Glasses in the system lithium chloride–lithium borate–tellurium dioxide have been prepared by the melt quenching route and characterised for their densities, glass transition temperatures and heat capacities. Their structures have been investigated using infrared, Raman and magic angle spinning nuclear magnetic resonance spectroscopies. While the structure consists of trigonal and tetrahedral borate groups, the tetrahedral boron in these glasses reaches much higher concentrations than in binary borate glasses. Tellurite species are present in both trigonal bipyramidal and trigonal pyramidal structures. The actual concentrations of the two borate and two tellurite species are interdependent. Their concentrations are also influenced by LiCl in the glass. The nature of speciation and chemical origin of the equilibration of the various species is examined using a structural model. The model has been used to rationalise the variation of the different properties in the glass system.

In this paper we report investigations on borotellurite glasses modified by Li2O in such a way that it formally corresponds to a pseudo-binary system consisting of LiBO2 and TeO2. We also report studies on pseudo-ternary, LiCl–LiBO2–TeO2 glasses. These glasses, which form relatively easily from melt quenching, are rather interesting from a structural point of view, because the components of this glass, namely alkali tellurites and alkali borates themselves, exhibit unique structural features associated with borate and tellurite units. The pseudo binary LiBO2–TeO2 glasses should therefore be expected to exhibit rich and complex equilibria between structural species.

Tellurite glasses have been studied fairly extensively because of their potential application as laser hosts and as nonlinear optical materials. TeO2 by itself is traditionally considered as a conditional glass former and it forms glasses in combination with a variety of other oxide materials such as B2O3, V2O5, WO3, PbO, ZnO, Ag2O and alkalis. The Te–O bond is more covalent than the Si–O bond on the basis of Pauling electronegativity differences.

In TeO2 Te is quadrivalent and therefore has a lone pair of electrons in the valence shell. This lone pair is generally considered to be present in one of the sp3d hybridised orbitals. In crystalline α-TeO2, Te is four coordinated to oxygen atoms forming a structural unit, [TeO4]6-. [TeO4]6- is a trigonal bipyramid (tbp) as shown schematically in Figure 1(a). In several tellurites, Te is also present in a trigonal pyramid (tp) structure (Figure 1 (b)) and is coordinated to just three oxygens, one of which is necessarily double bonded to Te. It is again required that the lone pair in Te be accommodated in a suitably hybridised orbital. Therefore, one would expect tellurite glasses to be capable of forming extensive 3-dimensional network based on [TeO4]6- units. However, uncharged trigonal pyramidal [TeO2]6- units would lead to glass structure based on polymeric chains.

Several structural studies using x-ray diffraction, extended x-ray absorption fine structure (EXAFS), x-ray photoelectron spectroscopy (XPS), Raman and infrared spectroscopies have all revealed the presence of both tbp and tp units in tellurite glass structures. However, EXAFS investigation, which addresses the local structure more directly seems to indicate the presence of only four coordinated (tbp) tellurite units in glasses. Another interesting aspect of the structure of tellurite glasses is that the addition of modifier oxides seem to favour the formation of tp units at the expense of tbp units.

Borate glasses also exhibit well-known and unique structural features particularly in binary alkali borate glasses. The glass structures consist of three coordinated trigonal (B3) and four coordinated tetrahedral...
(B₄) boron atoms. Tetrahedral borons are products of modification by the alkali. Combination of tetrahedral and trigonal borons gives rise to several unique borate species in glass such as modified boroxol, di-, tri-, tetra- and pentaborates. The trigonal to tetrahedral conversion, and formation of oxygen bridges by the oxide ion from the modifier reaches a maximum at the diborate composition (Li₂O/B₂O₃=0.5). The ratio \(N_{\text{tp}}/N_{\text{tbp}}\) is around 0.5 for this composition. When the modifier concentration is increased further (Li₂O/B₂O₃>0.5), the percentage of tetrahedral boron decreases indicating a structural instability of tetrahedra in the presence of higher modifier oxide concentrations. The notable feature is that there is no nonbridging oxygen (NBO) in the coordination of tetrahedral boron. The present glass system contains LiBO₂ where the Li₂O/B₂O₃ ratio is unity. The percentage of tetrahedral boron for this composition of Li₂O–B₂O₃ is expected to be much lower from a number of literature reports. In the ternary Li₂O–B₂O₃–TeO₂ glass in which TeO₂ is present, this value can be higher only if the modifier Li₂O is partially taken up by TeO₂, thereby pushing the Li₂O/B₂O₃ ratio to lower values (towards diborate) because tetrahedral borons can once again move up towards its value in diborate glass. It has been noted that binary B₂O₃–TeO₂ glass itself possesses a significant percentage of tetrahedral borons in the structure. It leads to speculation that TeO₂ itself may act as a modifier. There is an increase in \(t_p\) tellurium units also which is surprising because concentration of \(t_p\) generally goes up as a result of adding a modifier to TeO₂.

