

# Effect of compositional changes on the structure and properties of alkali-alumino borosilicate glasses

H. DARWISH<sup>1</sup>, M. M. GOMAA<sup>2</sup>

<sup>1</sup>*Glass Research Department, National Research Centre, El-Behoos St., Dokki, Cairo, Egypt*

<sup>2</sup>*Geophysics Department, National Research Centre, El-Behoos St., Dokki, Cairo, Egypt*

The effect of replacing BaO by SrO or Al<sub>2</sub>O<sub>3</sub> by MgO on the structure and some physical properties of the glasses of the system Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-(SrO)BaO-(MgO)Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>—containing TiO<sub>2</sub> have been investigated. Fourier transform infrared (FTIR) spectroscopy revealed that the addition of SrO at the expense of BaO gives no changes in the main structural building units. The addition of MgO instead of Al<sub>2</sub>O<sub>3</sub> decreases the fraction of BO<sub>3</sub> and increases the fraction of BO<sub>4</sub> groups.

Dilatometric measurements showed that the thermal expansion coefficients ( $\alpha$ -values) were increased by gradual addition of SrO or MgO instead of BaO or Al<sub>2</sub>O<sub>3</sub>, respectively, however the transformation ( $T_g$ ) and softening ( $T_s$ ) temperature values of the glasses were decreased. The density was found to decrease as SrO/BaO or MgO/Al<sub>2</sub>O<sub>3</sub> replacements increased.

The conductivity, dielectric constant and dielectric loss (dielectric constant  $\times$  loss tangent) of the glasses were investigated using the frequency response in the interval 200 Hz–100 KHz and the effect of compositional change on the measured properties was investigated. Measurements showed that the electric responses of samples were different and complex. The addition of SrO instead of BaO generally, increases the conductivity, dielectric constant and dielectric loss of the glasses. Increasing the MgO at the expense of Al<sub>2</sub>O<sub>3</sub>, the conductivity and dielectric constant of the glasses were decreased. However, the dielectric loss was increased.

The electrical properties were found to be factors that are able to distinguish the various electrical parameters as a result of the change in composition. The obtained data were correlated to the internal structure of the glasses and the nature and role played by glass forming cations. © 2006 Springer Science + Business Media, Inc.

## 1. Introduction

Alkaline earth alumino borosilicate glasses make up a large important group of materials, with a wide range of commercial applications. Knowledge of these glasses and melt structures are critical to understanding their chemical and physical properties and to wisely direct investigations of new materials [1].

Alkali [M<sup>+</sup>] or alkaline earth [M<sup>2+</sup>] cations act as network modifiers in the glass structure, breaking bridging oxygen bonds to form non-bridging oxygens (NBO) and residing in sites interstitial to the tetrahedral network in the vicinity of the negatively charged NBOs [1].

Aluminum acts as a network former in peralkaline compositions, replacing Si in tetrahedral coordination.

Peralkaline compositions are those in which the number of moles of Al is less than the total charge due to monovalent and divalent cations, i.e.  $[Al] < [M^+] + 2[M^{2+}]$ . The net negative charge due to this substitution is neutralized by a nearby network modifier. Charge balancer is a more appropriate name for cations in this structural role. Alkali or alkaline earth cations can obviously act as either charge balancer or network modifier in the same glass, balancing all the tetrahedral Al with the excess serving to depolymerize the structure [1].

Fourier Transform Infrared Spectroscopy, FTIR, has been widely applied to the interpretation of the structural modifications occurring in glasses [2–3]. Analysis of the vibrational spectra however can provide

structural information when a thorough analysis of the data is carried out [4]. Some authors [4–5] applied FTIR spectroscopy to aluminium borosilicate and sodium-silicate glass systems showing that the peak shift appears to be a sensitive tool for detecting the early stage of glass-in-glass phase separation induced by heat-treatment.

Hill *et al.* [5] revealed that substituting strontium for calcium has little influence on the structure of the glass and this is probably a result of the identical charge of the ions and their similar size. Strontium is suppressing the amorphous phase separation that is known to occur in the strontium free glass. Strontium is substituted for calcium to give the cements radio-opacity.

The wide variety of properties of glasses led to the wide interest in the investigation of physical and chemical properties of glasses and their composition dependence. The main reason for the interest in dielectric measurements of materials probably lies in the possibility of investigating their physical properties in a non-destructive, rapid, accurate manner and at a relatively low cost. Although no adequate models exist to explain experimental observations in detail, it is universally accepted that the dielectric and electrical transport properties of materials depend on the dielectric constant and conductivity of sample and its constituents. One of the properties that affect the electrical response of aluminoborosilicate glass is its connectivity or the bond strength [6–9].

Several dielectric mechanisms or polarization effects contribute to electrical properties response: electronic, atomic, dipole and interfacial (or Maxwell-Wagner) polarization. The first three mechanisms are always activated in the studied frequency range, providing a constant contribution to electrical properties response; whereas the Maxwell-Wagner (MW) polarization is frequency dependent [7–11]. Heterogeneity of samples governs the dielectric response in the MW polarization frequency range. Different dielectric behaviour is therefore found, depending on the composition of the samples and the used frequency range. These differences originate from the different distribution of charges in the samples. In D. C. case, free ions are responsible for the conductivity [9–13].

