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# Conductivity relaxation in mixed alkali fluoride glasses

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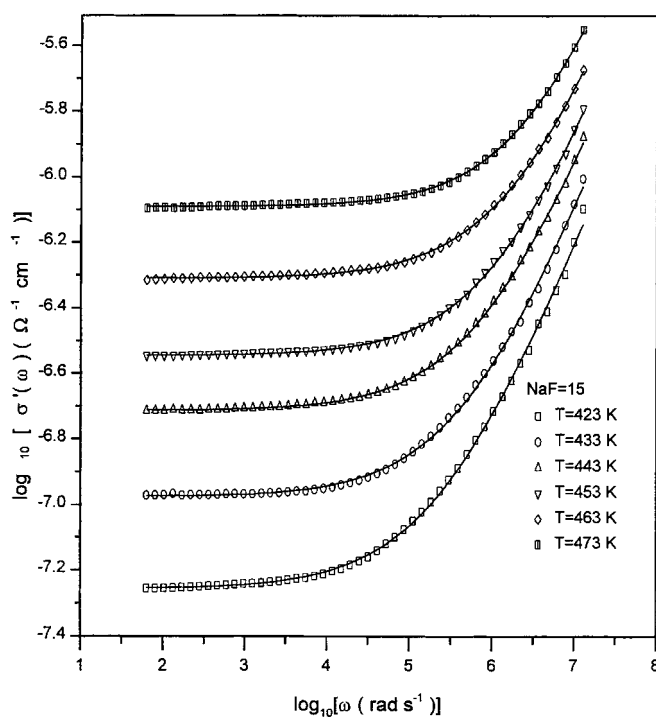
## Abstract

We have reported the electrical conductivity and the conductivity relaxation in fluoride glasses in the system  $40\text{ZrF}_4-20\text{BaF}_2-10\text{YF}_3-(30-x)\text{LiF}-x\text{NaF}$ ;  $0 \leq x \leq 30$ . We have observed a mixed mobile ion effect in these mixed alkali fluoride glasses. Using modulus formalism we have shown that the conductivity relaxation also exhibits the mixed mobile ion effect as does the dc conductivity. We have observed that the relaxation mechanism is independent of temperature but dependent on the composition.

## 1. Introduction

Fluoride glasses formed with heavy-metal network formers have received considerable attention recently because of their interesting physical properties, such as good infrared transmittivity and high ionic conductivity, which make them potential candidates for optical and solid electrolyte materials [1–5]. It has been observed that the conductivity of the alkali fluoride glasses depends on the concentration and the nature of alkali ions [6–10]. The conductivity of the lithium fluoride glasses decreases for low  $\text{Li}^+$  ion concentration ( $\text{LiF} < 0.20$ ) and increases for higher  $\text{Li}^+$  ion content ( $\text{LiF} \geq 0.20$ ) [6–8]. The variation of the conductivity has been explained mainly by a change of the  $\text{F}^-$  ion transport mechanism with the change in the LiF content. On the other hand, the conductivity of the sodium fluoride glasses decreases continuously with the increase of  $\text{Na}^+$  ion concentration [9, 10]. It has been shown that the  $\text{Na}^+$  ions do not contribute to the conduction process and the charge carriers in them are only  $\text{F}^-$  ions. Although there is a large number of reports on the conductivity of single-alkali fluoride glasses [1–10], there are a few reports on the electrical properties of fluoride glasses containing mixed alkali ions [11]. In contrast, oxide glasses containing mixed alkali ions have been studied extensively [12–24]. In the mixed alkali oxide glasses, the conductivity shows a minimum and the activation energy a maximum at a particular composition for a given overall alkali ion content. This phenomenon, known as the mixed alkali or mixed mobile ion effect, has also been observed in mechanical loss, internal friction and other properties of mixed alkali glasses [15, 16]. Although different theories [17–24] have been proposed to account for this effect in oxide glasses, to date the phenomenon lacks a convincing mechanism. In this paper,

