ions present in alkali containing glasses (Section 4.4).

Others found that the activation energy for the second peak in $Na_2O$–$SiO_2$ glasses was essentially twice (30 to 40 kcal mol$^{-1}$) that for Na ion diffusion and decreased almost linearly with

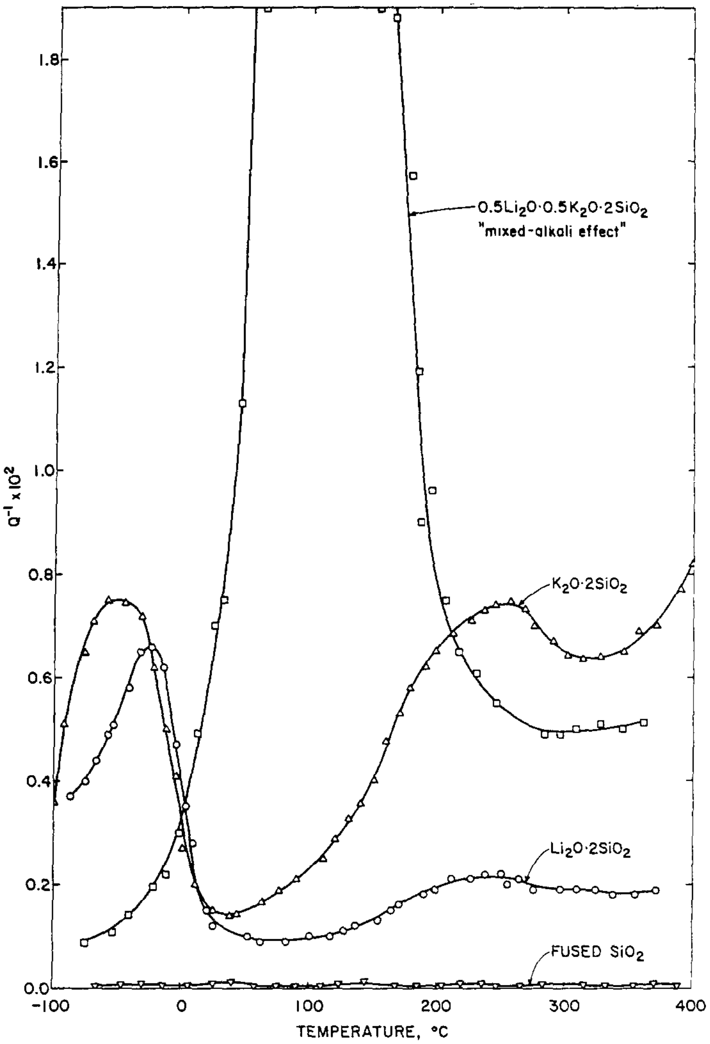

*Figure 1* Typical mechanical losses at a frequency of a few Hz shown by binary alkali–silicate glasses, corresponding mixed-alkali glass and vitreous $SiO_2$. Maxima $< 0°$ C are due to relaxation of alkali ions, while those between 200 and 300° C may be due to non-bridging oxygens or other causes (see text). Network relaxation increases $> 400°$ C. The sensitivity limit set by a torsional pendulum is $Q^{-1} \sim 10^{-4}$.

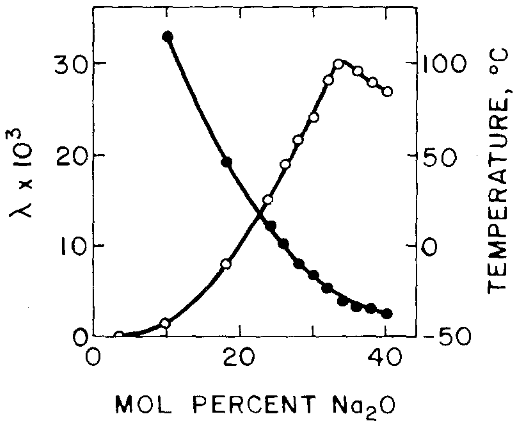

*Figure 2* Changes of the temperature (●) and height (○) of the "alkali" peak with varying content of $Na_2O$ in Na-silicate glass [35].

