Conductivity studies of lithium zinc silicate glasses with varying lithium contents

S K DESHPANDE*, V K SHRIKHANDE[†], M S JOGAD[‡], P S GOYAL and G P KOTHIYAL[†]

UGC–DAE Consortium for Scientific Research, Mumbai Centre, R5 Shed, [†]Technical Physics & Prototype Engineering Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[‡]S.B. College of Science, Gulbarga 585 103, India

Abstract. The electrical conductivity of lithium zinc silicate (LZS) glasses with composition, $(SiO_2)_{0.527}$ $(Na_2O)_{0.054}(B_2O_3)_{0.05}(P_2O_5)_{0.029}(ZnO)_{0.34-x}(Li_2O)_x$ ($x = 0.05$, 0.08, 0.11, 0.18, 0.21, 0.24 and 0.27), was studied as a function of frequency in the range 100 Hz–15 MHz, over a temperature range from 546–637 K. The a.c. conductivity is found to obey Jonscher's relation. The d.c. conductivity ($\sigma_{d.c.}$) and the hopping frequency (ω_h), inferred from the a.c. conductivity data, exhibit Arrhenius-type behaviour with temperature. The electrical modulus spectra show a single peak, indicating a single electrical relaxation time, τ, which also exhibits Arrhenius-type behaviour. Values of activation energy derived from $\sigma_{d.c.}$, ω_h and τ are almost equal within the experimental error. It is seen that $\sigma_{d.c.}$ and ω_h increase systematically with Li_2O content up to 21 mol% and then decrease for higher Li_2O content, indicating a mixed alkali effect caused by mobile Li^+ and Na^+ ions. The scaling behaviour of the modulus suggests that the relaxation process is independent of temperature but depends upon Li^+ concentration.

Keywords. Ionic conductivity; glasses; electrical modulus; dielectric relaxation.

1. Introduction

Glasses and glass–ceramics are technologically important materials. Glass–ceramics show superior thermo-mechanical, electrical and other physico-chemical properties, which make them suitable for use in vacuum, high-voltage, and biomedical applications (McMillan 1979). The lithium–zinc–silicate (LZS) glass containing Li_2O–ZnO–SiO_2–Na_2O–B_2O_3–P_2O_5 has been used as the base glass for producing glass ceramics that are suitable for applications in hermetic glass–ceramic–to–metal seals with a variety of metals and alloys (Sharma *et al* 2004). Various physical properties of these materials, like thermal expansion coefficients, electrical and thermal conductivity, micro-hardness, dielectric constant, etc can be controlled to suit different applications by varying the concentrations of the modifiers like Na_2O, Li_2O and ZnO in the base glass. In particular, the electrical and dielectric properties of these materials can be changed by varying the proportion of the alkali oxides, as the alkali ions are responsible for electrical conduction. The investigation of the conductivity behaviour in the base glass as a function of alkali oxide content is, therefore, of interest.

Lithium ion conduction has been the subject of study in different types of glasses (Ingram 1987; Meikhail *et al* 1993; Pan and Ghosh 1999; Bhat *et al* 2004), and some thermo-physical properties have been measured in LZS glass–ceramics (Sharma *et al* 2004). We have undertaken a study of the temperature and frequency dependence of electrical conductivity in LZS glasses containing different proportions of Li_2O and ZnO, keeping the total concentration of $Li_2O + ZnO$ constant. In this paper, we present the results of this study.

2. Experimental

LZS glasses having the nominal composition $(SiO_2)_{0.527}$ $(Na_2O)_{0.054}(B_2O_3)_{0.05}(P_2O_5)_{0.029}(ZnO)_{0.34-x}(Li_2O)_x$, where $x = 0.05$, 0.08, 0.11, 0.18, 0.21, 0.24, and 0.27, were prepared by the melt and quench method. The three-stage heating cycle, involving calcination, melting and quenching, as reported earlier (Shrikhande *et al* 1998), was used for the preparation of glasses. The amorphous nature of these glasses was confirmed by X-ray diffraction. Glass transition temperatures were determined by dilatometry.

