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Electrical conductivity and relaxation frequency of lithium borosilicate glasses

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Abstract

Electrical conductivity of glasses from the system $0.40Li_2O{\cdot}0.60(xB_2O_3(1-x)Si_2O_4)$ $(0 \le x \le 1)$ were measured by impedance spectroscopy. The influence of the substitution of the first glass former by the second in electrical conductivity and in the parameters of the Arrhenius expression, i.e., activation energy and pre-exponential factor, is discussed. The electrical conductivity increases from the silica to the boron oxide region, with an anomaly at $x = 0.3$ but with no evidence of a mixed glass-former effect. The relaxation frequency, which is an intrinsic characteristic of each glass sample and is independent of geometrical parameters, was also deduced from impedance diagrams and are also presented for all compositions.

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Keywords: Electrical conductivity; Relaxation frequency; Impedance spectroscopy; Lithium conductor; Mixed former effect

1. Introduction

The ionic conductivity of glasses has been widely investigated in recent decades [1,2] and special attention has been devoted to lithium conductor glasses due to their applicability as solid electrolytes in lithium cells [3].The electrical conductivity of ionic glasses may be increased by dissolving halides or other salts in the glass structure [4,5] or by mixing a second glass former in an originally binary glass constituted by a glass-former and a glass-modifier. In fact, the non-additive increase in electrical conductivity, observed when a second glass-former is added to a binary glass, is known as mixed former effect [1]. The most classical and remarkable example of the mixed former effect was found at the borophosphate system [6] in which the conductivity of the most conductive ternary compositions are two orders of magnitude higher than that of the binary glasses. In this system, the binary compositions, lithium borate and lithium phosphate, present very similar electrical conductivities values. The mixed-former effect has also been found in other glass systems such as: silver borophosphate [7], lithium borotelurate [8] lithium silicatelurate [9] and lithium selenoborate [10]. However, if both binary glasses at the given system present very different electrical conductivities, a monotonic change (when the first former is substituted by the second one) of electrical conductivity with no maximum, may not be considered a mixed former effect.

Although the lithium borosilicate glasses are mentioned as an example of mixed former effect [1], increased electrical conductivity in this system has been observed only in rapidly quenched glasses with concentrations of lithium oxide >60 mol% [11]. Nevertheless, glasses containing smaller concentrations of Li_2O were investigated by Otto [12]. Although those results show an increase in electrical conductivity when SiO_2 is added to the $Li_2O.B_2O_3$ glasses, Otto did not present data for the entire glass system, precluding conclusions about the existence or absence of a mixed former effect.

This work deals with the electrical conductivity and relaxation frequency of glasses in the lithium borosilicate system containing 0.40 mol% of Li_2O. Silica was written as Si_2O_4 to ensure that two atoms of the boron former were substituted by two atoms of the silicon former, thus keeping constant the lithium concentration and the number of former atoms in the ternary system $0.40Li_2O{\cdot}0.60(x$-

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$B_2O_3(1-x)Si_2O_4$), with $0 \le x \le 1$. Impedance spectroscopy was employed to measure the electrical conductivity. The relaxation frequency was also extracted from impedance data. Electrical conductivity, relaxation frequency, activation energy and the pre-exponential factor of the Arrehnius equations of both properties were investigated as a function of the composition, i.e., the substitution of the first glass former by the second one. Some considerations about the impedance spectroscopy method are presented.

2. Determination of electrical conductivity and relaxation frequency by impedance spectroscopy

Impedance spectroscopy is a powerful tool when applied to the study of all mobile charges in ionic conductors and semiconductors. This alternating current method allows for the resolution of phenomena with different time constants, τ ($\tau = RC$, R being the resistance, C the capacitance of sample). Impedance spectroscopy, in particular, can resolve the sample resistance from electrode phenomena. Since glasses are homogeneous media, the impedance data of an ionic glass plotted in a Nyquist diagram (i.e., the opposite of the imaginary part of impedance in the y axis and the real part in the x axis), results in a single semicircle followed by a straight line due to the diffusion of ions in the electrode or to electrode polarization (Fig. 1). The resistance of the sample is read at the intersection of the semicircle with the x axis at low frequency. The conductivity (σ) is then calculated by the relation:

$$\sigma = (1/R) \times (l/A) \tag{1}$$

where l/A is the geometrical factor, l is the thickness and A the area of the electrode.

