Electrical conductivity and conductivity relaxation in ZrF_4-BaF_2-YF_3-LiF glasses

Electrical conductivity and conductivity relaxation in ZrF$_4$–BaF$_2$–YF$_3$–LiF glasses

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Abstract. The electrical conductivity and the conductivity relaxation of the fluoride glasses in the system ZrF$_4$–BaF$_2$–YF$_3$–LiF with LiF content ranging from 10 to 60 mol% have been investigated in the frequency range 10 Hz–2 MHz and in the temperature range from 300 K to just below the glass transition temperatures. The conductivity shows a minimum and the activation energy a maximum for 20 mol% LiF content, which is interpreted as a crossover from F$^-$-dominated conductivity to Li$^-$-dominated conductivity at 20 mol% LiF. The glass decoupling index also shows a minimum for 20 mol% LiF, which is associated with the occurrence of the minimum for the conductivity. The conductivity relaxation parameter β, however, shows a minimum for 30 mol% LiF. A structural origin has been proposed to account for this.

1. Introduction

Heavy metal fluoride glasses have been the subject of much interest because of their potential applications in infrared optical components and ultra-low loss optical fibres [1–3]. These glasses are also likely candidates for use as solid electrolytes due to their relatively high electrical conductivity [4]. Glasses containing zirconium fluoride as a network former have been recently studied extensively [5–11]. The zirconium fluoride glasses are mainly fluorine ion conductors [5]. However, zirconium fluoride glasses containing alkali metals as modifiers are fluorine and/or alkaline ion conductors depending on the concentration and nature of alkali ions [8–11]. Some authors have observed the mixed alkali effect in zirconium fluoride glasses [6]. The effect of the replacement of Zr^{4+} by Al^{3+} and Y^{3+} on ionic motions in ZrF$_4$-based glasses has also been studied [7, 12]. A decrease in the electrical conductivity and an increase in the activation energy are observed by the progressive replacement of Zr^{4+} by Al^{3+} or Y^{3+}. A comparative study of the zirconium fluoride glasses containing lithium and sodium shows that glasses containing lithium ions are different from the glasses containing sodium ions with respect to the transport properties [8, 9]. The ionic conductivity results from the mixed contribution of mobile Li$^+$ and F$^-$ ions in the glasses containing lithium ions, while it is due only to motion of mobile F$^-$ ions in the glasses containing sodium ions. In this paper, we have studied the dc conductivity and conductivity relaxation in the glasses belonging to the quaternary ZrF$_4$–BaF$_2$–YF$_3$–LiF system with LiF content in the range 10–60 mol%.

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2. Experiment

Fluoride glass samples whose compositions are given in table 1 were prepared using the chemicals ZrF_4, YF_3, BaF_2 and LiF (Aldrich). The appropriate proportions of these chemicals were mixed with an excess of ammonium bifluoride. The mixtures were melted in a platinum crucible in an electrical furnace at $840\,°C$ for 15 minutes. The melts were then poured into a preheated aluminium mould. Residual mechanical stresses were removed by annealing the samples at a temperature $50\,°C$ below the glass transition temperatures (T_g) determined by the differential thermal analysis. The amorphous nature of the samples was confirmed from x-ray diffraction. For electrical measurements, gold electrodes were deposited on both surfaces of the polished samples by vacuum evaporation. The gold coated samples were then heat treated at $150\,°C$ for stabilization of the electrodes. The electrical measurements on the samples were carried out in the frequency range 10 Hz–2 MHz using a QuadTech *RLC* meter (model 7600) interfaced with a computer. Measurements were made over a temperature range from 300 K to just below T_g. The dc conductivity was obtained either from the extrapolation of the frequency dependent ac conductivity or from the complex impedance plots and these results agreed with each other within the experimental error.

Table 1. Compositions, activation energy, the preexponential factor and the conductivity at $200\,°C$ for the ZrF_4–BaF_2–YF_3–LiF glasses.