Impedance measurements were carried out on these samples (each about 10 mm in diameter and 2–3 mm thick) using an impedance analyser (HP 4194 A) in the fre-

quency range 100 Hz–15 MHz at five temperatures in the range 546–637 K. All measurements were carried out with the samples under a vacuum of 10^{-4} mbar. Gold film of about 500 Å was deposited on both sides of the samples for proper electrical contact, and the samples were sandwiched between two silver electrodes inside an indigenously made high-temperature cell (Balaya *et al* 2004). Four silver wires connected to the electrodes act as electric leads. The sample temperature was measured using a K-type thermocouple mounted close to the sample. A Eurotherm 818P PID controller was used to control the temperature within $\pm 0.2°C$. The impedance analyser was interfaced to a personal computer using a GPIB add-on card, and the recorded data was directly stored on the computer.

The frequency-dependent complex impedance, $Z^*(\omega)$, determined in our experiments is

$$Z^*(\omega) = Z'(\omega) - iZ''(\omega), \tag{1}$$

where $Z'(\omega)$ and $Z''(\omega)$ are, respectively, the measured real and imaginary parts of the impedance and ω the angular frequency ($\omega = 2\pi f$, where f is the frequency of applied field).

The measured impedance was used to extract information about the conductivity and electrical relaxation. The a.c. conductivity, $\sigma^*(\omega)$, was determined from the impedance using the relation

$$\sigma^*(\omega) = \sigma'(\omega) + i\sigma''(\omega) = (A/d)(1/Z^*(\omega)), \tag{2}$$

where A is the area of the sample surface under the electrodes and d the sample thickness. The d.c. conductivity was extracted from the a.c. conductivity.

To study the relaxation behaviour, the electrical modulus, $M^*(\omega)$, was also determined from the measured impedance using the relation

$$M^*(\omega) = M'(\omega) + iM''(\omega) = i\omega\varepsilon_0 Z^*(\omega), \tag{3}$$

where ε_0 is the permittivity of vacuum (Macedo *et al* 1972).

3. Results and discussion

A complex-plane plot of the measured impedance for one of the samples ($x = 0.18$) at selected temperatures is shown in figure 1. Each point on a given curve corresponds to one frequency value, with the frequency increasing in the direction of the arrow as shown in the figure. The d.c. resistance, obtained from the intercept on the low frequency side on the Z'-axis, decreases from about 400–30 kΩ as the temperature is increased from 565–637 K for this sample. Similar trend was observed for other samples.

In these glasses, both Na^+ and Li^+ ions are mobile and contribute to the conductivity. The d.c. conductivity, $\sigma_{d.c.}$, and ion hopping frequency, ω_h, were obtained by fitting the real part, $\sigma'(\omega)$, of the complex conductivity (2) to the relation (Almond *et al* 1993)

$$\sigma'(\omega) = \sigma_{d.c.}(1 + (\omega/\omega_h)^n), \tag{4}$$

where the exponent, n, takes values between 0 and 1. Figure 2 shows a plot of $\sigma'(\omega)$ as well as the fits to (4) at different temperatures for the sample with 8 mol% Li_2O. It is clear that $\sigma'(\omega)$ obeys the relation given by (4). The a.c. conductivity shows a plateau at lower frequencies and dispersion at higher frequencies. This behaviour is typical of ionic conductors (Angell 1983).