In view of the above structural aspects of TeO₂ and LiBO₂ glasses, we consider that an investigation of pseudo-binary LiBO₂–TeO₂ system of glasses would be very interesting. We have also examined the influence of the addition of LiCl to this system because we expect LiCl to open up the glass structure and stretch out the network forming elements, without itself chemically interfering with the network. This may reveal the influence of the ionicity of the environment on \(t_p\)-\(t_{bp}\) equilibrium of tellurium units. The behaviour of LiCl as a plasticiser in these glasses has been investigated elsewhere. The addition of LiCl introduces weaker, non-bonded and noncoulombic interactions into the \(>B–O–Te<\) network which is unimportant for our considerations here.

In this paper, we have studied 19 different compositions of glasses whose molar volumes, glass transition temperatures, heat capacities, infrared, Raman and ¹¹B HRMAS NMR spectra have been examined. In the following sections we present and discuss our experimental measurements and propose a structural model of borotellurite glasses, consisting of two network competitors for modifier oxygen, and show that it is consistent with the experimental observations.

### Experimental

Glasses were obtained using high purity commercial powders of TeO₂, LiCl and LiBO₂·2H₂O. Mixtures of these materials in appropriate proportions, Table 1, were taken in porcelain crucibles and slowly heated from 535 to 823 K (to remove water from LiBO₂·2H₂O) for 2 h. The resulting mixture was melted at 1223 K for 30 min and the melt was quenched between polished stainless steel plates. The amorphous nature of the samples was confirmed using x-ray diffraction (JEOL JOX–8P x-ray diffractometer). The densities of the glass pieces, free of air bubbles and cracks (visual examination), were determined through the apparent weight loss method in xylene. The molar volumes were calculated using the relation \(V_M=\frac{W_g}{\text{density}}\) where \(W_M\) are the corresponding formula weights. The glass transition temperatures (\(T_g\)) were determined using a differential scanning calorimeter (Perkin-Elmer DSC-2) employing dry nitrogen as purge gas.

The Fourier transform infrared (FTIR) spectra of the glasses were recorded on a Nicolet 740 FTIR spectrometer. The FTIR transmission spectra were recorded from 4000 to 400 cm⁻¹ using KBr pellets containing 2–5 mg of sample. Raman spectra were recorded on a Spex 1403 Raman spectrometer using 514.5 nm radiation from an Argon ion laser (Spectra-Physics Series 2000). The spectra were recorded in the current mode (40 amps) in reflection geometry at 90° incidence using a photo-multiplier tube. All spectra were recorded at room temperature (293 K) on large glass pieces. ¹¹B high resolution (HR) magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded on a Bruker MSL-300 solid state high resolution spectrometer operating at 90.4 MHz (magnetic field 7.05 T) using a DOTY probe. 90° pulses of 5 μs were employed with a delay time of 10 s between pulses in all the experiments. A spinning speed of 3–7 kHz was employed. All spectra were recorded at room temperature using freshly powdered samples.

