

Analysis of mechanical losses due to ion-transport processes in silicate glasses

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Ion-transport processes in silicate glasses containing alkali and alkaline-earth ions are studied using dynamic mechanical thermal analysis. The mechanical loss spectra are analyzed with respect to the frequency response, the height, and the activation energy of the loss peaks. It is found that the frequency response of all loss peaks is very similar, independent of the glass composition and the nature of the transport process. In the spectra of many mixed alkali-alkaline earth glasses, the low-temperature loss peak seems to be “suppressed” by intense high-temperature losses. This feature is well known from the mechanical loss spectra of mixed alkali glasses. We show that there is a correlation between this “suppression” effect and the difference between the activation energies of the low-temperature and the high-temperature peak. Furthermore, the “suppression” of the low-temperature losses seems to be accompanied by the occurrence of additional intermediate-temperature losses originating from the interaction of monovalent and divalent cations. [S0163-1829(98)01921-3]

I. INTRODUCTION

Mechanical spectroscopy is a powerful technique for the study of sub- T_g relaxations in glass. Relaxation processes occurring on different time scales can be detected in one experiment since the corresponding mechanical loss peaks are spread out on the temperature scale in an isochronal measurement. The classical studies of the mechanical loss properties of mixed alkali glasses performed by Day and others¹⁻⁵ have, e.g., revealed the existence of a relaxation mode that is connected with the transport of the slower alkali ions. By way of contrast, the electrical properties of a glass are usually dominated by the transport of most mobile ions. Therefore, no direct information on slower relaxation processes can be obtained from electrical measurements.

An important criterion for the applicability of mechanical spectroscopy to the detection of slow sub- T_g relaxations is the range of available frequencies. The lower the applied frequency, the more pronounced is the separation on the temperature scale between the sub- T_g loss peaks and the glass transition losses. The broader the range of available frequencies, the more precise are the values that can be obtained for the activation energies of the relaxation processes.

A large number of mechanical studies has been performed using the torsional pendulum at its natural frequency.¹⁻⁹ This method has a high sensitivity, i.e., mechanical losses of $\tan \delta > 10^{-4}$ can be detected, but the frequency range is relatively narrow. In order to overcome this limitation, pendulums working in forced oscillations have been designed.¹⁰⁻¹² Etienne *et al.* have used such a device to study sub- T_g relaxations in glasses.¹³⁻¹⁸ Their pendulum operates in the frequency range from 10^{-5} Hz to 1 Hz.

In a recent paper,¹⁹ we have shown that as an alternative to such specially designed pendulums, a commercially available instrumentation for dynamic mechanical thermal analysis (DMTA) can successfully be used for mechanical spectroscopy on glasses. We have described experiments on mixed alkali-alkaline earth glasses. In these systems, the alkaline-earth ions are much less mobile than the alkali ions.

Therefore, it was not initially clear if the alkaline-earth oxides should be considered as network modifiers or rather as network formers. The broad range of frequencies (0.01–200 Hz) provided by our DMT analyzer enabled us to examine in detail the mobility of the slow alkaline-earth ions.

Our results on glasses containing different alkaline-earth oxides, $\text{Na}_2\text{O}-2\text{MO}-4\text{SiO}_2$ with $M = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$, revealed that the motion of Ca^{2+} and Sr^{2+} is clearly more decoupled from the structural relaxations of the glass network occurring at the glass transition than the motion of Mg^{2+} and Ba^{2+} . So in this sense, MgO and BaO have more network former character than CaO and SrO. Furthermore, the mobility of the Na^+ ions decreases with the increasing size of the alkaline-earth cations.

We have also studied the effect of changing the relative amounts of alkali- and alkaline-earth oxides by comparing the mechanical loss spectra of the glasses $x\text{Na}_2\text{O}-(3-x)\text{CaO}-4\text{SiO}_2$ with $x = 0.4, 1.0, 1.5$. Contrary to what is found in mixed alkali glasses, in this system the mobilities of the slower alkaline-earth ions *increase* as they are replaced by alkali ions.

All the above conclusions have mainly been drawn from the loss peak temperatures and their frequency dependence. In the present paper, we consider how mechanical loss spectra can be analyzed in more detail, by taking into account peak shapes and peak intensities.

Such detailed analyses are relatively scarce in the literature. Some authors have determined the full width at half height (FWHH), δ , of loss peaks and have compared it with the FWHH of a Debye peak, $\delta_{\text{Debye}} = 1.14$ decades. Shelby and Day have done this for a large variety of single alkali and mixed alkali silicate glasses.² They find $\delta/\delta_{\text{Debye}} = 3.1-3.3$ for the alkali peak in single alkali glasses, and $\delta/\delta_{\text{Debye}} = 3.0-3.7$ for the alkali peak as well as for the mixed peak in mixed alkali glasses. Liu and Angell²⁰ have studied the mechanical losses of AgI-based fast ion conducting glasses. They find δ values for the Ag^+ ion-transport peaks similar to those of Shelby and Day. Green and co-workers²¹ report results for the mixed peak in a

TABLE I. Composition of the mixed alkali aluminosilicate glass, values in mol %.

