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The structure and electrical properties of lithium borate glasses containing thallic oxide

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Abstract. Lithium borate glasses containing Tl_2O_3 were prepared and annealed. The results of deconvolution analysis of infrared spectra, molar volume and electrical conductivities (DC and AC) show that thallium ions are distributed as network formers in the glass matrix. The analysis of IR spectra shows that the formation of BO_4^- tetrahedral groups is not affected by the addition of Tl^{3+} ions and that Li^+ ions are associated between Tl_2O_3 and B_2O_3 to convert them to TlO_4^- and BO_4^- units. The introduction of Tl^{3+} ions into lithium borate glasses causes a decrease in the conductivity while the associated activation energy increases.

1. Introduction

Thallium is a rare element of the boron–aluminium group and forms two oxides, thallose oxide Tl_2O and thallic oxide Tl_2O_3 , in which the element is univalent and trivalent respectively [1]. Previous studies [2, 3] showed that Tl ions exist in borate or silicate as Tl-rich clusters when they are introduced into the glass in the form of Tl_2O . It was found, in this case, that Tl ions are identical to alkali ions in terms of their electrical behaviour in borate and silicate glasses [4, 5]. This means that Tl ions can be introduced as glass modifiers in building the glass matrix. It was found, also, that the electrical conductivities of mixed-cation glasses of the $Tl_2O-Na_2O-B_2O_3$ system were identical to those of $Tl_2O-B_2O_3$ at the same Tl_2O content [6, 7]. This indicates that Tl ions are the only charge carriers in these glasses. On the other hand, the addition of Tl ions to silver borate glasses gives a minimum conductivity at the concentration ratio $[Ag_2O/(Ag_2O + Tl_2O)] \cong 0.25$.

A study by NMR technique [8] showed that some strange deviation occurs in the $Tl_2O-B_2O_3$ glass system. Within the composition range $0 < R < 0.2$ ($R = Tl_2O/B_2O_3$), one Tl_2O unit can convert approximately three boron atoms from three- to four-coordination.

Unfortunately, until now, there has been no investigation of the existence of Tl ions in the glass matrix when it is introduced as thallic oxide. The main object of this work is the study of the effect of the addition of Tl_2O_3 to some lithium borate glasses on their structure and physical properties.

2. Experimental procedure

2.1. Glass preparation

Samples of the glass systems $40Li_2O \cdot xTl_2O_3 \cdot (60 - x)B_2O_3$ were prepared from reagent-grade chemicals. 35 g batches of stoichiometric amounts of high-purity water-free Tl_2O_3 ,

B₂O₃ and Li₂O powders, see table 1, were thoroughly milled and mixed. The components were melted in porcelain crucibles in an electric furnace at a temperature in the range 950–1150 °C, depending on the glass composition. The crucible and its contents were kept in the furnace for about 30 min to 1 h and the melt was stirred several times. The samples were annealed at 340 °C and then they were slowly cooled to room temperature at a rate of about 60 °C h⁻¹. The obtained samples were homogeneous and transparent.

Table 1. The composition, activation energies and electrical conductivity of the studied glasses.

| Glass | Glass composition (mol%) | | | <i>E</i> (eV) | $\sigma_{200^\circ\text{C}}$ ($\Omega^{-1}\text{ cm}^{-1}$) |
|-------|--------------------------------|-------------------------------|-------------------|------------------|--|
| | Tl ₂ O ₃ | B ₂ O ₃ | Li ₂ O | | |
| G1 | 0 | 60 | 40 | 0.583 | 4.074×10^{-6} |
| G2 | 5 | 55 | 40 | 0.620 | 1.259×10^{-6} |
| G3 | 10 | 50 | 40 | 0.683 | 3.890×10^{-7} |
| G4 | 15 | 45 | 40 | 0.729 | 9.772×10^{-8} |
| G5 | 20 | 40 | 40 | 0.757 | 1.096×10^{-7} |
| G6 | 25 | 35 | 40 | | |

2.2. AC measurements

For the AC conductivity measurements, samples were prepared in the form of discs of diameter 1 cm and thickness in the range 0.1–0.3 cm. The parallel surfaces of the samples were coated with graphite as electrodes. Complex impedance measurements were performed in the frequency range from 1 Hz to 500 kHz using a calibrated impedance meter (TESLA BM 507). The sample cell was shielded to minimize the external noise and stray impedance. The error in the absolute value of the complex impedance was less than 5% and that in its phase was 1°. The thermocouple, kept near the sample, was used to control the temperature within the experimental accuracy of ± 1 °C.

The complex impedance (Z^*) is related to the complex conductivity (σ^*) and the complex electric modulus (M^*), such that

$$\sigma^* = (Z^*)^{-1} = \sigma' + i\sigma'' \quad (1)$$

$$\sigma' = Z'/(Z'^2 + Z''^2) \quad \sigma'' = Z''/(Z'^2 + Z''^2) \quad (2)$$

$$M^* = M' + iM'' = \omega\epsilon_0 Z^* \quad (3)$$

where σ' , Z' and M' and σ'' , Z'' and M'' are the real and imaginary parts of σ^* , Z^* and M^* respectively, ω ($= 2\pi f$) is the angular frequency and ϵ_0 is the permittivity of the vacuum.

