

## Li<sup>+</sup> ion conductivities in boro-tellurite glasses

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**Abstract.** Lithium ion conductivity has been investigated in a boro-tellurite glass system, LiCl·LiBO<sub>2</sub>·TeO<sub>2</sub>. In the absence of LiCl, the conductivity increases with increasing non-bridging oxygen (NBO) concentration. LiCl addition has little influence on total conductivity although the observed barriers are low. Formation of LiCl clusters appears evident. In the a.c. conductivity and dielectric studies, it is observed that the conductivity mechanism remains the same in all compositions and at all temperatures. A suggestion is made that Li<sup>+</sup> ion transport may be driven by bridging oxygen ↔ non-bridging oxygen (BO ↔ NBO) switching, which is why the two different types of Li<sup>+</sup> ions in the clusters and in the neighbourhood of NBOs, do not manifest in the conductivity studies.

**Keywords.** Tellurite glasses; Li<sup>+</sup> ion transport.

### 1. Introduction

Boro-tellurite glasses have been widely studied in literature because of the industrial importance of tellurites in making glasses with desirable optical properties (Nasu *et al* 1990; Tanabe *et al* 1990; Kim *et al* 1993; Wang *et al* 1994). Since both B<sub>2</sub>O<sub>3</sub> and TeO<sub>2</sub> are present in boro-tellurite glasses, it leads to complex specification in the glass structure (Rao and Harish Bhat 2001). Depending upon the Li<sub>2</sub>O concentration available for modification, the species present in the glasses can be [BO<sub>4/2</sub>]<sup>−</sup> (≡ B<sub>4</sub><sup>−</sup>) and [BO<sub>3/2</sub>]<sup>−</sup> (≡ B<sub>2</sub><sup>−</sup>), trigonal bipyramidal (*tbp*) [TeO<sub>4/2</sub>]<sup>0</sup> (≡ T<sub>4</sub><sup>0</sup>) and trigonal pyramidal (*tp*) [TeOO<sub>2/2</sub>]<sup>0</sup> (≡ T<sub>2</sub><sup>0</sup>) along with *tbp* [TeO<sub>3/2</sub>O]<sup>−</sup> (≡ T<sub>3</sub><sup>−</sup>) and *tp* [TeO<sub>1/2</sub>O]<sup>−</sup> (≡ T<sub>1</sub><sup>−</sup>) (Burger *et al* 1992; Mori *et al* 1995; Sabry and El-Samanoudy 1995; Akagi *et al* 1999; Blanchandin *et al* 1999; Komatsu and Mohri 1999; El-Damrawi and Abd-El-Maksoud 2000; Iwadata *et al* 2000; Arnaudov and Dimitriev 2001; Rao and Harish Bhat 2001) (note: the superscript on letters B and T represents the charge and the subscript represents the number of bridging oxygens attached to the central atom). Besides, in this glass system there are three structural conversion reactions of interest, viz. B<sub>4</sub><sup>−</sup> → B<sub>2</sub><sup>−</sup>, T<sub>4</sub><sup>0</sup> → T<sub>2</sub><sup>0</sup> and T<sub>4</sub><sup>−</sup> → T<sub>1</sub><sup>−</sup>. These conversions are promoted when the concentration of the modifier, Li<sub>2</sub>O, is increased. T<sub>4</sub><sup>0</sup> → T<sub>2</sub><sup>0</sup> conversion also appears to be promoted by the presence of ionic salts like LiCl; LiCl favours *tbp* to *tp* (Rao and Harish Bhat 2001). In turn, *tp* units in the structure appear to favour retention of B<sub>4</sub><sup>−</sup> in the borotellurites. A very important consequence of these structural features is that the effective dimensionality of the glass

structure itself is critically dependent on the concentration of various structural species because the connectivities of the structural species are quite varied: quite expectedly all the properties of the resulting glasses such as density, molar volume, glass transition temperature, etc manifest the structural changes which occur as a function of Li<sub>2</sub>O concentration. Some of these properties have been discussed in an earlier publication (Rao and Harish Bhat 2001). There have also been literature reports on alkali ion transport in tellurite and boro-tellurite glasses (Hampton *et al* 1987; Rodriguez and Duclot 1988; Tanaka *et al* 1988, 1991; Jaysinghe *et al* 1995; Reau *et al* 1995; Sabry and El-Samanoudy 1995; Sunandana 1996; Chowdari and Pramoda Kumari 1998; Pan and Ghosh 1999). Various influences including those of structural changes upon modification, nature of the added alkali-salt, changes in bonding features and also the equilibrium of tellurite species (*tbp* ↔ *tp*) upon the alkali ion transport have been discussed.

In this communication, we report our investigations of the Li<sup>+</sup> ion transport in the LiCl·LiBO<sub>2</sub>·TeO<sub>2</sub> glasses as a function of composition, temperature and frequency. This would lead to a better understanding of the role of the individual components of the glass, the two glass formers, B<sub>2</sub>O<sub>3</sub> and TeO<sub>2</sub>, the dissolved salt, LiCl, which is not expected to influence the network structure and the modifier, Li<sub>2</sub>O, which determines the concentration of non-bridging oxygens (NBOs) in the system, on the Li<sup>+</sup> ion transport.

### 2. Experimental

Boro-tellurite glasses discussed in this paper were prepared by melt-quenching technique as described elsewhere (Rao and Harish Bhat 2001). Glasses were obtained

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ned using high-purity (Analar Grade) commercial powders of TeO<sub>2</sub>, LiCl and LiBO<sub>2</sub>·2H<sub>2</sub>O. Mixtures of these materials in appropriate proportions were taken in porcelain crucibles and slowly heated to 535 K and then to 823 K (to remove water from LiBO<sub>2</sub>·2H<sub>2</sub>O) for 2 h. The mixture was then melted at 1223 K, kept at that temperature for 30 min, following which it was quenched between polished stainless steel plates.

Electrical conductivity measurements were carried out on a Hewlett-Packard HP 4192A LF impedance-gain phase analyser (Hewlett-Packard, USA) from 10 Hz to 13 MHz in the temperature range 200–625 K. A home built cell assembly (a 2-terminal capacitor configuration and spring loaded electrodes of silver) was used for the measurements. The sample temperature was measured using a Pt–Rh thermocouple (copper-constantan was used at low temperatures) positioned very close to the sample. The temperature was controlled using a Heatcon (Bangalore, India) temperature controller and the temperature constancy of  $\pm 1$  K was achieved in the entire range of measurements. Annealed circular glass pieces, coated with silver paint on both sides and having thickness of about 0.1 cm and 1 cm diameter were used for measurements. The real ( $Z'$ ) and imaginary ( $Z''$ ) parts of the complex impedance ( $Z^*$ ) were obtained from the measured conductance and capacitance using the relations

$$Z' = G/(G^2 + \omega^2 C^2),$$

$$Z'' = \omega C/(G^2 + \omega^2 C^2),$$

where,  $G$  is the conductance,  $C$  the parallel capacitance, and  $\omega$  the angular frequency. The real ( $\epsilon'$ ) and imaginary ( $\epsilon''$ ) parts of the complex dielectric constant were calculated from the relations

$$\epsilon' = Cd/(\epsilon_0 A),$$

$$\epsilon'' = \mathbf{s}/(\omega \epsilon_0),$$

where  $d$  is the sample thickness,  $A$  the cross-sectional area,  $\mathbf{s}$  the conductivity, and  $\epsilon_0$  the permittivity of free space.