increasing $Na_2O$ content from 17% to 34% [22]. The explanation offered was that this peak involved the co-operative action of two alkali ions. Further measurements of dielectric relaxation showed only maxima attributable to Na ions so the centres responsible for this peak would have to be unpolarized [44, 45]. It is unlikely that two Na ions would always move in such a fashion as to remain unpolarized [36]. A characteristic of this second peak is that its magnitude is proportional to alkali content [22, 24]. However, in alkali–silicate glasses the magnitude of this peak also increases with the amount of $H_2O$ dissolved in the glass. Since the number of single-bonded oxygen ions also increases with alkali or water content, it cannot be unequivocally concluded that differences in water content are the sole cause of the changes

TABLE I Temperatures corresponding to typical internal friction maxima in various binary alkali silicate glasses. Average values from [31, 37]. Frequency = 0.4 Hz.

| Glass | Temperature, (° C) | |
|---|---|---|
| | First peak (alkali ion) | Second peak (of controversial origin) |
| $Li_2O \cdot 3SiO_2$ | −38 | 150 |
| $Na_2O \cdot 3SiO_2$ | −33 | 179 |
| $K_2O \cdot 3SiO_2$ | −29 | 186 |
| $Rb_2O \cdot 3SiO_3$ | −25 | 205 |

in peak magnitude. Nevertheless, there is increasing evidence that the second peak is greatly affected by the presence of dissolved water [35, 46–49]. Theories for this peak are presented in Section 4.5.

## 4.3. Mixed-alkali glasses

Many properties of mixed-alkali glasses cannot be precisely correlated with linear relations between the molar proportions of each alkali oxide. When one alkali oxide is substituted for another in silicate, borate, phosphate or germanate glasses, many physical properties vary nonlinearly with glass composition. This behaviour is sometimes so pronounced that the initial trend is later reversed giving rise to a maximum or minimum which is known as the "mixed-alkali", "polyalkali", or "neutralization" effect.

The effect is most obvious in those properties dependent on alkali ion mobility; alkali diffusion [50, 51], electrical conductivity [50, 52–55] dielectric relaxation and loss [50,54–57] and mechanical damping [33, 37, 38, 50, 51, 54–61]. Alkali diffusion coefficients, for example, change by many orders of magnitude with the gradual substitution of one alkali oxide for another, but there is no unique mixed-alkali effect on the thermodynamic or structural properties of these glasses. Refractive index [37], thermal expansion coefficient [50, 54, 62, 63], elastic modulus [50, 64], heat capacity [63], density [50, 53, 54, 65] and molar volume [50, 53, 54, 66] either show additivity (linearity) or only slight deviations from additivity. Other structural properties, such as glass transition temperature [50, 54, 62, 63] and shear viscosity [50, 67] usually show negative deviations from additivity.

The internal friction of mixed-alkali glasses has been long known [4, 23, 33, 34] to differ substantially from that of single alkali glasses. The effect increases with the difference in size (or mass) between the alkali ions. When a second alkali oxide is added to a single alkali glass (total alkali oxide content held constant), a large internal friction peak appears at temperatures higher than that of the low temperature, single-alkali peak, Fig. 1. This "mixed-alkali peak" increases in height and moves to lower temperatures with further additions of the second alkali oxide. The single alkali peaks shifts to higher temperatures and becomes smaller until it disappears into the low-temperature portion of the much larger alkali peak, Fig. 3. In silicate glasses the mixed-alkali peak is usually located between 80 and 300° C at ~ 1 Hz.