Within the approximate temperature range 80–280 °C, the conductivity obeyed the Arrhenius equation

$$\sigma = \sigma_0 \exp[-E/(RT)] \quad (4)$$

where σ_0 is a constant, E is the activation energy for conduction, R is the universal gas constant and T is the absolute temperature. The activation energy for conduction E is calculated from the slopes of the $\ln(\sigma)$ versus $1000/T$ plot for various compositions. The experimental error in determining the activation energies is estimated to be less than 0.03 eV.

2.3. The molar volume

The molar volume, Mv , is defined as

$$Mv = \sum M_i n_i / D \quad (5)$$

where M_i is the molecular weight for the component i , n_i is its molar ratio and D is the glass density. To determine the molar volume of glass, density measurements were performed at room temperature, using a standard method based on Archimedes' principle with xylene as the immersion fluid. Three samples of each glass were taken to measure the density. Density values are precise to $\pm 0.01 \text{ g cm}^{-3}$.

2.4. Infrared spectroscopy

The IR spectra for the glass samples were recorded at room temperature using the KBr disc technique by a spectrophotometer (Perkin Elmer model PE 577 in the wavenumber range $200\text{--}2000 \text{ cm}^{-1}$ with a resolution of 2 cm^{-1}).

3. Results

Figure 1 illustrates the de-convolution infrared spectra of the studied glasses, G1–G6, and the difference between the experimental and simulated curves. The de-convolution processes have been described and discussed in other works [9, 10]. The best fitting was obtained when the bands were taken to be Gaussian. From the spectral analysis, the position, C , and the relative area, A , of the component bands of the studied glasses are listed in table 2. Only the interesting domain, $600\text{--}1750 \text{ cm}^{-1}$, is represented in figure 1. Figure 2 shows the effect of substitution of B_2O_3 by Tl_2O_3 on the molar volume for the studied glasses. It is clear from figure 2 that the molar volume increases almost linearly with increasing Tl_2O_3 content, which indicates that the structure of the studied glasses becomes more open and expanded. The temperature-dependence of the electrical conductivity for the studied glasses, G1–G6, measured at 1 kHz is given in figure 3. Figure 4 shows the effect of Tl_2O_3 content on the electrical conductivity at three different temperatures (150, 200 and 250°C). It is shown that the electrical conductivity rapidly decreases with increasing Tl_2O_3 content (up to 15 mol%) then takes constant values for Tl_2O_3 higher than 15 mol%. The variation of the activation energy for conduction, E , with Tl_2O_3 content is presented in figure 5. It is found that E increases almost linearly as the Tl_2O_3 content increases. The values of $\sigma_{200^\circ\text{C}}$ and E are listed in table 1.

4. Discussion

To illustrate the distribution of thallium ions in $\text{Tl}_2\text{O}_3\text{--Li}_2\text{O--B}_2\text{O}_3$ glasses, one must take into account the change in the glass structure caused by the substitution of B_2O_3 by Tl_2O_3 . In other words, one must first specify whether Tl^{3+} ions enter the glass network as glass modifiers or as glass formers.

4.1. IR spectra

Study of the IR spectra of the binary glass, G1, is very helpful in understanding the effects of addition of Tl_2O_3 to the boron–oxygen network of the ternary system. In figure 1, the spectrum of G1 is composed of five main bands at about 700, 830, 950, 1075 and