Li ₂ O	5.72
Na ₂ O	5.72
SiO ₂	71.16
Al ₂ O ₃	16.17
TiO ₂	0.62
B ₂ O ₃	0.36
As ₂ O ₃	0.19
K ₂ O	0.06

0.243Li₂O-0.263Na₂O-0.494P₂O₅ glass. For this peak, $\delta/\delta_{\text{Debye}} \approx 3$, also in good agreement with Shelby and Day.

All these results suggest that the peak width does not significantly depend on the glass composition nor on the nature of the underlying relaxation process.

On the other hand, some authors observe mechanical loss peaks in glasses that are either broader or narrower compared with the above. Examples for very broad peaks are $\delta/\delta_{\text{Debye}} \approx 4.3$ for the mixed peak in a 0.5Na₂O-0.5K₂O-2SiO₂ glass,²² and $\delta/\delta_{\text{Debye}} \approx 4.4$ for the high-temperature peak in a ‘‘bioactive’’ 0.243Li₂O-0.269CaO-0.026P₂O₅-0.462SiO₂ glass.¹⁵ An example of a loss peak clearly narrower than is usually observed is the F^- ion-transport peak in a 0.55ZrF₄-0.31BaF₂-0.05LaF₃-0.03AlF₃-0.06NaF (ZBLAN) glass with $\delta/\delta_{\text{Debye}} \approx 2$.¹⁶

In many of our mixed alkali-alkaline earth glasses, the half widths could not easily be determined since the losses caused by different relaxational modes overlap on the frequency/temperature scale. Therefore, we have decided to use more sophisticated fitting techniques.

In the literature, two functions have mainly been used to fit mechanical loss data. The first function is the Kohlrausch-Williams-Watts (KWW) function^{23,24}

$$\Phi(t, T) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right], \quad \text{with } \tau = \tau_0 \exp\left(\frac{E_A}{kT}\right) \quad (1)$$

and $0 < \beta \leq 1$.

The mechanical loss, $\tan \delta$, is then given by

$$\tan \delta(\omega, T) \propto \int_0^\infty \left(-\frac{d\Phi(t)}{dt}\right) \sin(\omega t) dt. \quad (2)$$

The second function is a double power law²⁵

$$\tan \delta(\omega, T) \propto \frac{1}{(\omega\tau)^{-n} + (\omega\tau)^m}. \quad (3)$$

In order to test these functions, we have fitted the mechanical loss spectrum of a mixed alkali aluminosilicate glass (composition given in Table I) showing only one intense sub- T_g loss peak. In Fig. 1, the mechanical loss $\tan \delta$ is plotted as a function of temperature at a constant frequency of $\nu = 1$ Hz. From measurements at different frequencies, we have determined the activation energy of the loss peak $E_A = 0.98$ eV from the equation $E_A = -k d \ln \nu / d(1/T)$. The shapes of the temperature-dependent spectra do not depend on frequency. Therefore, knowing the value of E_A , we can

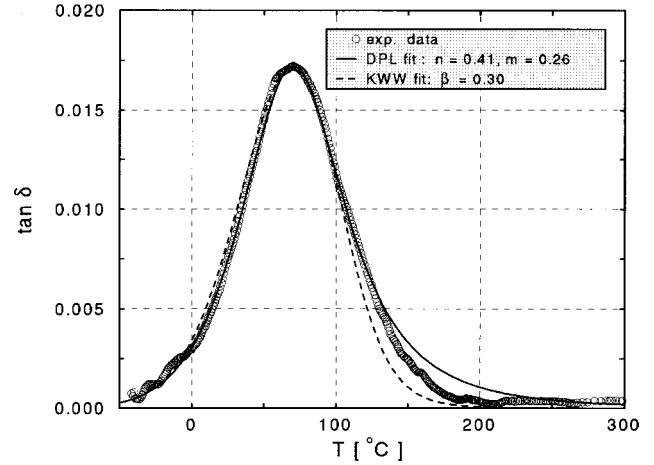


FIG. 1. Mechanical loss spectrum of the mixed alkali aluminosilicate glass at $\nu = 1$ Hz (circles) and fits (solid and dashed line).

now choose between fitting temperature-dependent loss spectra at constant frequency or frequency-dependent spectra at constant temperature. As the DMTA analyzer enables us to obtain higher resolution temperature-dependent spectra at constant frequency, we decided to fit this kind of spectra.

As can be seen from Fig. 1, the double power law provides a slightly better fit than the KWW function. The parameters chosen are $\beta = 0.3$, and $n = 0.41$, $m = 0.26$. We have, therefore, used the double power law to fit the mechanical loss spectra of the mixed alkali-alkaline earth glasses. Although in the case of the aluminosilicate glass, there are small deviations between double power law fit and experimental data at the high-temperature end of the relaxation peak, this feature does not affect the significance of the fits in the case of the mixed alkali-alkaline earth glasses.

II. DATA ANALYSIS

In the following, we analyze the mechanical loss spectra of one sodium silicate glass and several mixed alkali-alkaline earth silicate glasses. The method of sample preparation is described in Ref. 19. The DMTA experiments have been performed using the Rheometric Scientific Analyzer Mk III. Additionally, the frequency and temperature-dependent conductivities of the glasses have been measured using the Schlumberger SI 1260 impedance analyzer. Details of the measurements are presented in full in Ref. 19.