The values of $\sigma_{d.c.}$, ω_h and n are given in table 1 for sample with $x = 0.08$. The parameter, n, does not show a simple behaviour with temperature. It is seen to vary non-systematically in our study, but remains close to 0.5.
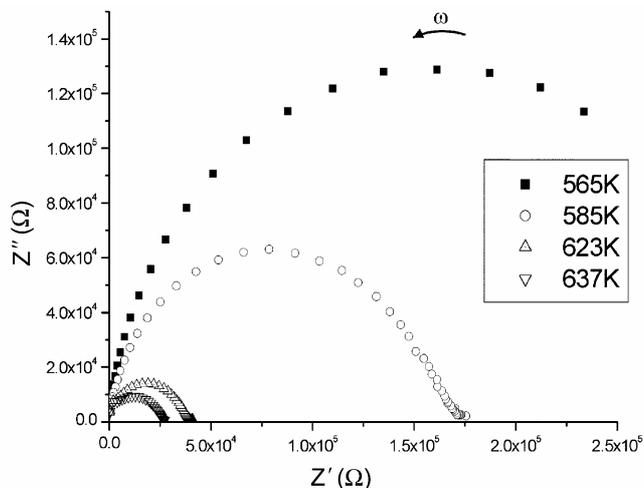

Figure 1. Impedance plot in the complex plane for sample with $x = 0.18$.
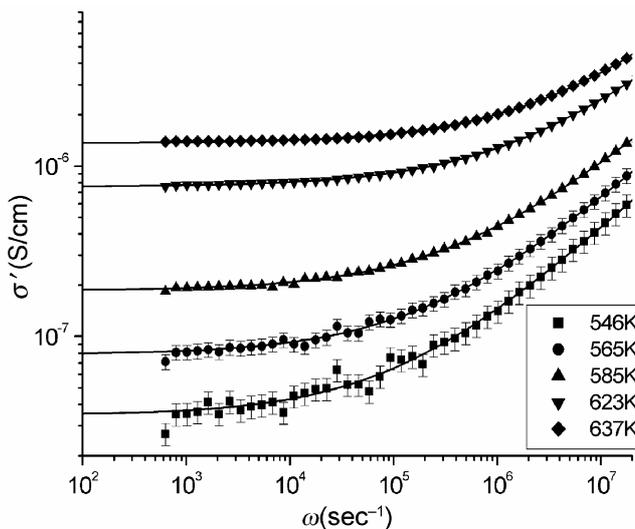

Figure 2. Real part of conductivity as a function of frequency at different temperatures for sample with 8 mol% Li_2O. Solid lines are fit to data according to $\sigma'(\omega) = \sigma_{d.c.}(1 + (\omega/\omega_h)^n)$. Error bars are smaller than the size of symbols for $T > 565$ K.

Similar analysis was done for the other samples also. It was seen that the real part, $\sigma'(\omega)$, of a.c. conductivity obeys (4) for all glass compositions at all reported temperatures.

The effect of concentration of Li_2O on the d.c. conductivity, as determined by above analysis was examined next. Figure 3 shows the variation of d.c. conductivity with Li_2O concentration at different temperatures. It is interesting to note that as the concentration of Li^+ ions increases, the d.c. conductivity increases for Li_2O content up to 21 mol% and then sharply decreases as shown in figure 3, i.e. the plot of $\sigma_{d.c.}$ vs Li_2O content goes through a maximum and then a minimum. This indicates that the conductivity is dependent upon relative concentration of Li^+
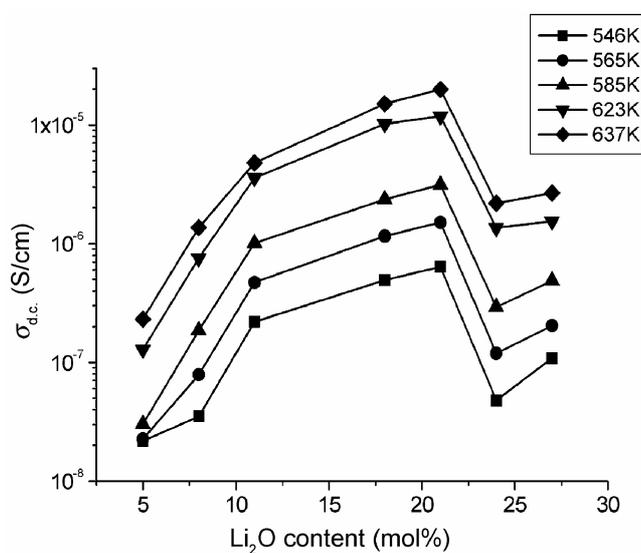