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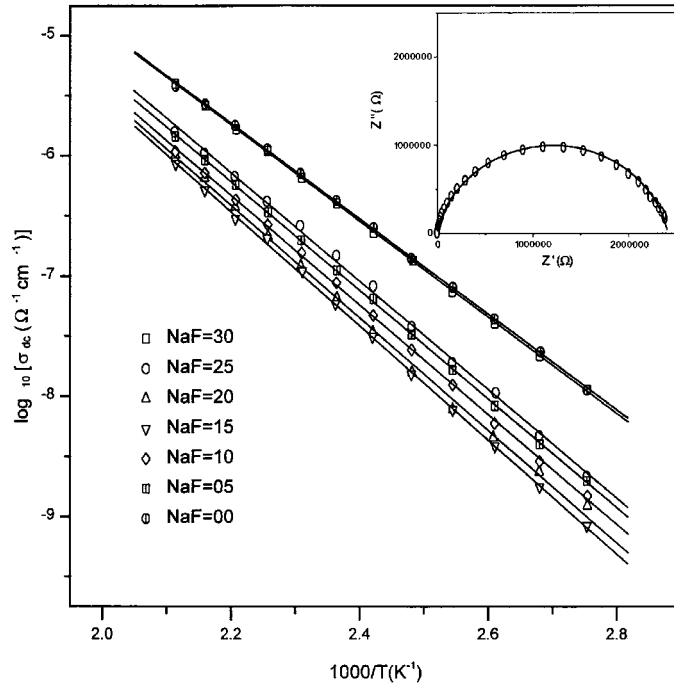


**Figure 1.** The frequency dependence of the conductivity of the  $40\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}10\text{YF}_3\text{-}15\text{LiF}\text{-}15\text{NaF}$  glass composition is shown for several temperatures. The solid curves are drawn through the data to guide the eye.

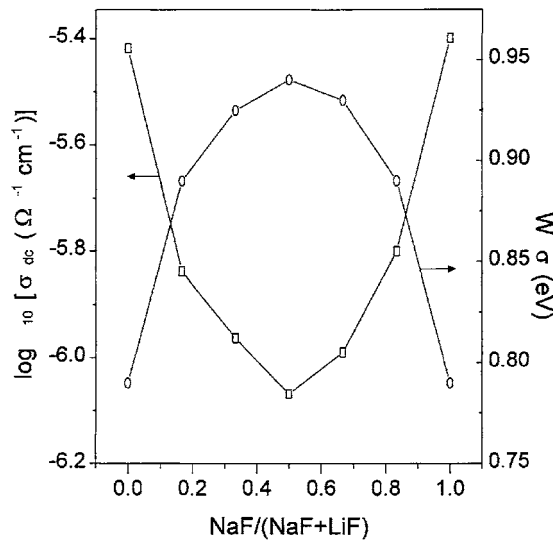
we report the electrical conductivity and conductivity relaxation of the mixed alkali fluoride glasses of compositions  $40\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}10\text{YF}_3\text{-}(30-x)\text{LiF}\text{-}x\text{NaF}$ ;  $0 \leq x \leq 30$ .

## 2. Experiment

Fluoride glass samples of compositions  $40\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}10\text{YF}_3\text{-}(30-x)\text{LiF}\text{-}x\text{NaF}$  were prepared using the chemicals  $\text{ZrF}_4$ ,  $\text{BaF}_2$ ,  $\text{YF}_3$ ,  $\text{LiF}$  and  $\text{NaF}$  (table 1). These chemicals were taken in appropriate proportions and mixed with an excess of ammonium hydrogen difluoride. The mixtures were then melted in a covered platinum crucible in an electrical furnace at  $800^\circ\text{C}$  for 15 min to avoid too much evaporation loss. The melts were finally poured into a preheated aluminum mould. Residual mechanical stresses were removed by annealing the samples at a temperature  $50^\circ\text{C}$  below the glass transition temperatures ( $T_g \sim 230\text{-}260\text{ K}$ ), which were determined from differential thermal analysis. The amorphous nature of the samples was confirmed by x-ray diffraction. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples of diameter  $\sim 1.5\text{ cm}$  and thickness ranging from 0.05 to 0.10 cm. The gold-coated samples were then heat-treated at  $150^\circ\text{C}$  for the stabilization of the electrodes. The electrical measurements such as capacitance and conductance of the samples were carried out in the frequency range  $10\text{ Hz}\text{-}2\text{ MHz}$  using an  $RLC$  meter (QuadTech, model 7600) interfaced with a computer. The measurements were made in the temperature range from 300 K to just below  $T_g$ . The dc conductivity was obtained either from the complex impedance plots or from the extrapolation of the frequency-independent conductivity (figure 1). The results of the two calculations agreed very well.