The electrical conductivity of a glass melt depends on the mobility of the mass particles, which increases with temperature. The particles must overcome the potential barriers between vacancies. The transfer of electrical current is provided primarily by the ions of monovalent alkali metals and, in alkali-free glass, e.g. The E-glass for fibres, by ions of bivalent alkaline earths. Element with a large effective radius (e.g., Ba) blocks the movement of alkali metal ions and suppress electrical conductivity [12] and reduces the dielectric loss. The dielectric loss factor is given by the product of dielectric constant and loss tangent [13].

The aim of the study was to verify the presence of systematic differences in the structure and some physical properties like thermal expansion,  $T_g$ ,  $T_s$ , density, and electrical characteristics of some alkali-alumino borosilicate glasses as a function of the change in compositions.

## 2. Experimental

The chemical compositions of the glasses are given in Table I. Analytical grade powders of  $\text{Li}_2\text{CO}_3$ ,  $\text{BaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{MgCO}_3$ ,  $\text{H}_3\text{BO}_3$  and  $\text{SiO}_2$  were used for the preparation of these glasses.  $\text{TiO}_2$  was added in amount of 10 g over 100 wt% of batch to decrease the viscosity of the glass melts. Calculated amounts of these powders were mixed and melted in Pt-2%Rh crucibles in an electric furnace with SiC heating elements at  $1350^\circ\text{--}1400^\circ\text{C}$  for 4 hrs. Melting was continued until a clear homogeneous melt was obtained; this was achieved by swirling the melt several times at about 30 min intervals. The melt was cast into rods and as buttons, which were then properly annealed in a muffle furnace at  $650^\circ\text{C}$  for 1 hour then cooled at a rate of  $1^\circ\text{C}/\text{min}$  to room temperature to minimize the strain.

The density ( $d$ ) of glass (at room temperature) was determined by the Archimedes method. The weight of glass samples was determined both (a) in air and (b) when immersed in xylene at  $25 \pm 2^\circ\text{C}$ . The density was calculated according to equation (1):

$$d = [(a)/(a - b)] \cdot [0.86] \quad (1)$$

where 0.86 is the density of xylene at  $25^\circ\text{C}$ .

TABLE I Composition of the studied glasses

| Glass no.      | $\text{Li}_2\text{O}$ | Composition of the glasses (mole%) |                         |                        |                |     | $\text{MgO}$ | Additive<br>+ $\text{TiO}_2$ | Thickness<br>(mm) | Diameter<br>(mm) |
|----------------|-----------------------|------------------------------------|-------------------------|------------------------|----------------|-----|--------------|------------------------------|-------------------|------------------|
|                |                       | BaO                                | $\text{Al}_2\text{O}_3$ | $\text{B}_2\text{O}_3$ | $\text{SiO}_2$ | SrO |              |                              |                   |                  |
| G <sub>1</sub> | 20                    | 10                                 | 10                      | 10                     | 50             | –   | –            | 10 g                         | 4.1               | 15.5             |
| G <sub>2</sub> | 20                    | 7                                  | 10                      | 10                     | 50             | 3   | –            | 10 g                         | 5.0               | 29.6             |
| G <sub>3</sub> | 20                    | 5                                  | 10                      | 10                     | 50             | 5   | –            | 10 g                         | 5.0               | 14.0             |
| G <sub>4</sub> | 20                    | –                                  | 10                      | 10                     | 50             | 10  | –            | 10 g                         | 4.7               | 19.0             |
| G <sub>5</sub> | 20                    | –                                  | 7                       | 10                     | 50             | 10  | 3            | 10 g                         | 5.0               | 26.7             |
| G <sub>6</sub> | 20                    | –                                  | 5                       | 10                     | 50             | 10  | 5            | 10 g                         | 5.8               | 16.5             |
| G <sub>7</sub> | 20                    | –                                  | –                       | 10                     | 50             | 10  | 10           | 10 g                         | 4.9               | 18.0             |

The density of the glasses at 300 °C could be calculated dependent on the coefficient of volume expansion  $\beta \approx 3\alpha$  [12] (below T<sub>g</sub>) according to the equation (2):

$$d_t = d_{25}/1 + 3\alpha(t - 25) \quad (2)$$

Dilatometric measurements were performed using Linseis L76/1250 Dilatometer. The glass samples were prepared by cutting the glass into rectangular slabs of 1.5 cm length and 0.5 cm thickness with exactly parallel two surfaces. The sample was fixed in its position in the Dilatometer, and then heated starting from the room temperature with a rate of 5 °C/min. The thermal expansion coefficient was measured up to 300 °C. The linear thermal expansion coefficient ( $\alpha$ ) was automatically calculated using the general equation (3):

$$\alpha = (\Delta L/L) \cdot (1/\Delta T) \quad (3)$$

where: ( $\Delta L$ ) is the increase in length, ( $\Delta T$ ) is the temperature interval over which the sample is heated and ( $L$ ) is the original length of the specimen.

FTIR transmittance spectra of the powdered glasses were measured in the range 2000–400 cm<sup>-1</sup> using the KBr-pellet method at room temperature. A recording spectrophotometer type, Jasco FTIR-300E (Japan) was used.

