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Electrical conduction in alkali borate glasses; a unique dependence on the concentration of modifier ions

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Abstract

The electrical conduction of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses seems, at first sight, to be dominated by the activation energy. Regardless of the size of the alkali ion, there is a unique dependence of conductivity, at a certain temperature, on the alkali-alkali distance and thus on N (the number of ions per cm^3). The linear dependence of $\log \sigma$ on $N^{-3/2}$ for all types of alkali ions reveals that N is the basic parameter that determines the conductivity at a certain temperature. A derived semi-empirical relation can be used to calculate the conductivity as a function of N and temperature.

1. Introduction

Electrical conduction in oxide glasses has been a subject of interest for many decades. Special attention has been given to the effect of the type and concentration of alkali ions on the transport properties of various glasses [1–6]. Apart from mixed alkali glasses, the results show a nonlinear increase in conductivity when increasing the concentration of alkali ions in glass. In addition, for a certain concentration of alkali oxide, glasses containing small ions such as Li^+ ions show higher conductivities than those with alkali ions of greater size.

Various models have been presented to clarify the nature and possible mechanisms of electrical conduction in ionic conducting glasses. The strong electrolyte model [7] is mostly the first quantitative treatment of the phenomenon. It represents, together with the weak electrolyte model [8], marked signs in understanding the basic concepts of the conduction process in such glasses. Further models have been developed in the last two decades and made considerable progress in this respect. The jump relaxation model [9–11], the dynamic structural model [12, 13], the counter-ion model [14, 15], the unified site relaxation model [16] and the free volume model [17] are important examples of this advance.

In the literature, the concentration of components is almost given in mol%. The present work investigates the correlation

of the electrical conduction of alkali borate glasses with the alkali ion concentration taken as the number of ions per cm^3 .

2. Experimental details

Alkali borate glasses (table 1) were prepared from reagent-grade chemicals. Li_2CO_3 , Na_2CO_3 , K_2CO_3 , and H_3BO_3 were used as sources for the oxides in the glasses. The glasses were melted in porcelain crucibles in an electric furnace. Melting was carried out in normal atmosphere at temperatures ranging between 800 and 980 °C, depending on the glass composition. The crucible and its contents were kept in the furnace for about 30 min. The melt was swirled frequently. The refined melt was quenched by pouring onto a ceramic plate and then pressed by another plate to obtain discs with a thickness of about 1–1.5 mm. The samples that were obtained were transparent and apparently homogeneous. The samples were preserved directly after preparation in sealed plastic sacks and stored in a desiccator until required.

For measuring the dc resistivity, polished discs with a thickness of about 1 mm were coated with graphite to serve as electrodes. The resistance was measured using a type TM14 insulation tester (Levell Electronics Ltd, UK) with a range of 10^3 – 10^{13} Ω . As a rule, three samples of each glass were used to measure the resistance. The experimental error in determining the activation energy for conduction is estimated to be less than 0.02 eV, whereas the relative error in the conductivities is

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Table 1. Composition (mol%), molar volume ($\text{cm}^3 \text{mol}^{-1}$) [19], $\log[\sigma_{473}(\Omega \text{cm})^{-1}]$, $\log[\sigma_0(\Omega \text{cm})^{-1}]$ and the activation energy (eV) of $\text{R}_2\text{O}-\text{B}_2\text{O}_3$ glasses.

