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Mixed mobile ion effect in fluorozincate glasses

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Abstract

The mixed mobile ion effect has been investigated for the first time in zinc fluoride glasses where in addition to alkali cations fluorine anions also participate in the diffusion process, unlike mixed alkali oxide glasses. The minimum in the conductivity, conductivity relaxation frequency, crossover frequency and decoupling index indicates the existence of the mixed mobile ion effect in these fluoride glasses. It has been observed that the non-exponential parameter and the frequency exponent are independent of temperature. It has been established that alkali ions and fluorine anions exhibit lower dimensionality of the conduction pathways in mixed alkali zinc fluoride glasses than that in the single alkali lithium based zinc fluoride glasses while they are migrating. From the scaling of the conductivity spectra, it has been established that the relaxation dynamics in mixed alkali zinc fluoride glasses is independent of temperature and composition.

1. Introduction

Many physical properties of alkali modified glasses show nonlinear behaviour as a function of alkali content, if one alkali type is gradually replaced by another alkali. This behaviour is referred to as the mixed alkali effect or mixed mobile ion effect [1–3]. The mixed alkali effect in glasses gives rise to a large change in many dynamic properties, particularly those related to ionic transport when a fraction of the mobile ions is substituted by another type of mobile ions [4–9]. Although several theories have been proposed, no single theory is universally accepted nor fully accounts for all features of the mixed alkali effect. Most models describing the ion dynamics in mixed alkali glasses focus on the long-range diffusivity of the ions. The reduced diffusivity in mixed alkali glasses as compared to single alkali glasses is attributed to interaction between dissimilar ions [3], to phase separation [10], or to cation sites of different sizes [11]. Most recently in the dynamic structure model the reduced ion diffusivity in mixed alkali glasses has been explained in terms of a site relaxation and memory effect [12], where each type of mobile cation is able to adapt the glassy nature according to its spatial and chemical

requirements. While all these models yield a qualitative composition dependence of the ionic diffusivity, none of them is able to account for the mixed alkali effect in the frequency response of the ionic conductivity.

For single alkali fluoride glasses containing LiF or NaF, it is observed that the conductivity of the LiF glasses decreases for low Li⁺ ion concentration LiF \sim 0.20 (mole fraction) and increases for higher Li⁺ ion content (LiF \geq 0.20). The variation of the conductivity has been explained mainly by the change of F⁻ ion transport mechanism with the change in the LiF content [13]. On the other hand, the conductivity of the sodium fluoride glasses decreases continuously with the increase of Na⁺ ion concentration. It has been shown that the Na⁺ ions did not contribute to the conduction process [14] and the charge carrier in them is only F⁻ ions. But in the case of oxide glasses, the conductivity increases with increase of monovalent Li⁺ or Na⁺ ion content [15, 16]. The remarkable difference between mixed alkali oxide and fluoride glasses is that in oxide glasses the two ions such as Na⁺ and Li⁺ ions participate, but an additional F⁻ ion is present in the mixed alkali fluoride glasses. The mixed mobile ion effect in these glasses is extremely complicated. Although there are a few reports on the mixed mobile ion effect in zirconium based fluoride glasses [17, 18], there is no report on the study of this effect for zinc based fluoride glasses. This present study explores the conductivity and relaxation mechanism in mixed alkali fluoride glasses in the system 25ZnF₂-25AlF₃-30PbF₂-(20 - x)LiF-xNaF in order to understand the dynamics of charge carriers in such complicated systems. The ac conductivity and relaxation mechanisms have been analysed in the framework of the conductivity and the modulus formalism. In the present work it has been shown that the conductivity formalism accounts for the same qualitative variation of relaxation parameters with composition as the modulus formalism.