Composition (mol%)				σ_0 (S cm^{-1})	W_σ (eV)	σ_{473} (S cm^{-1})
ZrF_4	BaF_2	YF_3	LiF			
50	30	10	10	1.2×10^3	0.78	2.54×10^{-6}
50	20	10	20	1.6×10^3	0.85	1.32×10^{-6}
40	20	10	30	7.1×10^3	0.83	6.84×10^{-6}
35	15	10	40	6.2×10^3	0.70	2.45×10^{-5}
25	15	10	50	3.4×10^3	0.70	9.57×10^{-5}
20	10	10	60	1.6×10^3	0.59	3.16×10^{-4}

3. Results and discussion

Figure 1 shows the logarithmic dc conductivity obtained from the complex impedance plot as a function of reciprocal temperature for all the glass compositions listed in table 1. In all cases, the variation of the conductivity with temperature can be described by an Arrhenius equation $\sigma = \sigma_0 \exp(-W_\sigma/kT)$. The values of the prefactor σ_0 and the activation energy W_σ obtained from the least squares straight line fits of the data are shown in table 1 for all glass compositions. We have shown in figure 2 the dependence of the conductivity at 473 K (σ_{473}) and the activation energy on the LiF content in the glass compositions. It may be noted that the conductivity exhibits a minimum and the activation energy shows a maximum at about 20 mol% LiF content. Similar effects have been also observed in ZrF_4–BaF_2–LaF_3–LiF glasses [11]. These results are in sharp contrast to ZrF_4–BaF_2–ThF_4–LiF glasses for which no conductivity minimum was observed [11]. It corresponds to a crossing from a conductivity due to F^- ions to a conductivity due to Li^+ ions. ^{19}F and ^7Li NMR investigations have shown that F^- and Li^+ participate as change carriers in the conduction mechanism [11]. For the present glasses with LiF content $\leqslant 20$ mol%, the conductivity arises from the migration of F^- ions while the conductivity is mainly due to the migration of Li^+ ions for glasses with more than 20 mol% LiF.
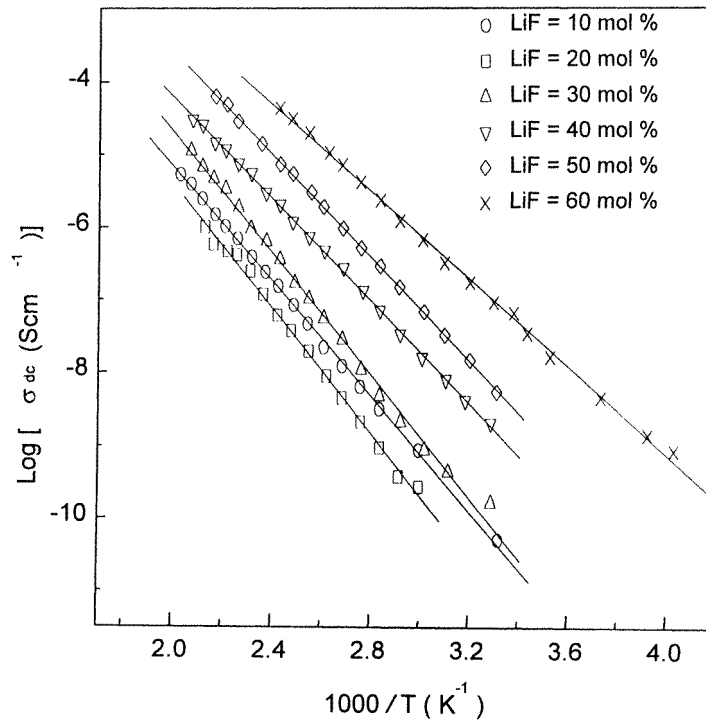
Figure 1. Temperature dependence of the dc conductivity of the ZrF$_4$–BaF$_2$–YF$_3$–LiF glasses for the different compositions shown.