The electrical conductivity, dielectric constant, and loss tangent of all the samples were measured using alternating current measurements analyzing their dependence on the frequency. The complex impedance of the samples was measured in the frequency range 200 Hz–100 KHz at room temperature, using a Hioki 3528–50 LCR Hitester Impedance Analyzer. A voltage of 1V was applied. All the analyzed samples were disk shaped with different diameters and thicknesses as shown in Table I. The sample to be analyzed is placed between parallel stainless steel plates of a flat capacitor (Agilent dielectric test fixture 16451B) and connected to the Impedance Analyzer (four leads). All the samples are measured at room temperature at completely dry state. The Impedance Analyzer measures the total impedance ( $Z_T$ ) of the equivalent circuit.  $Z_T$  is the sum of two contributions in series: the impedance  $Z_C$ , which accounts for the capacitance of the cell and of the inter-connecting wires, and the series impedance  $Z_L$  of the inter-connecting system.  $Z_L$  may be measured directly by short-circuiting the cell.  $Z_C$  is then calculated by the difference ( $Z_T - Z_L$ ) [6–11].

### 3. Results

#### 3.1. FTIR spectra

Fig. 1 represents the FTIR spectra of the investigated glasses. The IR spectrum of the base glass G<sub>1</sub> showed six main bands. Bands located at about 410, 464 and 711 cm<sup>-1</sup> are detected together with a stronger broad band located at about 996 cm<sup>-1</sup> and a small shoulder

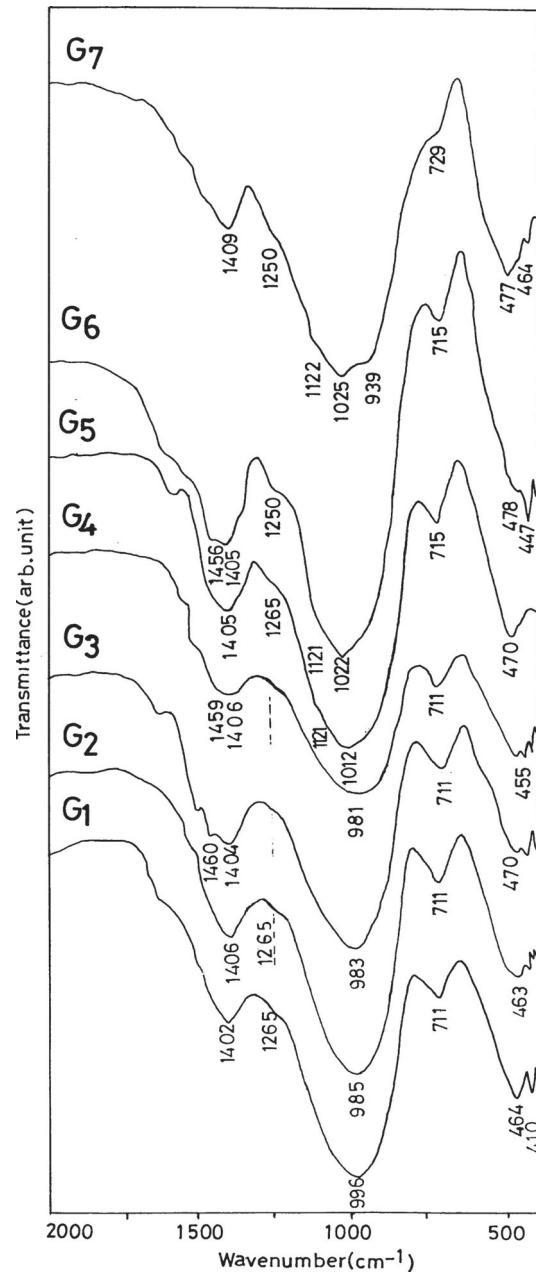


Figure 1 FTIR spectra of the studied glasses.

band located at 1265 cm<sup>-1</sup>. Another band was recorded at about 1402 cm<sup>-1</sup>. Fig. 1 also revealed that the gradual addition of SrO at the expense of BaO in glasses (G<sub>2</sub>–G<sub>4</sub>) gives no change in the spectra i.e., the IR spectra of the modified glasses reveals that the same bands of glass G<sub>1</sub> are repetitive at the same wavenumbers.

The addition of MgO instead of Al<sub>2</sub>O<sub>3</sub> in the glasses G<sub>5</sub>–G<sub>7</sub> (free of BaO) led to the following conclusions:

(a) the band located at 711 cm<sup>-1</sup> was decreased and shifted to higher wavenumber.

TABLE II The thermal expansion coefficient and the density values of the investigated glasses at different temperatures

| Glass no.      | Expansion coefficient $\times 10^{-7} \text{ } ^\circ\text{C}^{-1}$ |        |        |        | $T_g$ °C | $T_s$ °C | $d_{25^\circ\text{C}}$<br>( $\text{g cm}^{-3}$ ) | $d_{300^\circ\text{C}}$<br>( $\text{g cm}^{-3}$ ) |
|----------------|---------------------------------------------------------------------|--------|--------|--------|----------|----------|--------------------------------------------------|---------------------------------------------------|
|                | 25–100                                                              | 25–200 | 25–300 | 25–400 |          |          |                                                  |                                                   |
| G <sub>1</sub> | 83                                                                  | 84     | 89     | 91     | 470      | 493      | 2.82                                             | 2.799                                             |
| G <sub>2</sub> | 84                                                                  | 85     | 90     | 92     | 464      | 491      | 2.80                                             | 2.779                                             |
| G <sub>3</sub> | 86                                                                  | 88     | 91     | 93     | 463      | 487      | 2.78                                             | 2.759                                             |
| G <sub>4</sub> | 87                                                                  | 89     | 92     | 94     | 461      | 485      | 2.75                                             | 2.729                                             |
| G <sub>5</sub> | 90                                                                  | 91     | 93     | 96     | 459      | 484      | 2.74                                             | 2.721                                             |
| G <sub>6</sub> | 91                                                                  | 93     | 95     | 99     | 458      | 482      | 2.73                                             | 2.709                                             |
| G <sub>7</sub> | 92                                                                  | 95     | 99     | 107    | 451      | 480      | 2.72                                             | 2.697                                             |