2. Experiment

Fluoride glasses of compositions 25ZnF₂-25AlF₃-30PbF₂-(20 - x)LiF-xNaF, where $0 \leq x \leq 20$, were prepared. The appropriate amounts of chemicals ZnF₂, AlF₃, PbF₂, LiF, and NaF (Aldrich, 99+%) were melted in a platinum crucible at a temperature in the range 800–850 °C depending upon composition. Before melting, an excess amount of ammonium hydrogen difluoride was added to the mixture to avoid oxidation. The melts were finally quenched between two aluminium plates. The samples were annealed at 150 °C to remove residual stresses. All the samples were transparent and colourless. The amorphous nature of the samples was confirmed by x-ray diffraction. Gold electrodes were deposited on both surfaces of the polished samples. The electric measurements, such as capacitance and conductance, of the samples were carried out using a precision RLC meter (Quad Tech, model 7600) in the temperature range from room temperature to just below the glass transition temperature and in the frequency range from 10 Hz to 2 MHz.

3. Results and discussion

The temperature dependence of the dc conductivity obtained from the complex impedance plots are shown in figure 1 for all glass compositions. It is noted that the variation of the conductivity with temperature obeys an Arrhenius equation $\sigma T = \sigma_0 \exp(-\frac{E_\sigma}{kT})$, where σ_0 is a conductivity prefactor and E_σ is the activation energy. The values of the activation energy E_σ were obtained from the least-squares straight-line fits. The dependence of the conductivity at 423 K and its corresponding activation energy on the relative composition $\frac{\text{LiF}}{\text{NaF+LiF}}$ content are shown in figures 2(a) and (b), respectively. It is observed that the conductivity shows a

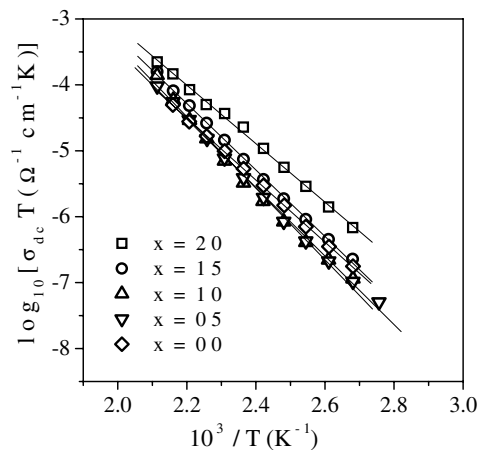


Figure 1. Plots of dc conductivity times temperature shown as a function of reciprocal temperature for all compositions of $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$ glasses shown in the inset. The solid lines are the least-squares straight-line fits.

minimum and the activation energy a maximum at a value of $\frac{\text{LiF}}{\text{NaF+LiF}} \approx 0.50$, which indicates the presence of the mixed mobile ion effect [3]. In the next three sections, the relaxation dynamics of mixed alkali fluoride glasses has been studied using a modulus formalism, the Almond–West conductivity formalism and the scaling of conductivity and modulus formalism.

3.1. Modulus formalism

In the modulus formalism [19], an electric modulus $M^*(\omega)$ is defined as the reciprocal of the complex dielectric permittivity $\epsilon^*(\omega)$ by

$$\begin{aligned} M^*(\omega) &= 1/\epsilon^*(\omega) = j\omega\epsilon_0\sigma^*(\omega) \\ &= M_\infty \left[1 - \int_0^\infty \exp(-j\omega t) \{-d\phi(t)/dt\} dt \right] \end{aligned} \quad (1)$$

where $M_\infty = \frac{1}{\epsilon_\infty}$, ϵ_∞ is the high-frequency asymptotic value of the real part of the dielectric constant, and $\phi(t)$ is the relaxation function, which gives the evolution of the electric field within the material. The relaxation function in this case is taken as the KWW function [20] given by