### Results and discussion

**Molar volumes, glass transition temperatures and heat capacities**

The nominal compositions, densities, molar volumes and glass transition temperatures of the three series, BT, CT and CL, of glasses are given in Table 1.
variation of molar volumes and glass transition temperatures are shown in Figures 2(a) and (b), respectively, for BT glasses as a function of TeO$_2$ concentration. Similar plots of variations of molar volumes and glass transition temperatures for the CT series (as a function of LiBO$_2$) and CL series (as a function of TeO$_2$) are shown in Figures 3(a) and (b) and 4(a) and (b) respectively. Variation of molar volume in Figure 2(a) indicates that addition of TeO$_2$ tends to increase the volume to about 50 mol% beyond which $V_M$ decreases. The occurrence of the maximum is an indication of structural rearrangements in which the 50 mol% composition is likely to have the most open structure. The molar volume of pure LiBO$_2$ glass (21.17 cm$^3$mol$^{-1}$) is in fair agreement with earlier values (21.57 cm$^3$mol$^{-1}$) where the glass was prepared using Li$_2$CO$_3$ and H$_3$BO$_3$ as starting materials. Extrapolation gives the volume of pure TeO$_2$ glass as 25.85 cm$^3$mol$^{-1}$. The glass transition temperature generally decreases with increasing TeO$_2$ concentration. The decrease is somewhat rapid in the region of 20–50 mol% TeO$_2$.

In the CT series of glasses the molar volumes do not vary much for the substitution of LiBO$_2$ by LiCl, the entire variation being under 1.5 cm$^3$mol$^{-1}$ over the whole composition range. However, a shallow minimum and a shallow maximum occur for the (40:30) and (60:10) combinations of (LiBO$_2$:LiCl), respectively. Substitution of LiCl by LiBO$_2$ leads to an essentially monotonic and almost sigmoidal increase in the glass transition temperatures. In the CL series, however, the variation of both $V_M$ and $T_g$, Figures 4(a) and (b), are rather complex. Up to 30 mol% substitution by TeO$_2$, the molar volume shows an increasing trend. A similar increase is noted in the molar volume above 50 mol% TeO$_2$. But in the region between 30 and 50 mol% TeO$_2$ the molar volume variation exhibits an anomalous decrease. The glass transition temperatures also exhibit remarkable behaviour. While up to 20 mol% substitution of LiBO$_2$ by TeO$_2$ leads to an increase in $T_g$, there is a sudden decrease in $T_g$ around 30 mol% TeO$_2$. $T_g$ again exhibits a slight increase until all the LiBO$_2$ is substituted by TeO$_2$. The $T_g$ behaviour of the 30 mol% TeO$_2$ glass exhibited a large scatter in $T_g$ and was found to be not very reproducible.

The somewhat smooth change in $V_M$ and $T_g$ observed in the BT series is disrupted by the presence of LiCl in the CL series. Therefore, LiCl plays a nontrivial role (not just addition of its own volume) in $V_M$ and $T_g$ variations. This is even more clearly demonstrated in the insets of the Figures 4(a) and (b) where we have plotted the variations of $V_M$ and $T_g$ as functions of TeO$_2$ for only the LiBO$_2$–TeO$_2$ glass portion in them. This is done by first subtracting a constant volume of 7.8 cm$^3$ for 0.3 mol LiCl (it is assumed that molar volume of hypothetical LiCl glass at 298 K = volume of LiCl melt (900–1050 K) at two-thirds its melting point (589 K)) from all the $V_M$ values and by disregarding LiCl in the composition representation. For example the CL2 glass, i.e.
30LiCl.20LiBO\textsubscript{2}.50TeO\textsubscript{2} is represented as 20:50 (20/0·7):(50/0·7)\textsubscript{28·57LiBO\textsubscript{2}:71·43TeO\textsubscript{2}). On comparing the variation of \(V_M\) in the inset with the same in Figure 2(a), the fact that LiCl influences \(V_M\) is quite evident.

Heat capacity plots for the three different series of glasses are shown in Figures 5(a), (b) and (c). Compositions like BT0, BT3, BT6 and CL6 exhibit pre-transition endotherms which we attribute to insufficient annealing. However, the \(\Delta C_p\) values have been calculated by extrapolation from lower temperatures in the plot. The CL6 glass exhibits a rather large spread of glass transition temperature, while other glasses in the same series exhibit fairly sharp rise in heat capacities in the transition region. Tellurite rich glasses in the BT series do not exhibit the characteristic humps and also their heat capacities continue to rise in the post glass transition region suggesting continuing degradation of the covalently bonded tellurite network even above \(T_g\).