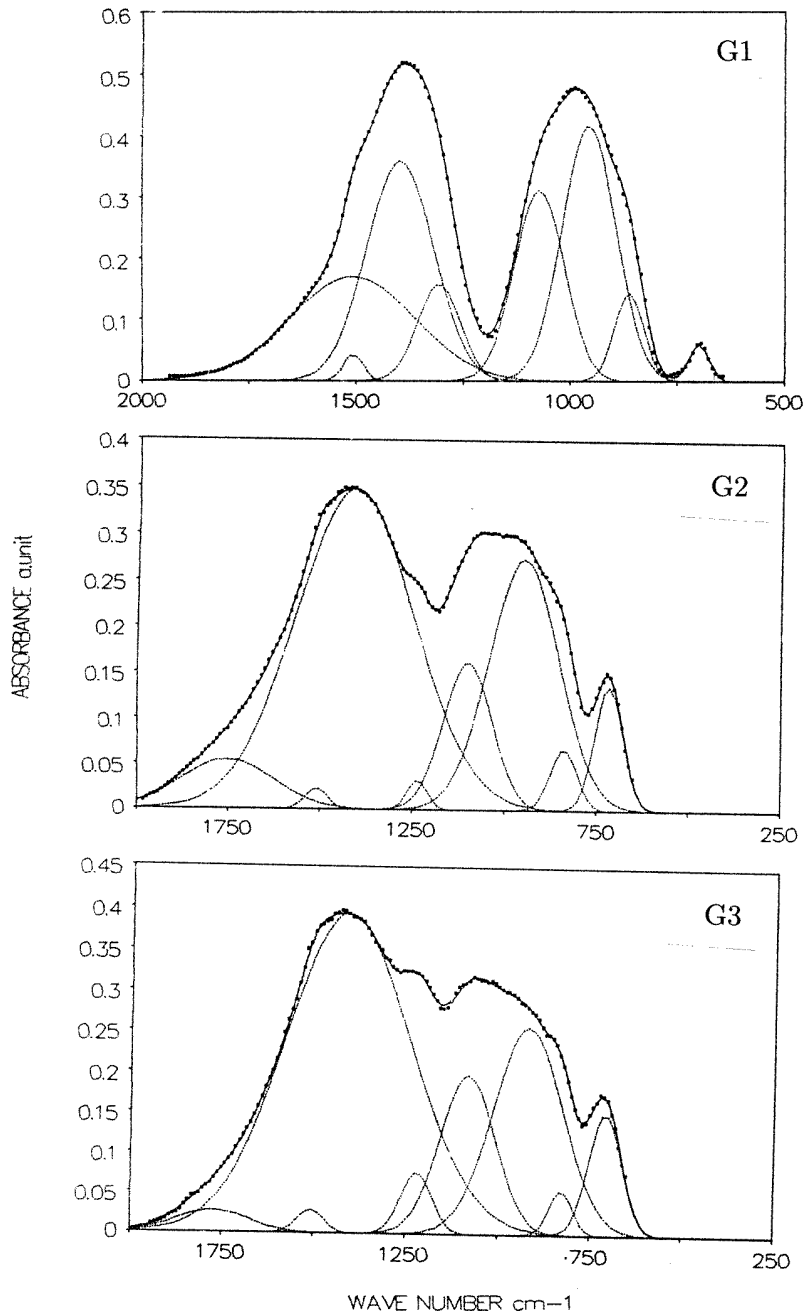


Figure 1. De-convolution of the infrared spectra of the studied glasses G1–G6. The component bands are the lines below the simulated spectra curve.

1400 cm^{-1} ; and furthermore, the bands in the region $350\text{--}550\text{ cm}^{-1}$ listed in table 2. According to Kamitsos *et al* [11] there are three active infrared spectral regions, at 600--

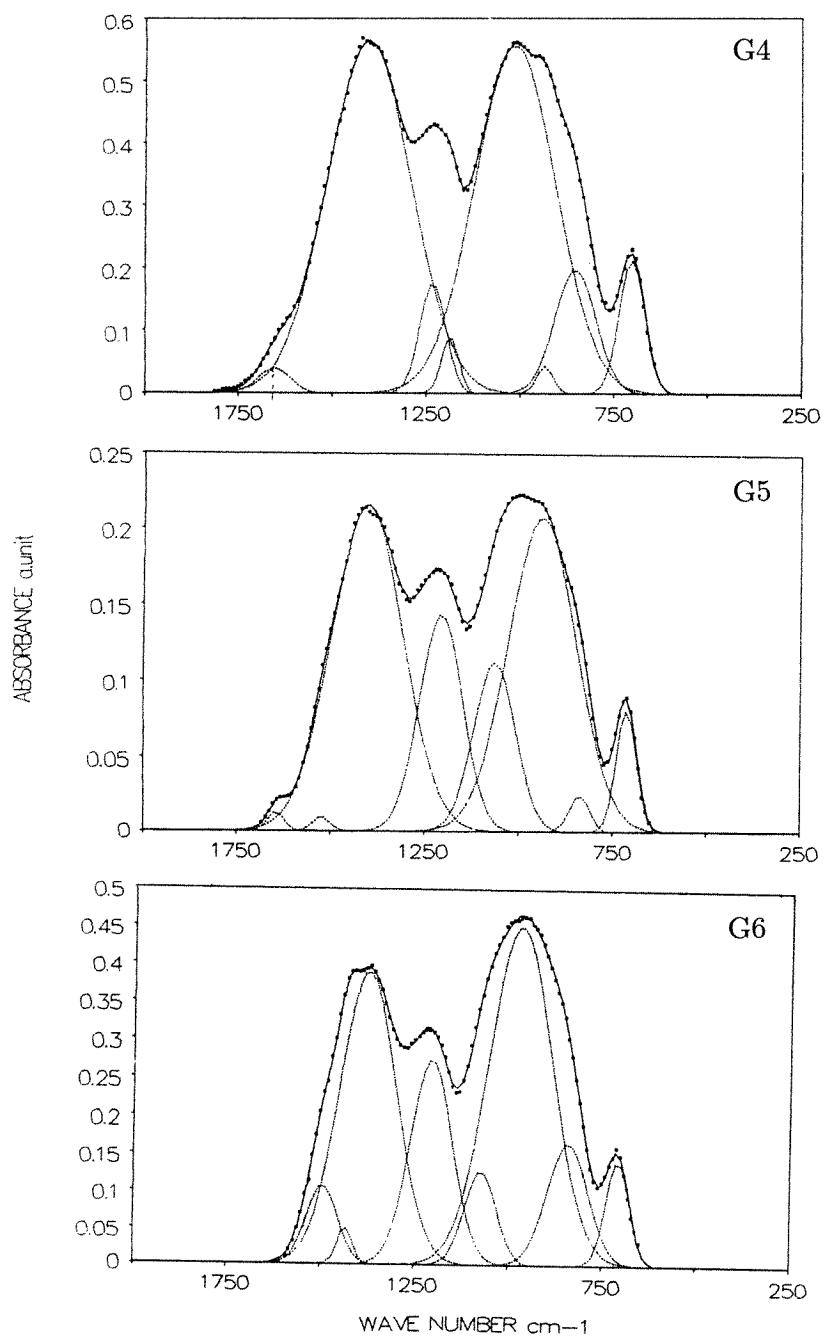


Figure 1. (Continued)