The loss spectra of all glasses consist of more than one relaxation peak. Therefore, in order to separate the contributions from different relaxational modes with different activation energies, temperature-dependent spectra taken at different frequencies have been fitted. We find that according to their mechanical loss behavior, the glasses examined can be divided into three classes:

(a) *Glasses where an intense loss peak caused by the alkali ion transport can be observed.* The spectra of the glasses Na₂O-4SiO₂ and Na₂O-2MgO-4SiO₂ at different frequencies were fitted by the superposition of one low-temperature peak, that can be attributed to the Na⁺ ion transport, and one additional high-temperature peak, see Figs. 2 and 4.

In the case of the Na₂O-4SiO₂ glass, the height of the

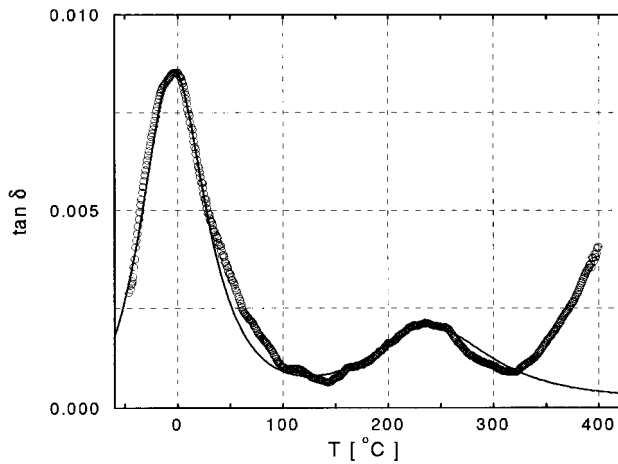


FIG. 2. Mechanical loss spectrum of the $\text{Na}_2\text{O}-4\text{SiO}_2$ glass at $\nu = 1$ Hz (symbols) and fit (solid line).

low-temperature peak is very similar to that found in other studies on alkali silicate glasses.^{1,2,26} The peak at $T \approx 235$ °C is probably due to the presence of H_2O in the glass,^{6,8,9} while the increase in $\tan \delta$ at $T > 325$ °C is caused by the onset of the glass transition ($T_g = 502$ °C). In Fig. 3, we present an Arrhenius plot of characteristic frequencies ν_m^* and ν_σ^* extracted from the mechanical spectra and from the conductivity spectra, respectively. In the former case, these are the frequencies of the mechanical loss peak maxima, while in the latter case, these are the crossover frequencies from dc conductivity to dispersive conductivity. In glasses, the activation energy of ν_σ^* is found to be identical with the activation energy of the dc conductivity, E_A^{dc} .³⁰ As can be seen from Fig. 3, the low-temperature mechanical losses and the conductivity are obviously due to the same microscopic process. On the other hand, the process causing the high-temperature mechanical losses does not contribute to the conductivity.

In the case of the $\text{Na}_2\text{O}-2\text{MgO}-4\text{SiO}_2$ glass, the increase in $\tan \delta$ at $T > 350$ °C is clearly connected with the presence

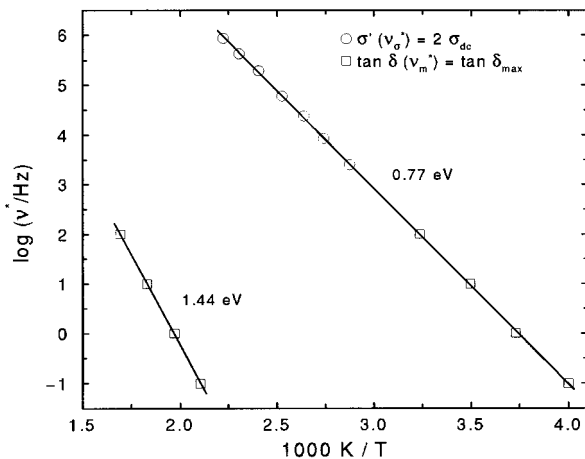


FIG. 3. Arrhenius plot of characteristic frequencies ν_m^* and ν_σ^* extracted from the mechanical loss spectra and from the conductivity spectra of the $\text{Na}_2\text{O}-4\text{SiO}_2$ glass.

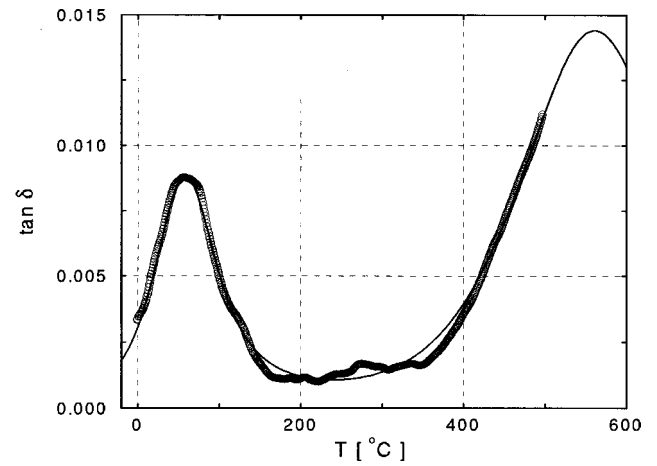


FIG. 4. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{MgO}-4\text{SiO}_2$ glass at $\nu = 1$ Hz (symbols) and fit (solid line).

of Mg^{2+} in the glass. A peak maximum cannot be detected at $\nu = 1$ Hz, but this is possible at lower frequencies. The results of isothermal multifrequency analyses have been presented in Ref. 19. The parameters for the fit of the high-temperature losses in Fig. 4 have been taken from a fit of these multifrequency data.