**IR spectra**

Infrared spectra of the three series of glasses are shown in Figures 6(a), (b) and (c), respectively, for the BT, CT and CL series. The BT0 spectra bears the signature of
tetrahedral and trigonal borons in the region of 1000 and 1400 cm\(^{-1}\), respectively. The B–O–B bending mode in the region of 700 cm\(^{-1}\) is also seen in the BT0. In the BT7, where the spectra is dominated by TeO\(_2\), one observes a rather intense peak at ~700 cm\(^{-1}\) with a shoulder on the high frequency side but with the characteristic 1000 cm\(^{-1}\) (tetrahedral, B\(_4\)) and 1400 cm\(^{-1}\) (trigonal, B\(_3\)) borate peaks present with a relatively lower intensity. The relative intensities of the B\(_4\) and B\(_3\) peaks decrease in the intermediate compositions in relation to the 700–800 cm\(^{-1}\) peak of tellurite groups, which increases towards BT7. The B–O–B bending vibration, whose contribution to the spectral intensity of the glasses towards BT7 is expected to decrease, is however subsumed in the characteristic tellurite peak. In the tellurite rich glasses, the trigonal boron peak splits into sub-peaks suggesting the presence of different trigonal species.

Infrared spectra of the CT series glasses are roughly similar to those in BT series. As LiBO\(_2\) concentration decreases, the relative intensity in the TeO\(_2\) region becomes prominent. But the spectra of CT3 and CT4 glasses reveal that increased percentages of LiCl affect the spectra in the region of 600–900 cm\(^{-1}\) significantly and the evolution of different tellurite species is suggested by the changes (see later).

In the CL series the spectra of CL0 is simply that of tellurite glass diluted by the largely infrared inactive LiCl. There is a sharp resonance at 635 cm\(^{-1}\) and a shoulder at 770 cm\(^{-1}\). But as more and more LiBO\(_2\) is added and the glass becomes more and more dilute with respect to TeO\(_2\), the TeO\(_2\) region of the spectra (600–800 cm\(^{-1}\)) is marked by evolution of distinct peaks. CL7 spectra reveals that LiCl affects the spectral region corresponding to trigonal borates also. The 1227 cm\(^{-1}\) feature is unique to this glass and we refer to it later.

**Raman spectra**

Raman spectra of the glasses are shown in Figures 7(a), (b) and (c) respectively for the BT, CT and CL series of glasses. The spectrum of BT0 corresponds to that of pure LiBO\(_2\) glass. It consists of four well defined peaks at 1475, 975, 780 and 530 cm\(^{-1}\). The 780 cm\(^{-1}\) peak is the most intense in the spectra and is attributed to the presence of four coordinated, B\(_4\) borons. Substitution of LiBO\(_2\) by TeO\(_2\) results in two notable changes. First, the higher frequency scattering at 1475 and 965 cm\(^{-1}\) and also the one at 530 cm\(^{-1}\) get suppressed. Second, the 780 cm\(^{-1}\) peak intensifies by virtue of additional scattering in the same region from tellurite species. In the spectra of intermediate compositions, from BT3 to BT7 glasses, a shoulder in the low frequency region around 680 cm\(^{-1}\) emerges which

![Figure 6](image-url) Infrared spectra of (a) BT series, (b) CT series and (c) CL series of glasses
eventually dominates so much that the 780 cm\(^{-1}\) scattering appears like a shoulder in the spectra of BT7 glass. A new feature in the 470–490 cm\(^{-1}\) region also becomes dominant in these glasses which correlates with increasing presence of TeO\(_2\).

The Raman spectra of the CT series reflect essentially the same features, except that in the low frequency region for the high LiCl containing CT4 there is a small feature in the 380–400 cm\(^{-1}\) region. This is likely to arise from the rattling (cage vibrational) modes of Li\(^+\) ions in their sites.

Effect of substitution of LiBO\(_2\) by TeO\(_2\) on the absorption peaks in 700–800 cm\(^{-1}\) region is clearly evident in the Raman spectra of CL glasses. While borate rich glasses show a unique sharp peak, they evolve into composites of two distinct scatterings due to the presence of borate and tellurite groups. In the CL0 glass containing only tellurite, the two peak character is indicative of the presence of two tellurite species, one of which scatters almost around the same frequency as the borate species, namely 740 cm\(^{-1}\). It also suggests that the absorption at 460 cm\(^{-1}\) is clearly due to some bending mode in tellurite units.