(b) the band located at about  $981 \text{ cm}^{-1}$  in G<sub>4</sub> was shifted to higher wavenumber with the appearance of small shoulder bands located at about  $1121 \text{ cm}^{-1}$  and  $1250 \text{ cm}^{-1}$  (G<sub>5</sub> – G<sub>7</sub>) and another shoulder band was appeared at  $939 \text{ cm}^{-1}$  in G<sub>7</sub> only.

### 3.2. Thermal expansion

Table II and Fig. 2 clearly indicated that the addition of SrO or MgO at the expense of BaO or Al<sub>2</sub>O<sub>3</sub>, respectively, resulted in an increase in the thermal expansion coefficients (i.e.  $\alpha$ -values) and a decrease in both the glass transition ( $T_g$ ) and softening ( $T_s$ ) temperature values of the glasses.

### 3.3. The density

It is shown that the systematic replacements of BaO by SrO or MgO by Al<sub>2</sub>O<sub>3</sub> caused a monotonic decrease in the density as shown in Table II.

It was also noted that the calculated density at high temperature (300 °C) was lower than that obtained at room temperature (25 °C) i.e., the density values were decreased at high temperature (below  $T_g$ ), Table II.

### 3.4. Electrical properties

Figs. 3 and 4 show the conductivity and dielectric constant of the samples as a function of frequency. From the study of the plots, it can be noticed to what limit

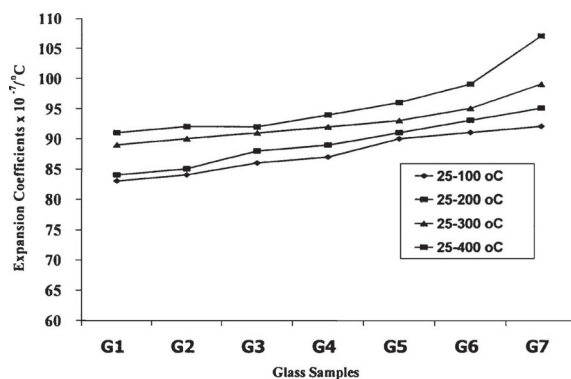


Figure 2 The thermal expansion coefficients of the studied glasses.

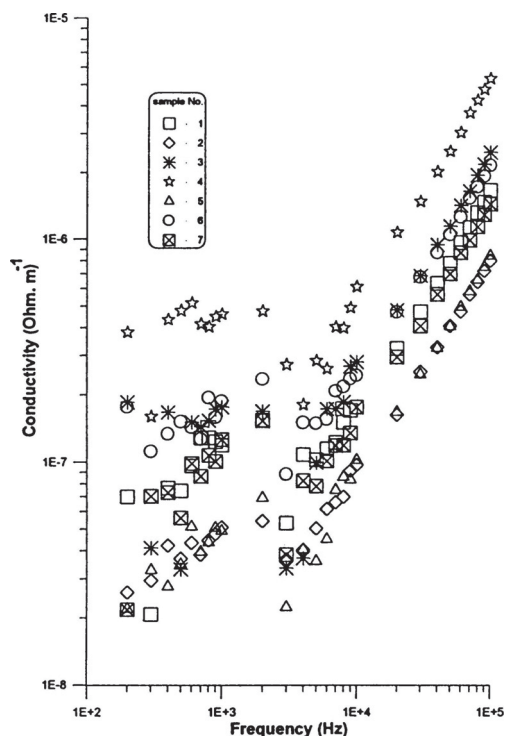


Figure 3 The conductivity of the samples as a function of frequency.

the change of composition clearly affects the electrical properties of the samples that were analyzed.

The loss tangent is another parameter, which makes it possible to distinguish between samples of different compositions. The loss tangent is defined as  $\tan(\delta) = \epsilon''/\epsilon'$ , and it is related to the ratio of the energy dissipated per radian in the material ( $\epsilon''$ ) to the energy stored ( $\epsilon'$ ) at the peak of polarization by the electric field. The behaviors of  $\tan(\delta)$  as a function of frequency for some samples of glass are shown in Fig. 5.