The relaxation frequency (f_r) may be understood as the relation between the electrical conductivity (σ) and the relative dielectric constant ε_s of the sample [13], following the expression:

$$f_r = \sigma/2\pi\varepsilon_s\varepsilon_0 \tag{2}$$

(ε_0 being the permittivity of the vacuum).

In the Nyquist diagram, the relaxation frequency is found at the apex of the semicircle (Fig. 1), and is the unique frequency which satisfies the relation:

$$\omega RC = 1 \tag{3}$$

where: $\omega = 2\pi f_r$.

It can be seen from expression (2) that the relaxation frequency is independent of the geometrical parameter of sample. Thus, it can be obtained, even if the sample's thickness or the area in contact with the electrode is not known.

The variation of relaxation frequency with temperature also follows an Arrhenius expression [16]:

$$f_r = f_{r0}\exp(-E_{f_r}/kT), \tag{4}$$

where f_{r0} = pre-exponential term, E_{f_r} = activation energy, and k and T have their usual meaning.

The impedance data obtained in this work were fitted according to a routine described by Kleitz and Kennedy [14], which calculates a samples' resistance by a minimum root mean square method and the relaxation frequency by a property pointed out by Cole and Cole [15]. The electrical sample's equivalent circuit is assumed to be a parallel RC circuit.

The activation energy of conduction, for temperatures under the glass transition, is calculated from the slope of the linear function obtained when the data are plotted against

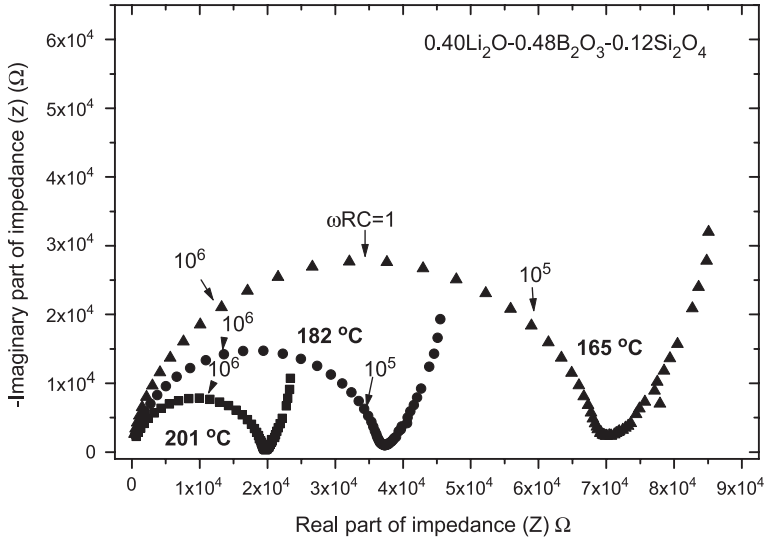

Fig. 1. Impedance data, in Nyquist diagram form, for the glass composition $x = 0.8$. Measurements were taken at indicated temperatures. Some frequency values (Hz) are given.

10^3/T. Since the relaxation frequency can also be fitted with an Arrhenius function [16], the same procedure is employed to obtain the activation energy of this property.

3. Experimental

3.1. Glass synthesis

The glass binary compositions, $0.40Li_2O{\cdot}0.60B_2O_3$ and $0.40Li_2O{\cdot}0.60Si_2O_4$, were melted in a platinum crucible, starting from lithium carbonate, silica reagent grade or boron oxide, previously melted to eliminate absorbed water. Appropriate amounts of the binary glasses were then melted to synthesize glasses with compositions $0 \le x \le 1$. The melting temperatures varied from 1250 to 900 °C when x increased from 0 to 1. The melted glasses were poured into a metal mold to form 14 mm diameter, 10–20 mm tall glass cylinders. These glass cylinders were then annealed at 420 °C (temperature that corresponds to T_g—30 °C) for 4–6 h to release internal stresses.

3.2. Electrical conductivity

Electrical conductivity measurements were taken of 2-mm-thick samples cut from the initial glass cylinder, with gold electrodes deposited on both faces. Measurements were carried out by impedance spectroscopy using an impedance analyzer (HP 4192A) in the 5 Hz–13 MHz frequency range, from 100 to 240 °C.