800 cm^{-1} , which is attributed to the bending vibrations of various borate segments; at 850–1200 cm^{-1} , which is attributed to stretching vibrations of tetrahedral BO_4^- units; and

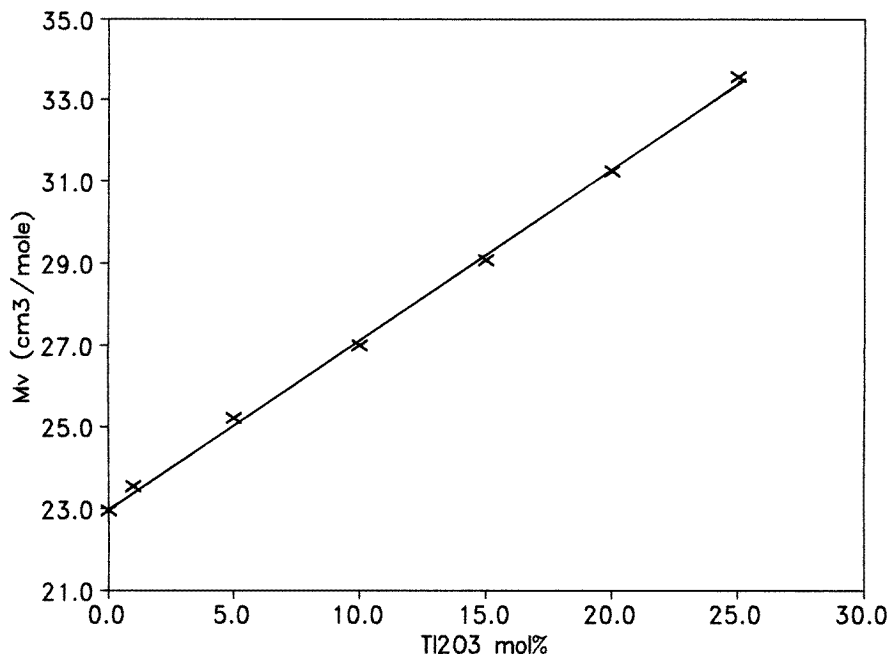


Figure 2. The dependence of the molar volume on the Ti₂O₃ content.

Table 2. De-convolution parameters of the infrared spectra of glasses G1–G6. *C* is the component band centre and *A* is the relative area of the component band.

| | | | | | | | | | | | | |
|----|------------------------------|------|------|------|------|------|------|------|------|------|------|------|
| G1 | <i>C</i> (cm ⁻¹) | 434 | 476 | 550 | 613 | 701 | 865 | 959 | 1075 | 1308 | 1399 | 1508 |
| | <i>A</i> (%) | 1.03 | 0.52 | 1.51 | 0.39 | 1.22 | 4.19 | 22.6 | 15.7 | 6.77 | 24.2 | 21.9 |
| G2 | <i>C</i> (cm ⁻¹) | 353 | 453 | 571 | 718 | 840 | 951 | 1103 | 1238 | 1413 | 1510 | |
| | <i>A</i> (%) | 1.18 | 2.73 | 0.78 | 4.37 | 2.16 | 22.9 | 9.43 | 0.78 | 49.3 | 0.60 | |
| G3 | <i>C</i> (cm ⁻¹) | 377 | 502 | 621 | 710 | 829 | 921 | 1085 | 1222 | 1413 | 1508 | |
| | <i>A</i> (%) | 1.65 | 5.45 | 0.29 | 4.63 | 1.34 | 18.6 | 11.4 | 2.45 | 51.6 | 0.77 | |
| G4 | <i>C</i> (cm ⁻¹) | 355 | 460 | 704 | 855 | 935 | 1017 | 1189 | 1236 | 1406 | | |
| | <i>A</i> (%) | 0.99 | 7.60 | 4.21 | 6.53 | 0.58 | 36.2 | 1.25 | 3.67 | 38.0 | | |
| G5 | <i>C</i> (cm ⁻¹) | 413 | 510 | 627 | 715 | 839 | 941 | 1067 | 1209 | 1406 | 1524 | |
| | <i>A</i> (%) | 6.38 | 3.65 | 0.08 | 3.22 | 1.04 | 29.8 | 9.90 | 13.1 | 32.2 | 0.33 | |
| G6 | <i>C</i> (cm ⁻¹) | 372 | 484 | 711 | 844 | 973 | 1076 | 1208 | 1378 | 1436 | 1497 | |
| | <i>A</i> (%) | 2.87 | 8.06 | 3.52 | 7.47 | 31.9 | 4.48 | 12.9 | 24.4 | 0.82 | 3.62 | |

at 1200–1500 cm⁻¹, which arises from B–O stretching vibrations of BO₃³⁻ units only [12–14]. More analyses of this spectrum indicate that the bands which appear in the region 350–475 cm⁻¹ should be assigned to the vibration of Li⁺ ions relative to their network sites [11, 15]. The band at 550 cm⁻¹ is attributed to in-plane bending vibrations of orthoborate