The present results revealed that an increase in the SrO content from 0 to 10 mole% instead of BaO in the glasses G<sub>1</sub>–G<sub>4</sub>, could increase the conductivity, dielectric constant and loss tangent. The sample G<sub>4</sub> show significantly high values of conductivity, dielectric constant ( $\sim 400$ ) at 200 Hz and loss tangent. However, the decrease in the Al<sub>2</sub>O<sub>3</sub> content from 10 to 0

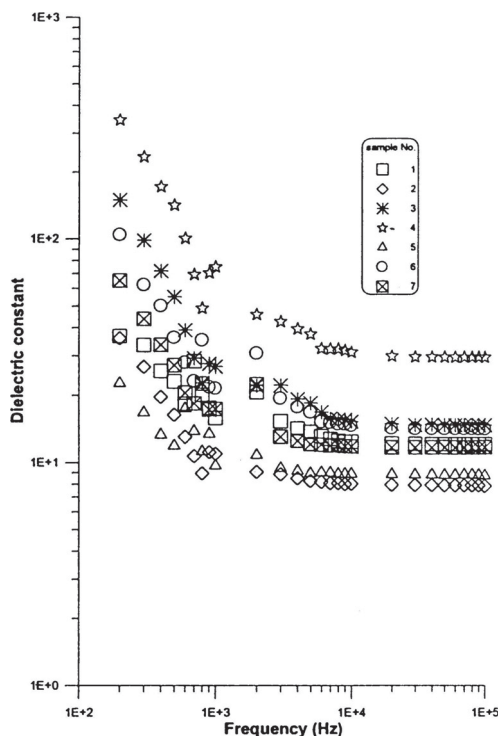


Figure 4 The dielectric constant of the glasses as a function of frequency.

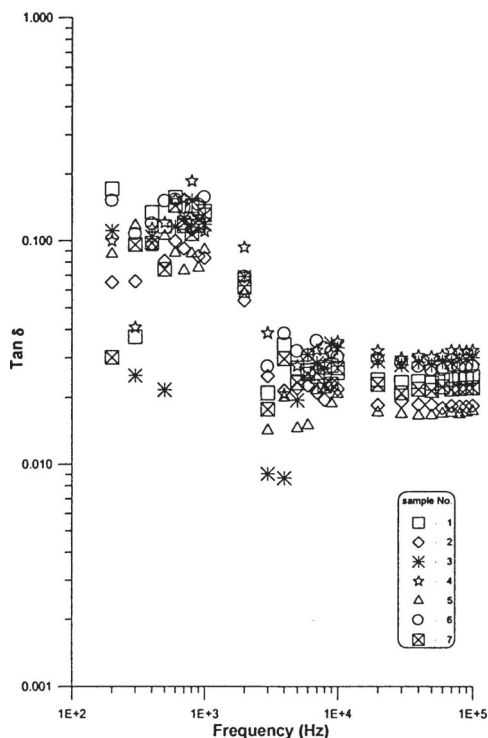


Figure 5 The log-log plot of the loss tangent as a function of frequency of the glasses.

mole% by increasing MgO, led to decrease in both the conductivity, dielectric constant and loss tangent values of the glasses G<sub>5</sub>–G<sub>7</sub>.

#### 4. Discussion

A discussion of the property trends found must take into account the effects of both atomistic and microstructural changes with composition. Therefore, it might be helpful to explain first, the FTIR spectra in order to correlate their indications with the other property trend.

The FTIR spectrum of the base glass (G<sub>1</sub>) is composed of six main bands characteristic of the silicon-oxygen and boron-oxygen networks. The bands at 410–478 cm<sup>-1</sup> are due to the Si–O–Si asymmetric bending vibrations [14–15].

The band located at 711 cm<sup>-1</sup> is attributed to oxygen between two trigonal BO<sub>3</sub> groups [16]. The region of 990–1200 cm<sup>-1</sup> can arise from the overlapping contributions of silicate and borate groups. It was not possible to separate the individual contributions in this region [17]. The strong broad band located at 996 can be seen to consist of overlapping contributions of the Si–O–Si and B–O–B vibrations modes i.e., it is attributed to Si–O–Si asymmetric bond stretching vibration [18] and B–O bonding vibration in BO<sub>4</sub> structural units [19].

On the other hand the bands located in the region between 1200 and 1600 cm<sup>-1</sup> are attributed to the B–O stretching vibration of BO<sub>3</sub> units [17] i.e., the shoulder located at 1265 cm<sup>-1</sup> is due to the stretching vibration of boroxol rings [20]. The band located at 1402 cm<sup>-1</sup> can arise from structural groups containing BO<sub>3</sub> units only [17]. The shoulder appeared at 939 cm<sup>-1</sup> is due to the B–O linkage of the BO<sub>4</sub> groups.

The present result revealed that the addition of SrO at the expense of BaO gives no changes in the main structural building units and the skeleton of the glass network remains the same and this is probably a result of the identical charge of the ions and their similar size.

The FTIR spectra revealed that the addition of MgO instead of Al<sub>2</sub>O<sub>3</sub> in the glasses G<sub>5</sub>–G<sub>7</sub> decreases the intensities of the bands located at 711 cm<sup>-1</sup>, 1265 cm<sup>-1</sup> and 1409 cm<sup>-1</sup> (characteristic for the BO<sub>3</sub> group) and shifted to higher wavenumbers. This indicated that the fractions of BO<sub>3</sub> units were decreased. However, the appearance of band located at 939 cm<sup>-1</sup> (characteristic for the BO<sub>4</sub> group [21]) in G<sub>7</sub> (free of Al<sub>2</sub>O<sub>3</sub>) and the increase of the intensity of the band located at 1025 cm<sup>-1</sup> indicated that the fractions of BO<sub>4</sub> units are increased. Measurements of the intensity ratio between the BO<sub>4</sub> and BO<sub>3</sub> bands  $I_{1025} : I_{1409}$  (Fig. 1), which increases with increasing MgO at the expense of Al<sub>2</sub>O<sub>3</sub>, indicated that the BO<sub>3</sub> structural units are transformed into BO<sub>4</sub> units.

