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Isothermal mechanical relaxations in single and mixed alkali silicate glasses.

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Abstract

Very low frequency damping measurements carried out in various mixed alkali silicate glasses $(1-x)\text{Na}_2\text{O}\cdot x\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ with $x = 0, 0.25, 0.5$ and 0.75 point out new experimental features. A new relaxation peak occurring at very low temperature is evidenced in the single alkali glass ($x = 0$) in addition to the two classical relaxation peaks previously described and assigned respectively to the motion of alkali ions (ionic peak) and to a local rearrangement of the glassy structure involving non-bridging oxygen (NBO peak). For the three mixed alkali glasses, the mixed alkali relaxation peak is shown to be superimposed to two satellite peaks corresponding to the ionic and NBO peaks. Moreover, Arrhenius plot of the mixed alkali peak shows that the apparent activation energy is different below and above 340 K. These experimental results are discussed using recent models proposed for the alkali effect and a model developed previously for mechanical relaxation in ionic glasses below T_g .

Keywords: Isothermal mechanical spectroscopy, internal friction, mixed alkali effect, inorganic glass.

1. Introduction

Various peaks are previously observed in single alkali silicate glasses: a first one, occurring near room temperature when the frequency of vibration is of the order of 1 Hz, is generally attributed to the action of the applied stress on alkali ions and called "ionic peak" [1-4]. The origin of a second peak observed at higher temperature is still debated: it appears only with the presence of non-bridging oxygen and of water. This peak is often called "non-bridging oxygen peak" (NBO peak) [2,4-7].

Mixed alkali silicate glasses exhibit a very large internal friction peak [4,5,8-12]. Some authors maintain that this peak takes the place of the ionic peak and others that it is superimposed to the peaks observed in the single silicate glasses. Another point of discussion concerns the results obtained for mixed alkali glass with a very low ratio of a second alkali ion [5,8,11]: a small relaxation peak is described by the authors as a mixed alkali peak but in fact this peak can correspond to the NBO peak.

In order to clarify this situation, new internal friction experiments were performed using the isothermal mechanical spectroscopy technique allowing very accurate measurements, for four silicate glasses of $(1-x)\text{Na}_2\text{O}\cdot x\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ type with $x = 0, 0.25, 0.5$ and 0.75 .

2 - Experimental procedure

Isothermal mechanical spectroscopy (IMS) consists in measuring internal friction in a very wide frequency range (10^{-4} Hz - 40 Hz) after stabilization of the temperature and of the sample microstructure. For materials with high stiffness, a good accuracy in damping ($\pm 10^{-4}$) can be obtained only using an inverted forced pendulum working in the subresonant frequency range [13,14]. Such a pendulum must have a very high resonance frequency (200 - 300 Hz) to allow the forced measurements until 40 Hz. In comparison with measurements at a fixed frequency, IMS presents decisive and basic advantages and allows a better

determination of the relaxation parameters.

The apparatus used for this work was already described in detail [15]. Measurements were carried out in a vacuum. In the case of the forced vibration technique, internal friction Q^{-1} is equal to $\tan \varphi$ where φ is the phase lag between the applied stress and the resulting strain. Isothermal experiments started three hours after each temperature change. The measurement frequencies (f) were ranged between 40 Hz and 10^{-4} Hz and ten discrete frequencies per decade were used. Internal friction was also measured at the free frequency of the pendulum (≈ 200 Hz) by the free decay method. The maximal strain amplitude was $\varepsilon_M = 5 \times 10^{-6}$. The dimensions of the specimens were $1.5\text{mm} \times 5\text{mm} \times 50\text{mm}$.

3. Experimental results and interpretation

3.1. Single alkali silicate glass

Isothermal spectroscopy experiments performed in the single alkali silicate glass $\text{Na}_2\text{O} \cdot 3\text{SiO}_2$ exhibit three mechanical relaxation peaks. In fact, a new relaxation peak is evidenced at very low temperature (Fig. 1). The corresponding activation energy (11.8 kJ/mole, 0.12 eV) corresponds to a local motion of sodium ions inside their sites. For an anelastic behavior, the applied stress does not act directly on the ions but the elastic deformation of the vitreous structure can induce change in ion position.