The mechanism responsible for this peak was originally believed to be the diffusion of alkali ions [4, 34] (i.e. the same as in single alkali glasses), but this explanation is now considered incorrect [38, 59]. As the alkali ratio varies, the height of the mixed-alkali peak passes through a maximum, Fig. 4, while the temperature goes through a broad minimum. Studies of internal friction accompanied by diffusion measurements in Na–Rb [38] and Na–K silicate glasses [51, 68, 69] showed that the mixed-alkali peak is always largest for a certain composition (alkali ratio) where the alkali ion mobilities (diffusion coefficients) are equal, Fig. 4. This equality of mobilities at some particular composition is a consequence of the reduction of the diffusion coefficient of the original alkali upon addition of a second alkali, irrespective of cation size. It has also been found in Na–Cs [54], Na–K [70] and Na–K–Ca [71] silicate glasses and in Na–Rb germanate glasses [72]. This critical composition is a function of the glass-former, alkali concentration and in some, but not all, glass systems is temperature dependent; for example, in Na–K glasses K/(Na + K) varies from 0.68 at 250° C to 0.78 at 450° C [73]. The activation energy for the mixed-alkali peak changes proportionally to the peak temperature, but does not correlate with that for single ion diffusion. It has been concluded that the mixed-alkali peak is due to a co-operative reorientation of dissimilar alkali ions which is controlled by the slower moving alkali ion (larger relaxation time). This mechanism contrasts with that of a single-alkali peak which is related to the mobility of the more mobile ion. The mechanism for the mixed-alkali peak is similar to that proposed for the stress-induced relaxation in substitutional alloys such as α-CuZn, or CuAl [74].