$$\phi(t) = \exp[-(t/\tau_m)^\beta] \quad (2)$$

where β measures the extent of the non-exponentiality. Figures 3(a) and (b) show the frequency dependence of the real and imaginary parts of the modulus spectra, respectively, at different temperatures for a glass composition $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-10\text{LiF}-10\text{NaF}$. The real part of the electric modulus $M'(\omega)$ exhibits very small values at lower frequencies, revealing the case of migration of the conducting ions. As the frequency of the applied field is increased, $M'(\omega)$ shows a dispersion and tends to saturate at M_∞ at higher frequencies. On the other hand, the imaginary part of the electric modulus $M''(\omega)$ shows an asymmetric maximum at frequency ω_m centred at the dispersion region of $M'(\omega)$. It is also observed in figure 3(b) that the maximum of $M''(\omega)$ shifts towards higher frequencies as the temperature is increased. The angular frequency ω_m corresponding to M''_{max} gives the most probable conductivity relaxation time τ_m from the condition [19] $\omega_m \tau_m = 1$. A similar temperature and frequency

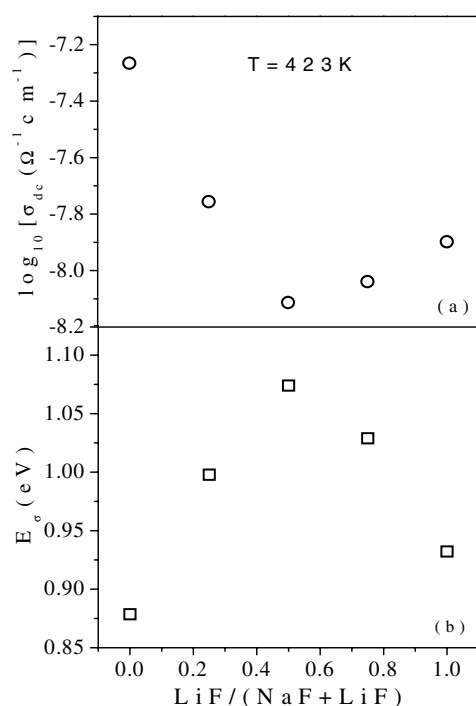


Figure 2. Composition dependence of the (a) dc conductivity at 423 K and (b) activation energy for dc conductivity for $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-}(20-x)\text{LiF-xNaF}$ glass series.

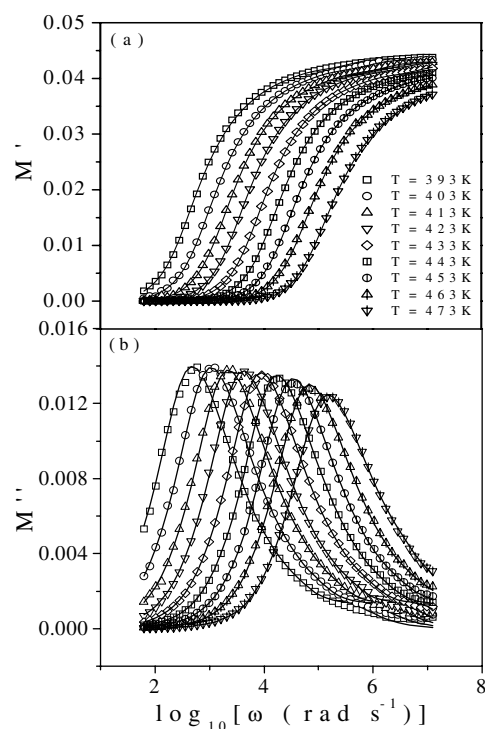


Figure 3. Frequency dependence of (a) the real and (b) the imaginary parts of modulus isotherms at different temperatures for $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-}10\text{LiF}\text{-}10\text{NaF}$ glass composition. The solid curves are the best fits to equations (1) and (2).

dependence of $M^*(\omega)$ for other glass compositions has been observed. It is shown in figure 4 that the reciprocal temperature dependence of the conductivity relaxation frequency obeys the Arrhenius relation $\omega_m = \omega_0 \exp(-\frac{E_a}{kT})$. The dependence of the conductivity relaxation frequency at 423 K and its corresponding activation energy (see table 1) on $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})}$ content is shown in figures 5(a) and (b), respectively. It is observed that the conductivity relaxation frequency shows a minimum, and the activation energy for that shows a maximum at a value of $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})} \approx 0.50$, which indicates the presence of the mixed mobile ion effect. The values of the non-exponent β (see table 1) obtained from the fits of equation (2) using the procedure of Moynihan *et al* [19] were found to be independent of temperature. We did not observe any systematic compositional dependence of β .