(b) *Glasses where the alkali ion-transport loss peak is "suppressed" and two loss peaks at higher temperatures are present.* The loss spectrum of a $\text{Na}_2\text{O}-2\text{BaO}-4\text{SiO}_2$ glass can best be fitted by superimposing three loss peaks with different activation energies, see Fig. 5. In this and in the following figures, the loss peaks and their superposition are shown as solid lines. The low-temperature peak is activated with the same activation energy as the dc conductivity, $E_A^{\text{dc}} = 1.15$ eV. This peak can be attributed to the Na^+ ion transport. The peak is clearly smaller than the corresponding Na^+ peak in the $\text{Na}_2\text{O}-2\text{MgO}-4\text{SiO}_2$ glass. The high-temperature losses ($T > 300$ °C) are again clearly connected with the presence of Ba^{2+} in the glass. A peak maximum could not be detected at $\nu = 1$ Hz. Therefore, the fit parameters have again been taken from a fit of isothermal multifrequency data. At

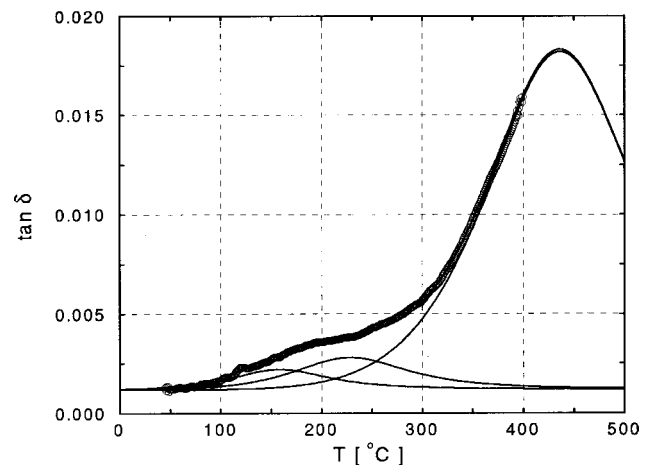


FIG. 5. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{BaO}-4\text{SiO}_2$ glass at $\nu = 1$ Hz (symbols) and fit (solid lines).

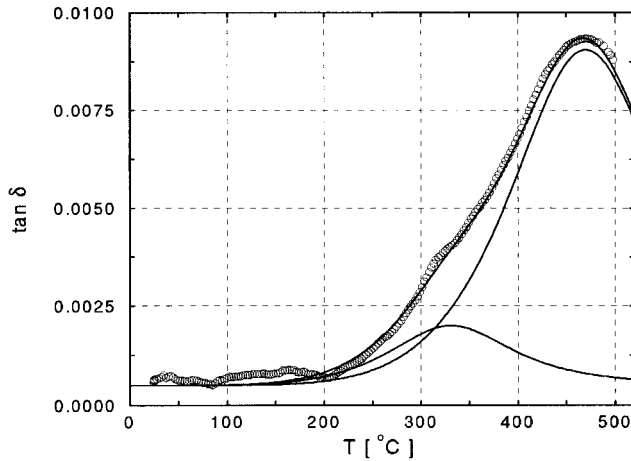


FIG. 6. Mechanical loss spectrum of the $0.4\text{Na}_2\text{O}-2.6\text{CaO}-4\text{SiO}_2$ glass at $\nu=0.1$ Hz (symbols) and fit (solid lines).

intermediate temperatures, a loss peak with an activation energy of $E_A=1.35$ eV was required to obtain a good fit.

The situation is similar in the case of a $0.4\text{Na}_2\text{O}-2.6\text{CaO}-4\text{SiO}_2$ glass, see Fig. 6. The activation energy of the dc conductivity is $E_A^{\text{dc}}=1.48$ eV. This relaxational mode cannot be detected in the mechanical loss spectrum, so the spectrum can be fitted by the superposition of two peaks with $E_A=1.74$ eV and $E_A=2.11$ eV.

In Fig. 7, the mechanical loss spectrum of a $0.5\text{Na}_2\text{O}-0.5\text{K}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass is presented. This spectrum can be fitted by the superposition of three peaks with $E_A=1.52$ eV, $E_A=1.77$ eV, and $E_A=2.18$ eV. The activation energy of the low-temperature peak is higher than the activation energy of the dc conductivity, $E_A^{\text{dc}}=1.33$ eV, see Fig. 8. This Arrhenius plot clearly demonstrates that mixed cation glasses as compared to single cation glasses (Fig. 3) show a more complex response to different external perturbations. The low-temperature mechanical loss peak is attributed to