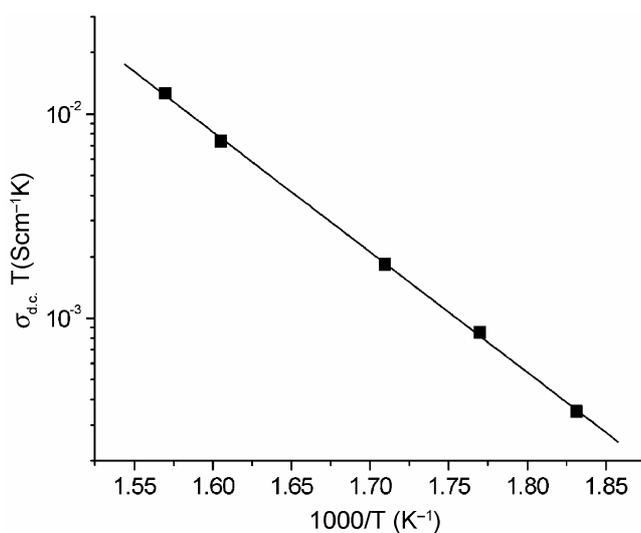**Figure 3.** Variation of d.c. conductivity with Li_2O content. The solid line is a guide to the eye.

Figure 4. Temperature dependence of $\sigma_{d.c.}T$ for the sample containing 21 mol% Li_2O. Solid line is linear fit to the data.

and Na^+ ions. This behaviour is due to the 'mixed alkali effect' observed in mixed alkali glasses (Ingram 1987), and reviewed by Isard (1969) and Day (1976). The hopping frequency, ω_h, also shows a maximum at $x = 0.21$ and goes through a minimum beyond this concentration.

The temperature dependence of the d.c. conductivity and hopping frequency was also examined. Figure 4 shows the variation of d.c. conductivity with temperature for the sample containing 21 mol% Li_2O. A similar trend was seen for ω_h.

It is seen that both $\sigma_{d.c.}$ and ω_h obey the Arrhenius-type relationships

$$\sigma_{d.c.}T = \sigma_0 \exp(-E_\sigma/kT), \tag{5}$$

$$\omega_h T = \omega_0 \exp(-E_h/kT), \tag{6}$$

where k is the Boltzmann constant, T the temperature, E_σ the activation energy for d.c. conduction, and E_h the activation energy for local ion hopping process.

We have found that E_σ shows no systematic variation with Li^+ content, within the experimental error. It is expected that E_σ will go through a maximum corresponding to the minimum in $\sigma_{d.c.}$ (Ingram 1987), but we find that it does not show a maximum as d.c. conductivity drops to a minimum at $x = 0.24$. The values of the activation energies, E_σ, for all the samples studied are given in table 2.

The d.c. conductivity was plotted against the hopping frequency for each glass composition. Figure 5 shows a plot of $\sigma_{d.c.}$ vs ω_h for the sample with 21 mol% Li_2O. We have found that, for all the samples studied, $\sigma_{d.c.}$ and ω_h obey the Barton–Nakajima–Namikawa (BNN) relationship (Kremer and Rozanski 2003)

$$\sigma_{d.c.} \propto \omega_h. \tag{7}$$

This indicates that the mechanism responsible for observed d.c. and a.c. conduction in these samples is identical.

The electrical relaxation behaviour was examined by determining the electrical modulus using (3). As an example, figure 6 shows the variation of M'', the imaginary part of the modulus, with frequency for the sample with 21 mol% Li_2O at different temperatures. The shape of the spectrum is identical for all temperatures and shows a single relaxation peak. The maxima in these spectra occur at $\omega_m = 1/\tau$, where τ is the relaxation time. The peak frequency, ω_m, shifts to higher values with increasing temperature.

From the values of ω_m, the values of relaxation times, τ, have been obtained. The temperature dependence of τ is shown in figure 7 for sample with 21 mol% Li_2O.