**Figure 2.** Temperature dependence of the dc conductivity of 40ZrF<sub>4</sub>-20BaF<sub>2</sub>-10YF<sub>3</sub>-(30-x)LiF-xNaF glasses for different values of x. The inset shows a complex impedance plot at T = 473 K for x = 15.



**Figure 3.** Composition dependence of the dc conductivity at 473 K (□) and the activation energy (O) for 40ZrF<sub>4</sub>-20BaF<sub>2</sub>-10YF<sub>3</sub>-(30-x)LiF-xNaF glasses.

**Table 1.** The activation energies for the dc conductivity and the relaxation time and the stretched exponent for  $40\text{ZrF}_4-20\text{BaF}_2-10\text{YF}_3-(30-x)\text{LiF}-x\text{NaF}$  (where  $x = 0-30$ ) glasses.

Composition $x$	$W_\sigma$ (eV) $\pm 0.01$	$W_c$ (eV) $\pm 0.01$	$\beta$ $\pm 0.01$
0	0.79	0.78	0.42
5	0.89	0.90	0.44
10	0.93	0.91	0.49
15	0.94	0.94	0.54
20	0.93	0.93	0.56
25	0.89	0.88	0.54
30	0.79	0.79	0.50

### 3. Results and discussion

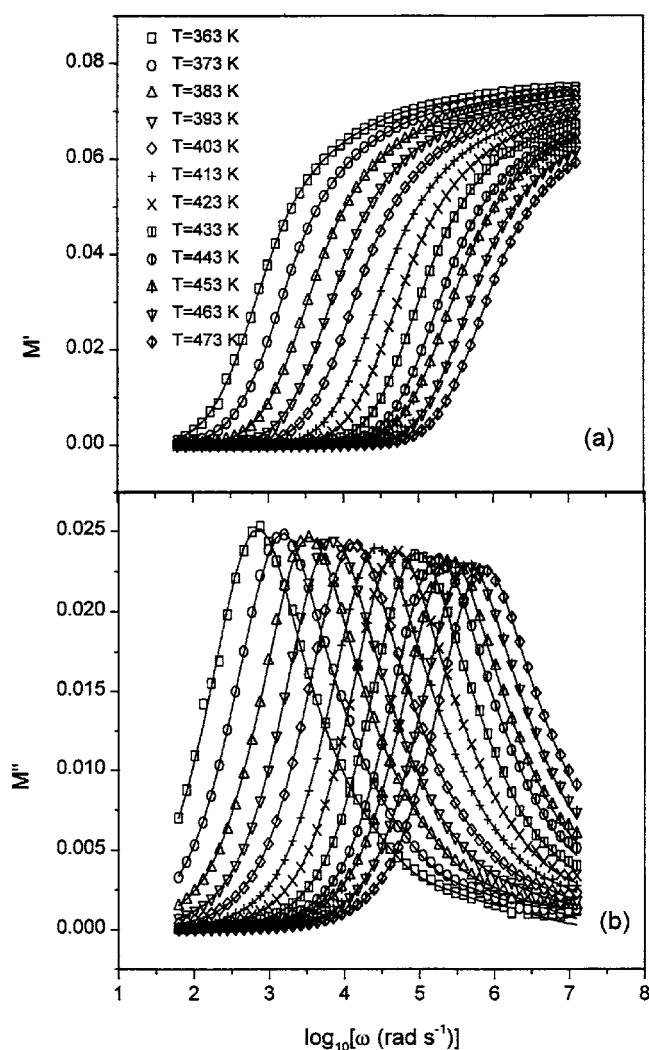
The frequency dependence of the conductivity for a glass composition is shown in figure 1 at several temperatures. It is observed that at low frequencies the conductivity is independent of frequency at all temperatures, indicating that the electrode polarization is absent and the dc conductivity can be obtained from the extrapolation of the frequency-independent conductivity. It is also observed that as the frequency is increased the conductivity shows a dispersion, which shifts to higher frequencies with the increase in temperature.