The data were also analysed using the electrical modulus formalism. The real ( $M'$ ) and imaginary ( $M''$ ) parts of the complex electrical modulus ( $M^* = 1/\epsilon^*$ ) were obtained from  $\epsilon'$  and  $\epsilon''$  values using the relation,

$$M' = \epsilon'/((\epsilon')^2 + (\epsilon'')^2),$$

$$M'' = \epsilon''/((\epsilon')^2 + (\epsilon'')^2).$$

### 3. Results and discussion

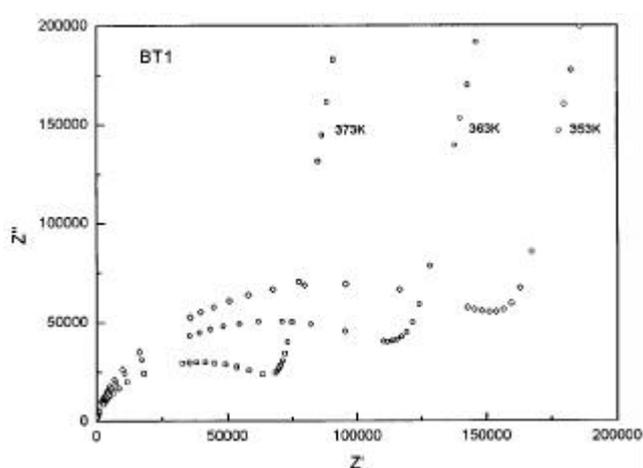
Compositions of the glasses studied are indicated in table 1. Typical impedance plots (Cole–Cole plots) are shown in figure 1 for the case of BT1 glass for three different temperatures. Semicircle fits were used to determine the zero frequency impedances (resistances) and using known geometrical dimensions of the pellet (glass piece), the d.c. conductivities were determined. The variation of the corresponding conductivities ( $\mathbf{s}_{d.c.}$ ) for the BT series of glasses are shown in figure 2 in a semi-log plot as a function

**Table 1.** Compositions, molar volumes, d.c. conductivity (at 463 K) and d.c. activation barriers for boro-tellurite glasses.

Code	Composition	Molar volume* (cc)	$\mathbf{s}_{d.c.}$ (463 K) (S cm <sup>-1</sup> )	$E_{d.c.}$ (eV)
BT0	100LiBO <sub>2</sub> : 0TeO <sub>2</sub>	21.17	$9.99 \times 10^{-5}$	0.62
BT1	90LiBO <sub>2</sub> : 10TeO <sub>2</sub>	23.00	$7.16 \times 10^{-5}$	0.66
BT2	80LiBO <sub>2</sub> : 20TeO <sub>2</sub>	24.31	$6.96 \times 10^{-6}$	0.76
BT3	70LiBO <sub>2</sub> : 30TeO <sub>2</sub>	25.52	$1.51 \times 10^{-6}$	0.86
BT4	60LiBO <sub>2</sub> : 40TeO <sub>2</sub>	26.24	$2.54 \times 10^{-7}$	0.94
BT5	50LiBO <sub>2</sub> : 50TeO <sub>2</sub>	27.05	$1.61 \times 10^{-8}$	1.07
BT6	40LiBO <sub>2</sub> : 60TeO <sub>2</sub>	26.77	$2.80 \times 10^{-9}$	1.23
BT7	30LiBO <sub>2</sub> : 70TeO <sub>2</sub>	26.55	$5.58 \times 10^{-10}$	1.18
CT0	0LiCl : 70LiBO <sub>2</sub> : 30TeO <sub>2</sub>	25.52	$1.51 \times 10^{-6}$	0.86
CT1	10LiCl : 60LiBO <sub>2</sub> : 30TeO <sub>2</sub>	25.53	$1.69 \times 10^{-6}$	0.76
CT2	20LiCl : 50LiBO <sub>2</sub> : 30TeO <sub>2</sub>	24.99	$2.58 \times 10^{-6}$	0.62
CT3	30LiCl : 40LiBO <sub>2</sub> : 30TeO <sub>2</sub>	24.62	$5.41 \times 10^{-6}$	0.65
CT4	40LiCl : 30LiBO <sub>2</sub> : 30TeO <sub>2</sub>	24.85	$6.52 \times 10^{-6}$	0.59
CL0	30LiCl : 00LiBO <sub>2</sub> : 70TeO <sub>2</sub>	25.87	—	—
CL1	30LiCl : 10LiBO <sub>2</sub> : 60TeO <sub>2</sub>	24.82	—	—
CL2	30LiCl : 20LiBO <sub>2</sub> : 50TeO <sub>2</sub>	23.94	$1.34 \times 10^{-8}$	0.68
CL3	30LiCl : 30LiBO <sub>2</sub> : 40TeO <sub>2</sub>	24.66	$4.61 \times 10^{-8}$	0.65
CL4	30LiCl : 40LiBO <sub>2</sub> : 30TeO <sub>2</sub>	24.62	$5.41 \times 10^{-8}$	0.65
CL5	30LiCl : 50LiBO <sub>2</sub> : 20TeO <sub>2</sub>	23.48	$5.30 \times 10^{-7}$	0.52
CL6	30LiCl : 60LiBO <sub>2</sub> : 10TeO <sub>2</sub>	23.60	$1.78 \times 10^{-5}$	0.41
CL7	30LiCl : 70LiBO <sub>2</sub> : 00TeO <sub>2</sub>	22.32	$6.3 \times 10^{-5}$	0.36

\*from reference 5.

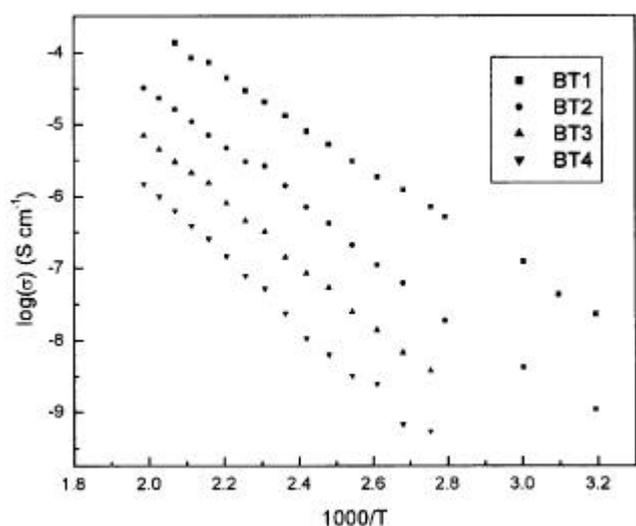
of inverse temperature. The temperature behaviour of d.c. conductivities of all the glasses were similar. The activation barriers ( $E_{d.c.}$ ) have been calculated and their variation as a function of  $\text{TeO}_2$  concentration are shown for BT and CL series (figures 3(a) and (c)). The variation of activation barrier for CT series of glasses is shown as a function of LiCl concentration (figure 3(b)). In general, increase of  $\text{TeO}_2$  concentration leads to increase of the activation barrier (Jayasinghe *et al* 1995; Sabry and El-Samanoudy 1995; Pan and Ghosh 1999). On the contrary, increase in LiCl concentration leads to decrease of the activation barrier (Tanaka *et al* 1988, 1991; Reau *et al* 1995). It was shown earlier by us (Rao and Harish Bhat 2001) that in all the three series of glasses, the concentration of  $N_4$  ( $\equiv [B_4]/\{[B_3] + [B_4]\}$ ) is very high, and it reaches peak values in intermediate compositions. However, molar volume variations suggest LiCl does not simply dissolve in  $\text{LiBO}_2\text{-TeO}_2$  glasses, but it strongly influences the structure of tellurite species in glasses by favouring formation of  $T_3^0$  units. Increasing concentration of LiCl would be expected to lead to increased d.c. conductivity, but the increase is marginal as evident in figure 4(b) for CT series. Since concentration of  $\text{Li}^+$  ions decreases in BT and CL series as the concentration of  $\text{TeO}_2$  is increased, a decrease in conductivity is anticipated and the observed behaviour (figures 4(a) and (c)) is also consistent. It is interesting to note from figures 3(a) and (c) that with increasing  $\text{TeO}_2$  content activation barriers increase almost linearly. Activation barriers also decrease in a similar way with increasing LiCl in CT series. From table 1, it may be seen that increase of activation barriers is in apparent inconsistency with the observed increase in molar volumes. Conductivity decrease is about four orders of magnitude. Although there is a significant decrease in  $\text{Li}^+$  ion concentration itself (in BT and CL series), the more significant reason for the observed decrease in conductivity is the increased activation barrier. Since in