The compositional dependence of the dc conductivity is consistent with that of the decoupling index. Angell [21] defined the glass decoupling index $R_\tau(T_g)$ as the ratio $\tau_s(T_g)/\tau_m(T_g)$, where $\tau_s(T_g)$ and $\tau_m(T_g)$ are the average structural and the conductivity relaxation times respectively at the glass transition temperature T_g . $R_\tau(T_g)$ determines the extent to which motion of the conducting ions is decoupled from the viscous motion of the glassy network and is related to the ability of the mobile ions to migrate in the glassy electrolytes at T_g . The values of $\tau_m(T_g)$ have been calculated by extrapolating the plots of $\log_{10}(\omega_m)$ versus $\frac{10^3}{T}$ (figure 4) at T_g and assuming $\tau_s(T_g)$ equal to 200 s. Figure 6 shows the dependence of $\log_{10}[R_\tau(T_g)]$ on the $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})}$ content. It is observed that the variation of $R_\tau(T_g)$ is similar to

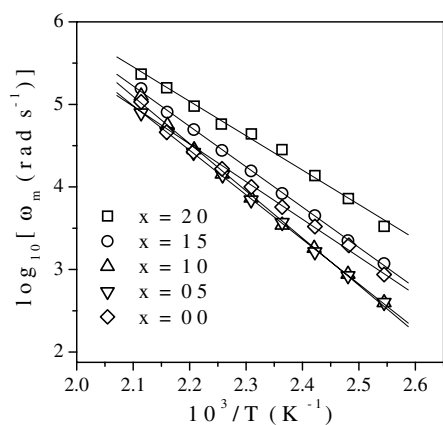


Figure 4. Reciprocal temperature dependence of the conductivity relaxation frequency for different compositions of $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$ glasses shown in the inset. The solid lines are the least-squares straight-line fits to the data.

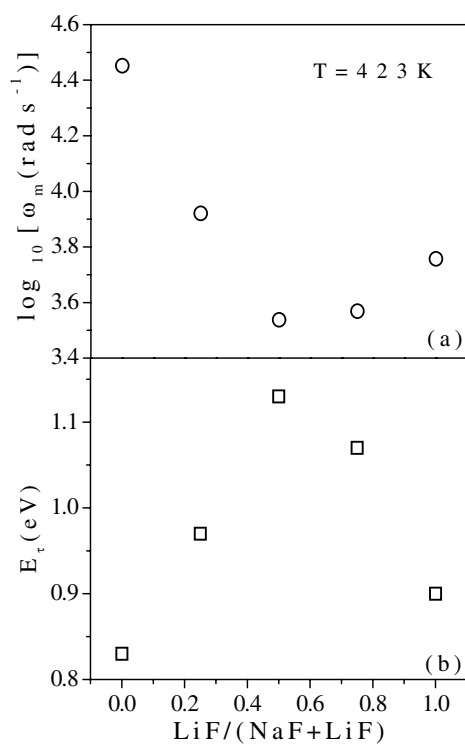


Figure 5. Compositional dependence of (a) the conductivity relaxation frequency at 423 K and (b) the activation energy for conductivity relaxation frequency for the $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$ glass series.

the variation of dc conductivity, which suggests the existence of the mixed mobile ion effect in the decoupling index also.

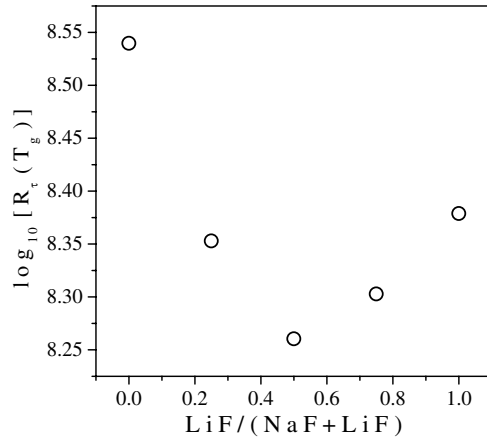


Figure 6. The compositional dependence of decoupling index for the glass series $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-(}20-x\text{)LiF-xNaF}$.