The modulus formalism [13] has been employed to analyse the ac conductivity data. This formalism discriminates against electrode polarization and other interfacial effects in solid electrolytes [14]. Macedo *et al* [13] defined the electric modulus M^* as the analogue of the dynamical mechanical modulus and it is given by the inverse of the complex dielectric permittivity ε:

$$M^* = 1/\varepsilon^* = \left(\varepsilon' - j\varepsilon''\right)\big/\left|\varepsilon^*\right|^2 = M' + jM'' = M_\infty\left[1 - \int_0^\infty e^{-j\omega t}\{d\phi(t)/dt\}\,dt\right]$$

where M' and M'' are the real and imaginary parts of the complex modulus M^*, $M_\infty = 1/\varepsilon_\infty$ is the inverse of the high frequency dielectric constant ε_∞ and the function $\phi(t)$ gives the time evolution of the electric field and hence the distribution of relaxation time within the material. Figure 3(a) and (b) shows the frequency dependence of M' and M'' respectively at several temperatures for the 40ZrF$_4$–20BaF$_2$–10YF$_3$–30LiF glass composition. At higher frequencies, M' tends to saturate at M_∞, while at lower frequencies it approaches zero, which indicates that the contribution of electrode polarization to M' is negligible. M'' shows an asymmetric maximum (M''_{max}) centred at the dispersion region of M'. It may be observed in figure 3(b) that the maximum shifts towards higher frequencies with the increase in temperature. The frequency ω_c where the maximum in M'' occurs is indicative of a transition from a short range to a long range mobility at decreasing frequency and is defined by the condition $\omega_c\tau_c = 1$, where τ_c is the most probable conductivity relaxation time. A similar temperature and frequency dependence of M^* has been observed for other glass compositions. A master plot of M'/M_∞ and M''/M_{max} is shown in figure 4 as a
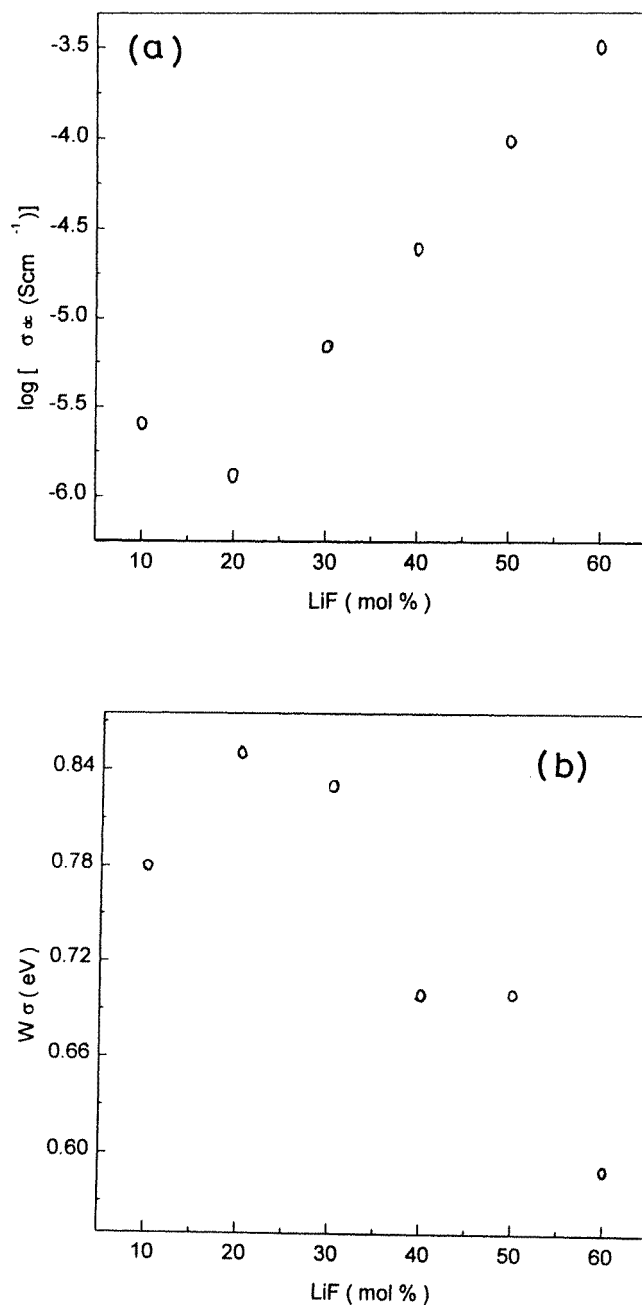
Figure 2. (a) Dependence of the dc conductivity at 473 K (σ_{473}) for the ZrF_4–BaF_2–YF_3–LiF glasses on the LiF content in the compositions. (b) Dependence of the dc activation energy (W_σ) for the ZrF_4–BaF_2–YF_3–LiF glasses on the LiF content in the compositions.
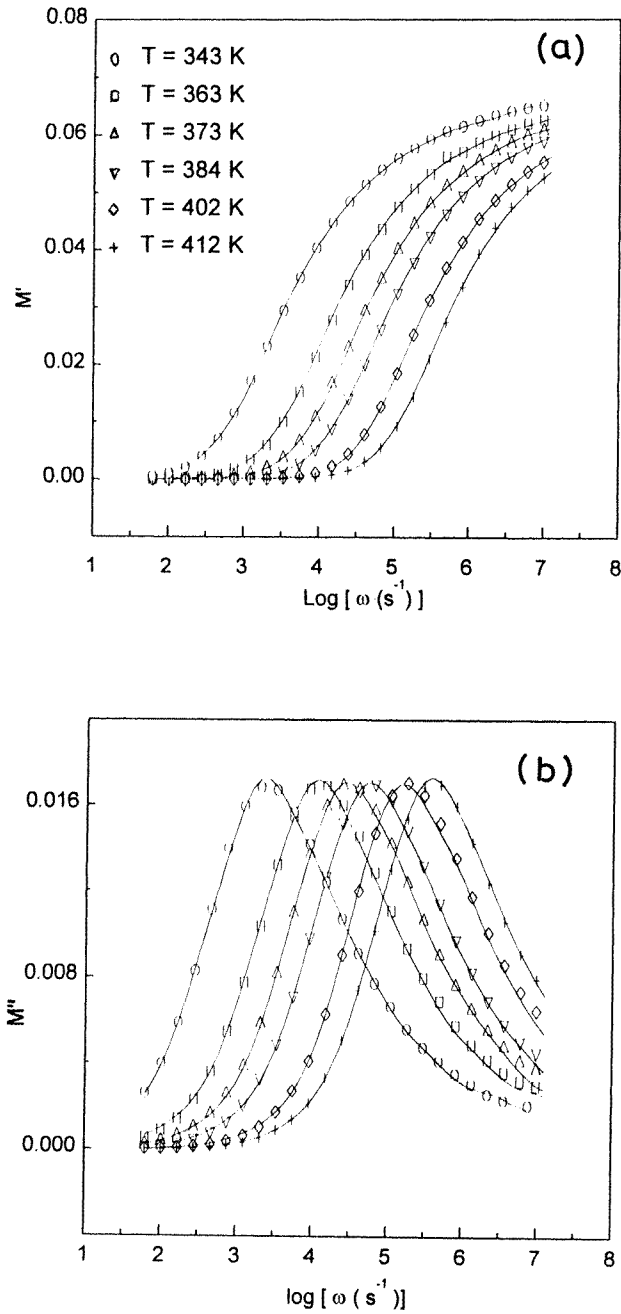
Figure 3. Frequency dependence of M' and M'' at different temperatures for the 40ZrF$_4$–20BaF$_2$–10YF$_3$–30LiF glass composition. Solid curves are the best fits to the modulus formalism.