It is again found that the relaxation time obeys the Arrhenius-type relation

$$\tau = \tau_0 \exp(E_\tau/kT), \tag{8}$$

where E_τ is the activation energy. Activation energy thus obtained for all samples is tabulated in table 3. It is observed that the values of E_τ are in good agreement with those of E_σ, indicating that the mechanism of ion migration

Table 1. Physical parameters for the sample with 8 mol% Li_2O.

$T(K)$	$\sigma_{d.c.}$ (Scm^{-1})	Hopping frequency, ω_h (s^{-1})	n	Mobile ion concentration factor, $K = (\sigma_{d.c.} T/\omega_h)$ (S cm^{-1} s^{-1} K)
546	$3 \cdot 50 \times 10^{-8}$	131270	0·56	$1 \cdot 4 \times 10^{-10} \pm 1 \times 10^{-11}$
565	$7 \cdot 87 \times 10^{-8}$	247364	0·54	$1 \cdot 8 \times 10^{-10} \pm 1 \times 10^{-11}$
585	$1 \cdot 86 \times 10^{-7}$	543100	0·53	$2 \cdot 0 \times 10^{-10} \pm 1 \times 10^{-12}$
623	$7 \cdot 59 \times 10^{-7}$	$2 \cdot 1174 \times 10^6$	0·52	$2 \cdot 2 \times 10^{-10} \pm 1 \times 10^{-12}$
637	$1 \cdot 37 \times 10^{-6}$	$4 \cdot 175 \times 10^6$	0·54	$2 \cdot 1 \times 10^{-10} \pm 1 \times 10^{-12}$

Table 2. Variation of activation energy, E_σ, with concentration of Li_2O.

Concentration (mol% Li_2O)	E_σ (eV)
5	0·87 ± 0·18
8	1·25 ± 0·05
11	1·09 ± 0·02
18	1·18 ± 0·02
21	1·17 ± 0·03
24	1·31 ± 0·01
27	1·10 ± 0·04

Table 3. Variation of activation energy, E_τ, with concentration of Li_2O.

Concentration (mol% Li_2O)	E_τ (eV)
5	1·19 ± 0·21
8	1·13 ± 0·03
11	1·09 ± 0·02
18	1·33 ± 0·08
21	1·05 ± 0·03
24	1·28 ± 0·05
27	1·04 ± 0·02

Figure 6. The imaginary part of electrical modulus as a function of frequency for 21 mol% Li_2O.
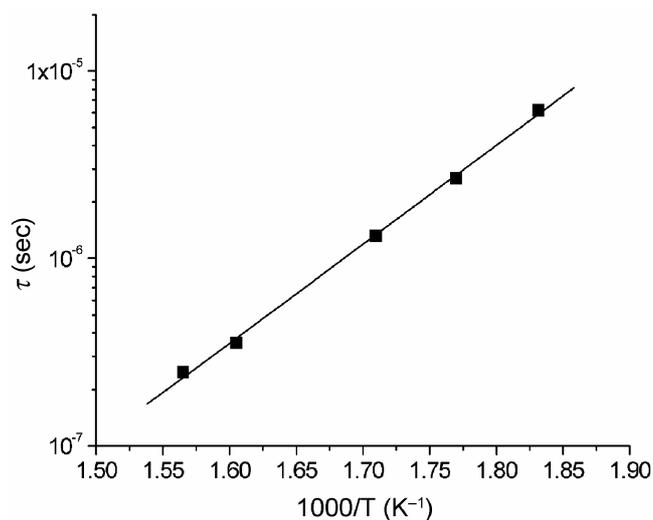
Figure 7. Variation of relaxation time with temperature for 21 mol% Li_2O. Solid line is a linear fit to the data.