The classical ionic peak corresponding to the jump of sodium ions to a vacant neighboring site and the non-bridging oxygen peak were also evidenced in the sample. Fig 2 displays the Arrhenius plots (Napierian logarithm of the peak maxima versus the corresponding inverse measurement temperature) for the three relaxation peaks.

The relaxation parameters (the apparent activation energy E_a and the limit relaxation time τ_0) are: $E_a \approx 58$ kJ/mol (0.6 eV) and $\tau_0 = 8 \times 10^{-14}$ s for the ionic peak and $E_a \approx 94$ kJ/mol (0.95 eV) and $\tau_0 = 1.5 \times 10^{-11}$ s for the non-bridging oxygen peak.

[insert Figs. 1 and 2 here]

3.2. Mixed alkali silicate glasses

For the three mixed alkali silicate glasses $(1-x)\text{Na}_2\text{O} \cdot x\text{Li}_2\text{O} \cdot 3\text{SiO}_2$, isothermal internal friction measurements exhibited an apparent peak of large amplitude. Fig.3 shows the internal friction spectrum versus frequency for each glass ($x=0.25, 0.5$ and 0.75) at the same temperature 350K. It is noticeable that the height and the location of this apparent maximum depend on the glass composition. From the experiments performed at different temperatures, this apparent peak shifts to higher frequency with increasing temperature and covers about 3 decades. However, for each composition, the height depends on the temperature of the measurement as shown in Fig. 4 corresponding to the $0.5\text{Na}_2\text{O} \cdot 0.5\text{Li}_2\text{O} \cdot 3\text{SiO}_2$ mixed alkali silicate. In such case, the relaxation peaks plotted against the inverse temperature are not symmetrical. More often such relaxation spectra are complex and a relaxation peak is generally superimposed on a background or other peaks. For relaxation spectra plotted against the temperature, the use of symmetrical functions to deduce the relaxation peak introduces systematically a mistake on the determination of the temperature of the peak maximum. On the contrary, isothermal experiments exhibit always symmetrical peaks which can be easily and accurately subtracted from the experimental spectra.

[insert Figs. 3 and 4 here]

From the isothermal experiments performed in frequency sweep, internal friction can also be plotted against the temperature T at a given frequency, as illustrated in Fig. 5 at 0.0032Hz for

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the $0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ glass: the internal friction spectrum can be separated into a high intensity peak (mixed alkali peak) at about 330K and, at higher temperature ($\sim 410\text{K}$), a lower intensity peak (NBO peak) which appears as a shoulder at the bottom of the high peak. Fig. 5 shows also the decrease of the modulus accompanying each of the relaxation phenomena. So, the NBO peak is still present in mixed alkali glasses.

The ionic peak is also evidenced in mixed alkali silicate glasses as shown in Fig. 6. This peak corresponds to the jump of both sodium and lithium ions. The relaxation strength is much larger for the single alkali silicate glass than for the $0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ glass and, in this case, only few ions jump directly to a neighboring site.

[insert Figs. 5 and 6 here]

In Fig. 7 the Arrhenius plots corresponding respectively to the ionic and NBO peaks obtained for the single alkali glass and the three mixed alkali glasses are reported. The plots corresponding to the NBO peaks are quite similar for all the glasses. On the contrary, Fig. 7 shows that the ionic peak shifts to lower frequency (at fixed temperature) for the mixed alkali glasses. This fact was previously mentioned [4, 5, 8, 10-12].

The Arrhenius plots corresponding to the mixed alkali peak are displayed in Fig. 8. For each sample, the experimental points cannot be aligned in a single straight line and the Arrhenius spectra correspond to two different energy activation values; the transition temperature being about 340 K.

[insert Figs. 7 and 8 here]

The experimental relaxation parameters are displayed in Table 1 for the three mixed alkali glasses.