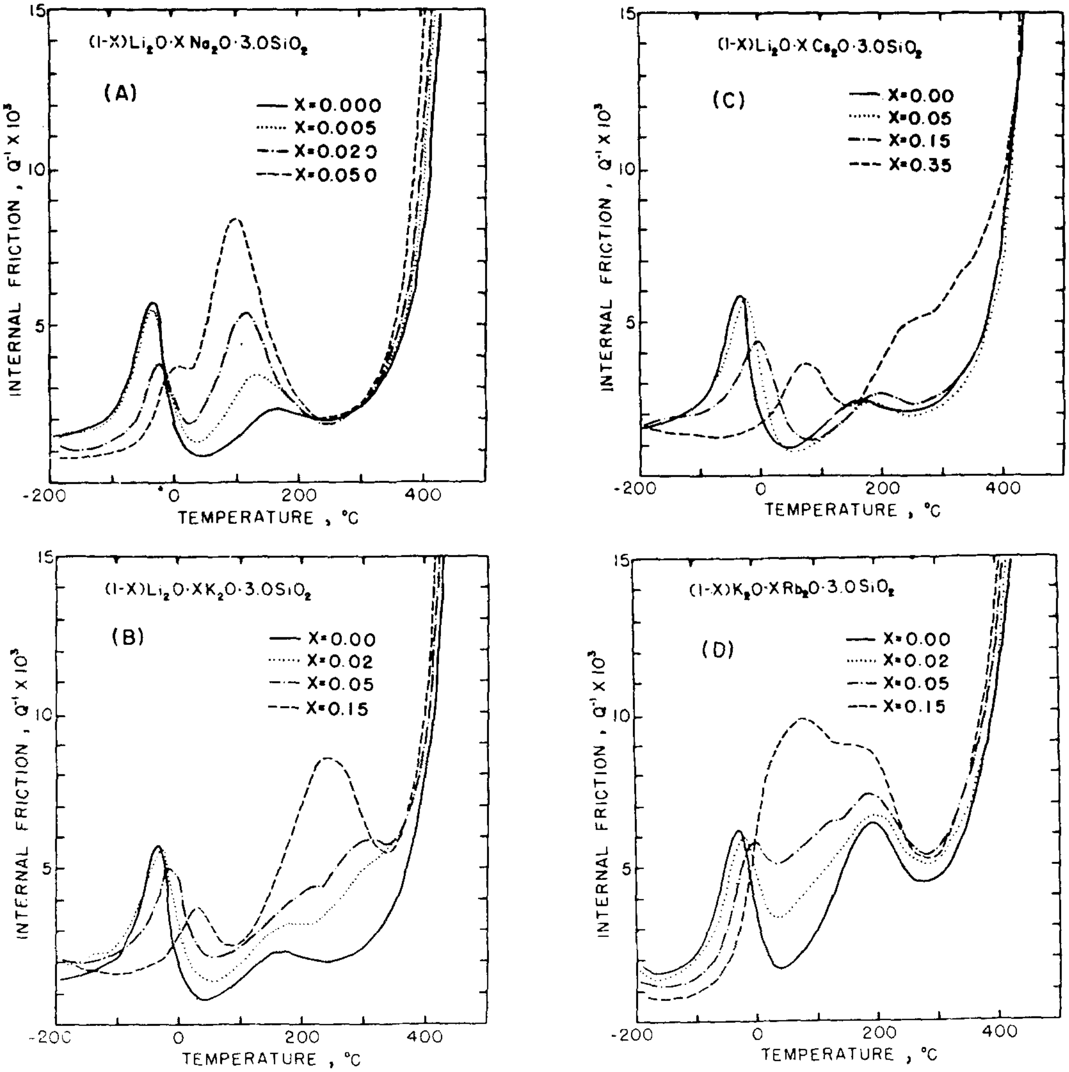

*Figure 3* Progressive changes of the internal friction curves and the appearance of a mixed-alkali peak during gradual substitution of alkalis in silicate glasses. (A) $(1-x)$ $Li_2O{\cdot}xNa_2O{\cdot}3SiO_2$, (B) $(1-x)$ $Li_2O{\cdot}xK_2O{\cdot}3SiO_2$ with a new peak appearing at ~ 300° C in $x = 0.02$ glass, (C) $(1-x)$ $Li_2O{\cdot}x$ $Cs_2O{\cdot}3SiO_2$ with the inflection at 300° C in curve for $x = 0.35$ glass and (D) $(1-x)$ $K_2O{\cdot}xRb_2O{\cdot}3SiO_2$ with a new peak at ~ 100° C in $x = 0.05$ and $x = 0.15$ glasses. $\omega = 0.4$Hz. [37].

If there is an electric moment associated with the elastic dipole involved in the mixed-alkali mechanical relaxation, it remains to be determined by parallel mechanical and electrical measurements. Currently, the elastic dipoles are thought to be electrically neutral because the relaxation time for mechanical and electrical relaxation do not correlate [73].

Effects similar to those in mixed alkali glasses are found in Na–Cu and Ag–Cu borate glasses (Section 4.6), in some liquids, molten silicates [75], molten nitrates [76] and in polycrystalline solids [77]. The latter have not been investigated extensively.

It is emphasized that the term "mixed-alkali effect" should be reserved for those glass properties related to alkali ion motion since properties associated with structural relaxation in mixed-alkali glasses are almost additive functions of chemical composition. A significant feature of commercial glasses is that mixing the alkalis increases volume instability (the well-known zero point depression of thermometers) and reduces the electrical losses. Other features of the mixed-alkali

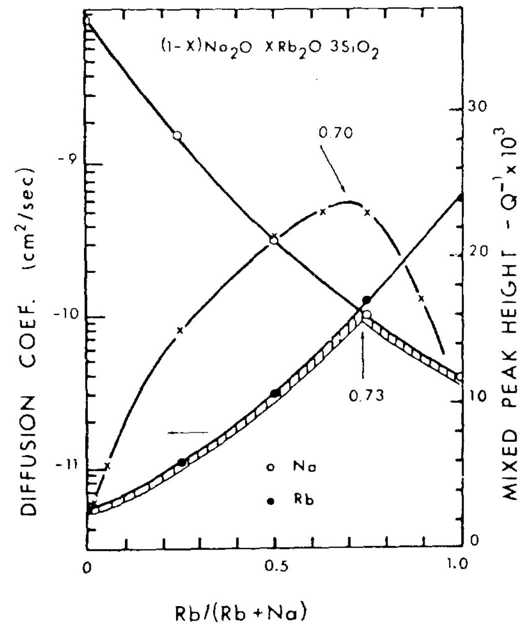

*Figure 4* Correlation between the Na and Rb diffusion coefficients (o, •) (400° C) and the height ($x$) of mixed-alkali internal friction peak as a function of $Na_2O/Rb_2O$ ratio in trisilicate glass [38].

effect and the validity of theories advanced to explain this effect can be found in reviews by Isard [50] and Day [73].

## 4.4. Silicate glasses containing alkalis and alkaline earth oxides

Alkaline earth ions, which have higher ionic potentials than the alkalis, substantially improve the chemical durability of silicate glasses. They decrease the polarizability of the single-bonded oxygen ions and reduce the diffusion coefficients of both alkali ions and protons [78, 79]. Because of their good corrosion resistance, Na–Ca silicate glasses have wide practical use.