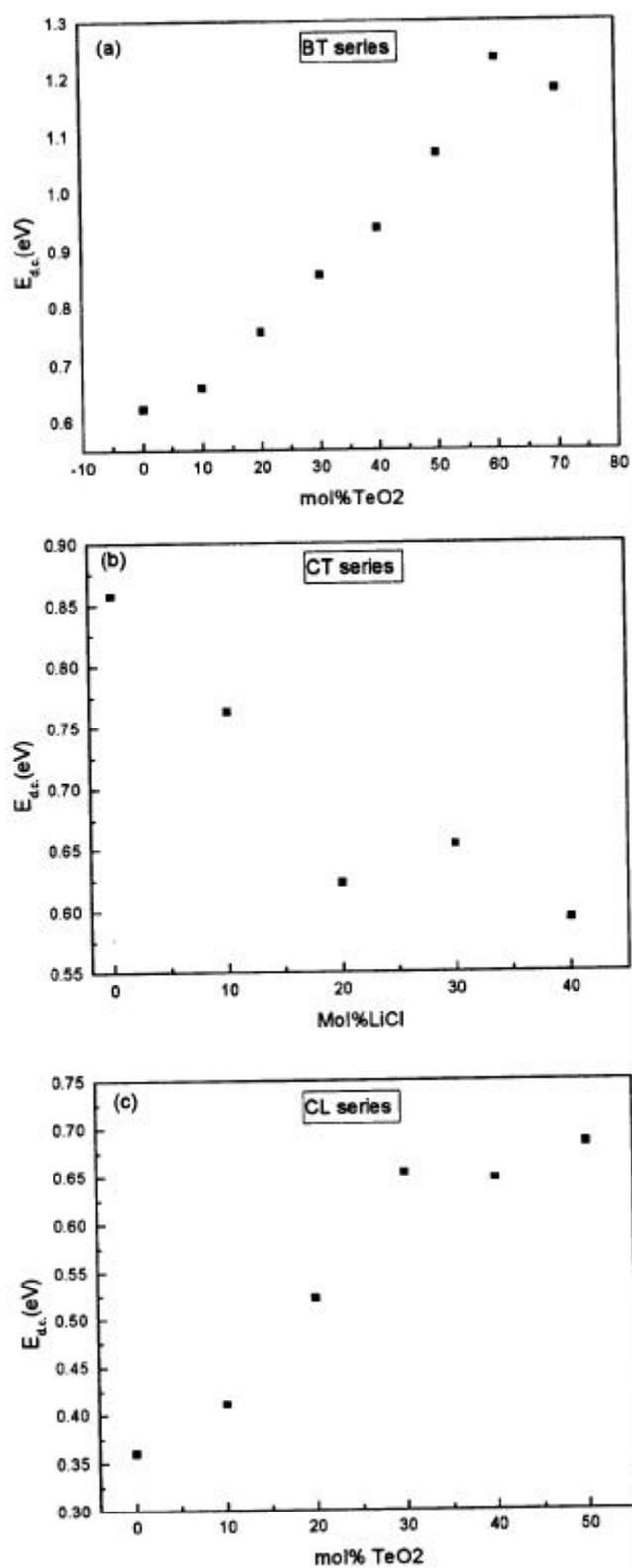
**Figure 1.** Typical impedance plots with increasing temperature for the glass sample BT1.

CT series, concentration of  $\text{TeO}_2$  is held constant, and there is an effective substitution of borate  $\text{BO}_2^-$  by  $\text{Cl}^-$ , we would expect the network to be broken down and reorganized by the substitution. The  $\text{TeO}_2$  part of the network may survive. The substitution, however, leads to significant decrease of  $E_{d.c.}$ , but the corresponding increase in  $s_{d.c.}$  is just under one order of magnitude in spite of the large decrease in  $E_{d.c.}$  This is contrary to expectation. We may also note that the variation in molar volumes in this series is very little (table 1). Therefore, the influence of  $\text{TeO}_2$  on  $E_{d.c.}$  is inferred from the behaviour of transport in BT and CL series and the influence of  $\text{B}_2\text{O}_3$  from the behaviour of transport in CT series. Together, they point towards the dominant role played by glass former network on conductivity.