[insert Table 1 here]

4. Discussion and conclusion

The use of isothermal mechanical spectroscopy provides new and more accurate experimental results:

- a new relaxation peak was evidenced for the first time at very low temperature in single alkali silicate $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ glass; the associated activation energy (11.8 kJ/mole, 0.12 eV) allows to assign this peak to very small motion of alkali ions inside their sites.
- contrary to previous works [10,12,16], our experimental results show that NBO peak is still present in mixed alkali silicate glasses; this peak is quite similar in single and mixed alkali glasses and corresponds to a relaxation inside the vitreous structure.
- as predicted in a theoretical approach suggested by Meyer and Bunde [17], the ionic peak is also still present in mixed alkali silicate glasses and corresponds to jumps of both sodium and lithium ions. The very small relaxation strength indicates that only few ions can jump directly to a vacant neighboring site.
- the shift of the ionic peak to higher temperature for the mixed alkali glasses are in agreement with previous papers [1-3].
- the Arrhenius plots corresponding to the mixed alkali peaks indicates a transition temperature (about 340 K).

The very large relaxation strength of the mixed alkali peak can be explained by recent theories about the mixed alkali effect [18, 19, 20]. According to these theories, the both kinds of mobile ions have different jump paths. The mutual interception of these jump paths involves a freeze of the ions and consequently a decreasing of the electrical conductivity. So, a great number of sodium ions are close to a lithium one (and vice versa). If the elastic deformation allows one ion to jump, the second one will also jump quite automatically. Such correlative

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3 jumps concerning a large number of alkali ions induce a very large relaxation peak.
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4 Figure captions

5 Fig. 1 - Very low temperature internal friction peak in single alkali silicate glass $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$
6 measured at 145 K (∇) and 154 K (Δ).
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8 Fig. 2 - Arrhenius plot of the three peaks observed in single alkali silicate glass $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$:
9 very low temperature peak (∇), ionic peak (\circ) and NBO peak (Δ).
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11 Fig. 3 - Mixed alkali peak measured at 350 K in the three mixed alkali silicate glasses
12 $(1-x)\text{Na}_2\text{O}\cdot x\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ for $x = 0.25$ (∇), 0.5 (\circ) and 0.75 (Δ).
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14 Fig. 4 - Mixed alkali peak in $0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ mixed alkali silicate glass measured at
15 350 K (∇), 375 K (\circ) and 396 K (Δ).
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17 Fig. 5 - Mixed alkali silicate glass $0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ - Internal friction (Δ) and modulus
18 effect (∇) measured at 0.0032 Hz.
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21 Fig. 6 – Ionic peak measured at 292 K in single alkali silicate glass $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ (Δ) and in
22 mixed alkali silicate glass $0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$ (∇) after background subtraction.
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25 Fig. 7 - Arrhenius plot of the ionic (empty symbols) and NBO (full symbols) peaks in single
26 alkali silicate glass $\text{Na}_2\text{O}\cdot 3\text{SiO}_2$ (\diamond, \blacklozenge) and the three mixed alkali silicate glasses
27 $(1-x)\text{Na}_2\text{O}\cdot x\text{Li}_2\text{O}\cdot 3\text{SiO}_2$: $x = 0.25$ ($\nabla, \blacktriangledown$), 0.5 (\circ, \bullet) and 0.75 (Δ, \blacktriangle).
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30 Fig. 8 - Arrhenius plot of the mixed alkali peak in the three mixed alkali silicate glasses
31 $(1-x)\text{Na}_2\text{O}\cdot x\text{Li}_2\text{O}\cdot 3\text{SiO}_2$: $x = 0.25$ (∇), 0.5 (\circ) and 0.75 (Δ). The arrow indicates the
32 transition temperature.
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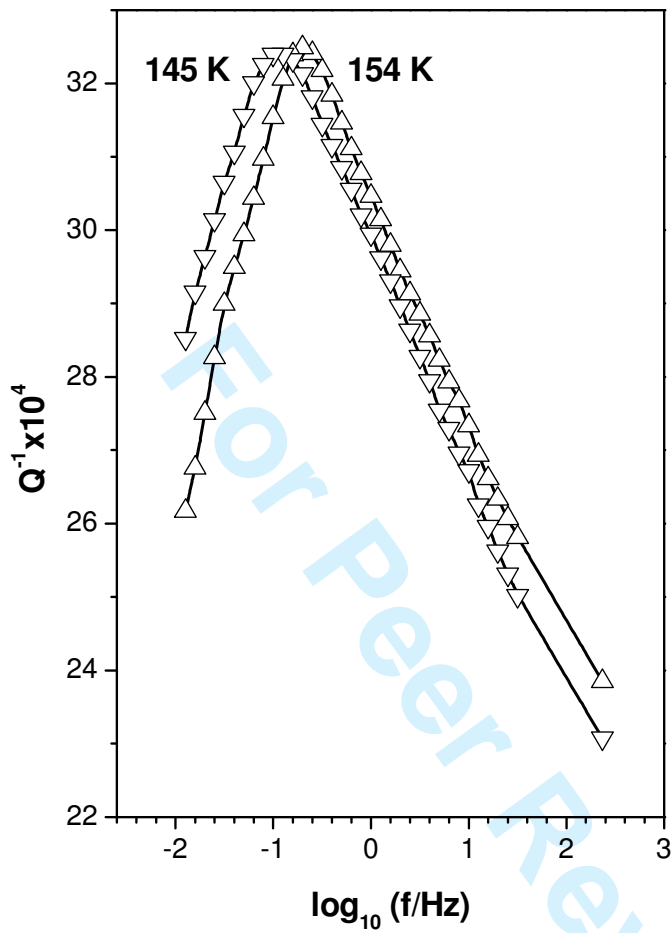