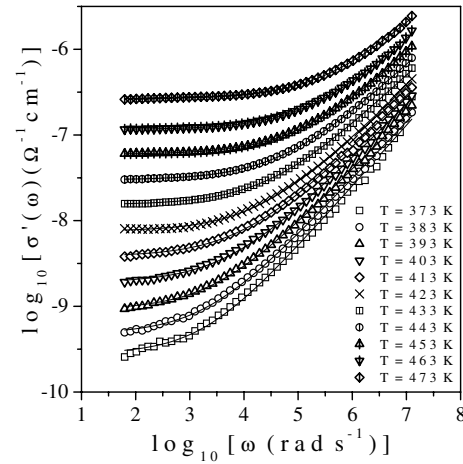


Figure 7. The frequency spectra of the real conductivity $\sigma'(\omega)$ for different temperatures (shown) for a typical glass composition $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-}10\text{LiF-}10\text{NaF}$. The solid lines are the best fits to equation (3).

Table 1. The dc activation energy, activation energy for conductivity relaxation, non-exponent parameter, activation energy for cross-over frequency and the frequency exponent for $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-(}20-x\text{)LiF-xNaF}$ glasses.

Compositions x	E_σ (eV) $\pm(0.01)$	E_τ (eV) $\pm(0.01)$	β $\pm(0.01)$	E_H (eV) $\pm(0.01)$	n $\pm(0.01)$
20	0.88	0.83	0.61	0.87	0.58
15	1.00	0.97	0.63	0.92	0.60
10	1.07	1.13	0.59	0.98	0.60
05	1.03	1.07	0.64	0.92	0.62
00	0.93	0.90	0.60	0.77	0.62

3.2. The Almond–West conductivity formalism

The frequency spectra of the measured real part of the conductivity for a glass composition are shown in figure 7 for several temperatures. It is observed that, at lower frequencies, the conductivity is almost independent of frequency, approaching the dc conductivity with decreasing frequency. As the frequency is increased, the conductivity shows a dispersion, which shifts to higher frequencies with the increase in temperature. Other glass compositions also showed similar frequency and temperature dependence. The conductivity spectra have also been analysed in the framework of the Almond–West formalism [22]. In this formalism the bulk frequency-dependent conductivity $\sigma'(\omega)$ (real part) in ionic crystals and glasses is described by

$$\sigma'(\omega) = \sigma_{\text{dc}} \left[1 + \left(\frac{\omega}{\omega_H} \right)^n \right] \quad (3)$$

where σ_{dc} is the dc conductivity, ω_H is the cross-over frequency of the charge carriers and n is the frequency exponent parameter in the range $0 \leq n \leq 1$ measuring the interaction between the mobile ions. The conductivity spectra are fitted to equation (3) for different temperatures

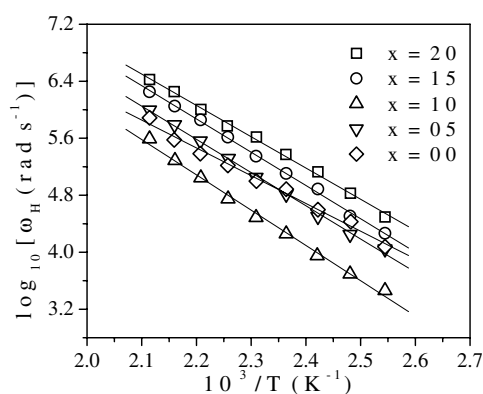


Figure 8. Temperature dependence of the hopping frequency for different glass compositions of $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-(}20-x\text{)LiF-xNaF}$ shown in the inset. The solid lines are the least-squares straight-line fits.