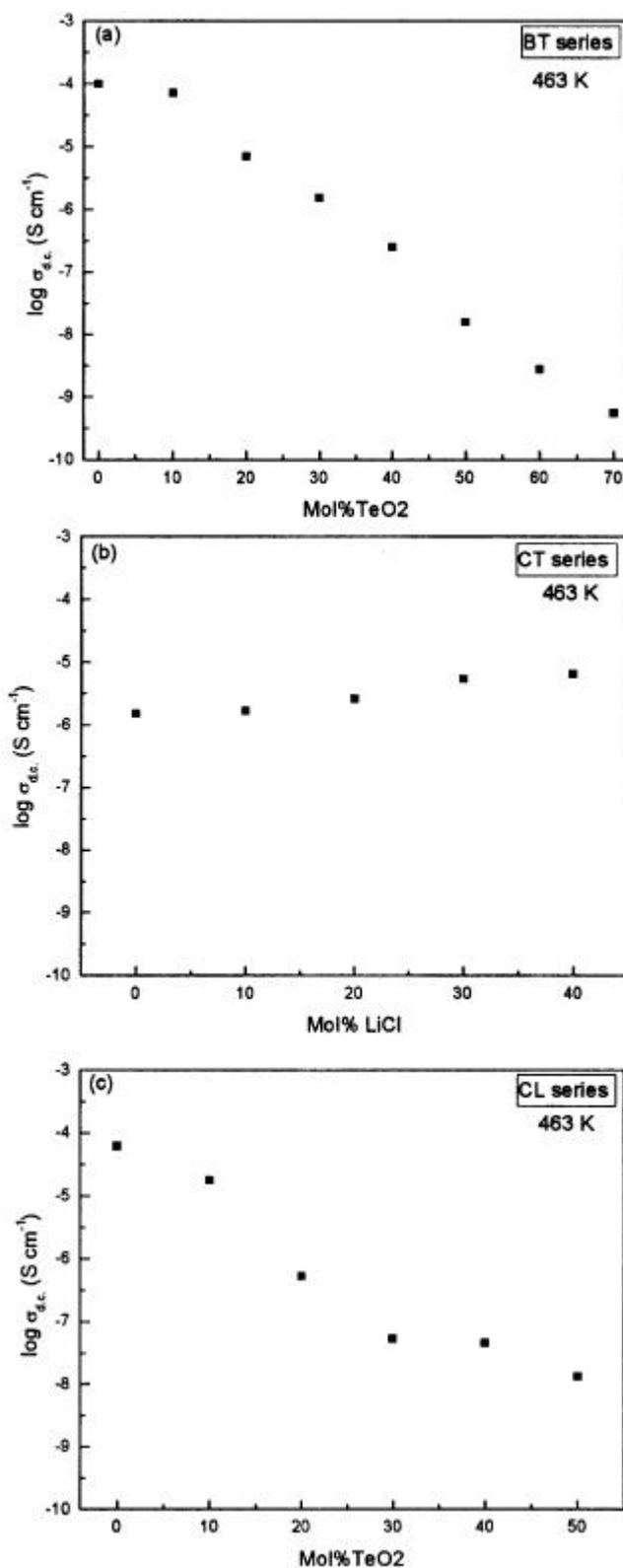
In order to examine the influence of LiCl itself on the observed conductivity,  $\log s_{d.c.}$  has been re-plotted as a function of mole%  $\text{TeO}_2$  for glasses of both BT and CL series, by ignoring the presence of LiCl and treating the glasses of CL series as binaries,  $\text{LiBO}_2\text{-TeO}_2$  (figure 5(a)). For example,  $30\text{LiCl}\cdot30\text{LiBO}_2\cdot40\text{TeO}_2$  is treated as  $30\text{LiBO}_2\cdot40\text{TeO}_2$  or simply as  $42.8\text{LiBO}_2\cdot57.2\text{TeO}_2$  glass. The corresponding variation of  $E_{d.c.}$  are re-plotted in figure 5(b). It appears that the conductivities in the two series are surprisingly very close which suggests that  $s_{d.c.}$  is determined by the network formers,  $\text{B}_2\text{O}_3$  and  $\text{TeO}_2$ , rather than LiCl. But the activation barriers are themselves much lower in LiCl containing glasses. This is possible only if the effective concentration of  $\text{Li}^+$  ions participating in transport is much lower in LiCl containing glasses. Similar observations, which indicate the participation of only a part of the cations from added salts in the transport, has been made in lithium and silver tellurite glasses (Tanaka *et al* 1988; Rossignol *et al* 1993; Pan and Ghosh 1999). This strongly supports the view that LiCl



**Figure 2.** Arrhenius plots of d.c. conductivity of BT series of glasses.



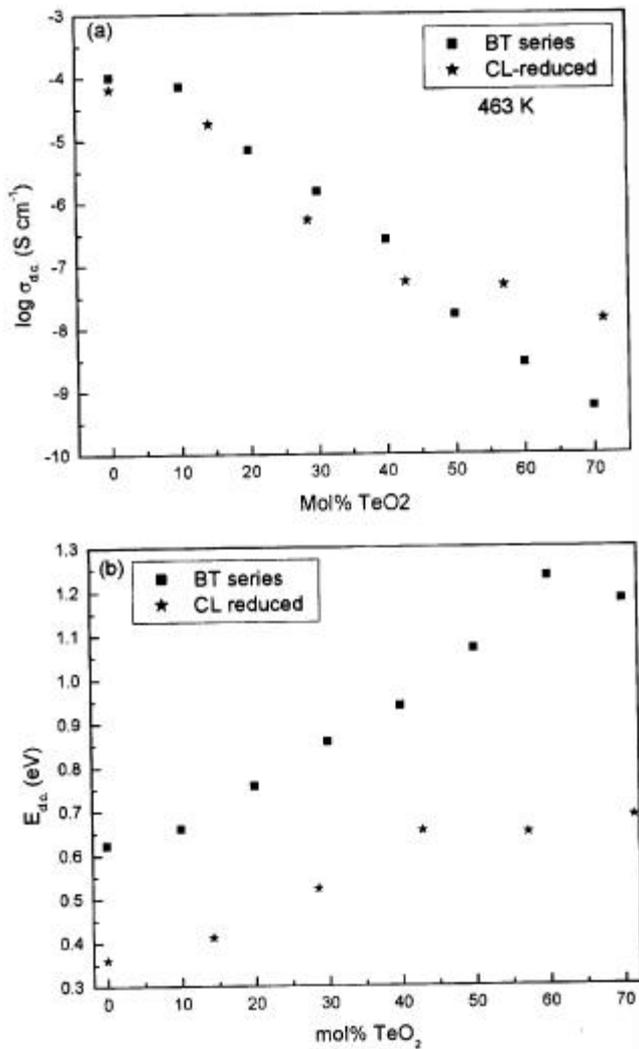
**Figure 3.** Variation of d.c. activation energies ( $E_{d.c.}$ ) with composition for (a) BT series, (b) CT series and (c) CL series of glasses.



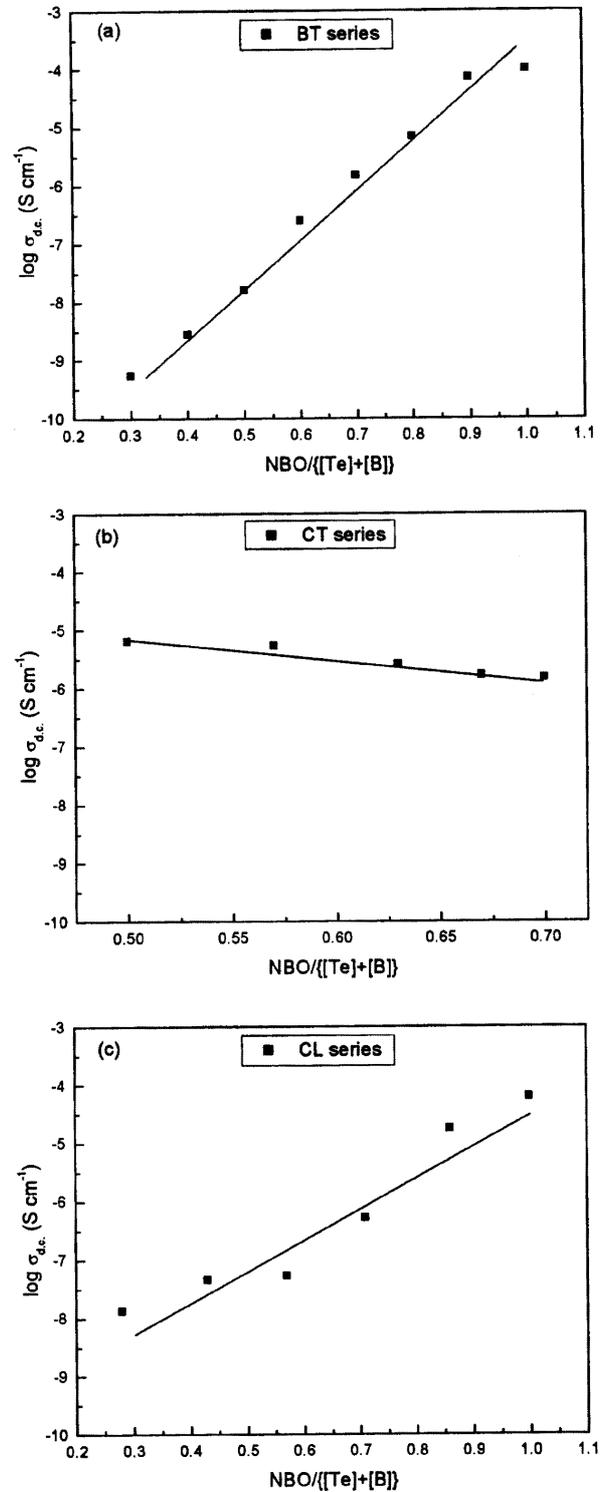
**Figure 4.** Variation of log of conductivity (at 463 K) for (a) BT series, (b) CT series and (c) CL series of glasses.