Fig. 1

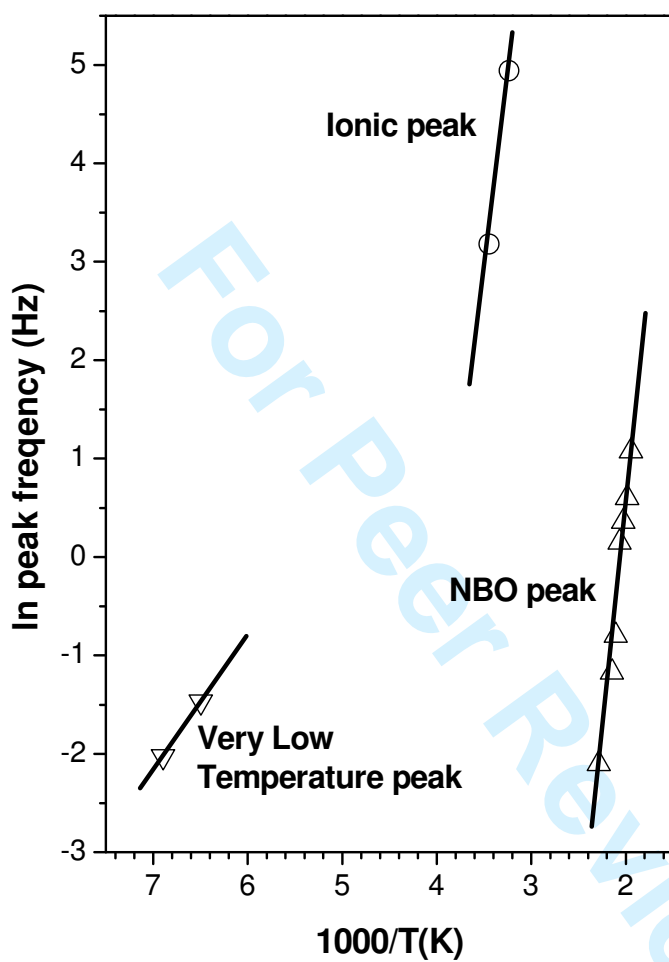


Fig. 2

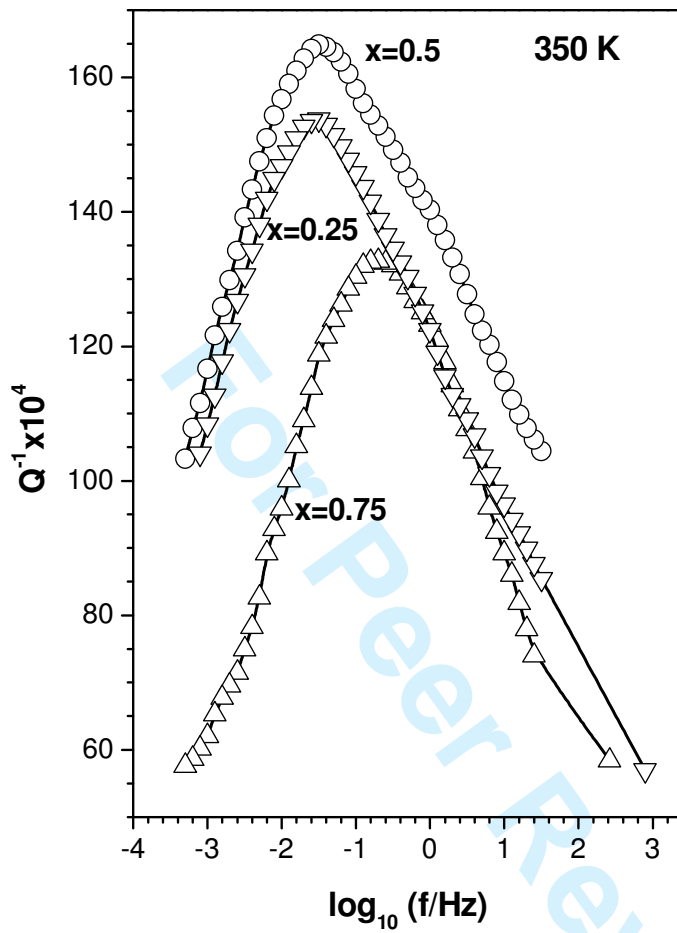


Fig. 3