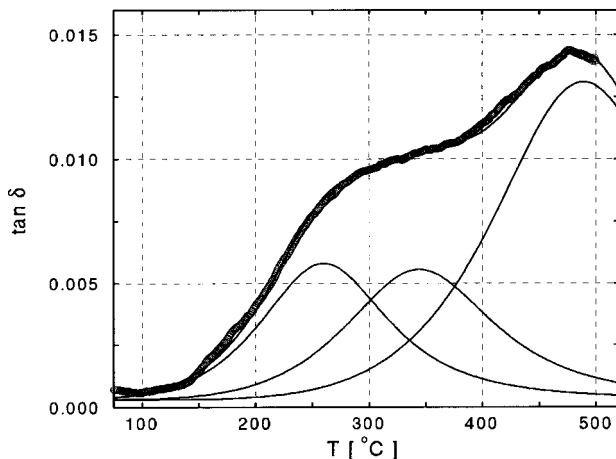


FIG. 7. Mechanical loss spectrum of the $0.5\text{Na}_2\text{O}-0.5\text{K}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass at $\nu=1$ Hz (symbols) and fit (solid lines).

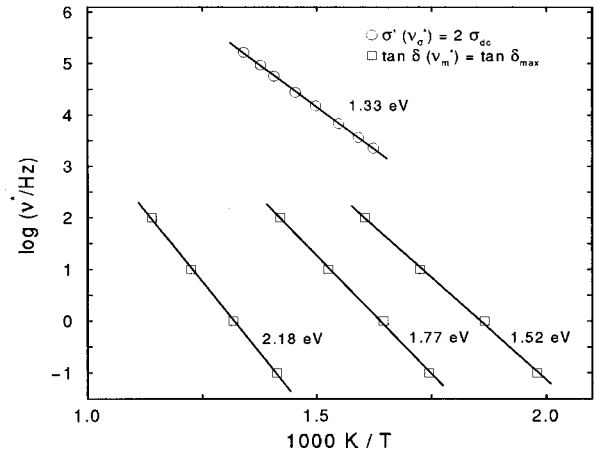


FIG. 8. Arrhenius plot of characteristic frequencies ν_m^* and ν_σ^* extracted from the mechanical loss spectra and from the conductivity spectra of the $0.5\text{Na}_2\text{O}-0.5\text{K}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass.

the coupled transport of both alkali ions, and will, therefore, in the following be called the “mixed alkali peak.” It is well known from the mechanical spectra of pure mixed alkali glasses that the activation energy of the mixed alkali peak is usually higher than E_A^{dc} .²² Compared with pure mixed alkali glasses, the mixed alkali peak of the $0.5\text{Na}_2\text{O}-0.5\text{K}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass is, however, less intense, i.e., it seems to be “suppressed” by the intense high-temperature peak ($E_A=2.18$ eV) that is clearly connected with the presence of Ca^{2+} in the glass. Again, this feature is accompanied by the occurrence of an intermediate-temperature peak with $E_A=1.77$ eV.

The obvious question is whether the intermediate-temperature peaks identified in Figs. 5, 6, and 7 are “water peaks” just like the one that presents such a prominent feature of Fig. 2. Such a suggestion may not seem unreasonable for the $\text{Na}_2\text{O}-2\text{BaO}-4\text{SiO}_2$ glass, in view of the very similar temperatures (ca. 230°C) at which the intermediate-temperature peaks appear in Figs. 2 and 5. If the peaks appearing in the range from 330°C to 350°C in Figs. 6 and 7 are also “water peaks,” then it is, indeed, remarkable that they are so strongly shifted to higher temperatures by the presence of calcium ions but do *not* suffer the same suppression effect as do the sodium peaks at lower temperatures. General considerations of glass chemistry would suggest that glasses rich in calcium and poor in sodium (such as is exemplified in Fig. 6) would in fact contain much less water than the binary sodium silicate glass (which is the progenitor of “water glass”) and yet the intermediate-temperature peaks are of very similar intensity. Based on these arguments we propose that the intermediate-temperature peaks seen in Figs. 5–7 differ in kind from those previously reported.^{6,8,9}

(c) *Glasses where the alkali ion-transport loss peak is “suppressed,” but it is not clear how many loss peaks at higher temperatures are present.* In Fig. 9, the mechanical loss spectrum of a $\text{Na}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass is shown. At first sight, this spectrum seems to consist of two loss peaks. It, however, cannot be fitted by the superposition of two peaks according to Eq. (3) with $n=0.41$ and $m=0.26$, see Fig. 9. The deviation between data and fit at temperatures $T > 450^\circ\text{C}$ is probably due to extra losses caused by the glass

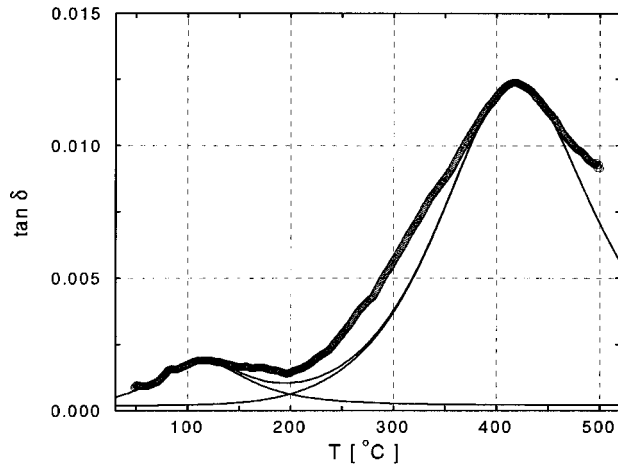


FIG. 9. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass at $\nu=1$ Hz (symbols) and fit (solid lines). Obviously, the high-temperature losses cannot be fitted by one peak with $m=0.26$.

transition ($T_g=605$ °C). The deviations at temperatures, 200 °C $< T < 375$ °C, however, must be of different origin.