\(^{11}\)B HRMAS NMR spectra

\(^{11}\)B HRMAS NMR spectra of the three series of glasses are shown in Figures 8(a), (b) and (c) respectively for the BT, CT and CL glasses. All show sharp resonances due to tetrahedral boron located roughly at the centre of the quadrupolar split resonance of trigonal borons. In all series side bands are observed and their intensities are low. The areas under the tetrahedral and trigonal boron signals were determined as well as the relative proportions of the tetrahedral boron (\(N_t=[B_4]/([B_3]+[B_4])\)). These \(N_t\) values have been plotted as a function of reduced LiBO\(_2\) concentration, \(R=([LiBO_2]/([LiBO_2]+[TeO_2]))\) for all three series of glasses in Figures 9(a), (b) and (c), respectively. There is some amount of scatter in the \(N_t\) values in the BT series. The scatter is much less in the other two series. All three series of glasses uniformly exhibit high values of \(N_t\), the maxima being as high as 0·63 in the BT series and 0·59 and 0·58 respectively in the CT and CL series. It may also be noted that pure LiBO\(_2\) glass in the BT series exhibits an \(N_t\) value of 0·46, whereas TeO\(_2\) free LiCl–LiBO\(_2\) glass in the CL series (CL7) has maximum value of about 0·41. Therefore, LiCl may not be responsible for increased \(N_t\) concentration in these glasses. On the contrary, TeO\(_2\) may be directly responsible for pushing up the values of \(N_t\). However, the \(N_t\) maximum in BT series occurs around \(R=0·8\) (reduced LiBO\(_2\) concentration) and at around \(R=0·3\) in the CL series. Therefore, there appears to be some influence of LiCl on \(N_t\) concentration contrary to our earlier observation. But we believe that the influence of LiCl on \(N_t\) concentration is only indirect and occurs via its influence on the structural preference for \(tp\) tellurite units in the structure. We discuss this aspect in the following section. The occurrence of \(N_t\) maximum in the CT series is also due to the indirect influence of the same nature.
The structural model

We first recognize that there are two structural equilibria which influence each other in this rather interesting system of glasses. First is the equilibrium in borate moieties as B$_4$ and B$_3$ structural units. Second is the equilibrium of TeO$_2$ moieties as T$_4$(thp) and T$_3$(tp) units. All the three spectroscopies, namely infrared, Raman and $^{11}$B NMR, indicate that with increasing percentage of TeO$_2$, B$_4$ increases. There is a corresponding decrease in T$_4$ units which is not so obvious but the decrease is an essential concomitant as we see below. In pure TeO$_2$ the preferred structural units are T$_2$(thp) (superscripts indicate the charge). The structural units in equilibrium in LiBO$_2$ are B$_4$ ([BO$_4$]$_2^-$) and B$_3$([BO$_3$O]$_2^-$). The experimentally measured B$_4$ in NMR is a sum of B$_4^0$([BO$_4$]$_2^-$) and B$_3^-$ units. In pure lithium borate glasses, the N$_4$ maximum occurs at the diborate composition with a value of ~0.5 and corresponds to the ratio $[B_4]^-/[B_4]^-+[B_3]^-+[B_3]^-$. For Li$_2$O/B$_2$O$_3$ ratio greater than unity, N$_4$ decreases approximately linearly. Therefore, in this region, B$_4^0$ is converted into B$_3^-$ by the modifier. B$_3^-$ is also destabilised and converted into B$_4^-$. 

\[
\text{BO}_{4/2} \quad \text{increased modifier} \quad \text{BO}_{2/2} \text{O}
\]

Therefore, in LiBO$_2$ (Li$_2$O/B$_2$O$_3$=1) we would expect N$_4$ to be less than 0.5. In fact, in pure LiBO$_2$ glass a value of 0.42 is obtained (this value is slightly higher than earlier values obtained in binary Li$_2$O–B$_2$O$_3$ glasses prepared from Li$_2$CO$_3$ and H$_3$BO$_3$. However, we may note that there is a significant scatter in the reported values of N$_4$ in this region).

Therefore the observed increase of N$_4$ in the present system of glasses is possible only if the Li$_2$O:B$_2$O$_3$ stoichiometry is affected adversely by the presence of TeO$_2$. 