Isolated internal friction measurements of commercial glasses have been reported [22, 80], but the most extensive work is that of Ryder and Rindone [31]. They studied 39 three-component glasses of the general composition $Me_2O{\cdot}xMeO$ $(3-x/2)\,SiO_2$. The ratio of alkali ions (Li, Na, or K) to oxygen ions was held constant as the content of Mg, Ca or Ba varied between 0.0 and 0.5 mol. These glasses generally exhibited two internal friction peaks; the alkali peak and a broader, higher temperature peak called the non-bridging oxygen peak. Sometimes a third peak at still higher temperature was observed.

Alkaline earth oxides (MeO) shift the alkali peak to above 0° C, sometimes to as much as +40° C. This effect is proportional to the MeO content and is largest for Li-glasses and somewhat smaller for Na and K-glasses. BaO is most effective, while MgO is least effective in increasing the temperature of the alkali peak in Na and K-glasses, Fig. 5, but in Li-glasses all three alkaline earth oxides produce rather similar increases at MeO $<$ 0.5 mol. At the same time, the alkali peak magnitude decreases. The effectiveness of the MeO oxides is: BaO $>$ CaO $>$ MgO in Na and K-glasses, but this is reversed in Li-glasses. The decrease in height and simultaneous shift to higher temperatures (indicating an increase in activation energy) suggest that partial immobilization of both the non-bridging oxygen ions and the alkali ions occurs in Li, Na and K-glasses with additions of MeO. Dielectric loss measurements also support this hypothesis [44].

Alkaline earth oxides also cause the second peak to broaden and shift to higher temperatures, depending on glass composition. With the exception of the $Li_2O$–BaO, $Na_2O$–MgO, $K_2O$–MgO and $K_2O$–CaO glasses, more than 0.25 mol of CaO or MgO either eliminated this peak completely or possibly shifted it to still higher temperatures where a third peak was observed. The decrease in peak intensity and shift to higher temperatures, regardless of the type of alkaline earth cations present, supported, according to Ryder and Rindone [31], the contention that the movement

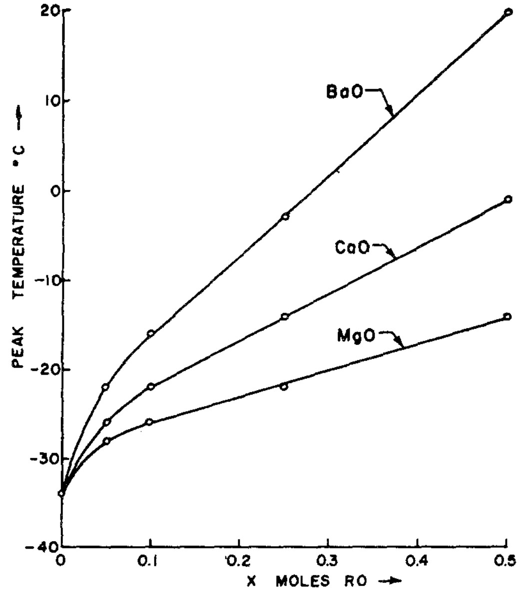

*Figure 5* An increase of the alkali relaxation temperature due to addition of RO (BaO, CaO or MgO) to the glass $Na_2O{\cdot}xRO{\cdot}(3-x/2)\,SiO_2$ [31].

of the non-bridging oxygens was the major relaxation mechanism in this temperature range. A large number of relaxing single-bonded oxygens become partially immobilized upon MeO additions so they required higher activation energies (30 to 40 kcal mol$^{-1}$) distributed over a broader energy range.

In $Li_2O$–MgO, $Li_2O$–CaO, $Na_2O$–CaO, $Na_2O$–BaO and $K_2O$–BaO glasses a third peak was observed between 265 and 380° C. The behaviour of this peak was opposite to that of the other two peaks. With increasing MeO additions, its intensity increased in proportion to MeO content, and with the exception of $Li_2O$–CaO glasses, always shifted to lower temperatures. At 0.1 mol MeO, this peak was only partially resolved from the second peak and appeared as an inflection. Two possibilities may account for the third peak. First, the basic mechanism of the non-bridging oxygen relaxation is unchanged and only the activation energy for the process is increased because of stronger bonds in the structure. The second possibility is that a new type of relaxation unit is formed in some glasses.Ryder and Rindone [31] favoured an interaction between alkali-rich clusters and the glass network. They suggested that a portion of the alkali ions may have been transferred from those positions in the glass network where they normally relax at $<0°$ C, to new positions within the MeO-rich clusters. This explanation was proposed to account for the temperature shift of the alkali peak being opposite to that of the second peak with increasing MeO content.