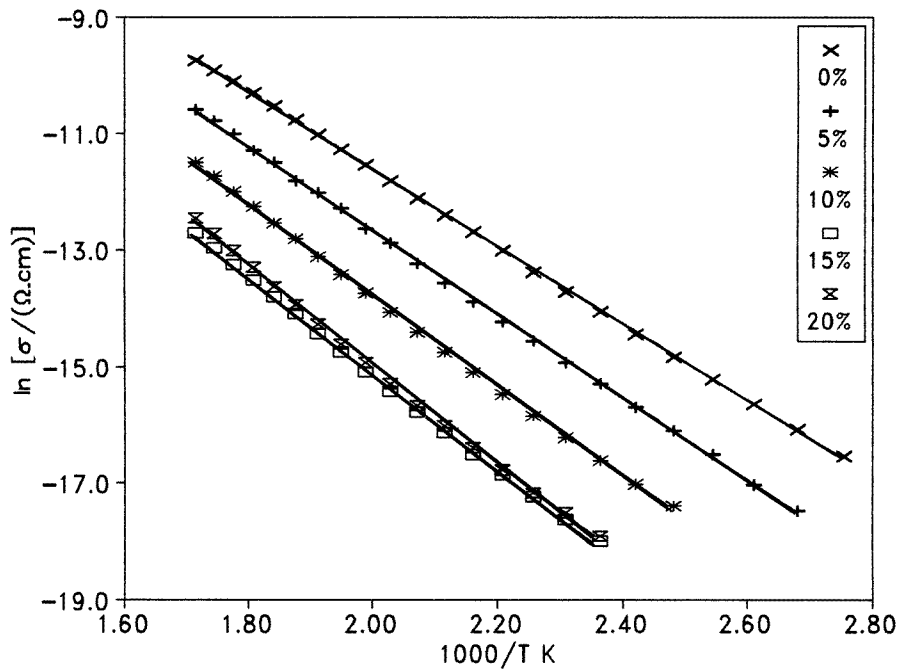


Figure 3. The temperature-dependences of the conductivity of the studied glasses G1–G6 measured at 1 kHz.

units [11]. The band at about $700\text{--}720\text{ cm}^{-1}$ corresponds to the bond-bending vibration of B–O–B bridges to the boron–oxygen network [12]. The band at about $820\text{--}865\text{ cm}^{-1}$ is attributed to the stretching vibrations of tetrahedral BO_4^- units [11]. In addition, the band at about $900\text{--}950\text{ cm}^{-1}$ has been assigned to diborate groups [10, 11]. The band at 1064 cm^{-1} is similar to that at 1080 cm^{-1} , which has been assigned to vibrations of pentaborate groups [11].

The IR spectra of the ternary glasses are presented in figure 1, G2–G6, for different Tl_2O_3 contents. There were no new observations due to the addition of Tl_2O_3 compared with the binary system except for two effects. First, a new band appears at about 1240 cm^{-1} when Tl_2O_3 is added and shifts to lower frequencies as the Tl_2O_3 content decreases (it is at about 1208 cm^{-1} at 25 mol% Tl_2O_3). The component band in this region has been attributed to the metaborate chains [11]. Secondly, bands at 975 and 1017 cm^{-1} appear which have been attributed to the formation of triborate groups [11].

As previously reported by Moustafa *et al* [10, 16], the fraction of four-coordinated borons, N_4^{IR} , in the glass is calculated from the relative area of the component bands such that $N_4^{IR} = (\text{concentration of } \text{BO}_4^- \text{ tetrahedral}) / (\text{concentration of } \text{BO}_3^{3-} \text{ triangles plus concentration of } \text{BO}_4^- \text{ tetrahedral})$. Table 3 represents the values of the fraction of four-coordinated borons (N_4) with the molar ratio (R' and R'') of the studied glasses, where R' is $[(\text{Li}_2\text{O} - \text{Tl}_2\text{O}_3) / \text{B}_2\text{O}_3]$ in mol% in the case of Tl_2O_3 introduced as a glass former, R'' is $[(\text{Li}_2\text{O} + \text{Tl}_2\text{O}_3) / \text{B}_2\text{O}_3]$ in mol% in the case of Tl_2O_3 introduced as a glass modifier, $N_4^{C'}$ and $N_4^{C''}$ represent the calculated values of N_4 which are equal to