function of normalized frequency ω/ω_c for all temperatures for the same glass composition as in figure 3. Superposition of the plots for all temperatures implies that the dynamical
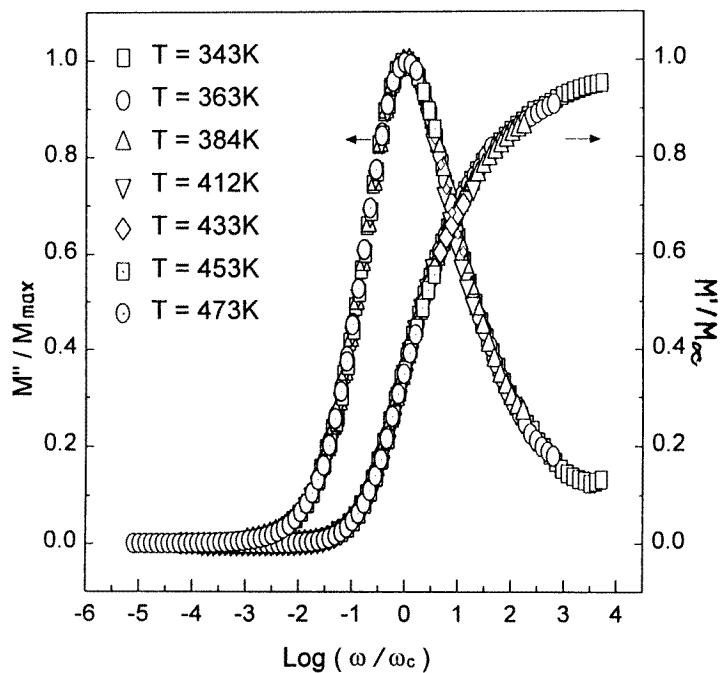
Figure 4. Plot of M'/M_∞ and M''/M_{max} versus $\log_{10}(\omega/\omega_c)$ at different temperatures for the same glass composition as in figure 3.