There are now two ways to fit the spectrum. The first one is to assume that the high-temperature mechanical loss peak is broader than in the glasses of class (a) and class (b). The second way is to assume that there is a third loss peak at intermediate temperatures. In principle, it should be possible to decide from spectra taken at different frequencies which of the two ways is the more appropriate. If the first way were more appropriate, the shape of the high-temperature loss peak should be frequency independent, while if the second way were more appropriate, then the shape of the high-temperature losses should depend on frequency. However, it is difficult to make a decision from the experimental data. Within experimental error, both ways could be appropriate. The high-temperature losses can either be fitted by two peaks according to Eq. (3) with $m=0.26$, see Fig. 10, or by one peak with $m=0.185$, see Fig. 11.

The same applies for the spectra of the glasses $\text{Na}_2\text{O}-2\text{SrO}-4\text{SiO}_2$ and $1.5\text{Na}_2\text{O}-1.5\text{CaO}-4\text{SiO}_2$. In Figs. 12 and 13, the high-temperature loss peaks are fitted by two peaks with $m=0.26$. However, bearing in mind that in class (c) behavior the two upper peaks are much closer together than in class (b) behavior, it is difficult to decide just how many peaks do indeed exist.

III. DISCUSSION

As can be seen from our results, mechanical spectroscopy spreads out very conveniently the fast and slow processes on the temperature scale. In all our glasses, we find an Arrhenius-type relation between peak temperature T and applied frequency, $\nu = \nu_0 \exp(-E_a/kT)$. The values for the pre-exponential factor ν_0 are similar for different glasses and different relaxation processes ($10^{13.5}$ Hz $< \nu_0 < 10^{14.5}$ Hz). Therefore, the spread of the relaxation peaks on the temperature scale corresponds directly to the spread in the activation energies. The spread on the temperature scale is the more

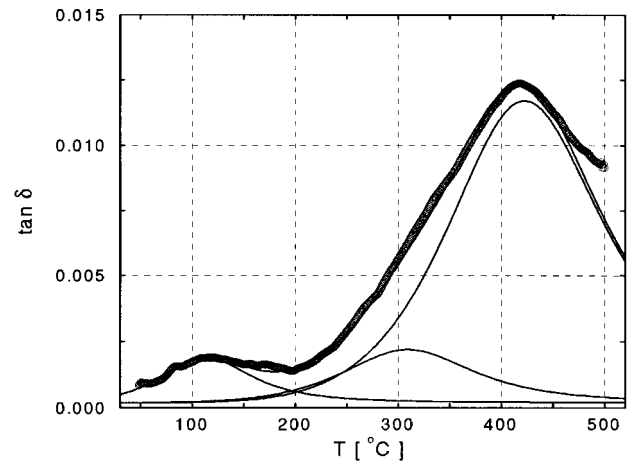


FIG. 10. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass at $\nu=1$ Hz (symbols) and fit (solid lines). The high-temperature losses are fitted by two peaks with $m=0.26$.

pronounced, the lower is the applied frequency. It would, e.g., be impossible to analyze the slow relaxations of the alkaline-earth ions with ultrasonic methods (MHz regime) because the alkaline-earth ion loss peaks will coalesce with the glass transition losses.

An important finding from the present study is that all loss spectra can be fitted by superimposing loss peaks described by Eq. (3) with $m=0.26$ and $n=0.41$. This corresponds to $\delta/\delta_{\text{Debye}}=3.1$. The high-temperature losses of the glasses of class (c) can alternatively be fitted by one peak with $m=0.185$ corresponding to $\delta/\delta_{\text{Debye}}=3.7$. So, in either case, our results are in good agreement with those of Shelby and Day. The frequency response of ion-transport mechanical losses in glass seems, indeed, to show a universal kind of behavior analogous to the universal phenomena observed in the frequency response of low-frequency electrical losses in glass.²⁷⁻³⁰

According to linear-response theory, the density fluctuations caused by an ion-transport process lead to a mechanical loss that is given by³¹

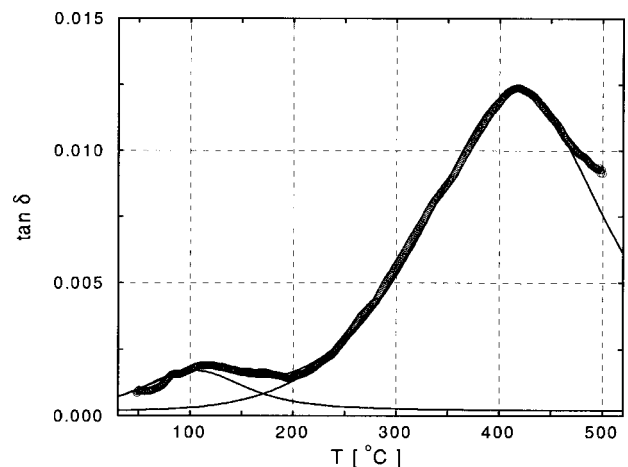


FIG. 11. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{CaO}-4\text{SiO}_2$ glass at $\nu=1$ Hz (symbols) and fit (solid lines). The high-temperature losses are fitted by one peak with $m=0.185$.