It is known that [22], the structure of borate and borosilicate glasses is greatly affected by the addition

of  $\text{Al}_2\text{O}_3$  content. The infrared spectra of borate glasses show that the intensities of bands in the area  $900\text{--}1100\text{ cm}^{-1}$  decrease with increasing  $\text{Al}_2\text{O}_3$  content, indicating a decrease in the concentration of  $\text{BO}_4$  units. It was known also that the addition of  $\text{Al}_2\text{O}_3$  to alkali borosilicate glasses reduces both the number of non-bridging oxygens and the number of  $\text{BO}_4$  units [22].

In the present work, it could be concluded that the addition of  $\text{MgO}$  instead of  $\text{Al}_2\text{O}_3$  decreases the fraction of  $\text{BO}_3$  and increases the fraction of  $\text{BO}_4$  groups.

#### 4.1. Thermal expansion

The increase in the thermal expansion of the glass in the transformation range was attributed by Wely and Marboe [23] to the formation of defects such as vacant anion sites or incomplete coordination. These defects introduce asymmetries into the short range of glasses and increase the thermal vibration. In the transformation range, glass behaves as a plastic material.

The thermal expansion of glass is not only a function of temperature but also depends, among other factors, on composition. The thermal expansion is also sensitive to the structure of the glass, e.g., degree of polymerization, type of structural units, the nature and contribution of the different cations, whether they occupy forming or modifying positions in the glass network [24].

The thermal expansion may be related to the internal structural and to the number and size of the ionic aggregates [25]. The nature of the particular cations should be also taken into consideration. The bond strength and character were suggested to govern the thermal expansion [26]. The open, less rigid or loosely compact nature of the structure favours the increase in thermal expansion. Also, the replacement of a cation with another of lower bond strength will increase the thermal expansion coefficient. The binding energy increases with increasing valency and decreasing size of the atom [26–27]. The thermal expansion is also assumed to increase with increasing ionic character of the bonding.

The addition of  $\text{SrO}$  to replace  $\text{BaO}$  of the present glasses ( $G_1\text{--}G_4$ ) slightly increases the thermal expansion coefficient and decreases both  $T_g$  and  $T_s$  values of the studied glasses, and this is probably a result of the identical charge of the ions and their similar size. It may be suggested therefore, that the  $\text{Sr}^{2+}$  possesses relatively lower single-bond strength with oxygen ( $32\text{ kcal mole}^{-1}$ ) [26] compared with that of  $\text{Ba}^{2+}$  ( $33\text{ kcal mole}^{-1}$ ) [26]. Therefore, the thermal expansion coefficient of the glasses is then slightly increased and the decrease in both  $T_g$  and  $T_s$  values could be expected.

The formation of  $\text{BO}_4$  groups at the expense of  $\text{BO}_3$  groups in glasses  $G_5\text{--}G_7$  can be explained on the basis that the lithia is assumed to donate its oxygen to form  $\text{BO}_4$  groups, thus the negative charge is also assumed to be in the boron ion, and not more on the oxygen ion. Thus, the lithium ion is loosely bound to the boron

with heteropolar bond, which is much weaker than the lithium-oxygen bond facilitating its higher mobility. At the same time, the network coherence and viscosity are increased as a result of the strengthening of the network by the formation of  $\text{BO}_4$  groups. Therefore, the two changes may cancel each other [28] i.e., the effect of  $\text{B}_2\text{O}_3$  on the measured physical properties is constant in the glasses  $G_5\text{--}G_7$ .

As previously mentioned, Kim and Bray [29] reported that both  $\text{MgO}$  and  $\text{Na}_2\text{O}$  behave as network modifiers for  $\text{MgO}$  content smaller than 15 mole%. Therefore, on increasing the  $\text{MgO}/\text{Al}_2\text{O}_3$  replacements ( $G_5\text{--}G_7$ ), the increase in the expansion coefficients of the glasses and the decrease in both  $T_g$  and  $T_s$  values are expected. This could be explained on the basis that on increasing the  $\text{MgO}/\text{Al}_2\text{O}_3$  replacements led to decrease the amount of  $\text{AlO}_4$  tetrahedra i.e. the numbers of non-bridging oxygen ions could be relatively increased which led to a more open and less strongly bonded network that tend to cause an increase in the thermal expansion coefficients of the glasses.

#### 4.2. The density

Density responds to variations in glass composition sensitively in technological practice. Density of glass, in general, is explained in terms of a competition between the masses and sizes of the various structural groups present in glass. Accordingly, the density is related to how tightly the ions and ionic groups are packed together in the substructure. [12]. The decrease in density observed as  $\text{SrO}$  and  $\text{MgO}$  (of lower single-bond strength with oxygen) systematically replaces  $\text{BaO}$  and  $\text{Al}_2\text{O}_3$  (of higher single-bond strength with oxygen), respectively, could be reasonably understood in terms of the decrease of both average atomic mass and single-bond strength of the cations.

#### 4.3. Electrical properties

The electrical properties of the studied glass samples were investigated using the frequency response in the interval  $200\text{ Hz--}100\text{ KHz}$  and the effect of change in composition on the measured properties was investigated. Samples were tested and showed markedly different responses.