## 4.5. Effect of dissolved water

Water vapour dissolves chemically in glasses, and by breaking the strong network former–oxygen bonds, significantly affects physical and structural properties of glasses. Conventional silicate glasses may contain $<0.1$ wt % $H_2O$, borate and phosphate glasses $<1$ wt%, and natural volcanic glasses as much as 5% $H_2O$ [81].

Vacuum fusion techniques [82–86] infra-red absorption [87–96], tracer diffusion [97–104], internal friction [47–49, 105–111] ion exchange [106, 108, 112] and recent ESCA studies [113, 114] have provided considerable information on the reaction of water vapour and protons with glasses and melts.

It is well known that the equilibrium water solubility (saturation concentration of hydroxyl) is proportional to the square root of the $H_2O$ vapour pressure in simple [90, 93, 98] and complex oxide glasses [82–85, 96] over a wide composition range. The linear relationship between solubility and $(P_{H_2O})^{1/2}$ implies the dissociation of water molecules and the formation of (≡Si–OH) groups in silicate glasses. These groups remain stable even to 1000° C. Experimental evidence also indicates that protons can diffuse under an applied electrical field [115] or in ion exchange reactions [106, 108, 112]. Also, small quantities of molecular water may predominate in the surface reactions with glass [116].

The mechanical damping of glasses is particularly sensitive to either water dissolved in the bulk or absorbed on the surface. Vitreous $SiO_2$, and especially $B_2O_3$ [105], show increased losses due to dissolved $H_2O$. As little as 0.001% $H_2O$ produces substantial losses in Na-phosphate glasses [48]. In binary alkali silicate glasses containing dissolved water the equilibrium distribution of protons attached to non-bridging oxygens (i.e., $OH^-$ groups) affects the alkali mobility which in turn changes the mechanical damping. The internal friction peak caused by alkali relaxation decreases in magnitude and shifts to higher temperature (increased activation energy) with increasing dissolved water concentration. The second peak (between 100 and 300° C) increases in height and shifts to lower temperature which indicates that water decreases the activation energy for the second peak [107]. Thus, non-bridging oxygen ion motion cannot be the sole mechanism responsible for the second peak. Two other mechanisms have been proposed; an interaction between the alkali ions, oxygen ions and protons in hydrogen bonded bridging positions [35], or the motion of protons [46]. No theory is generally accepted.

As shown in Fig. 6, the $H_2O$ concentration and the magnitude of the second internal friction peak in sodium silicate glasses vary systematically with alkali content. Similarly, the magnitude of this peak in Li, Na, and K glasses of the same total alkali content (thus approximately equal concentration of non-bridging oxygen ions), agrees reasonably well with their estimated $H_2O$ content [111]. Investigations of Na- and Li-phosphate glasses of varying water content further support the hypothesis that protons rather than oxygen ions are responsible for the second peak in alkali silicate glasses [48–110]. Taylor and Rindone [40], however, calculated the degree of interaction between two dissimilar ions in a glassy matrix and compared the interaction energy between two

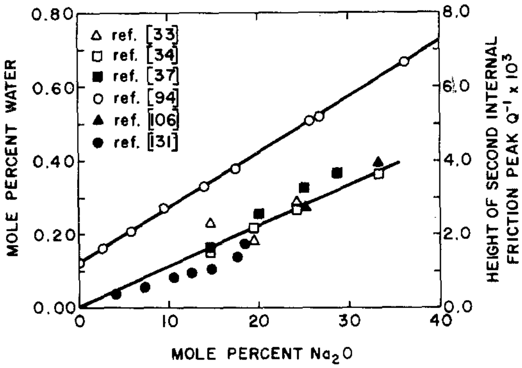

*Figure 6* Relationship between $H_2O$ content (upper line), $Na_2O$ content (lower line) and the height of the second internal friction peak in Na–silicate glasses [111].

sodium ions in non-equivalent sites (one site having been modified by converting oxygen ions into hydroxyl ions), to that for $Na^+$–$H^+$ interaction. Since the interaction energy between two sodium ions in non-equivalent sites was almost two orders of magnitude greater than the energy between a proton and a sodium ion, Taylor and Rindone proposed that the $Na^+$–$Na^+$ non-equivalent interaction is the more plausible.