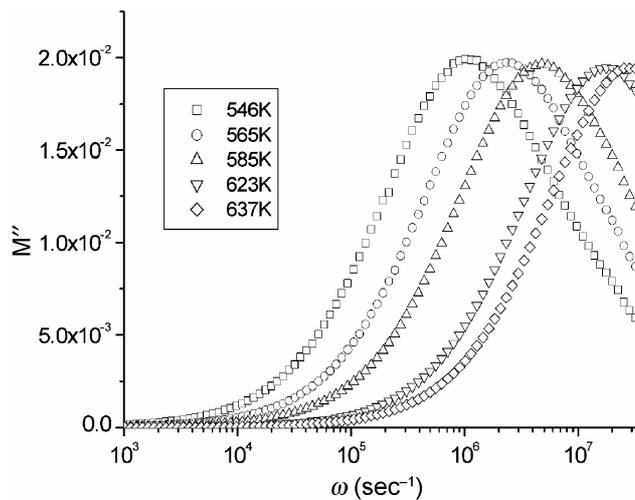**Figure 5.** Relationship between $\sigma_{d.c.}$ and ω_h for sample with $x = 0 \cdot 21$. Solid line is a linear fit to the data.

is responsible for both the observed d.c. and a.c. conductivities, and electrical relaxation (Macedo *et al* 1972).
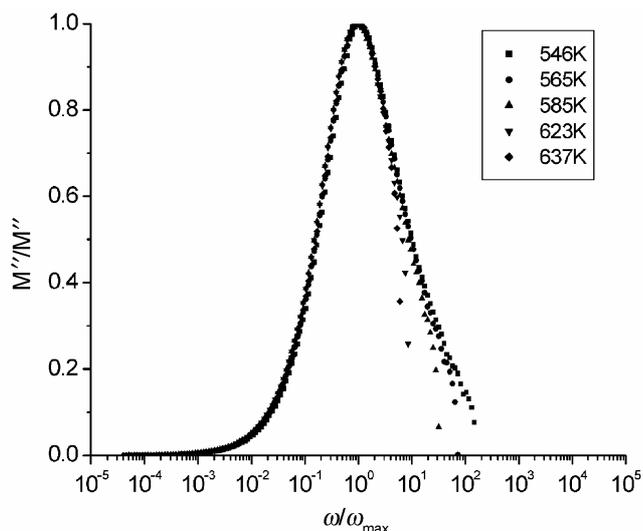
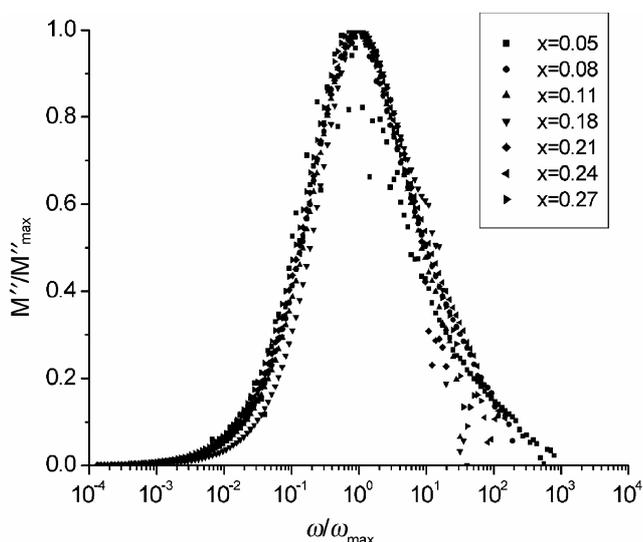**Figure 8.** Temperature dependence of the scaling of M'' ($x = 0.11$).

Figure 9. Composition dependence of the scaling of M'' at 585 K.

We have also examined the scaling behaviour of the modulus function. The M'' spectra were scaled by M''_{max}, and the ω axis is scaled by the relaxation frequency, ω_m. It is observed that for any particular composition, the M'' spectra at different temperatures merge very well into a single master curve, as shown in figure 8 for one of the samples. This indicates that the relaxation process is independent of temperature for a given concentration of Li^+ ions. A similar analysis for composition dependence of the scaling behaviour was carried out, and we find that the M'' spectra at any particular temperature for different compositions do not merge into a single master curve (see figure 9). This indicates that the relaxation dynamics varies with glass composition (Ghosh and Ghosh 2002).