4. Results

The Arrhenius plot of electrical conductivity and relaxation frequency for all the samples studied is shown in Fig. 2. All Arhenius functions were fit to the data with correlation coefficients >0.9995. As expected, both properties had the same activation energy, taking into account the errors (Fig. 3). Both activation energy of the electrical conduction and the relaxation frequency, decreases with increasing x, after a maximum for the composition $x = 0.3$ (Fig. 3). Fig. 4 shows the influence of the composition on the pre-expo-

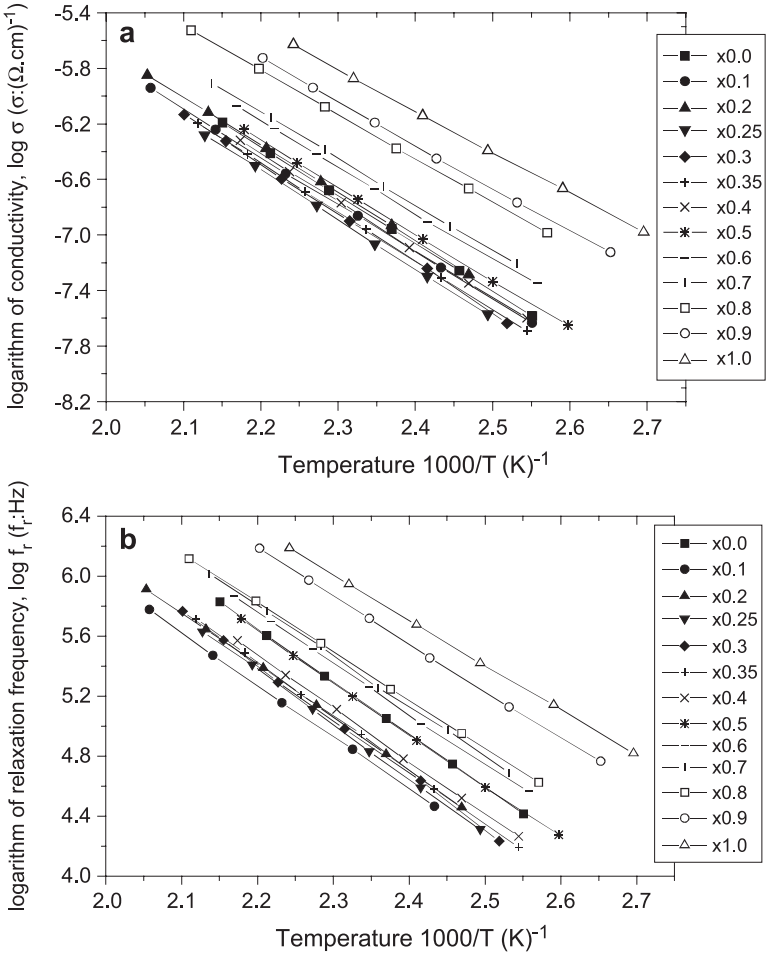

Fig. 2. Arrhenius plot of electrical conductivity (a) and relaxation frequency (b). The solid lines represent a linear regression analysis of the experimental data points. All the correlation coefficients are above 0.9995.