The electrical properties of glasses are also markedly dependent on the chemical compositions. This is expected as a result of changing the spatial arrangements of the network forming structural units and the available interstices and cavities, and hence the change of the ease of jumping of the migrating ions between different sites. Generally, the electrical conductivity and dielectric constant are directly proportional to the number of free or bond charge carriers as well as their mobility. For the latter, it is not only their valence and size that are decisive but also the compactness of the network, which changes with the concentration of alkali contents [30].

Zarzycki [26] revealed that the largest increase of the resistivity is observed for CaO, BaO and B<sub>2</sub>O<sub>3</sub>, which consolidate the network and thus reduce the mobility of alkali ions.

The present results showed that the electrical responses of the samples were complex. The conductivity, dielectric constant and loss tangent were found to be factors that are able to distinguish the various electrical parameters as a result of the change in composition. The samples show significantly high values of dielectric constant (~400) at 200 Hz that may correspond to the accumulation of space charges at the broken bonds and/or to the broken chains and/or to the band shift to higher wavenumbers.

Dielectric investigations provide a fundamental basis for studying the rotational and hopping electron processes involved in conduction. They also account for the dispersion behaviour associated with the molecular configuration and its ordering as it affects the conductivity behaviour [31]. Values of the dielectric constant could be explained qualitatively by assuming a decrease in the band energies. Relaxation phenomena are associated with the frequency dependence of orientational polarization and hence with polar dielectric substances. In static or slowly varying fields, the permanent dipoles align themselves along the field acting upon them and thus contribute fully to the total polarization of the dielectric [32].

Glasses with high dielectric constant and low dispersion with frequency are desirable for some other technological applications. It is being argued that a large dielectric dispersion with frequency in conducting glasses is mainly due to the interaction among mobile ions. The ionic conductivity in alkali silicate glass arises largely because of mobile alkali ions [33].

Glass containing larger alkali content exhibits lower dielectric constant. It is likely that as the concentration of total mobile ions increases the alkali-alkali distance is reduced, thereby increasing the interaction between them [34]. Such an increase in interaction among mobile ions could possibly reduce the dipole-dipole interaction, leading to a reduction in the dielectric constant [35]. Further, it is seen that the dielectric dispersion, which is the variation of dielectric constant over the measured frequency range, is less than 3% at high frequencies as shown in Fig. 4. The present glass system with high dielectric constant at low frequencies and a low dielectric dispersion (at high frequencies) could be considered as a possible candidate for many applications. Availability of these charged particles increases the conductivity whereas the formation of space charge increases the dielectric constant.

The addition of SrO instead of BaO increases the conductivity and dielectric constant of the glasses G<sub>1</sub>–G<sub>4</sub>. This can be explained on the basis that the addition of SrO reduces the consolidation of the network caused by BaO in the glasses and thus increases the mobility of

Li<sup>+</sup> ions. Also, the presence of Al<sub>2</sub>O<sub>3</sub> in the glasses increases the mobility of Li<sup>+</sup> ions by suppressing non-bridging oxygens and forming Al-O-Al bridges, which do not restrain the alkali metal cations as much [26].

However, on increasing the MgO/Al<sub>2</sub>O<sub>3</sub> replacements led to decrease the amount of AlO<sub>4</sub> tetrahedra i.e. the numbers of non-bridging oxygen ions could be increased giving more occasion for self-trapping of the Li<sup>+</sup> ions. This could cause a decrease of Li<sup>+</sup> ions mobility and led to decrease in the conductivity and dielectric constant of the glasses G<sub>5</sub>–G<sub>7</sub>.

It could be concluded that there is a small deviation in the values of the measured electrical properties of the glass samples. This may be attributed to the fact that the studied glasses are composed of a random-network structure.

The dielectric loss factor which is given by the product of dielectric constant and loss tangent [13] is affected by the presence of a large ion such as barium, and is particularly effective in reducing the losses since they tend to block the motion of the mobile alkali metal ion (Li<sup>+</sup>). The replacement of BaO by SrO tend to decrease the blocking action of barium and this led to increase the mobility of the mobile alkali metal ion (Li<sup>+</sup>) and increase the dielectric loss. Also, The replacement of MgO by Al<sub>2</sub>O<sub>3</sub> in the glasses led to a more open and less strongly bonded network that tend to cause an increase in the dielectric losses [13].

## 5. Conclusion

The effects of replacement of BaO by SrO or Al<sub>2</sub>O<sub>3</sub> by MgO on the structure and some physical properties of the glasses of the system Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-(SrO)BaO-(MgO)Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>—containing TiO<sub>2</sub> have been investigated.

FTIR spectroscopy revealed that the addition of SrO at the expense of BaO in the investigated glasses gives no changes in the main structural building units. However, the addition of MgO instead of Al<sub>2</sub>O<sub>3</sub> decreases the fraction of BO<sub>3</sub> and increases the fraction of BO<sub>4</sub> groups.

The obtained data of density and thermal expansion properties were correlated to the internal structure of the glasses, nature and role played by glass forming cations.

The electrical properties of the studied samples were investigated using the frequency response in the interval 200 Hz-100 KHz and the effect of change in composition on the measured properties was investigated. Samples were tested and showed markedly different responses.