tends to cluster and hence do not participate in conductivity, although by virtue of expanding the network volume of the glass,  $E_{d.c.}$  is lowered. This is also supported by the molar volume behaviour itself. The observed molar volume of LiBO<sub>2</sub> (BT0, table 1) is 22.17 cc. The molar volume of hypothetical LiCl glass obtained from extrapolation is 26.00 cc. The calculated molar volume, for example, of CL7 glass should be  $0.3 \times 26.00 + 0.7 \times 21.17 = 22.62$  cc, which is in close agreement with the observed 22.32 cc. This represents near-ideal mixing. Therefore, LiCl itself simply acts as a plasticizer opening up the network and Li<sup>+</sup> ion transport is likely to be confined to the regions of the network formers in the glass. The volume fraction of LiCl in the glasses is also nearly 30% and therefore, the quantity of LiCl clusters as envisaged to be present in the CL series of glasses are already well above the percolation limit. The fact that inter-substitution of

LiBO<sub>2</sub> by TeO<sub>2</sub> still affects conductivities very drastically in CL series of glasses indicates that clusters, in spite of percolation, do not contribute significantly to the conductivity. Formation of such clusters and domains has



**Figure 5.** (a) Variation of log of conductivity (at 463 K) of BT series and CL-reduced (reduced to binary B<sub>2</sub>O<sub>3</sub>-TeO<sub>2</sub>) series of glasses and (b) variation of corresponding activation barriers.



**Figure 6.** Variation of log of conductivity (at 463 K) with NBO/([Te]+[B]) for (a) BT series, (b) CT series and (c) CL series of glasses (line is drawn as a guide to the eye).

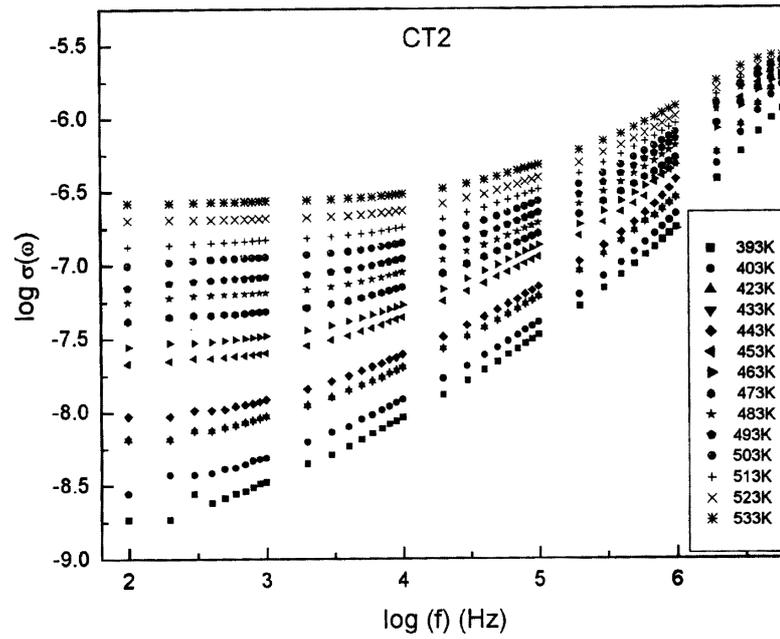


Figure 7. Variation of log of conductivity with frequency at various temperatures for CT2 glass.

been observed in LiX (X = F,Cl) substituted Li<sub>2</sub>O·TeO<sub>2</sub> glasses and also in AgI substituted Ag<sub>2</sub>O·TeO<sub>2</sub> glasses (Reau *et al* 1992, 1995; El-Damrawi and Abd-El-Maksoud 2000).

The general conductivity behaviour of BT and CL series of glasses may also be considered as implying a (direct) correlation between log  $s_{d.c.}$  and NBOs (LiBO<sub>2</sub> can be written as 0.5Li<sub>2</sub>O·0.5B<sub>2</sub>O<sub>3</sub> and NBO concentration is twice the Li<sub>2</sub>O concentration or is simply equal to LiBO<sub>2</sub> concentration itself. It may be assumed that B<sub>4</sub><sup>-</sup> → B<sub>2</sub><sup>-</sup> conversion is structurally facile and therefore, B<sub>4</sub><sup>-</sup> is also effectively NBO bearing group. But there is a slight increase in conductivity in the CL series inspite of the decrease in NBO concentration. If we recall that LiCl addition favours formation of T<sub>2</sub><sup>0</sup> units in place of T<sub>4</sub><sup>0</sup> units along with the corner-sharing B<sub>4</sub><sup>-</sup> units (readily convertible to B<sub>2</sub><sup>-</sup>), the resulting structure could provide a facile Li<sup>+</sup> transportation path (effective increase of mobility). Therefore, it compensates for the decrease in conductivity to be expected from decrease in NBO concentration. Conductivity variation as a function of the ratio of NBO to the sum of [Te] and [B] is shown in figure 6 for the three series of glasses. Although it would have been more appropriate to plot log  $s$  as a function of [NBO]/[BO], quantification of BO is difficult since the actual concentration of the structural species, B<sub>4</sub><sup>-</sup>, B<sub>3</sub><sup>0</sup>, B<sub>2</sub><sup>-</sup>, T<sub>4</sub><sup>0</sup>, T<sub>3</sub><sup>0</sup>, T<sub>2</sub><sup>0</sup> and T<sub>1</sub><sup>-</sup> has not been determined. There is the expected direct and almost linear correlation between log  $s$  and NBO/{[Te] + [B]} in BT and CL series although in CT series this fails due to the reason given earlier. Therefore, NBO concentration appears to be a more critical determinant of conductivity than the concentration of Li<sup>+</sup>.