The temperature dependence of the dc conductivity, obtained from the complex impedance plots, is shown in an Arrhenius fashion in figure 2. A typical complex impedance plot is also shown in the inset of figure 2. The values of the activation energy  $W_\sigma$  (table 1) were obtained from the least-squares straight-line fits of the data (figure 2). The composition dependence of the dc conductivity and the activation energy is shown in figure 3. We note that the conductivity shows a minimum and the activation energy a maximum at a concentration ratio  $\text{NaF}/(\text{NaF} + \text{LiF})$  of about 0.5. This phenomenon is known as the mixed mobile ion effect [12, 13]. It was mentioned in the introduction that charge carriers in fluoride glasses containing NaF are fluoride anions, while charge carriers in fluoride glasses containing LiF are fluoride anions and alkali cations for LiF content  $< 20$  mol% and only alkali cations for LiF content  $> 20$  mol% [6–10]. We have studied mixed alkali fluoride glasses with total alkali fluoride contents in the range 16–35 mol% [25]. We have observed that there exists in each case a mixed mobile ion effect, the magnitude of which decreases with the decrease of the total alkali fluoride content, similar to mixed alkali oxide glasses [12, 13]. This suggests that the main charge carriers responsible for the ionic conductivity in these mixed alkali fluoride glasses are alkali cations. Further studies regarding the transference number of cations and anions are necessary to resolve the issue.

It is mentioned in the introduction that many theories have been proposed to explain the mixed mobile ion effect in oxide glasses [17–24]. These theories cannot be directly applied to explain the mixed mobile ion effect in fluoride glasses. It is necessary to know the mechanism of the electrical conduction in alkali fluoride glasses to interpret the mechanism of the mixed mobile ion effect in fluoride glasses. We have studied the ionic relaxation of these glasses in order to gain some insight into the mixed mobile ion effect.

In general, two formalisms such as the electric modulus and the conductivity formalisms have been adopted in the literature to study the ionic relaxation [26, 27]. We have used the modulus formalism [26] to study the conductivity relaxation of the present mixed alkali glasses. In this formalism an electric modulus  $M^*$  is defined as the reciprocal of the complex dielectric permittivity  $\epsilon^*$ :

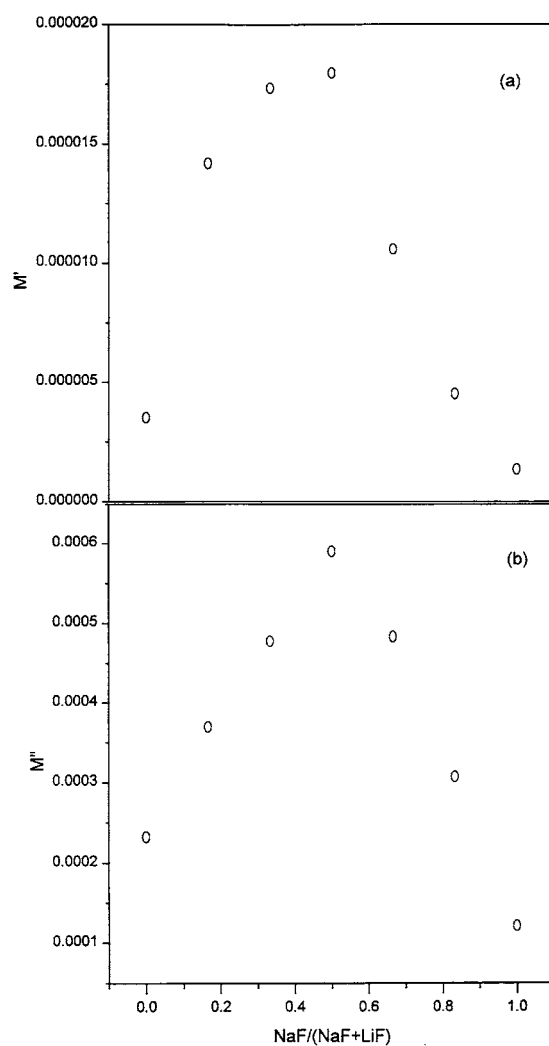
$$M^* = M' + jM'' = 1/\epsilon^* = M_\infty \left[ 1 - \int_0^\infty \exp(-j\omega t) \{ -d\varphi(t)/dt \} dt \right] \quad (1)$$