R_2O	Li_2O				Na_2O				K_2O			
	V_m	$\log \sigma_{473}$	$\log \sigma_0$	E	V_m	$\log \sigma_{473}$	$\log \sigma_0$	E	V_m	$\log \sigma_{473}$	$\log \sigma_0$	E
20	29.09	-8.07	2.15	0.94	31.04	-8.73	2.20	1.00	34.82	-9.36	1.90	1.04
24	27.60	-7.20	1.92	0.85	29.98	-7.61	1.78	0.87	34.31	-8.20	1.61	0.90
30	25.76	-6.34	0.89	0.64	28.68	-6.70	1.37	0.74	33.95	-7.22	1.78	0.83
35	24.53	-6.14	-0.03	0.57	27.86	-6.23	0.16	0.59	33.93	-6.56	1.50	0.75
40	23.48	-5.92	-0.38	0.51	27.25	-6.12	-0.36	0.54	34.08	-6.31	1.64	0.70
45	22.56	-5.77	-0.42	0.45	26.85	-5.94	-1.20	0.49	34.31	-6.18	1.11	0.64
50	21.69	-5.67	-0.55	0.43	26.65	-5.84	-0.94	0.46	34.55	-6.04	1.22	0.62

expected to be $\pm 5\%$. The Ohmic nature of the graphite–glass contact was tested by drawing the dependence of the current on the applied voltage across the sample. A linear dependence was obtained, revealing good Ohmic contact for all glasses.

3. Results

Over a certain temperature region, which depends on the glass composition, there is a linear dependence of the logarithm of conductivity ($\log \sigma$) on the reciprocal of the absolute temperature, for the glasses that were investigated. The behavior that is observed can be expressed by the Arrhenius relation:

$$\sigma = \sigma_0 \exp(-E/kT). \quad (1)$$

Here σ_0 is a constant for the glass that is investigated, E is the activation energy for the conduction process, k is Boltzmann’s constant and T is the absolute temperature. In studying ionic conduction in glass, the quantity (σT) is frequently used to correlate conductivity with various parameters. There is also an alternative way of analyzing conductivity data in ionic conductors where σ is used instead of σT . Because the present work aims to derive a relation that describes conductivity, it is adequate to take the second choice. A comparison between both types of representation (some plots have been tested using σT) showed that the differences are too small to be considered.

Figure 1 shows that $\log \sigma_{473}$ (the logarithm of conductivity at 473 K) increases with a decreasing rate when increasing the concentration of alkali oxide (R_2O) in borate glasses. It is noticed that, at a certain content of alkali oxide, the conductivity decreases from $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses to $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses.

Electron diffraction patterns of selected glasses revealed the amorphous nature of the structure. Transmission electron micrographs show an apparent, but weak, tendency for phase separation. The features that are observed are similar to those of model alkali borate glasses [18], which reflect good homogeneity of the glasses that are studied.

4. Discussion

The electrical conductivity of alkali borate glasses increases nonlinearly with increasing alkali oxide content. The behavior observed in figure 1 agrees with the results of various investigators [1–6]. It is known that the field strength of an ion

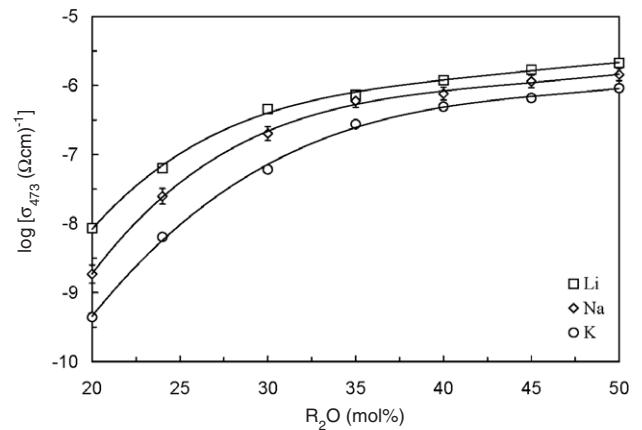


Figure 1. Logarithm of conductivity at 473 K as a function of the alkali oxide content in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The lines are fitting plots.

increases with decreasing ion radius. This may lead to stronger binding with the surroundings and lower conductivities for smaller ions. The results that are presented show the opposite trend. This reveals that the volume of alkali ion plays a dominant role in the electric conduction of these glasses. It is then concluded that the mobility of the alkali ions would be in the sequence $\text{Li}^+ > \text{Na}^+ > \text{K}^+$.