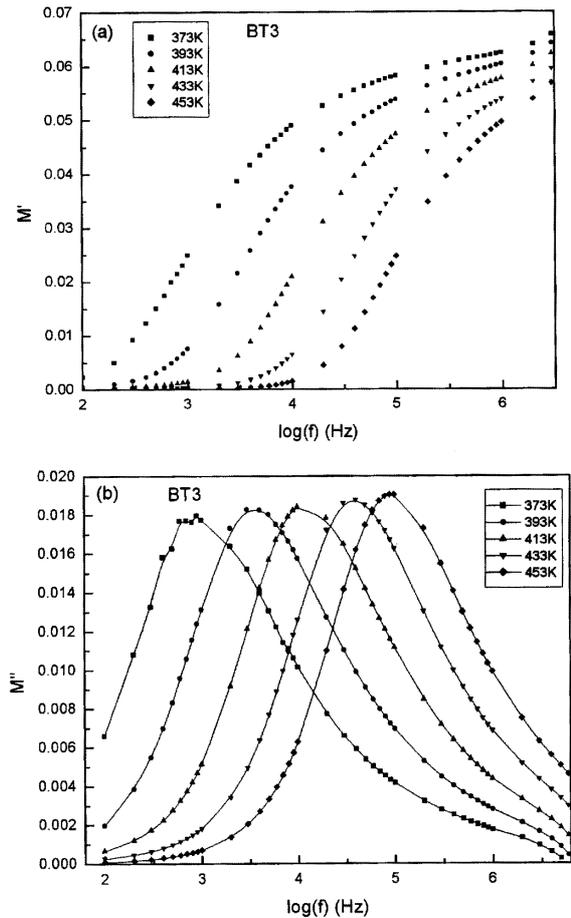


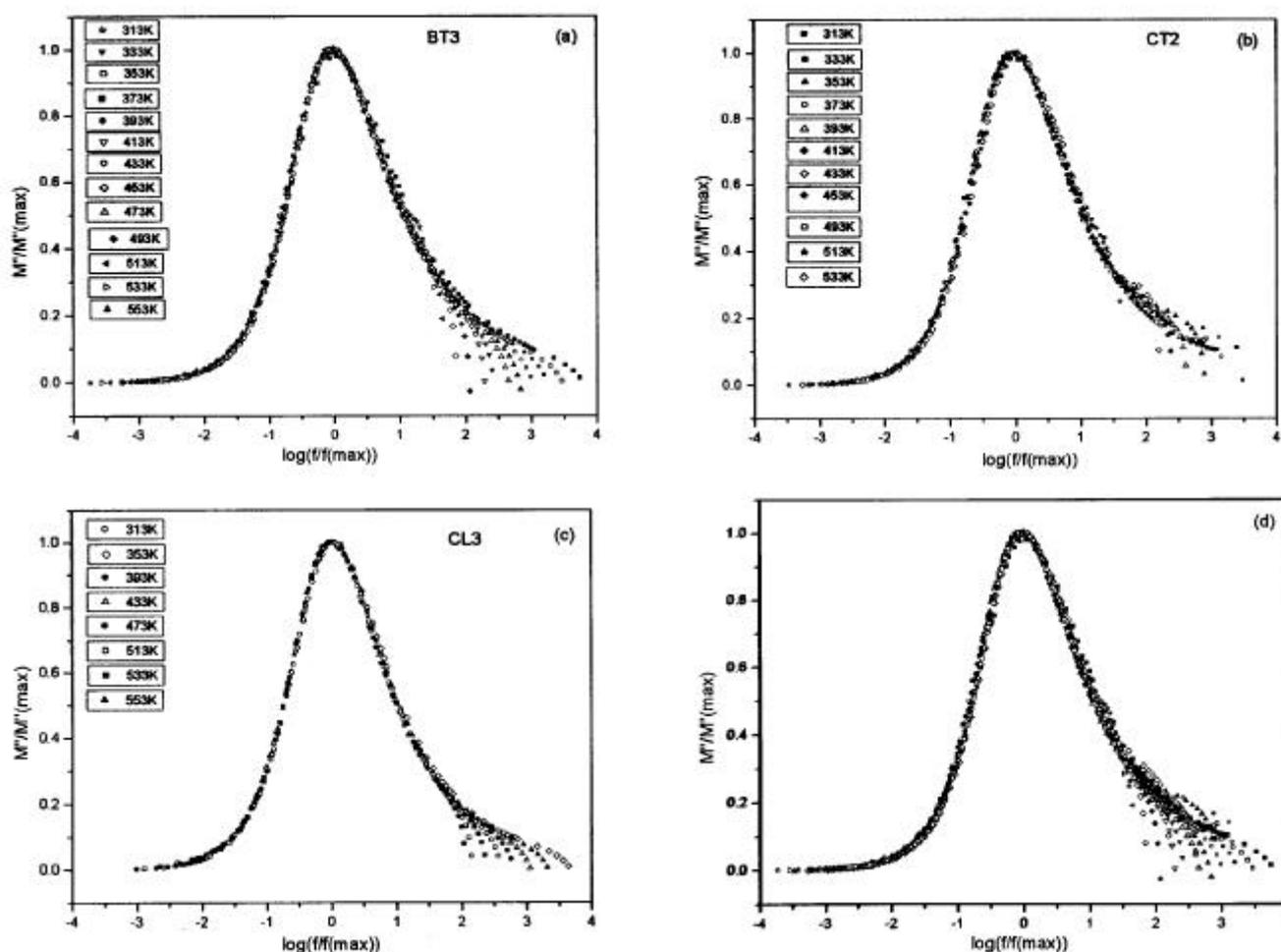
Figure 8. Variation of the (a) real ( $M'$ ) and (b) imaginary ( $M''$ ) parts of the dielectric modulus with frequency for BT3 glass at different temperatures.

In the complex equilibria of structural species in these glasses, we may note the following important feature.  $B_4^- \rightarrow B_2^-$  and  $T_4^0 \rightarrow T_2^0$  conversions reduce the number of BOs to half the value in a single step. In the glass structure, therefore, such BO reduction can be accommodated locally by either  $(B_4^- + B_4^-) \rightarrow (B_2^- + B_2^-)$  and  $(T_4^0 + T_4^0) \rightarrow (T_2^0 + T_2^0)$  reactions or a coupled  $(B_4^- + T_4^0) \rightarrow (B_2^- + T_2^0)$  reaction. When such changes are induced in the structure, locally the dimensionality of the glass itself changes from 3 to 1 (Rao and Harish Bhat 2001). The concentrations of the individual oxides in the glass composition undoubtedly determine the course of the above conversions. This is the reason why it is difficult to determine NBO/BO ratio. When the structure has an extended chain-like feature built from  $B_2^-$  and  $T_2^0$ , NBO/BO ratio reaches a maximum for a given concentration of modifier oxide. Figure 6 implies that the highest conductivity should be expected when this ratio is very high.

Conductivity behaviour in a.c. measurements are quite typical and is shown in figure 7 for the case of CT2 glass for various temperatures. The data were fitted to power

law expression with a single exponent,  $s(\omega) = s(0) + A\omega^s$ , using a regression fitting procedure. Values of  $s$  were determined for a number of temperatures for all the glasses.  $s(0)$  obtained from plots of this kind were compared with  $s_{d.c.}$  calculated from  $Z'$  values. For example, in the case of CL2 glass, at 493 K,  $s(0) = 3.8 \times 10^{-8} \text{ Scm}^{-1}$  and  $s_{d.c.} = 4.0 \times 10^{-8} \text{ Scm}^{-1}$ . The two values are in very good agreement in all cases.