**Figure 4.** Frequency dependence of (a)  $M'$  and (b)  $M''$  shown for several temperatures for the 40ZrF<sub>4</sub>-20BaF<sub>2</sub>-10YF<sub>3</sub>-15LiF-15NaF glass composition. Solid curves are the best fits to equation (1).

where  $M'$  and  $M''$  are the real and imaginary parts of the complex modulus  $M^*$  and  $M_\infty$  is the high-frequency value of  $M'$ . The function  $\varphi(t)$  gives the time evolution of the electric field within the materials.

Figures 4(a) and (b) present respectively the real and imaginary modulus at different temperatures for a glass composition. We note that the real modulus  $M'$  shows a dispersion as the frequency is increased and tends to saturate at  $M_\infty$  at higher frequencies. The imaginary modulus  $M''$  exhibits a maximum ( $M''_{\max}$ ) centred at the dispersion region of  $M'$ . We note that the position of  $M''_{\max}$  shifts to higher frequencies as the temperature is increased. The angular frequency  $\omega_c$  corresponding to  $M''_{\max}$  gives the conductivity relaxation time  $\tau_c$  from the condition  $\omega_c \tau_c = 1$  [26]. We also observed a similar temperature dependence of  $M'$  and  $M''$  for other glass compositions. The composition dependence of the real and imaginary



**Figure 5.** Composition dependence of (a) the real and (b) the imaginary modulus at 1 kHz and 473 K for the 40ZrF<sub>4</sub>-20BaF<sub>2</sub>-10YF<sub>3</sub>-15LiF-15NaF glass composition.

modulus for a glass composition at a fixed temperature and frequency is shown in figures 5(a) and (b) respectively. We note that both the moduli show a maximum at the same composition as the dc conductivity.

The temperature dependence of the relaxation time  $\tau_c$  is shown in figure 6 for all glass compositions. It is noted that  $\tau_c$  exhibits an activated behaviour. We note in table 1 that the values of the activation energy  $W_c$  for the relaxation times, obtained from the least-squares straight-line fit, are close to those for the dc conductivity. The composition dependence of the relaxation frequency  $\omega_c$  (i.e. inverse relaxation time  $\tau_c^{-1}$ ) and the activation energy  $W_c$  for the relaxation time is shown in figures 7(a) and (b) respectively. We note that the relaxation frequency exhibits a minimum and the activation energy a maximum at  $\text{NaF}/(\text{NaF} + \text{LiF}) \approx 0.5$ , similar to the dc conductivity and its activation energy. Thus the conductivity relaxation exhibits the same mixed mobile ion effect as the dc conductivity.

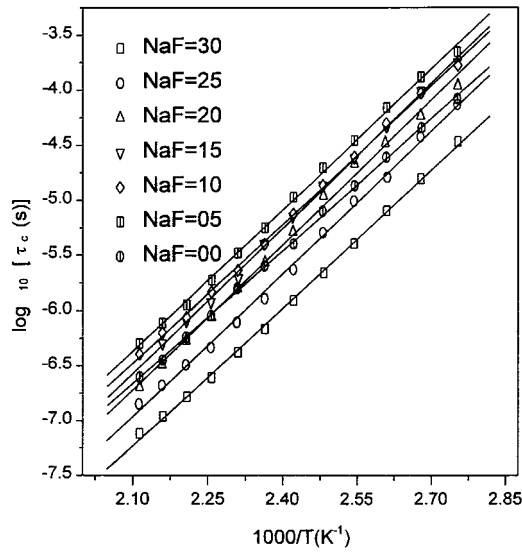


Figure 6. Temperature dependence of the conductivity relaxation time for different glass compositions.