The addition of SrO instead of BaO increases the conductivity and dielectric constant of the glasses. However, on increasing the MgO at the expense of Al<sub>2</sub>O<sub>3</sub>, the conductivity and dielectric constant of the glasses were decreased. The replacements of BaO by SrO or Al<sub>2</sub>O<sub>3</sub>

by MgO tend to increase in the dielectric losses. It could be concluded that the electrical properties of the samples are influenced by the distribution of its constituents, connectivity, and number of free charges.

## References

1. C. I. MERZBACHER and W. B. WHITE, *J. Non-Cryst. Solids* **130** (1991) 18.
2. Y. KATO, H. YAMAZAKY and M. TOMOZAWA, *J. Am. Ceram. Soc.* **84**(9) (2001) 2111.
3. S. FUJITA, Y. KATO and M. TOMOZAWA, *J. Non-Cryst. Solids* **328** (2003) 64.
4. J. WONG and C. A. ANGELL, *Glass structure by spectroscopy*, Marcel Dekker, New York, 1967.
5. R. G. HILL, A. STAMBOULIS, R. V. LAW, A. CLIFFORD, M. R. TOWLER and C. CROWLEY, *J. Non-Cryst. Solids* **336** (2004) 223.
6. M. M. GOMAA, S. A. HUSSAIN, E. A. EL-DIWANY, A. E. BAYOUMI and M. GHOBASHY, Renormalization group modeling of A. C. electrical properties of natural hematitic sandstone including texture effects, presented at the 69th annual international meeting: Society of Exploration Geophysics (SEG) and international Exposition, Session "Borehole/Rock Physics characterization of rock and fluid properties", Oral PHRP7, Oct. 31 Nov. 5, Houston, Texas (1999) pp. 204–207.
7. P. N. SEN, C. SCALA and M. H. COHEN, *Geophysics* **46**(5) (1981) 781.
8. W. E. KENYON, *Journal of Applied Physics* **55** (1984) 3153.
9. R. KNIGHT and A. NUR, *Geophysics* **52**(5) (1987) 644.
10. E. HASLUND, B. D. HANSEN, R. HILFER and COHENB. N. ST., *J. Applied Physics* **76** (1994) 5473.
11. B. NETTELBLAD and G. A. NIKLASSON, *J. Phys. Condens. Matter* **8** (1996) 2781.
12. M. B. VOLF, *Mathematical approach to glass*, *Glass Science and Technology*, Vol. 9, Elsevier Science Publishing Co., Inc., New York, 1988.
13. P. W. MCMILLAN, *Glass Ceramics*, Academic Press, London, (1979).
14. R. A. B. DEVINE, *J. Non-Cryst. Solids* **152** (1993) 50.
15. M. ROKITA, M. HANKE and W. MOZGAWA, *J. Mol. Struct.* **511/512** (1999) 277.
16. E. I. KAMITSOS, M. A. KARAKASSIDES and G. D. CHRYSIKOS, *J. Phys. Chem.* **91**(22) (1987) 5807.
17. K. EL-EGILI, *Physica B* **325** (2003) 340.
18. M. A. VILLEGAS and J. M. F. NAVARRO, *J. Non-Cryst. Solids* **100**(1–3) (1988) 453.
19. C. JULIEN, M. MASSOT, M. BALKANSKI, A. KROL and W. NAZAREWICZ, *Mater. Sci. Engng.* **B3** (1989) 307.
20. J. A. DEAN, *Analytical Chemistry Handbook*, McGraw-Hill, New York, Chapter 6, 1995.
21. E. I. KAMITSOS, M. A. KARAKASSIDES and G. D. CHRYSIKOS, *J. Phys. Chem.* **91** (1987) 1073.
22. W. L. KONIJNENDIJK, *Philips Res. Suppl.* **1** (1975).
23. W. A. WEYL and E. C. MARBOE, *The Constitution of Glasses, A Dynamic Interpretation*, Academic Press, N.Y., Vol. 1 (1962) 353.
24. A. A. AHMED, A. F. ABBAS and S. M. SALMAN, *Phys. Chem. Glasses* **36**(1) (1985) 17.
25. Z. STRNAD, *Glass-Ceramics Materials*, in *Glass Science and Technology*, Vol. 8, Elsevier, Amsterdam, The Netherlands (1986) p. 185.
26. J. ZARZYCKI, "Glass and Vitreous State", Cambridge Univ. Press, N.Y., Port Chester (1991).
27. P. W. MCMILLAN, In *Advances in Nucleation and Crystallization in Glasses*, Am. Ceram. Soc., Columbus, Ohio (1971).
28. M. M. A. SEKKINA, A. A. MEGAHED and I. A. GOHAR, *Glass and Ceramic Bulletin* **31**(1–4) (1984) 28.
29. K. S. KIM and P. J. BRAY, *Phys. Chem. Glasses* **17** (1976) 205.
30. M. A. KANEHISA, *J. Non-Cryst. Solids* **151** (1992) 155.
31. EL-DESOKY, *J. Phys. Chem Solids* **59**(9) (1998) 1659.
32. A. A. ZAKY and R. HAWLEY, *Dielectric Solid*, Routledge and Kegan Paul Ltd, London (1970) 37.
33. K. L. NGAI and C. LEON, *Phys. Rev. B* **60** (1999) 9396.
34. H. K. PATEL and S. W. MARTIN, *Phys. Rev. B* **45** (1992) 10292.
35. P. BALAYA, V. K. SHRIKHANDE, G. P. KOTHIYAL and P. S. GOYAL, *Current Science* **86**(4) (2004) 553.

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