independently for all glass compositions using the parameters σ_{dc} , ω_H and n as variable parameters. Such fits are shown in figure 7 for the $25\text{ZnF}_2\text{-}25\text{AlF}_3\text{-}30\text{PbF}_2\text{-}10\text{LiF}\text{-}10\text{NaF}$ glass composition; the solid lines are the best fits of equation (3). The other compositions also showed similar fits. The temperature dependence of the cross-over frequency ω_H obtained from the best fits for all glass compositions is shown in figure 8; it exhibits an Arrhenius behaviour. The values of the activation energy E_H for cross-over frequency of charge carriers were obtained from the least-squares fits of data in figure 8 and are displayed in table 1. The dependence of the cross-over frequency at 423 K and its corresponding activation energy on $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})}$ content is shown in figures 9(a) and (b) respectively. It is observed that cross-over frequency shows a minimum and the activation energy of the cross-over frequency shows a maximum at a value of $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})} \approx 0.50$, which strongly supports the existence of the mixed mobile ion effect in the present zinc fluoride glass compositions. It may be noted that the values of the frequency exponent n obtained from the fits are almost independent of temperature, but depend on composition. It is also observed that the values (see table 1) of n are lower for mixed alkali zinc fluoride glasses than those containing LiF as single alkali. Also, a decrease in the exponent has been observed with decreasing dimensionality of the conduction pathways [23]. The lower values of the frequency exponent for mixed alkali glasses than those for the single alkali fluoride glasses confirm the existence of the mixed mobile ion effect in zinc fluoride glasses. These results also indicate lower dimensionality of the conduction pathways in mixed alkali zinc fluoride glasses than that in the single alkali zinc fluoride glasses.

Although the qualitative changes in n and β are in conformity with the fact that both represent the interaction between the charge carriers, they do not, however, exactly obey the theoretical relationship between n and β , $n = 1 - \beta$, proposed by Ngai [24].

3.3. Scaling of the conductivity spectra

In this section there is a discussion on another interesting problem: does the relaxation mechanism depend on temperature or glass composition in mixed alkali zinc fluoride glasses? To get the answer to this question several scaling formalisms [25–28] have been developed. In these formalisms different scaling parameters were used for the frequency axis, while the conductivity axis was scaled by the dc conductivity. Here we have scaled the conductivity spectra following a newly developed scaling approach [25]. The conductivity axis of each

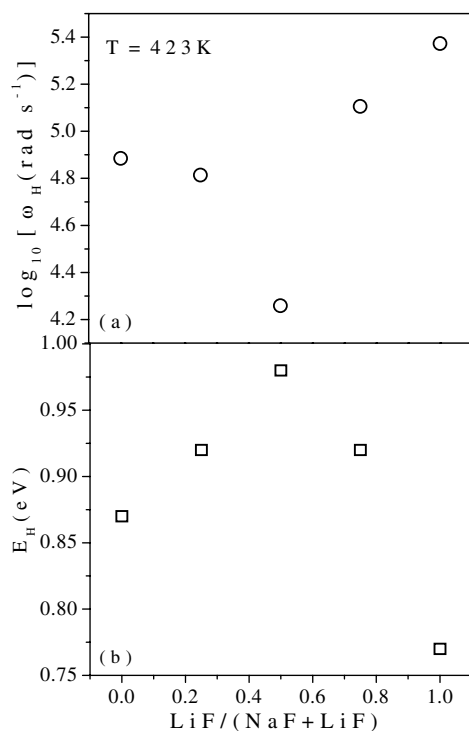


Figure 9. Composition dependence of (a) the hopping frequency at 423 K and (b) the activation energy for hopping frequency for $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$ glass compositions.