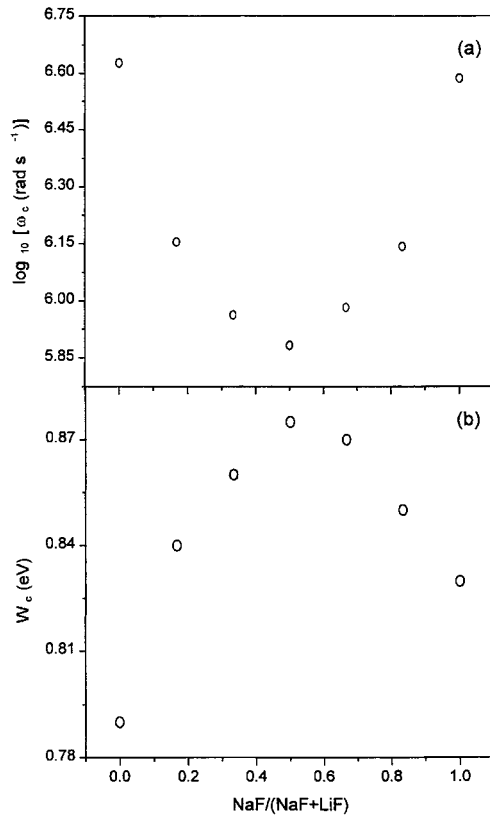
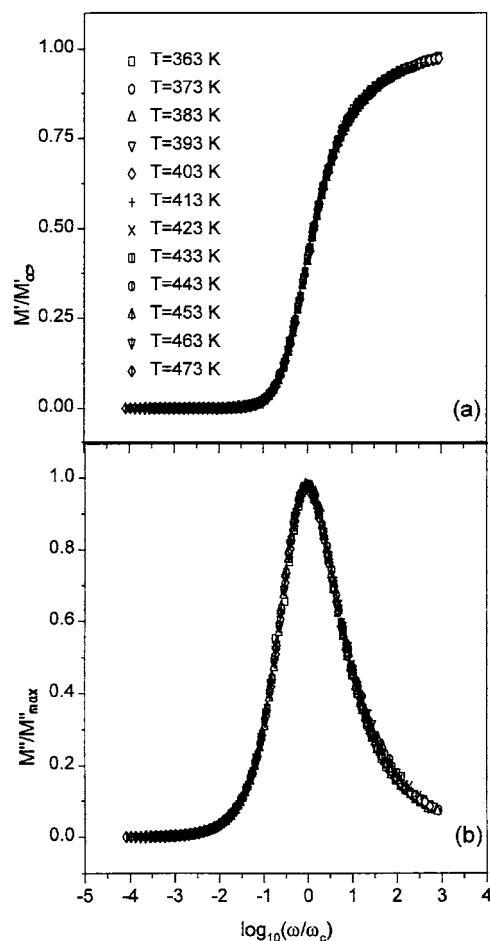


Figure 7. Compositional dependence of the conductivity relaxation frequency at 473 K (a) and its activation energy (b) for the  $40\text{ZrF}_4\text{-}20\text{BaF}_2\text{-}10\text{YF}_3\text{-(}30-x\text{)LiF-}x\text{NaF}$  glasses.