In the complementary analyses of a.c. response, dielectric constant and loss measurements were made using standard expressions.  $e'(\omega)$  and  $e''(\omega)$  were converted into dielectric moduli,  $M'(\omega)$  and  $M''(\omega)$ . Variation of  $M'(\omega)$  and  $M''(\omega)$  for the case of BT3 glass is shown in figures 8(a) and (b) which is quite typical of the glasses investigated in this study. It is evident that  $M''$  values exhibit characteristically asymmetric peaks. The full-width-at-half maximum (FWHM) values of the  $M''$  peaks were used to evaluate  $b$  values (FWHM =  $1.14 \times b$  decades), where  $b$  is the exponent in the stretched exponential relaxation function,  $f = f(0) \exp\{-(t/\tau)^b\}$ , which is known to provide satisfactory fits for the asymmetrical  $M''$  peaks ( $t$  is the



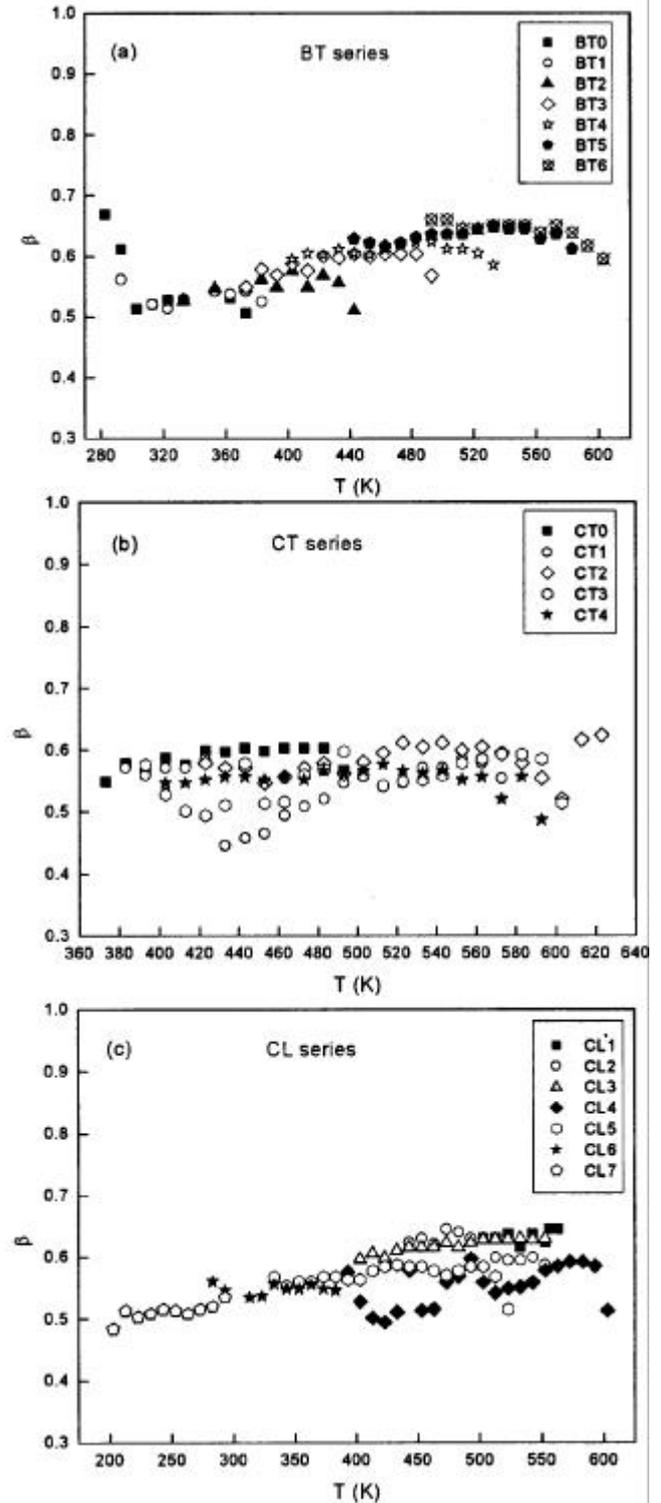
**Figure 9.** Normalized plot of  $M''$  against normalized frequency ( $f(\max)$ ) for (a) BT3, (b) CT2, (c) CL3 and (d) all the glasses at various temperatures.

characteristic relaxation time). The well-known very high frequency departures in the fits to stretched exponential function, however, have not been examined in this work.  $M''/M''(\max)$  were plotted against  $\log(f/f(\max))$  where  $M''(\max)$  and  $f(\max)$  refer to the peaks in figure 8(b). In figures 9(a), (b) and (c), these reduced plots measured at various temperatures are shown again for the three randomly chosen glasses, one each from BT, CL and CT series. Except at very high frequencies, the collapse of the data appears to be excellent suggesting that the transport mechanism is unaffected by the temperature and independent of the variations in compositions. In fact, all such  $M''/M''(\max)$  plots (as a function of reduced frequency) have been seen to collapse (figure 9(d)) very satisfactorily indicating that the mechanism of charge transport is independent of both temperature and composition. We may note that this is important because if charge transport were to be primarily due to  $\text{Li}^+$  ions, then there should be two different  $\text{Li}^+$  responses in a.c. measurements. One, due to  $\text{Li}^+$  ions held in NBO environment and the other due to  $\text{Li}^+$  ions in LiCl clusters. This is because there should be differences in the mechanisms of transport. Arguably,  $\text{Li}^+$  ions in clusters may make use of vacancies and interstitials in a manner somewhat similar to the nature of transport in crystalline LiCl, whereas  $\text{Li}^+$  ions associated with NBO environments in the region of glass formers may hop from one site to another of similar energy and environment. We are, therefore, led to infer that either only one particular type of  $\text{Li}^+$  ions contribute to a.c. conductivity, which is primarily polarization current or the basic mechanism of conductivity itself is different, unique, and involves  $\text{Li}^+$  ion transport only as a secondary event. We will discuss this aspect later.

The values of  $b$  and  $s$  determined for all the glasses at various temperatures are presented together in figures 10 and 11, respectively for the three series of glasses. Both  $s$  and  $b$  values exhibit dispersion. The spread in  $s$  values is somewhat greater than in  $b$  values. Several compositions in CL and BT series of glasses exhibit very high values of  $s$ . In some of the glasses such as CL1, CT4 and BT2 it is possible to discern manifestation of  $s_{\text{minimum}}$  as a function of temperature. However, this aspect is not discussed in this paper. The spread in  $b$  values is much smaller in comparison and values of  $b$  are generally close to 0.6, particularly at higher temperatures.  $b$  and  $s$  do not bear out the relation  $b = 1 - s$ . However, neither  $s$  nor  $b$  indicate features which can be associated with the two different  $\text{Li}^+$  ion populations implied in the d.c. conductivities as discussed above.