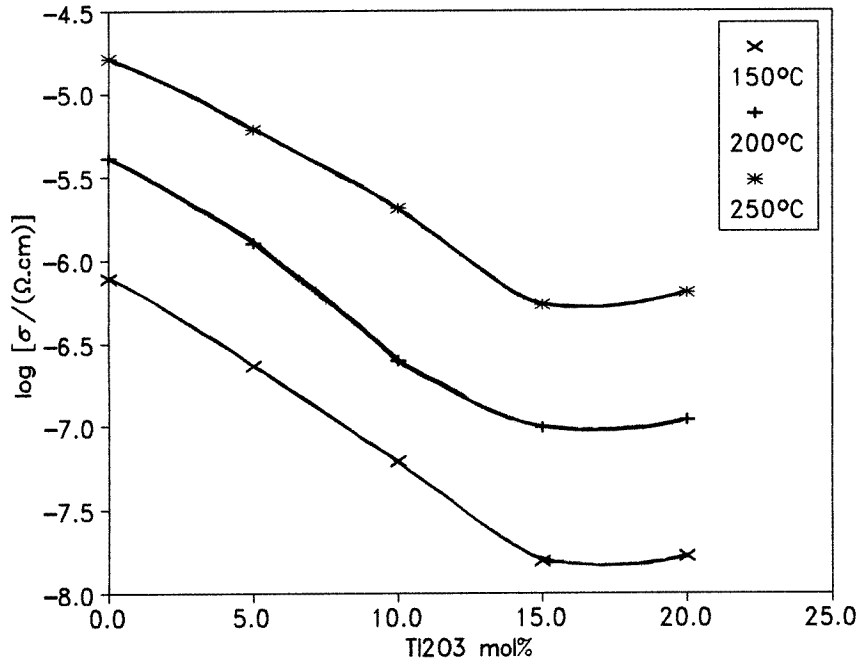


Figure 4. The dependence of the electrical conductivity at three different temperatures on the Tl_2O_3 content.

Table 3. The values of the mole fractions R' and R'' . Also, the calculated and the experimental values of the fraction of four-coordinated borons $N_4^{C'}$, $N_4^{C''}$, N_4^{IR} and N_4^{NMR} , see the text.

| Glass | R' | $N_4^{C'}$ | R'' | $N_4^{C''}$ | N_4^{NMR} | N_4^{IR} |
|-------|------|------------|-------|-------------|-------------|------------|
| G1 | 0.67 | 0.46 | 0.67 | 0.46 | 0.46 | 0.439 |
| G2 | 0.64 | 0.465 | 0.82 | 0.42 | | 0.449 |
| G3 | 0.60 | 0.475 | 1.00 | 0.375 | 0.46 | 0.431 |
| G4 | 0.56 | 0.485 | 1.22 | 0.32 | | 0.436 |
| G5 | 0.50 | 0.50 | 1.50 | 0.25 | 0.475 | 0.444 |
| G6 | 0.43 | 0.43 | 1.857 | 0.161 | | 0.433 |

the same values of R' or R'' for R' or $R'' \leq 0.5$ and equal to $0.375 - 0.25(R'$ or $R'' - 1)$ for R' or $R'' > 0.5$ [17], N_4^{NMR} is taken from NMR measurements for the binary lithium borate glasses [17] and N_4^{IR} is calculated from IR spectra of the studied glasses.

It is clear from table 3 that the values of N_4^{IR} are generally in agreement with the values of N_4^{NMR} and $N_4^{C'}$ within experimental error. This means that the formation of tetrahedral BO_4^- is not affected by the addition of Tl^{3+} ions and Tl_2O_3 enters the glass structure as a network former in the form of TlO_4^- . From the previous representation, one can conclude that not all of the Li_2O content is associated with B_2O_3 but rather that the Li_2O content should associate both with Tl_2O_3 and with B_2O_3 to convert them to TlO_4^- and BO_4^- units.

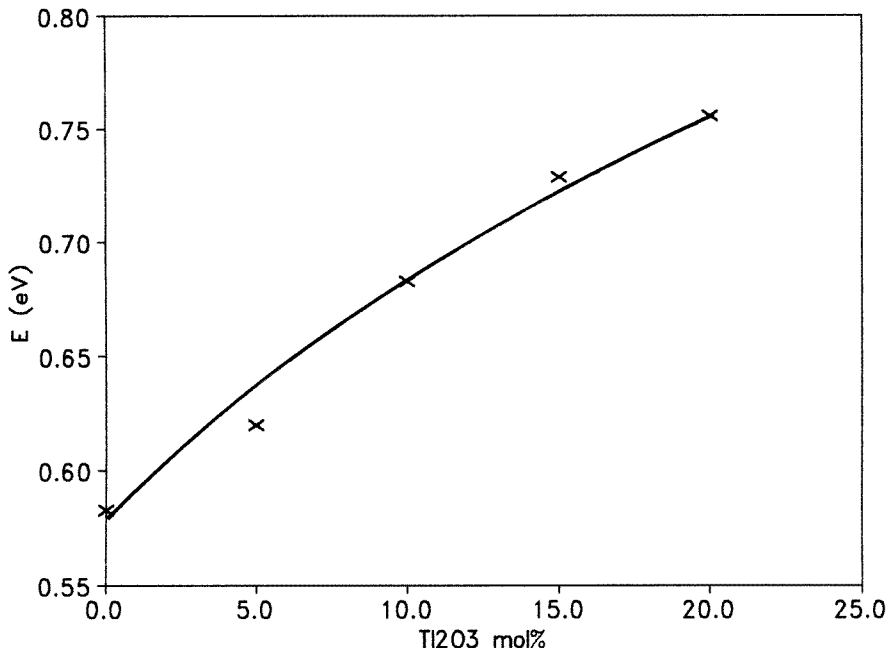
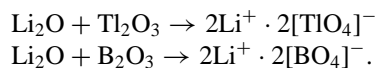


Figure 5. The dependence of the activation energy on the Tl₂O₃ content.