processes occurring at different frequencies have the same thermal energy. The data for M' and M'' for all temperatures were fitted simultaneously to the values obtained from the modulus formalism. In the fitting process, the Kohlrausch–William–Watts (KWW) function $\phi(t) = \exp[-(t/\tau_c)^\beta]$, where the stretched exponent β indicates departure from the Debye relaxation, was used. A best fit for a glass composition is shown in figure 3(a) and (b). Other glass compositions also showed similar fits. The values of the exponent β and the high frequency dielectric constant ε_∞ obtained from the fits are shown in table 2. Values of β were found to be independent of temperature, which is also evident from figure 4. The composition dependence of the exponent β is shown in figure 5, from which it is clear that β shows a minimum at about 40 mol% of LiF. The temperature dependence of the inverse of the conductivity relaxation time τ_c obtained from the maximum of M'' is shown in figure 6 for all glass compositions. It is evident that τ_c^{-1} exhibits the same temperature dependence as σ_{dc} (figure 1) and can be fitted to $\tau_c^{-1} = \tau_0^{-1} \exp[-W_c/kT]$. The values of the activation energy W_c and the preexponential term τ_0 obtained from the fits are shown in table 2 for all glass compositions. It may be noted that the values of W_c are very close to the values of W_σ, which suggests a hopping mechanism of charge carriers in the glasses.

Angel [15, 16] has defined the glass decoupling index $R_\tau(T_g)$ as the ratio $\langle \tau_s(T_g) \rangle / \langle \tau_c(T_g) \rangle$, where $\langle \tau_s(T_g) \rangle$ and $\langle \tau_c(T_g) \rangle$ 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 glass network and is thus related to the ability of the mobile ions to migrate in the glass electrolytes at T_g. We have calculated $\tau_c(T_g)$ by extrapolating the $\log_{10}(\tau_c^{-1})$ versus
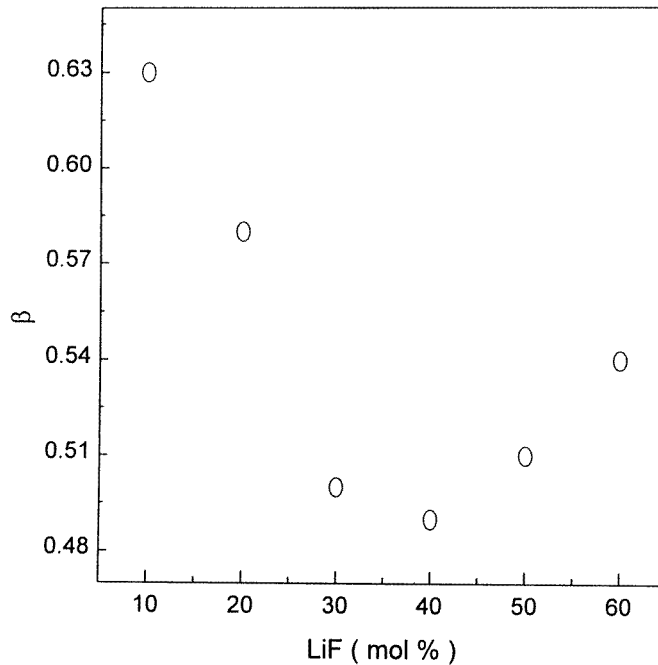
Figure 5. Variation of the stretched exponent β with the LiF content in the compositions for the ZrF$_4$–BaF$_2$–YF$_3$–LiF glasses.