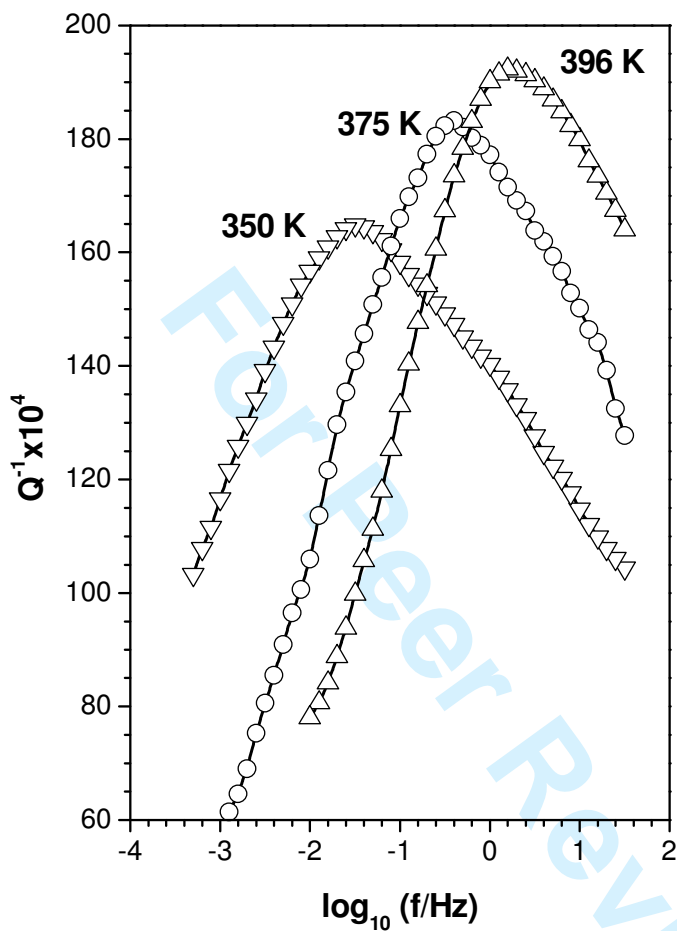


Fig. 4

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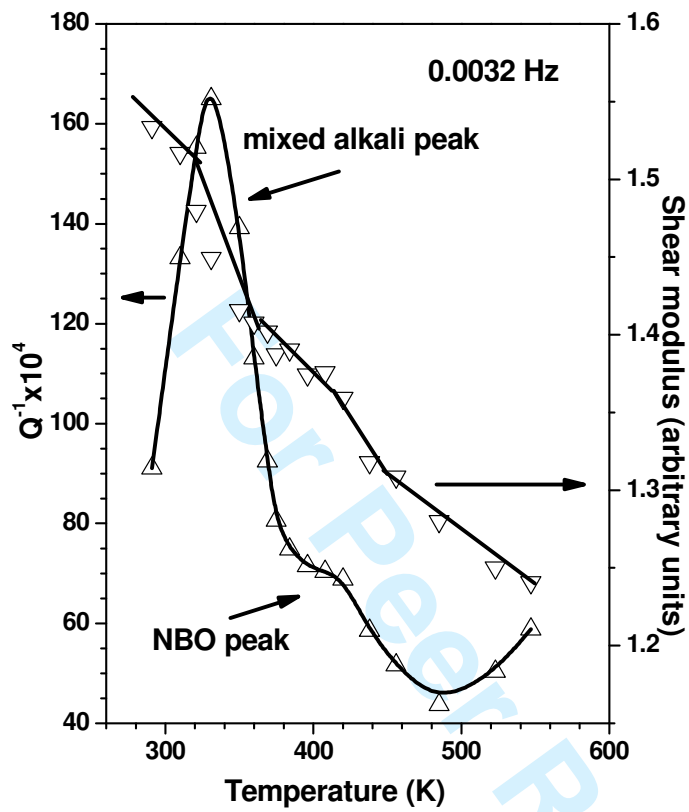