conductivity isotherm for a particular glass composition for different temperatures has been scaled (shown in figure 10(a)) by the dc conductivity σ_{dc} and the frequency axis by the crossover frequency ω_{H} obtained from the fitting of conductivity isotherms to equation (3). It is noted that all the conductivity isotherms fall on a single master curve, which indicates that the relaxation mechanism is independent of temperature. In figure 10(b) the same scaling results as above are shown for several compositions for a particular glass system having different fraction of $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})}$. Surprisingly, it is observed that all the isotherms for all temperatures for all glass compositions superpose on a single master curve, independent of concentration and type of the ionic charge carriers. As the conductivity isotherms superpose on a single master curve, this may imply that the relaxation mechanism is not only independent of temperature but also independent of concentration and type (i.e. concentration of Na^+ , Li^+ and F^- ion) of the ionic charge carriers. The scaling property presented above for these mixed alkali zinc fluoride glasses can be expressed by

$$\frac{\sigma'(\omega)}{\sigma_{\text{dc}}} = F\left(\frac{\omega}{\omega_{\text{H}}}\right). \quad (4)$$

The dynamics of the charge carriers is described by a universal function F , which is independent of temperature and composition. This indicates that the relaxation process is independent of the fraction of mobile ions in the composition and suggests the existence of a universal ionic relaxation process in mixed alkali zinc fluoride glasses. Although theoretical models have been developed focusing on the motion of ionic glasses determined by the interaction between the ions and the network structure and also by the long-range Coulomb interaction between

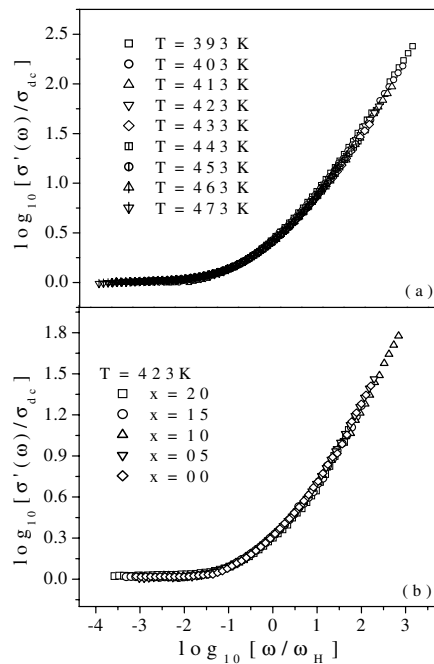


Figure 10. A plot of $\log_{10}(\sigma'(\omega)/\sigma_{dc})$ versus $\log_{10}(\omega/\omega_H)$ (a) at different temperatures (shown in the inset) for the same glass composition as in figure 6 and (b) at a temperature 423 K for compositions $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$ (shown in the inset).

the ions themselves [29–33], a theoretical understanding of these experimental observations has yet to be achieved because of the lack of information on the fluoride glass structure.

4. Conclusions

Here the result of an investigation of the mixed mobile ion effect in zinc fluoride glasses in the system $25\text{ZnF}_2-25\text{AlF}_3-30\text{PbF}_2-(20-x)\text{LiF}-x\text{NaF}$, where $0 \leq x \leq 20$, in the frequency range from 10 Hz to 2 MHz and in the temperature range from room temperature to just below the glass transition temperature has been reported. A minimum in the dc conductivity and a maximum in the activation energy were observed, which indicate the existence of the mixed mobile ion effect. A minimum in the conductivity relaxation frequency and decoupling index and a maximum in the activation energy for conductivity relaxation frequency were observed, which support the existence of the mixed mobile ion effect in these glasses. The cross-over frequency observed from the Almond–West formalism and its activation energy show a minimum and a maximum respectively at a composition $\frac{\text{LiF}}{(\text{NaF}+\text{LiF})} \approx 0.50$, similar to the dc conductivity and the conductivity relaxation frequency, which is strong evidence of the mixed mobile ion effect. It has been observed that the non-exponential parameter and the frequency exponent are independent of temperature. Lower dimensionality of the conduction pathways in mixed alkali zinc fluoride glasses than that in the single alkali lithium based zinc fluoride glasses was observed. From the scaling of conductivity spectra, it is established that the relaxation dynamics in mixed alkali zinc fluoride glasses is independent of temperature and composition.

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