Figure 8. $^{11}$B HRMAS NMR spectra of (a) BT series, (b) CT series and (c) CL series of glasses.
A portion of the Li₂O is reclaimed by TeO₂ for its own structural modification as follows:

\[
[\text{BO}_2\text{O}]^+ + [\text{TeO}_4]^{3-} \rightarrow [\text{TeO}_2\text{O}]^2- + [\text{BO}_3\text{O}]^2-
\]

This reaction is expected to be favoured on simple electronegativity considerations, because the molecular electronegativities of the various species are \([\text{BO}_2\text{O}]^+ (1.74); [\text{TeO}_4]^{3-}, 1.96; [\text{TeO}_2\text{O}]^2-, 2.71; [\text{BO}_3\text{O}]^{2-}, 2.92; [\text{BO}_2\text{O}]^+, 2.22\). The electronegativities of the products, \([\text{BO}_3\text{O}]^2-\) and \([\text{TeO}_2\text{O}]^2-\), lie between the electronegativities of the reactants, \([\text{BO}_2\text{O}]^+\) and \([\text{TeO}_4]^{3-}\). Thus, by addition of TeO₂ we would expect Li₂O used in modifying B₂O₃ to be consumed so that the corresponding Li₂O/B₂O₃ ratio also decreases in the glass. Therefore, the equilibrium value of \(N_4\) shifts towards larger values. Addition of more TeO₂ would not only deplete Li₂O from LiBO₂ glass and increase B₄, but more importantly tellurite units position themselves between borate units in the structure. The B₄ units are thus isolated from other similar borate units in the structure by the intervening tellurite units. This, we believe, exerts a stabilising influence on B₄ units. Thus we observe that even when \(R\) has decreased to only 0.8 at about 20 mol% TeO₂, the \(N_4\) value reaches a maximum. Therefore, the presence of LiCl promotes \(T_4\) units in the glass structure. The \(T_4\) species gives a band at 635 cm⁻¹. The shoulder of this band can be attributed to \(T_3\) units. In the spectra of CL0, the same band corresponds to \(T_4\) and \(T_3\) peaks. The spectra are essentially similar. Therefore, we feel that in the presence of highly ionic components in the glass, such as LiCl, \(T_4\) units get preferentially transformed into \(T_3\) units. We further argue that the facile nature of this transformation is because of the small difference in energies of the two species. The chemical binding in \(T_4\) and \(T_3\) units can be understood with the help of simple molecular orbital schemes. In both \(T_3\) and \(T_4\), the Te atom is assumed to use one 5s, three 5p and one 4d orbital for bonding. \(sp^3d\) hybridisation (\(d_{zx}\) orbital), gives rise to trigonal bipyramidal, \(tpb\), geometry where the lone pair can be accommodated in an equatorial orbital. The other four orbitals form \(\sigma\) bonds with \(p\) (or \(sp'\) hybridised) orbitals of four surrounding oxygens. This accounts well for the \(T_4\) species. On the other hand, the \(5s\) with \(5p\) orbitals on Te can hybridise and give four \(sp^3\) hybrid orbitals. The lone pair can be placed in one of them and the three other orbitals are used in bonding to three oxygens. The \(4d\) orbital can then make a \(d_{zx}\)-\(p\) type of \(\pi\) bond with one of the oxygens which now becomes a double bond. This accounts for the \(T_3\) species. Although the formation of both \(T_4\) and \(T_3\) units use the same set of orbitals, namely \(sp^3d\), the nature of the lone pair orbital is different in the two species. In \(T_3\) the lone pair orbital is present in a hybridised orbital with a larger \(s\) contribution. It is likely that \(sp'\) orbital is relatively more stabilised by association with a Li⁺ ion from LiCl than an \(sp'\) orbital. This is because the increased \(s\) character in \(sp'\) orbital gives rise to an enhanced polarisation energy. Further the coulombic interaction in the system is also optimised because the linear polymeric \([\text{TeO}_2\text{O}]^\text{2-}\) chains enable better packing of the constituent. Therefore, the presence of LiCl promotes \(T_4\rightarrow T_3\) structural transformation (this argument can be extended to \(T_2\rightarrow T_1\) also). Such \(T_4\rightarrow T_3\) conversions in binary alkali tellurites have been well-known in earlier experiments. Therefore, \(T_4\rightarrow T_3\) conversion is a consequence not only of modification in the sense of formation of negatively charged tellurite species, but also is due to addition of highly ionic salts to the glass (like LiCl).