Fig. 5

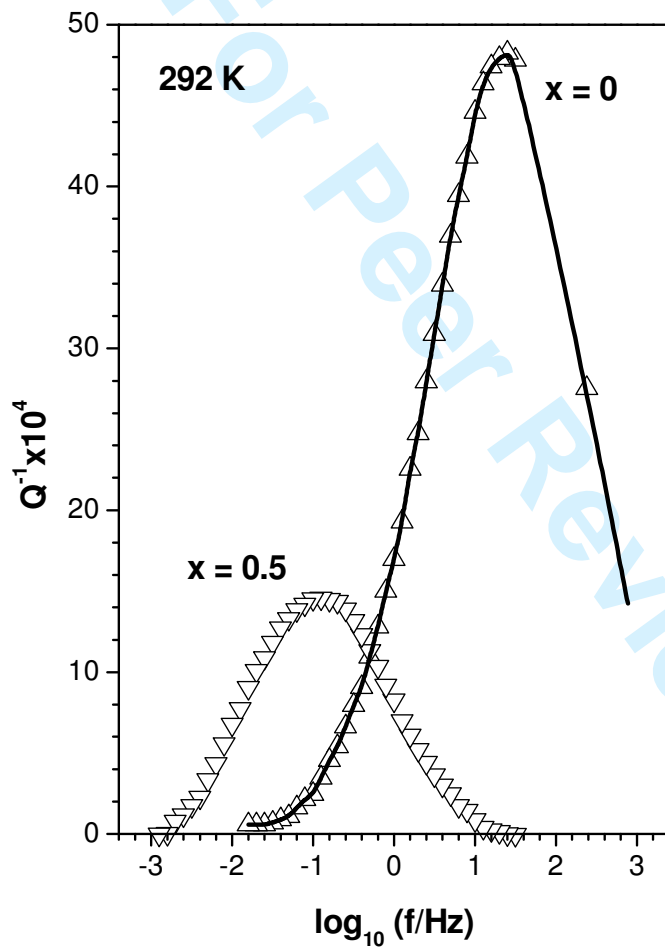


Fig. 6

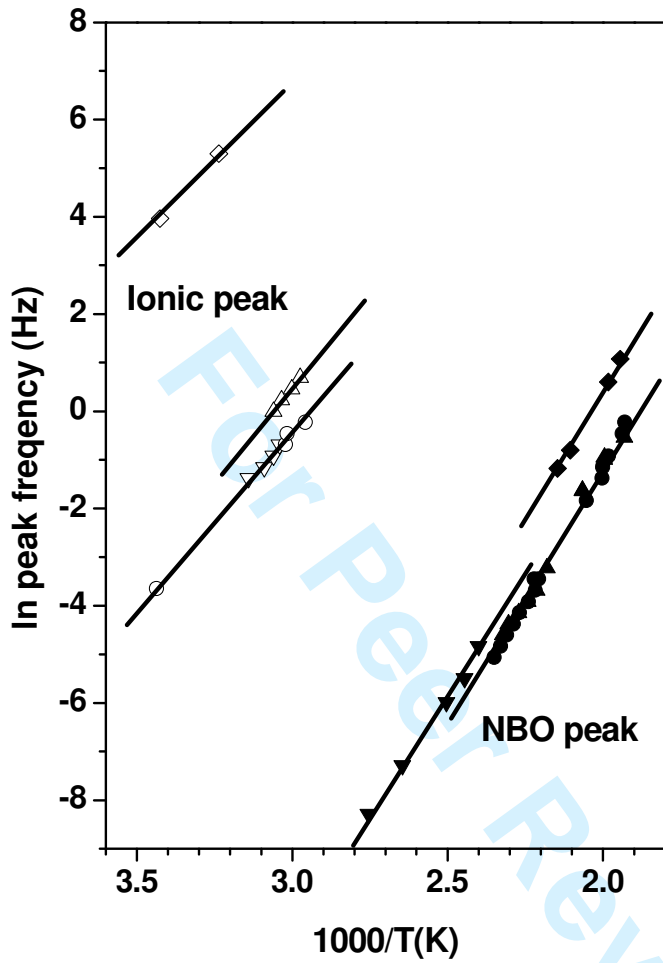


Fig.7

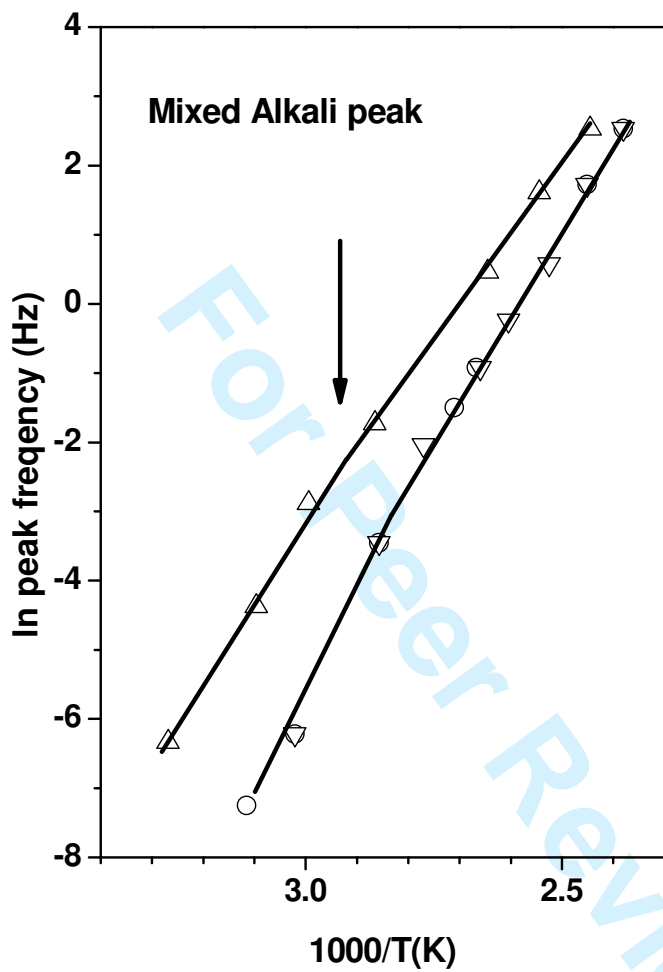


Fig. 8

	Low temperature	High temperature
$0.75\text{Na}_2\text{O}\cdot 0.25\text{Li}_2\text{O}\cdot 3\text{SiO}_2$	$E_a = 104 \text{ kJ/mole (1.1 eV)}$ $\tau_0 = 2 \times 10^{-16}$	$E_a = 85 \text{ kJ/mole (0.9 eV)}$ $\tau_0 = 2 \times 10^{-13}$
$0.5\text{Na}_2\text{O}\cdot 0.5\text{Li}_2\text{O}\cdot 3\text{SiO}_2$	$E_a = 123 \text{ kJ/mole (1.3 eV)}$ $\tau_0 = 2 \times 10^{-18}$	$E_a = 102 \text{ kJ/mole (1.05 eV)}$ $\tau_0 = 3 \times 10^{-15}$
$0.25\text{Na}_2\text{O}\cdot 0.75\text{Li}_2\text{O}\cdot 3\text{SiO}_2$	$E_a = 139 \text{ kJ/mole (1.4 eV)}$ $\tau_0 = 1 \times 10^{-20}$	$E_a = 104 \text{ kJ/mole (1.08 eV)}$ $\tau_0 = 2 \times 10^{-15}$

Table 1 - Relaxation parameters for the three mixed silicate glasses