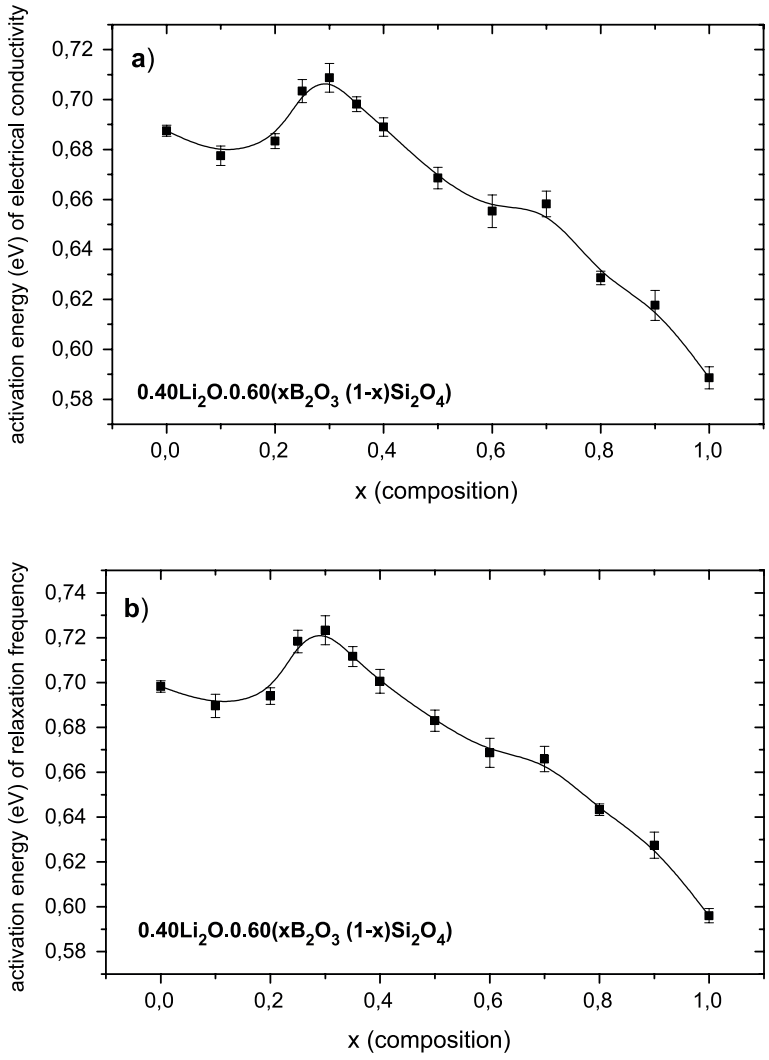

Fig. 3. Activation energy of electrical conduction (a) and relaxation frequency (b) as a function of glass composition. The lines serve as guides for the eyes.

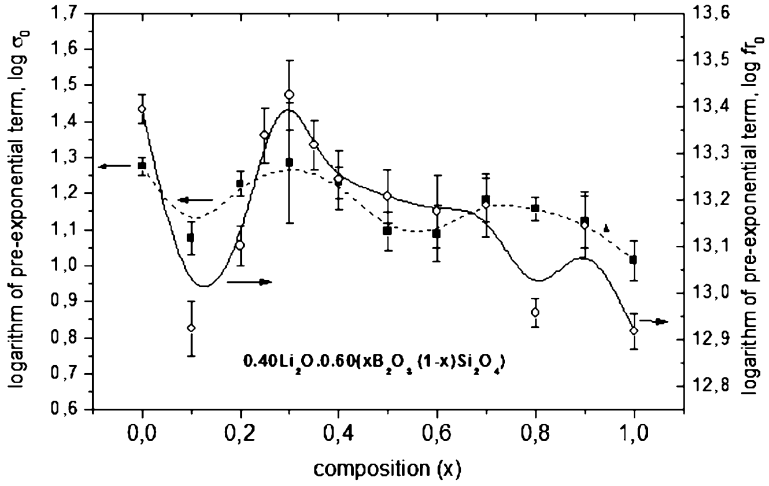

Fig. 4. Pre-exponential term of the Arrhenius expression of the electrical conductivity (σ_0) and of the relaxation frequency (f_{r0}), as a function of glass composition (x). The lines serve as guides for the eyes.