In this case, we expect that the oxygen atoms introduced by the Li₂O are consumed first for the four-coordination of thallium (TlO₄⁻) and the rest for the four-coordination of boron (BO₄⁻) as follows:



4.2. Molar volume and DC conductivity

As shown in figure 2 the network of the studied glasses expands with the addition of Tl₂O₃ content almost at the expense of B₂O₃ content. This trend can be attributed to the so-called open structure which may be attributed to the introduction of Tl³⁺ ions as network modifiers or formers into the glass network. When Tl³⁺ ions are introduced as modifiers, the increase in molar volume with increasing Tl₂O₃ content may be attributed to the large radius of the thallium ions (the Tl ion is much larger and heavier than the other ion in the present glasses) which cannot be accommodated in the voids associated with BO₄⁻ units without any expansion of the glass matrix. On the other hand, the direct substitution of one B₂O₃ by one Tl₂O₃ keeps the amount of oxygen atoms constant while the amount of boron decreases by two atoms. This means that the ratio of oxygen to boron atoms (O/B) must increase, see table 4. In this case, the formation of BO₄⁻ units must decrease and the non-bridging oxygen ions (NBOs) increase in number in the borate network. Consequently, the number of charge carriers must increase and their mobilities will increase where the ions can move easily in the conduction pathways within the open structure network. Therefore, one would expect the electrical conductivity to increase and the associated activation energy

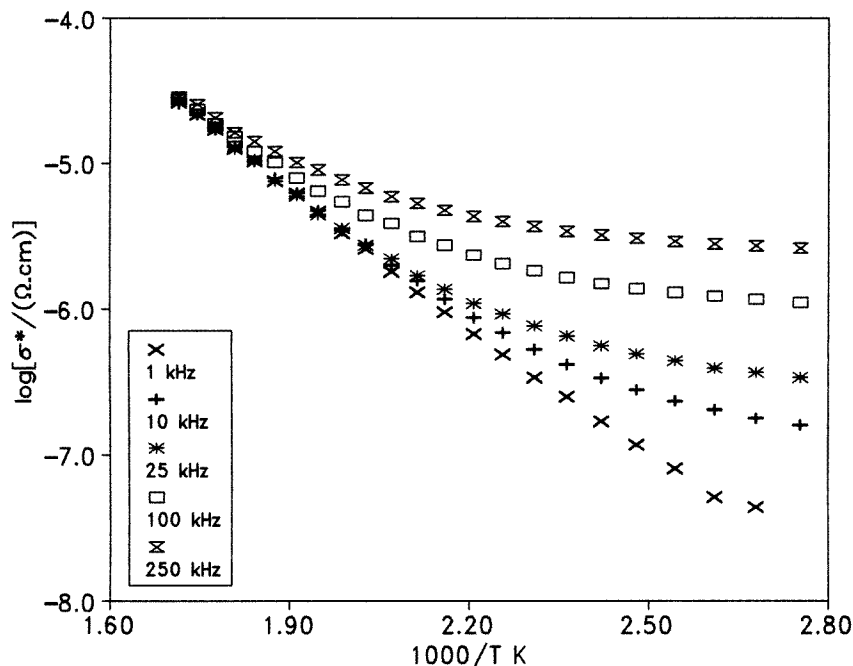


Figure 6. The temperature-dependence of the complex conductivity, σ^* , of the glass G2 measured at different frequencies.

Table 4. The density, mobility and concentration of Tl ions in the studied glasses.

| Glass | d (g cm ⁻³) | O/B ratio | $\mu_{200^\circ C}$ (m ² V ⁻¹ s ⁻¹) | η_{Tl} (10 ²¹ cm ⁻³) |
|-------|------------------------------|--------------|--|---|
| G1 | 2.342 | 1.83 | 48.44×10^{-10} | |
| G2 | 2.897 | 2 | 16.45×10^{-10} | 2.388 |
| G3 | 3.424 | 2.2 | 5.45×10^{-10} | 4.461 |
| G4 | 3.846 | 2.44 | 1.47×10^{-10} | 6.216 |
| G5 | 4.198 | 2.75 | 1.78×10^{-10} | 7.712 |
| G6 | 4.483 | 3.14 | | 8.971 |

to decrease with increasing Tl₂O₃ content. In fact, the results obtained from figures 4 and 5 are in conflict with this assumption because the electrical conductivity decreases and the associated activation energy rapidly increases as the Tl₂O₃ content increases. This leads one to conclude, again, that Tl³⁺ ions do not act as network modifiers but rather are introduced as network formers in the form of TlO₄⁻, that Li⁺ ions are the only charge carriers in such glasses and that they are responsible for the conduction mechanism. This formation of TlO₄⁻ units is responsible for the increase in molar volume and at the same time for blocking the glass structure by linkage to BO₄⁻ groups; therefore, the mobility of the charge carriers decreases (see table 4) and consequently the electrical conductivity decreases and the associated activation energy increases.