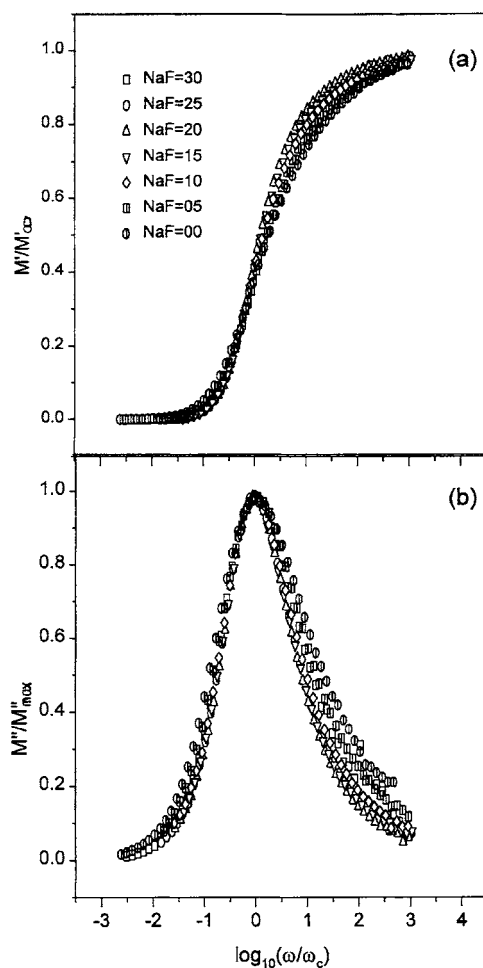




**Figure 8.** Plots of (a)  $M'/M_\infty$  versus  $\log(\omega/\omega_c)$  and (b)  $M''/M''_{\max}$  versus  $\log(\omega/\omega_c)$  at different temperatures for 40ZrF<sub>4</sub>–20BaF<sub>2</sub>–10YF<sub>3</sub>–15LiF–15NaF glass composition.

The experimental data for  $M'$  and  $M''$  at different temperatures for different compositions were fitted simultaneously to the values obtained from equation (1), using the procedure adopted by Macedo *et al* [26]. In the fitting procedure, we have used the non-exponential Kohlrausch–Williams–Watts (KWW) function  $\varphi(t) = \exp[-(t/\tau_c)^\beta]$ , where  $\beta$  is an exponent indicating departure from the Debye relaxation. Best fits for  $M'$  and  $M''$  at different temperatures for a glass composition are shown in figures 4(a) and (b) respectively. Other glass compositions also showed similar fits. The values of  $\beta$  obtained from different compositions are included in table 1. We note that  $\beta$  shows an increasing trend with the composition.

We have scaled the spectra for  $M'$  and  $M''$  at different temperatures for a glass composition in figures 8(a) and (b) respectively. In the scaling process,  $M'$  and  $M''$  are scaled by  $M_\infty$  and  $M''_{\max}$  respectively, while the frequency axis is scaled by the relaxation frequency  $\omega_c$ . We observe that the spectra for  $M'$  and  $M''$  for different temperatures merge on a single master curve. This result indicates that the dynamical processes occurring at different temperatures are independent of temperature. Such results were also observed for other glass compositions.



**Figure 9.** Plots of (a)  $M'/M_\infty$  versus  $\log(\omega/\omega_c)$  and (b)  $M''/M''_{\max}$  versus  $\log(\omega/\omega_c)$  at 433 K for different glass compositions.

Now it is interesting to note the composition dependence of the scaling behaviour of the modulus spectra. In figures 9(a) and (b) we have shown the scaled spectra for  $M'$  and  $M''$  respectively for different compositions at a fixed temperature. We note that the spectra for different compositions do not merge on a single master curve in both cases, which implies that the conductivity relaxation depends on the glass composition.

#### 4. Conclusions

We have studied the electrical conductivity and the conductivity relaxation in mixed alkali fluoride glasses in the system  $40\text{ZrF}_4-20\text{BaF}_2-10\text{YF}_3-(30-x)\text{LiF}-x\text{NaF}$ ;  $0 \leq x \leq 30$ . The dc conductivity exhibits a minimum and the activation energy a maximum (mixed mobile ion effect) at  $\text{NaF}/(\text{NaF} + \text{LiF}) \approx 0.5$ . The conductivity relaxation also exhibits the same effect at the same composition. The relaxation mechanism in these glasses is observed to be temperature independent but composition dependent.

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