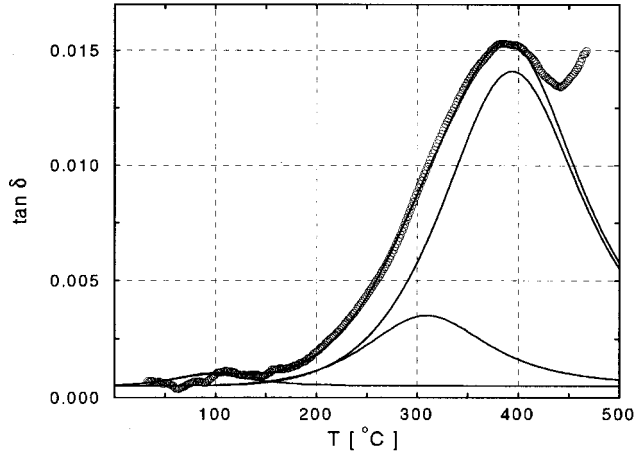


FIG. 12. Mechanical loss spectrum of the $\text{Na}_2\text{O}-2\text{SrO}-4\text{SiO}_2$ glass at $\nu=0.1$ Hz (symbols) and fit (solid lines). The high-temperature losses are fitted by two peaks with $m=0.26$.

$$\tan \delta(\omega) = \frac{N_V \omega}{M' k_B T} \sum_{\mathbf{Q}} |\hat{\epsilon}(\mathbf{Q})|^2 S_{\text{coh}}(\mathbf{Q}, \omega). \quad (4)$$

Here, N_V and M' are the number density of the mobile ions and the real part of the complex mechanical modulus, respectively. S_{coh} denotes the coherent dynamic structure factor of the mobile ions, while $\hat{\epsilon}(\mathbf{Q})$ are the Fourier components of the coupling function between mechanical deformation of the sample and the potential energy of the mobile ions, $\epsilon(\mathbf{r})$.

Equation (4) implies that the mechanical loss is the larger (a) the higher is the number density of mobile ions, (b) the more the potential energy of the ions is affected by the mechanical deformation of the sample, and (c) the more easily the ions can relax with respect to the changes in the potential landscape, i.e., the more easily density fluctuations are allowed. Furthermore, it follows from Eq. (4) that there are two prerequisites for a universal behavior of $\tan \delta(\omega)$. The

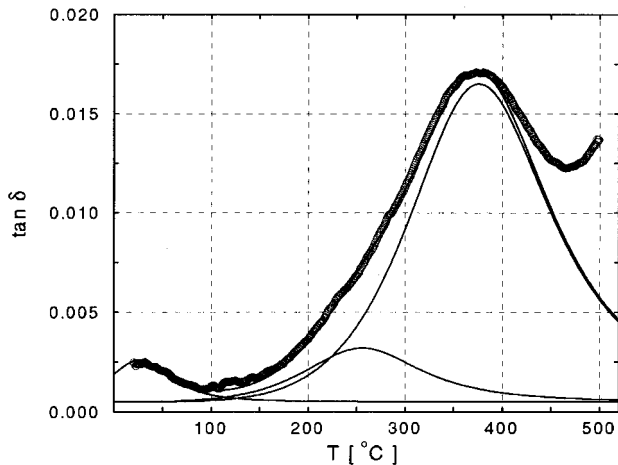


FIG. 13. Mechanical loss spectrum of the $1.5\text{Na}_2\text{O}-1.5\text{CaO}-4\text{SiO}_2$ glass at $\nu=1$ Hz (symbols) and fit (solid lines). The high-temperature losses are fitted by two peaks with $m=0.26$.

coupling function between mechanical deformation and potential energy of the mobile ions must be universal, and the dynamic structure factor of the underlying transport process must be universal, at least for the \mathbf{Q} components contributing significantly to $\hat{\epsilon}$. In particular, a universality in $\hat{\epsilon}(\mathbf{Q})$ is not obvious as the coupling between the mechanical deformation and the potential energy of the mobile ions should generally depend on the glass structure. This is contrary to the electrical case where the coupling between the electrical field and the mobile ions only depends on the ionic charge and the hopping distance. Therefore, a universality in the mechanical loss behavior is even more remarkable than the universality in the electrical loss behavior.

Another remarkable feature in the mechanical loss spectra of glasses with more than one mobile ion is the ‘‘suppression’’ of low-temperature peaks in the presence of intense high-temperature peaks. We have observed this feature in all our mixed alkali-alkaline earth glasses except in the $\text{Na}_2\text{O}-2\text{MgO}-4\text{SiO}_2$ glass. In this glass, the difference between the activation energy of the low-temperature Na^+ peak and the activation energy of the high-temperature peak, $\Delta E_A = 1.42$ eV, is much larger than in the case of the Ca, Sr, and Ba containing glasses, where ΔE_A is in the range 0.85 ± 0.05 eV. This comparison suggests that the ‘‘suppression’’ effect is greater the smaller the difference is between the activation energies of the high- and low-temperature peaks.