Table 2. Different parameters of the studied glasses obtained from the conductivity relaxation model.

Composition (mol%) LiF	W_c (eV)	τ_0 (s)	β	ε_∞ $= 1/M_\infty$	$\log(R_\tau(T_g))$
10	0.80	1.3×10^{-15}	0.63	10.99	10.18
20	0.85	7.6×10^{-15}	0.58	11.81	9.57
30	0.87	6.5×10^{-15}	0.50	14.52	10.09
40	0.70	1.4×10^{-15}	0.49	13.81	10.31
50	0.70	2.8×10^{-15}	0.51	12.91	10.69
60	0.60	1.4×10^{-15}	0.54	15.38	10.97

$10^3/T$ plots at T_g and assumed $\tau_s(T_g)$ equal to 200 s [16, 17]. The calculated values of $R_\tau(T_g)$ are shown in figure 7 as a function of LiF content in the glass compositions. It is observed that $R_\tau(T_g)$ shows a minimum at ∼20 mol% LiF. The composition dependence of $R_\tau(T_g)$ is very similar to that of the dc conductivity (both showing minimum for 20 mol% LiF). The conductivity minimum for 20 mol% LiF is therefore related to a minimum in the extent to which the motion of the mobile ions is decoupled from the viscous motion of the glass network. Similar results have been reported for ZrF$_4$–BaF$_2$–LaF$_3$–LiF fluoride [11] and Al(PO$_3$)$_3$–PbF$_2$–LiF oxyfluoride glasses [18]. But these results are in sharp contrast to those for ZrF$_4$–BaF$_2$–ThF$_4$–LiF glasses where $R_\tau(T_g)$ was observed to increase regularly with the increase of LiF content in the glasses.

It may be noted from table 2 that the variation of the values of β with composition is very
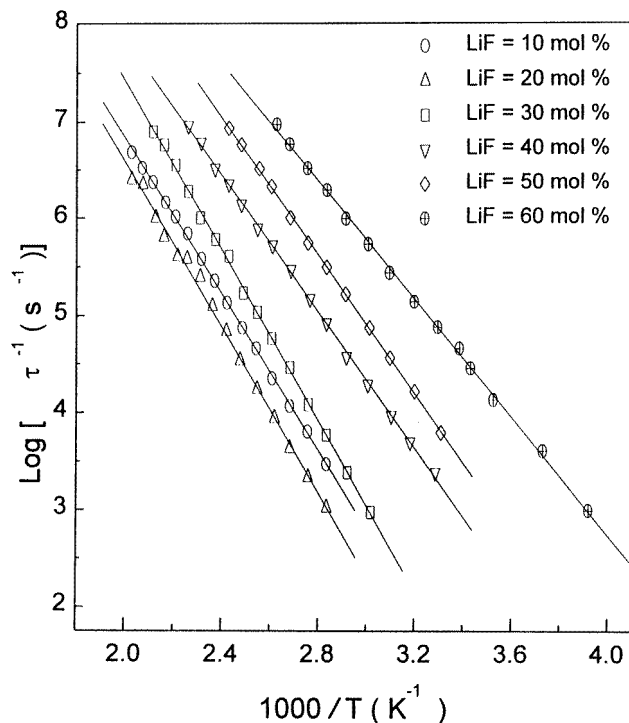
Figure 6. Temperature dependence of the inverse conductivity relaxation time for the same glass compositions as shown in figure 1.