The d.c. conductivity in ionic materials may be written as

$$\sigma_{d.c.} = KT^{-1}\omega_h, \tag{9}$$

where K is a factor that depends upon the concentration of mobile ions (Almond *et al* 1993; El-Egili 1996). Using (9), the mobile ion concentration factor, K, was calculated for each glass composition. As an example, the values of K for the sample with 8 mol% Li_2O are given in table 1. Within experimental errors, K remains unchanged as temperature is raised, which indicates that the mobile ion concentration is not thermally activated, and increase in conductivity is due to greater hopping rate as indicated by the large increase in hopping frequency with temperature. This is borne out in the scaling behaviour of M'' (figure 8), as the width of the M'' spectra, which is sensitive to the mobile ion concentration (Ngai *et al* 1989), does not change with temperature.

4. Conclusions

The d.c. conductivity and the ion hopping frequency in lithium zinc silicate glasses containing varying amounts of Li_2O and ZnO obey Arrhenius behaviour. It is seen that $\sigma_{d.c.}$ increases with lithium content up to 21 mol% and then sharply decreases to a minimum by an order of magnitude beyond this concentration indicating a mixed alkali effect. The hopping frequency, ω_h, also shows a similar trend. However, the activation energy for d.c. conduction, E_σ, neither shows systematic variation with concentration of Li_2O, nor an increase corresponding to the minimum in $\sigma_{d.c.}$, within the experimental error.

The relaxation time, τ, also shows Arrhenius behaviour and the values of activation energy, E_τ, obtained from the relaxation times are in good agreement with those of E_σ indicating that the mechanism of ion migration is responsible for the observed d.c. and a.c. conductivities and electrical relaxation.

The scaling behaviour of the electrical modulus indicates that the relaxation process is independent of temperature. There is no scaling with respect to concentration of Li^+ ions. Our results also suggest that the mobile ion concentration is not thermally activated.

References

Almond D P, Duncan G K and West A R 1993 *Solid State Ionics* **8** 159

Angell C A 1983 *Solid State Ionics* **9–10** 3

Balaya P, Shrikhande V K, Kothiyal G P and Goyal P S 2004 *Curr. Sci.* **86** 553

Bhat Harish M, Kandavel M, Ganguli Munia and Rao K J 2004 *Bull. Mater. Sci.* **27** 189

Day D E 1976 *J. Non-Cryst. Solids* **21** 343

El-Egili K 1996 *J. Phys.: Condens. Matter* **8** 3419

Ghosh S and Ghosh A 2002 *J. Phys.: Condens. Matter* **14** 2531

Ingram M D 1987 *Phys. Chem. Glasses* **28** 215

Isard J O 1969 *J. Non-Cryst. Solids* **1** 235

Kremer F and Rozanski S A 2003 *Broadband dielectric spectroscopy* (eds) F Kremer and A Schonhals (Berlin: Springer Verlag) Ch. 12

Macedo P B, Moynihan C T and Bose R 1972 *Phys. Chem. Glasses* **13** 171

McMillan P W 1979 *Glass ceramics* (London: Academic Press) 2nd edn

Meikhail M S, Gohar I A and Megahed A A 1993 *J. Phys. D: Appl. Phys.* **26** 1125

Ngai K L, Mundy J N, Jain H, Kannert O and Balzer-Jollenbeck G 1989 *Phys. Rev.* **B39** 6169

Pan A and Ghosh A 1999 *Phys. Rev.* **B60** 3224

Sharma Indrajit B, Goswami Madhumita, Sengupta P, Shrikhande V K, Kale G B and Kothiyal G P 2004 *Mater. Letts* **58** 2423

Shrikhande V K, Mirza T, Sawant B B, Sinha A K and Kothiyal G P 1998 *Bull. Mater. Sci.* **21** 493