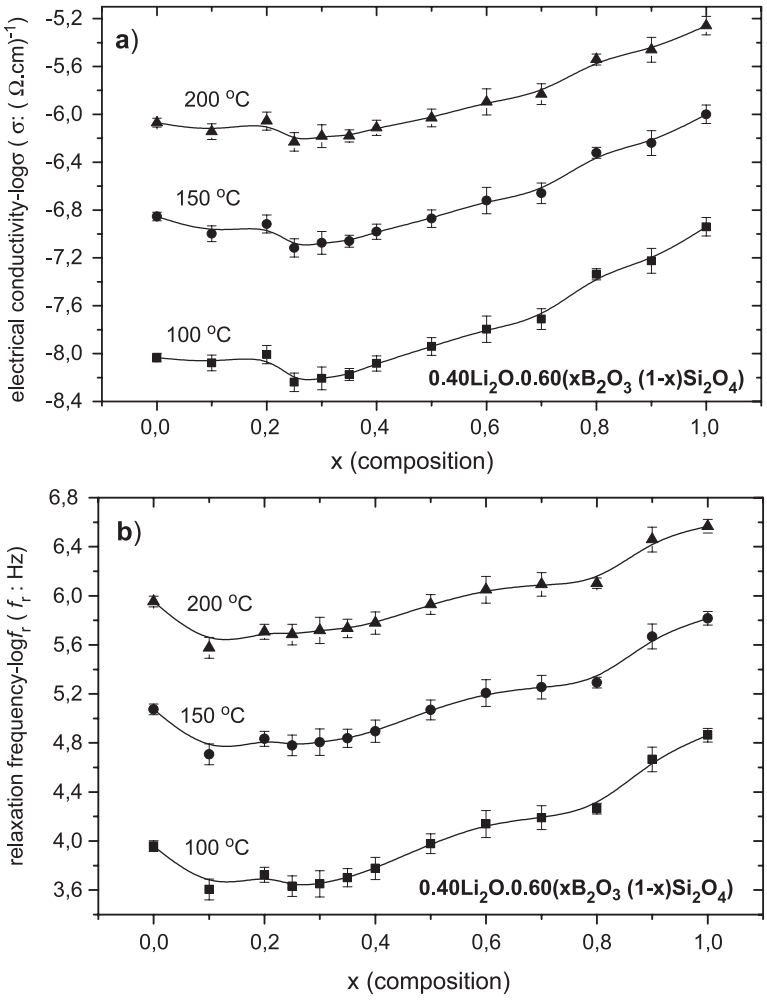

Fig. 5. Variation of electrical conductivity (a) and relaxation frequency (b) with glass composition, at different temperatures. The lines serve as guides for the eyes.

nential factors. In this case, too, both properties have the same variation and tend to decrease with the increase of x. Finally, Fig. 5 illustrates the isothermal variation of electrical conductivity and relaxation frequency; once again, both have similar temperature dependencies.

5. Discussion

It is well established that alkali oxides introduce non-bridging oxygen into the silica tetrahedra group in silicates glasses. On the other hand, alkali borate glasses are structured by planar BO_3 triangles, which can be transformed to BO_4 tetrahedra with increasing alkali content. This change in boron coordination, known as "boric anomaly" is reverted with increased alkali content. As in borate glasses, the addition of alkali to borosilicate glasses causes the formation of four-coordinated BO_3 groups, which competes with non-bridging oxygen formation in the SiO_4 tetrahedra [17]. In fact, the structure of alkali borosilicate glasses is composed of SiO_4 units with zero, one, or two non-bridging oxygens [18], boroxol rings consisting of BO_3 triangles and six-rings with one or two non-bridging BO_4 groups [17].

Fig. 5 shows that, despite these complex structural variations, the electrical conductivity in the $0.40Li_2O{\cdot}0.60(xB_2O_3(1-x)Si_2O_4)$ glass system shows a constant increase in electrical conductivity from the silica-rich to the boron-rich area in the graph, with only an anomaly at $x=0.3$. Since no glass composition in the system presents higher electrical conductivity than the most conductive binary glass ($0.40Li_2O{\cdot}0.60B_2O_3$), there is evidence, here, of the nonexistence of a mixed former effect in this glass system. It is worth noting that the mixed former effect has only been observed in rapidly quenched borosilicate glasses containing large amounts (>0.60 mol%) of lithium oxide [11].

The relaxation frequency, which is an intrinsic characteristic of the material, presents the same variation as the electrical conductivity. The variation in activation energy of both properties focused on here shows a maximum in the $x=0.3$ composition. This maximum

was confirmed by melting close compositions having $x=0.25$ and $x=0.35$, which have also been characterized (Figs. 3–5). After this maximum, the activation energy decreased with further increases of the B_2O_3 content in the glass. The pre-exponential term of both electrical conductivity and relaxation frequency shows a tendency to decrease with increasing x (Fig. 4), indicating the importance of this parameter, which should be investigated in greater detail even though some authors consider it constant [19].

Another aspect revealed by the results presented in Figs. 3–5 is the connection between the behavior of the electrical conductivity and its parameters and the relaxation frequency and its corresponding parameters. The relaxation frequency has the advantage of being independent of geometrical parameters and is easily applicable, for instance, to the study of phase-separated materials, in which the geometrical parameters of each phase are not simply identified.

6. Conclusion

Electrical conductivity and relaxation frequency were determined in glasses from the $0.40Li_2O{\cdot}0.60(xB_2O_3(1-x)Si_2O_4)$ system. The electrical conductivity increased from the silica-reach to the boron-rich area in the graph, with no evidence of a mixed former effect, but an anomaly at the $x=0.3$ composition, due possibly to structural modifications introduced by the substitution of SiO_2 by B_2O_3. The variation of the parameters of the Arrhenius expression of electrical conductivity showed a behavior similar to that of its equivalent in the relaxation frequency.

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