This hypothesis gains further support from earlier results on mixed alkali glasses.¹ If smaller alkali ions are partially replaced by larger alkali ions, the ‘‘suppression’’ of the alkali peak is the more pronounced and the difference between the activation energy of the alkali peak and the mixed peak is the larger, the smaller is the radius ratio of the two ions, e.g., the ‘‘suppression’’ is more pronounced in Li-Na glasses compared with Li-K glasses. The more pronounced the ‘‘suppression’’ effect, the faster the mixed peak grows with an increasing relative concentration of the larger ions.

In mixed alkali-alkaline earth glasses, the radius ratio of alkali ions to alkaline-earth ions does not obviously determine the difference between the activation energy of the alkali peak and the high-temperature peak, see Ref. 19, but the same relation between ‘‘suppression’’ of the alkali peak and difference between the activation energies seems to be valid. This indicates that there is a *direct* correlation between peak height and difference between the activation energies. This difference determines the ratio of the ion hopping rates.

A correlation between peak height and ratio of hopping rates suggests that the ‘‘suppression’’ of the low-temperature peaks and the high intensity of the high-temperature peaks are caused by an increasing coupling between the ion-transport processes with a decreasing ratio of hopping rates.

The low-temperature peaks in mixed alkali glasses as well as in mixed alkali-alkali- and alkali-earth glasses can be attributed to the transport of the fast alkali ions. The high-temperature peaks are clearly connected with the presence of the divalent ions in the glass. Sakai and co-workers³² have recently shown for a $\text{Na}_2\text{O}-2\text{CaO}-3\text{SiO}_2$ glass that the activation energy of the high-temperature mechanical loss peak is very close to the activation energy of the Ca^{2+} diffusion. On the other hand, we have observed that the height of the high-temperature peak in $x\text{Na}_2\text{O}-(3-x)\text{CaO}-4\text{SiO}_2$ glasses increases with x in the range $0.4 < x < 1.5$, see Figs. 6, 9, and

13. This strongly indicates that Na^+ ions play an important role with respect to the underlying relaxation process. Therefore, the high-temperature loss peaks can best be considered as involving interdiffusion of the fast alkali ions and the slower alkali- or alkaline-earth ions. This suggests that the coupling between the relaxation processes responsible for the low-temperature and the high-temperature loss peaks, respectively, should be closely related to the fact that the fast alkali ions are involved in both diffusion processes. The coupling between the processes could also be responsible for the additional relaxation modes that we have observed as intermediate-temperature losses in the spectra with "suppressed" low-temperature peaks.

The phenomenon of *coupling* has been discussed in very general terms in the literature, e.g., by Ngai and Tsang,^{29,33} Funke and co-workers,^{34,35} and Maass *et al.*^{36,37} Until now, attention has been focused on the universal nonexponential relaxation in glasses and other complex systems when recovering, for example, from electrical, thermal, and mechanical stresses. As presently formulated, the above theoretical approaches describe the phenomena observed when just one microscopic process dissipates energy in the system. The results presented here reopen the question (first posed by Shelby and Day following their work on mixed alkali glasses) of how "fast" and "slow" processes will couple when different atomic species are involved. In glasses containing both alkali- and alkaline-earth cations, it becomes important to establish just how far the major changes in mobilities of the unipositive and dipositive cations produced by varying the relative amounts of these species¹⁹ occur in response to "coupling" or can be attributed more straightforwardly to changes in the glass structure. Seeking the answers to these questions will help shed light on relaxation processes in ionic glasses more generally, and very likely will stimulate further investigations of mechanical loss spectra in these multicomponent systems.

Reference has already been made to the possible role of water in relaxing mechanical stresses in glass, especially at intermediate temperatures between the alkali loss peaks and T_g . This suggests that there is a clear need for additional studies on the behavior of protons and water molecules in glass, using complementary techniques for identifying

chemical species *and* ion dynamics, such as nuclear magnetic resonance. These studies should indicate unambiguously which mechanical loss peaks are related to water and which are not.

IV. CONCLUSIONS

We have analyzed in detail the mechanical loss spectra of a variety of silicate glasses containing both alkali- and alkaline-earth ions. Three important results have been obtained.

First, the frequency response of the mechanical loss peaks shows a universal kind of behavior analogous to the frequency response of electrical losses in glass. In a first approximation, the frequency response seems to be independent of the glass composition and the nature of the relaxation process.

Second, in many mixed alkali-alkaline earth glasses, we find a "suppression" of the low-temperature loss peak in the presence of an intense high-temperature loss peak. As in mixed alkali glasses, the degree of "suppression" is related to the difference between the activation energies of the low-temperature and the high-temperature peak.

Third, the suppression of the low-temperature peak seems to be accompanied by the occurrence of additional intermediate-temperature losses, that do *not* originate from the presence of water. A possible explanation for the latter two findings is a coupling between the two ion-transport processes responsible for the low-temperature and the high-temperature losses, the degree of coupling being large for small differences between the activation energies of the separate transport processes.

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