Figure 9. \(N_4\) vs reduced LiBO₂ concentration \((R)\) for (a) BT series, (b) CT series and (c) CL series of glasses.
Table 2  Change in connectivities and dimensionalities during modification of borate and tellurate species.

<table>
<thead>
<tr>
<th>Conversion</th>
<th>Change in number of bonds</th>
<th>Net change</th>
<th>Change in dimensionalities</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂⁺→B₄⁺</td>
<td>4→3</td>
<td>-1</td>
<td>3→2</td>
</tr>
<tr>
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<td>4→2</td>
<td>-2</td>
<td>3→1</td>
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<tr>
<td>T₃⁺→T₄⁻</td>
<td>4→1</td>
<td>-3</td>
<td>3→0</td>
</tr>
<tr>
<td>T₄⁻→T₁⁻</td>
<td>4→2</td>
<td>-2</td>
<td>3→1</td>
</tr>
</tbody>
</table>

Glass properties and the model

Simultaneous B₂⁺→B₄⁺ and T₃⁺→T₄⁻ conversions in the present glass system have profound consequences on the overall structure and thermal properties of these glasses. For example, B₂⁺→B₄⁺ conversion brings about a change in structure, from linear (2 covalent linkages) to a 3-dimensional (4 covalent linkages), which increases the volume, thereby creating more open structures. The nature of conversion and the associated change in number of covalent bonds and dimensionality of the structures are summarised in Table 2. We now examine the expected consequences of such structural changes on the properties of the different glasses.

In the BT series, Figure 2(a), the volume increases rapidly with TeO₂ addition because of the effect of conversion of B₂⁺→B₄⁺ and the formation of B₄⁺ units. Together, B₂⁺ and B₄⁺ create the open network of the borate consisting of an excess of tetrahedrally connected borons. When the ratio of TeO₂/LiBO₂ increases to unity this effect B₂⁺→B₄⁺ conversion and B₄⁺ production reaches a maximum. The TeO₂ rich region consists of a combination of T₃⁻, T₄⁻ and T₁⁻ units formed at the expense of B₂⁺, B₃⁺ and B₄⁺ units. This is responsible for the decreasing trend of molar volumes.

In the CT series of glasses the concentration of TeO₂ is constant. Therefore the changes in properties are presented as a function of LiBO₂ concentration in these glasses, Figure 3(a) and (b). In this series the first member, 40LiCl.30LiBO₂.30TeO₂ (CT4) glass, already corresponds to a composition of maximum volume originating from LiBO₂–TeO₂ part of the glass. Further increase of LiBO₂ would only increase the concentration of B₂⁺. Therefore, the volume has a slightly decreasing trend. In the same region the LiCl concentration continues to decrease and therefore the LiCl influence on T₃⁺→T₁⁻ conversion decreases. This will manifest in the recovery of T₁⁻ units which is reflected in a slightly increasing trend in volumes. At much lower concentration of LiCl (and much higher concentration of LiBO₂) the volume change essentially saturates because there are no important structural conversions. This is well reflected in the experiments, Figure 3(a).

The trend in volume change in the CL series (plotted as a function of TeO₂ in Figure 4(a)) perhaps represents an acute test of the model (consequences of concentration dependent speciation envisaged in this model). Initially as TeO₂ concentration increases, the volume changes are very much the same as in BT series, the volume increases primarily because of the formation of B₂⁺. Once the ratio of LiBO₂ to TeO₂ reaches unity (~35 mol% TeO₂) the increase in volume reaches a maximum. The next phase of changing volumes is dominated by the breakdown of T₁⁻ to T₄⁻ induced by the ionic environment of LiCl. But as TeO₂ concentration increases above 50 mol% TeO₂, T₄⁻→T₁⁻ conversion not only stops but is reversed (T₁⁻ is regenerated) because there is little LiBO₂, and LiCl/TeO₂ is much less than unity. The dominant influence of regenerated T₁⁻ in the structure leads to volume increase in the region 50–70 mol% TeO₂. Thus the molar volume behaviour of the glasses in all the three series is completely consistent with the expectation of the model.