Higher $H_2O$ content in glasses slightly decreases the ionic mobility by increasing the activation energy [117]. In Na-silicate glasses, variations in the $H_2O$ concentration can alter the activation energy by up to 10%. The good correlation observed [111] between the magnitude of the alkali peak and the alkali diffusion coefficient implies that a decrease in the alkali diffusion coefficient with increasing concentration of $H_2O$ [117] should result in a smaller alkali peak. This is illustrated by the data shown in Fig. 7. Other properties of $Na_2O \cdot 3SiO_2$ glass, such as viscosity and thermal expansion decrease monotonically with increasing $H_2O$ content, while the activation energy for viscous flow is reduced [118].

Qualitatively, the effect of dissolved water upon the alkali peak is similar to decreasing the alkali concentration or the addition of a second alkali. The effect upon the second peak is similar to an increase in alkali concentration. However, $<1\%$ $H_2O$ will produce changes equivalent to a several per cent variation in alkali concentration. The technique is unable to distinguish between protons or OH groups. Introducing protons into a glass by ion exchange in molten $NH_4HSO_4$ [108] produces the same changes in the mechanical damping as when a glass is melted in a humid atmosphere.

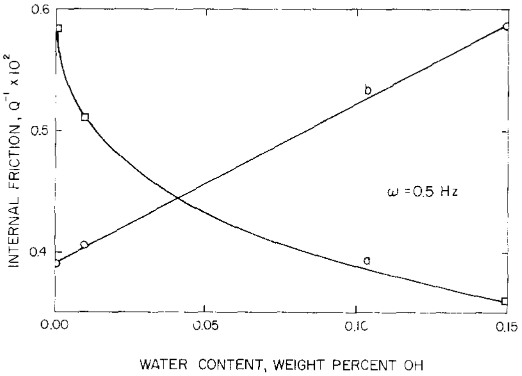

*Figure 7* Effect of $H_2O$ on the height of (a) the "alkali" peak and (b) the "high temperature" peak in 18% mol $Na_2O$–82% $SiO_2$ glass. Peaks height uncorrected for background absorption [107].

## 4.6. Borate glasses

In pure $B_2O_3$ glass, the boron ions are triangularly co-ordinated by oxygen ions ($[BO_3]^{-3}$ units). The addition of alkali oxides introduces oxygens which convert $BO_3$ units to $[BO_4]^{-4}$ units. This change in co-ordination number is thought to be the reason why some properties (viscosity, thermal expansion) of borate glasses show an extreme value at compositions between 13 to 16 mol% $Me_2O$. This is referred to as the boron anomaly [119, 120]. Internal friction investigations of alkali–borate glasses are few, compared to alkali silicate glasses, but both show similar relaxational and alkali transport behaviour; e.g., the electrical conductivity of both reaches a minimum when one alkali is replaced by another [121].

### *4.6.1. Binary borate glasses containing alkalis, Ag or Cu*

In contrast to silicate glasses, borate glasses of 15 to 32 mol% $Na_2O$ show only a network relaxation, $>350°$ C, and a single peak between 210 and 35° C, (5 Hz) whose activation energies are 32 and 16.5 kcal $mol^{-1}$, respectively. The magnitude of this peak increases with increasing soda content and shows no anomalous behaviour. However, measurements have not been made for $Na_2O$ contents below the critical 15 mol% of $Na_2O$ [122]. Fair agreement between the activation energy for the internal friction peak and that for d.c. conductivity in K–Al–borate glasses [123] suggests that the peak is due to alkali ion motion.