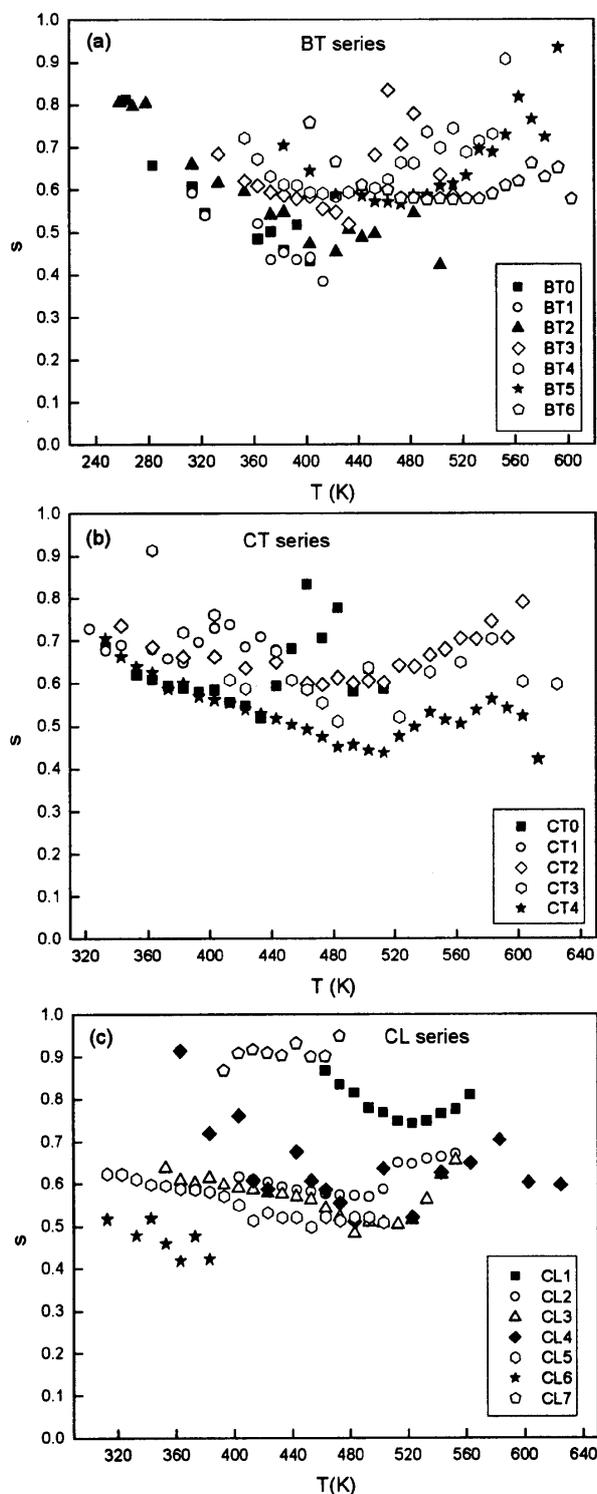
The a.c. response is generally assumed to arise from local hopping of  $\text{Li}^+$  ions between equivalent positions around an NBO (Elliott 1983; Rao 2002). NBO itself is assumed to be fixed in position on the time scales of ion hops. We may, therefore, expect that  $\text{Li}^+$  ions in LiCl clusters and also those  $\text{Li}^+$  ions moving along the contours of the network bound NBOs, contribute to a.c. res-

ponse. Their responses in principle cannot be identical. In such a situation a clear indication of this is expected to be revealed in the behaviour of  $s$  and  $b$ . Absence of two  $s$



**Figure 10.** Variation of stretched exponent  $b$  with temperature for (a) BT series, (b) CT series and (c) CL series of glasses.

values or two  $b$  values or any such features suggest that the primacy of Li<sup>+</sup> ion jumps invoked in conductivity mechanism may not represent the correct situation. In this context, we may note that in all network forming



**Figure 11.** Variation of power law exponent,  $s$ , with temperature for (a) BT series, (b) CT series and (c) CL series of glasses.

oxide glasses, the NBOs and BOs do switch positions—NBOs are therefore mobile (Karthikeyan *et al* 1999). If the timescales of NBO  $\leftrightarrow$  BO switching and Li<sup>+</sup> ion jumps are similar we cannot tell whether NBOs switch following Li<sup>+</sup> ion jumps or *vice versa*. Indeed, if NBO  $\leftrightarrow$  BO switching is the primary event and Li<sup>+</sup> ion jump is an event that follows, the ion dynamics is dictated by NBO  $\leftrightarrow$  BO switching. If so, NBO  $\leftrightarrow$  BO switching provides a rationalization of the observed absence of any signature of two Li<sup>+</sup> ion populations. Because the a.c. response is controlled by NBO  $\leftrightarrow$  BO switching, the NBO population is of only one type which migrates over both the glass former networks during transport. This aspect needs to be examined further and is currently being investigated in other systems which are designed to reveal the role of NBO  $\leftrightarrow$  BO switching.

#### 4. Conclusions

The conductivity behaviour of LiCl-LiBO<sub>2</sub>-TeO<sub>2</sub> glasses has been examined. It is found that the d.c. conductivities are well correlated to NBO concentration. LiCl appears to form clusters so that they do not contribute to conductivity although the effective barriers decrease. More importantly, a.c. conductivity studies reveal a single unchanging mechanism of charge transport which is inconsistent with the presence of two different populations of Li<sup>+</sup> ions. The possibility that NBO  $\leftrightarrow$  BO switching may be the first transport step whereas Li<sup>+</sup> ion movements are secondary steps is suggested.

#### References

- Akagi R, Handa K, Ohtori N, Hannon A C, Tatsumisago M and Umesaki N 1999 *J. Non-cryst. Sol.* **256** & **257** 111
- Arnaudov M and Dimitriev Y 2001 *Phys. Chem. Glasses* **42** 99
- Blanchandin S, Marchet P, Thomas P, Champarnaud-Mesjard J C, Frit B and Chagraoui A 1999 *J. Mater. Sci.* **34** 4285
- Burger H, Kneipp K, Hobert H, Vogel W, Kozhukharov V and Neov S 1992 *J. Non-cryst. Sol.* **151** 134
- Chowdari B V R and Pramoda Kumari P 1998 *Solid State Ionics* **113–115** 665
- El-Damrawi G and Abd-El-Maksoud S 2000 *Phys. Chem. Glasses* **41** 6
- Elliott S R 1983 *Physics of amorphous materials* (London: Longman)
- Hampton R N, Hong W, Saunders G A and El-Mallawany R A 1987 *J. Non-cryst. Sol.* **94** 307
- Iwodate Y, Kenmotsu H, Hattori T, Nishiyama S, Fukushima K, Umesaki N, Nakazawa T and Noda K 2000 *J. Alloys and Compounds* **305** 130
- Jayasinghe G D L K, Coppo D, Bandaranayake P W S K and Souquet J L 1995 *Solid State Ionics* **76** 297
- Karthikeyan A, Vinatier P, Levasseur A and Rao K J 1999 *J. Phys. Chem.* **103** 6185
- Kim S H, Yoko T and Sakka S 1993 *J. Am. Ceram. Soc.* **76** 865
- Komatsu T and Mohri H 1999 *Phys. Chem. Glasses* **40** 257
- Mori H, Igarashi J and Sakata J 1995 *Glasstech. Ber.* **68** 327

- Nasu H, Matsushita O, Kamiya K, Kobayashi H and Kubodera K 1990 *J. Non-cryst. Sol.* **124** 275
- Pan A and Ghosh A 1999 *Phys. Rev.* **B60** 3224
- Rao K J 2002 *Structural chemistry of glasses* (London: Elsevier)
- Rao K J and Harish Bhat M 2001 *Phys. Chem. Glasses* **42** 255
- Reau J M, Tanguy B, Portier J, Rojo J M, Sanz J and Herrero M P 1992 *J. Phys.* **2** C2-165
- Reau J M, Rossignol S, Tanguy B, Paris M A, Rojo J M and Sanz J 1995 *Solid State Ionics* **80** 283
- Rodrigues A C M and Duclot M J 1988 *Solid State Ionics* **28-30** 729
- Rossignol S, Reau J M, Tanguy B, Videau J J and Portier J 1993 *J. Non-cryst. Sol.* **155** 77
- Sabry A I and El-Samanoudy M M 1995 *J. Mater. Sci.* **30** 3930
- Sunandana C S 1996 *Bull. Mater. Sci.* **19** 1105
- Tanabe S, Hirao K and Soga N 1990 *J. Non-cryst. Sol.* **122** 79
- Tanaka K, Yoko T, Yamada H and Kamiya K 1988 *J. Non-cryst. Sol.* **103** 250
- Tanaka K, Yoko T, Kamiya K, Yamada H and Sakka S 1991 *J. Non-cryst. Sol.* **135** 211
- Wang J S, Vogel E M and Snitzer E 1994 *Opt. Mater.* **3** 187