The variation of glass transition temperature in the BT series, Figure 2(b), is also consistent with the above model. The Tₛ of pure LiBO₂ glass is highest in BT series. Perhaps this is because of a very efficient packing of B₂⁺ and Li⁺ in the structure, so that full advantage is taken by the coulombic interactions. Since the addition of TeO₂ rebuilds the open structure based on B₂⁺ and also since T₁⁻ is a large ion, the cohesive energy density in the glass decreases resulting in a rapid decrease in glass transition temperature until 50 mol% addition of TeO₂. Above 50 mol% TeO₂ it is the T₄⁻ units which dominate the structural reorganisations, which again leads to a lower energy density and hence lower Tₛ values. However, the slope of variation of Tₛ decreases above 50 mol% TeO₂.

In the CT series of glasses, Figure 3(b), Tₛ increase is due to LiBO₂ because TeO₂ concentration is a constant. As noted earlier, LiBO₂/TeO₂ is always greater than unity in this series and ranges between 1:33 and 2:33. The trend is similar to that of BT series for the same region as TeO₂ decreases between 0:43 to 0:30. However, LiCl does have its own influence on Tₛ and can be seen in the extrapolated value of Tₛ towards 0 mol% LiBO₂. Here the Tₛ should correspond to that of 70LiCl.30TeO₂ which is ~590 K. This value is (~2/3)Tₑₑ of LiCl (589 K). Extrapolation of Tₛ in the BT series Tₛ gives the Tₛ of pure TeO₂ glass as only 530 K. Therefore the Tₛ is indicative of the influence of the major component in the glass, namely LiCl.

In the CL series the Tₛ behaviour, Figure 4(b), is rather complex. We offer here a rather tentative explanation. The starting point is the extreme right which corresponds to LiBO₂ free LiCl–TeO₂ glass (CL0) with a somewhat low Tₑₑ. Substitution of TeO₂ by LiBO₂ in this region breaks down the TeO₂ structure by converting T₃⁻→T₁⁻. Although B₂⁺ units are introduced and their concentration is on the rise, the net effect is a weakening of the structure and it pushes down the Tₛ values to some extent. But around 25 mol% LiBO₂ it would generate more than 12-5% B₄⁺ units which along with B₂⁺ units creates a 3-dimensional network which permeate the glass structure. It is our speculation that the Tₛ is controlled by the stronger borate network above this concentration of LiBO₂. It is also likely that the inter-penetration of tellurite and borate networks pushes up the Tₛ to about 50LiBO₂. Above this composition, TeO₂ percentage being small, the B₂⁺ content drops (there is more LiBO₂), the network strengthening influence of the permeating TeO₂ network wanes and the strength of the glass structure decreases. This manifests as a decreasing trend in glass transition. Thus the Tₛ behaviour can also be considered as broadly consistent with the proposed structural model.
The ΔCₚ values obtained from the heat capacity plots vary widely. In general, ΔCₚ values can be related to the configurational excitation entropy on the basis of bond-lattice model. The plurality of speciation in these glasses and the associated change in the nature of number of bonds in unit composition makes it difficult to understand quantitatively the ΔCₚ variations and, therefore, these are not discussed any further.

Conclusions

LiCl–LiBO₂–TeO₂ glasses investigated in this paper are characterised by complex structural and bonding variations. On the basis of infrared, Raman and ¹¹B HRMAS NMR spectroscopy, it is observed that TeO₂ takes away part of the modifier oxide ion from BO₂ by virtue of its higher molecular electronegativity. This is followed by a series of structural rearrangements: (1) [B₄]/([B₃]+[B₄]) ratio is pushed in a direction that increase the relative concentration of B₄; (2) TeO₄/2 units, which have tp structure transform into [TeOO₁/₂O]⁻ which are tp units; (3) TeO₄/2 units themselves are induced to transform [TeOO₂³/₂] units in the prevailing ionic environment; (4) Addition of LiCl induces the transformation of T₃ units and also favours the stabilisation of B₃ units. The variation in molar volumes and glass transition temperatures observed in these glasses is well understood on the basis of such changes.

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References

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