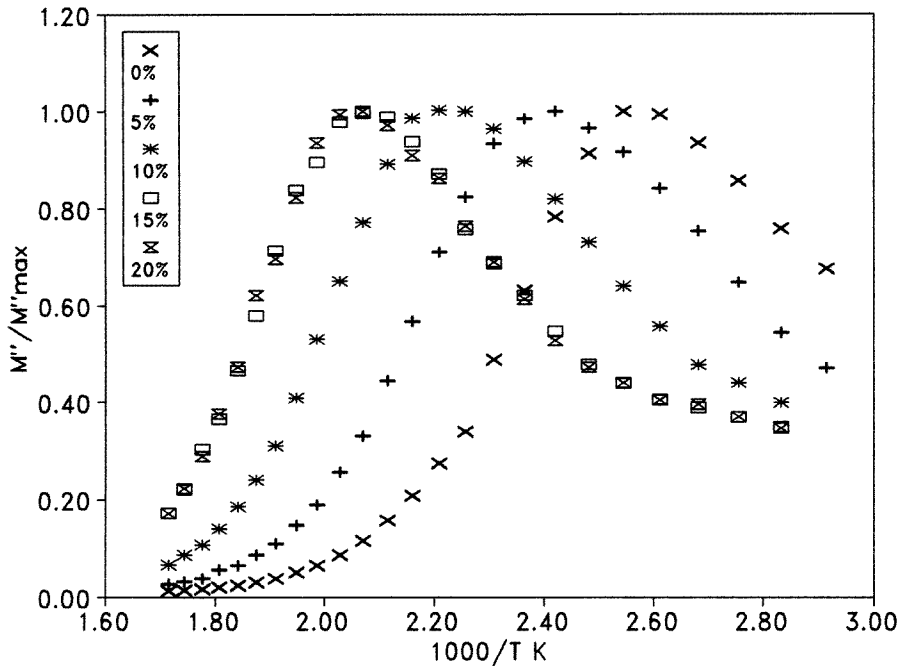


Figure 7. The effect of temperature on the normalized modulus, M''/M''_{max} , of the glasses G1–G6 measured at 25 kHz.

4.3. The AC conductivity

The variation of the complex conductivity, $\sigma^*(\omega)$, of the glass containing 5 mol% Tl_2O_3 (as an example) at different fixed frequencies is shown in figure 6 as a function of temperature. The general behaviour in figure 6 is very similar to that of the other ionic and transition metal oxide glasses [18, 19]. At higher temperatures, the temperature-dependence of the conductivity becomes strong and $\sigma^*(\omega)$ becomes equal at all frequencies. However, at low temperatures, $\sigma^*(\omega)$ is weakly dependent on temperature and it increases with increasing frequency at any fixed temperature. Similar behaviour was observed for the other glass compositions.

The effect of the temperature of the normalized modulus M''/M''_{max} for the studied glasses measured at constant frequency, 25 kHz, is plotted in figure 7. Figure 7 shows that the relaxation behaviour of the normalized peaks is characterized by a single relaxation time. Furthermore, the full-width at half-maximum of the normalized modulus decreases with increasing Tl_2O_3 content. It is found [20] that there is a correlation between the concentration of the mobile ions or the conductivity and the breadth of the distribution of the relaxation times. As the concentration of the mobile ions and/or the conductivity increases, the broad peak width of M'' becomes wider [21–23]. In our glasses, the concentration of Li_2O is constant, see table 1. Therefore, the results obtained from figure 7 indicate, again, that Tl^{3+} ions enter the glass network as glass formers, causing a narrower distribution of the relaxation times by decreasing the conductivity.

5. Conclusions

In this paper, structural investigations by IR spectroscopy and molar volume determination and the electrical conductivities (DC and AC) are reported for lithium borate glasses containing Ti_2O_3 of composition $40\text{Li}_2\text{O} \cdot x\text{Ti}_2\text{O}_3 \cdot (60 - x)\text{B}_2\text{O}_3$, where x is varied in the range 0–25.

Analysis of the IR spectra shows that the formation of BO_4^- tetrahedral is not affected by the addition of Ti_2O_3 . Replacing B_2O_3 by Ti_2O_3 in such glasses increases the molar volume while the DC conductivity decreases and the associated activation energy increases. The electrical modulus results show that the peak width at half-maximum decreases with increasing Ti_2O_3 content.

On this basis, one can suggest that Ti_2O_3 enters the glass structure as a glass former and that Li_2O should associate both with Ti_2O_3 and with B_2O_3 to convert them into TlO_4^- and BO_4^- units. This formation of TlO_4^- units is responsible for the increase in molar volume and at the same time for blocking the glass structure by linkage to BO_4^- groups. Consequently the electrical conductivity decreases and the associated activation energy increases.

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