small (0.54 to 0.63), similar to those observed in ZrF_4–BaF_2–LaF_3–LiF and ZrF_4–BaF_2–ThF_4–LiF glasses and also in superionic glasses [19, 20]. Small β values for the superionic glasses are associated with very low activation energy W_σ. However, high values of W_σ observed for the fluoride glasses in the composition range where the β minimum occurs imply that there is no correlation between W_σ and β for these fluoride glasses. It may also be noticed in figure 5 that the minimum of β values occurs for a composition different from that of the conductivity, similar to the results obtained for ZrF_4–BaF_2–LaF_3–LiF and ZrF_4–BaF_2–ThF_4–LiF fluoride [11] and $Al(PO_3)_3$–PbF_2–LiF oxyfluoride glasses [18]. The results for the oxyfluoride glasses are interpreted in terms of a crossover in principal current carriers [18]. However, this interpretation is not valid for the lithium fluoride glasses, because the NMR results for ZrF_4–BaF_2–LaF_3–LiF and ZrF_4–BaF_2–ThF_4–LiF glasses [11] confirm the crossover from F^- conductivity to Li^+ conductivity for 20 mol% LiF where the minimum in the conductivity occurs. A structural origin for ZrF_4–BaF_2–LaF_3–LiF and ZrF_4–BaF_2–ThF_4–LiF glasses [11] has been proposed to account for these results. The small β values occur for the compositions in which the migration topology of the modifier cation distribution is very complicated which results from the competitive influence of Ba^{2+} and Li^+ cations on the mobility of the F^- ions mobile at long range and also from the large perturbation caused by the long range motion of Li^+ ions themselves. The latter influence might be responsible for the occurrence of the β minimum for a composition different from that of the conductivity. This interpretation is extended to the present ZrF_4–BaF_2–YF_3–LiF glasses.
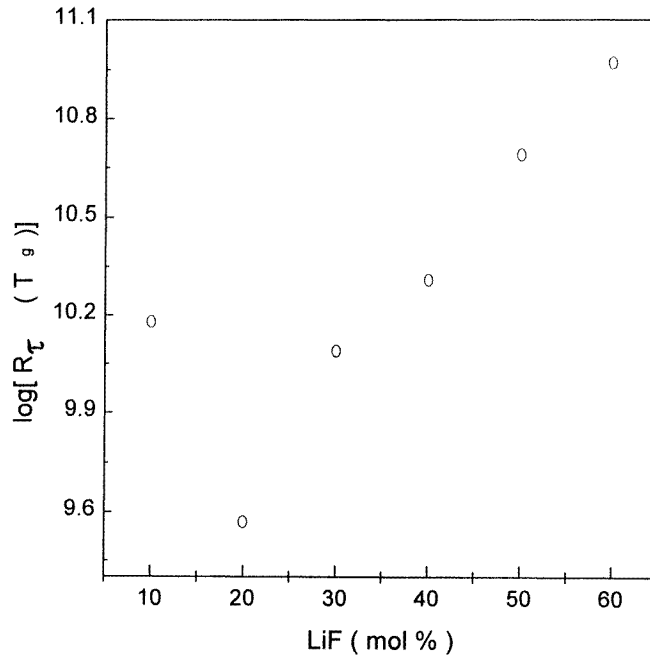
Figure 7. Variation of $R_\tau(T_g)$ with the LiF content in the composition for the ZrF$_4$–BaF$_2$–YF$_3$–LiF glasses.

4. Conclusions

The composition dependence of the conductivity and the activation energy clearly shows that there is a crossover from an F$^-$ ion conductivity to an Li$^+$ conductivity at 20 mol% LiF content in the glass composition. The conductivity is also associated with a minimum in the extent to which the motion of the mobile ions is decoupled from the viscous motion of the glass matrix. The relaxation parameter β, however, exhibits a minimum at a different LiF content, which results from the competitive influence of Ba^{2+} and Li$^+$ cations on the mobility of F$^-$ ions mobile at long range.

Acknowledgment

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