Similarly, Ag-borate glasses containing 10 to 30 mol% $Ag_2O$ show a single peak whose temperature is sensitive to glass composition, varying from

$\sim 110$ to $-100°$ C, and which increases in height with increasing Ag concentration. At $\sim 34$ mol % $Ag_2O$ a second, broad maximum appears at 95° C. This peak is similar to the second peak in alkali silicate glasses, but its occurrence can be related to B ions in tetrahedral co-ordination. Reduction of $Ag^+$ to $Ag^0$ does not alter the mechanical damping [124]. Increasing the Ag concentration $> 33$ mol % causes the $BO_4$ units to transform to $BO_3$ groups and the majority of oxygen ions become non-bridging [125]. In general, the peaks in Ag-borate glasses are at lower temperatures (lower activation energy) than in alkali borate glasses. Electrical conductivity [126] indicates that the $Ag^+$ ions have a higher mobility and lower activation energy than $Na^+$ ions.

### 4.6.2. *Mixed-alkali effect*

Small additions ($< 1$ mol %) of $Na_2O$ to Ag–borate glass or of $Ag_2O$ to Na–borate glass causes the low temperature peak to decrease in size and to shift to higher temperatures. A second peak begins to appear at $\sim 140°$ C in the Ag glass doped with $Na_2O$; this peak is only partially resolved in the Na glass doped with $Ag_2O$. A glass containing equimolar proportions of Ag and Na oxides shows a large "mixed-alkali" peak at $\sim 250°$ C [125]. In borate glasses, silver and copper behave as alkali oxides providing they are present as ions, a conclusion substantiated by White [127, 128] in silicate and alumino-silicate systems. Generally, the mixed-alkali effect in borate glasses is similar to that for mixed alkali phosphate and silicate glasses [129].

## 5. Summary

The need for understanding the anelastic behaviour of materials used for engineering applications has long been appreciated and internal friction techniques offer one means for studying the structure and atomic motion in vitreous solids. The position, magnitude and shape of the internal friction maxima, measured as a function of temperature (or frequency), are characteristic of glass composition and provide data for the activation energy and the type and concentration of relaxing units participating in a particular activated process. Such information is independent of, but often complementary to that obtained from diffusion and conductivity, SAXS, NMR, infra-red spectroscopy and other techniques used to study the motion, interaction and co-ordination of the structural units present in vitreous solids.

All common multicomponent oxide glasses, irrespective of the modifying and network-forming ions present (silicate, alumino-silicate, borate, boro-silicate, germanate and phosphate glasses) show specific damping peaks closely related to ionic mobility. Very mobile ions like the alkalis, $Cu^+$, $Ag^+$, and $Au^+$ produce a relaxation at temperatures $< 0°$ C (at $\omega \sim$ few Hz) with the lowest temperature corresponding to the highest ionic mobility (lowest activation energy). Since, however, the relaxation is governed not only by the type of alkali but is also related to its immediate environment, the relaxation need not be a direct function of the alkali concentration. Less mobile and more complex structural units such as non-bridging oxygen ions, oxygen–proton dipoles or alkali–proton pairs, have higher activation energies for relaxation (30 to 40 kcal $mol^{-1}$) so the damping peaks occur at higher temperatures and may often overlap. A reduction in alkali mobility occurs upon introducing bivalent cations with higher ionic potentials, whose presence cause an increase in the activation energy and a decrease in the alkali peak height. Below a certain alkali concentration ($\sim 15\%$ for Na–Ca–$SiO_2$ glass) the alkali peak disappears completely. On the other hand, mixing different alkalis reduces the mobility of the predominate alkali due to the formation of elastic dipoles which are thought to consist of two dissimilar alkali ions. These units have a higher activation energy for motion, but once activated, produce very large mechanical losses which reach a maximum at that composition where both alkalis have the same mobility.

Nucleation and crystallization [29, 130], phase separation [131–136] and ion exchange [108, 137–139] have also been studied by internal friction techniques. Nucleation in alkali silicate glasses does not produce significant changes in internal friction. Some authors postulate that liquid immiscibility in mixed-alkali glasses [140] and Na-borosilicate glasses [132, 135] produces an internal friction peak, but others report that phase separation was not detectable by $Q^{-1}$ measurements. A few investigations of non-oxide glasses ($BeF_2$) have also been reported [141, 142].

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