Opposite trends are observed for the activation energy (E) of the electrical conduction for these glasses (figure 2). The decrease in E with increasing modifier oxide content is common behavior for alkali borate glasses. Equation (1) reveals that, at a certain temperature, an increase in σ might be expected when increasing σ_0 or decreasing E . The behavior observed in figure 2 is in harmony with the change of $\log \sigma_{473}$ (figure 1). In contrast, from table 1, there is a slight decrease in $\log \sigma_0$ with composition for $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses, whereas $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ glasses show a marked decrease in $\log \sigma_0$ when increasing the modifier oxide content. The change in $\log \sigma_0$ of all these glasses is inconsistent with the change in $\log \sigma_{473}$. It is then concluded that E dominates the change in conductivity of these glasses.

The activation energy for ionic conduction is considered [7] to be the sum of two terms. One of these is the electrostatic binding energy (E_b) of the movable ion with its immediate surroundings. The second one is the energy needed for a jump from one site to the next. This part of the energy would

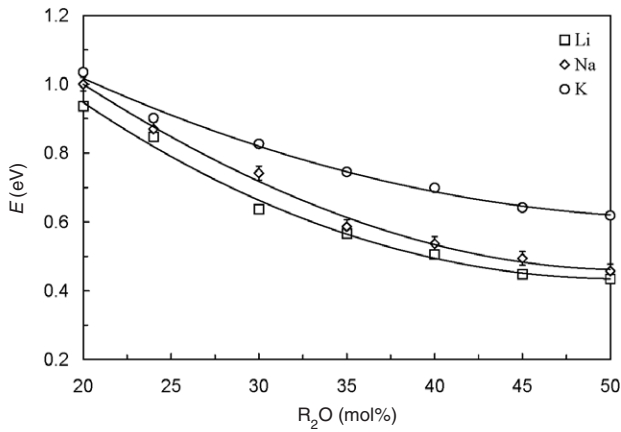


Figure 2. The dependence of the activation energy E on the alkali oxide content in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The lines are fitting plots.

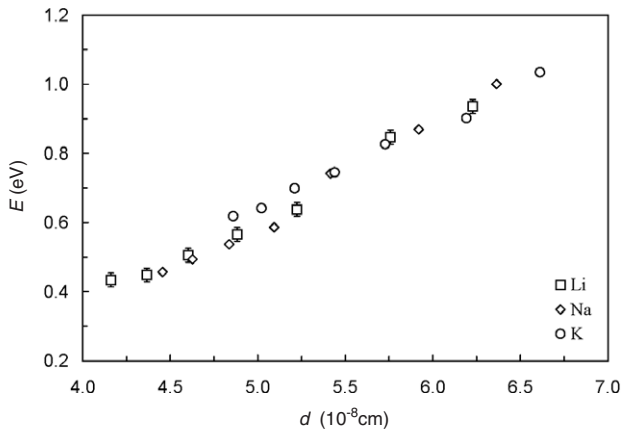


Figure 3. The activation energy E as a function of the average separation distance d between alkali ions in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses.

be consumed for straining a doorway between adjacent sites and is called the ‘strain energy’, E_s . The activation energy is then given by

$$E = E_b + E_s. \quad (2)$$

The strain energy is given [7] as

$$E_s = 4\pi G r_d (r - r_d) \quad (3)$$

where G is the shear modulus of glass, r_d is the radius of the opening between adjacent interstices, and r is the radius of the migrating ion. One may think about another term that must be included in the strain energy. This is the inter-ionic separation distance, i.e. the distance (d) between adjacent alkali ion sites. Work would be done in moving the alkali ion the distance d in the direction of the applied electric field. This means that E_s may be given as

$$E_s = E_g + E_w. \quad (4)$$

Here E_g is the energy needed to create and overcome an opening between sites, and E_w is the work equivalent for the displacement of the alkali ion between adjacent sites. A greater d value means a higher value of E . Figure 3 is in agreement

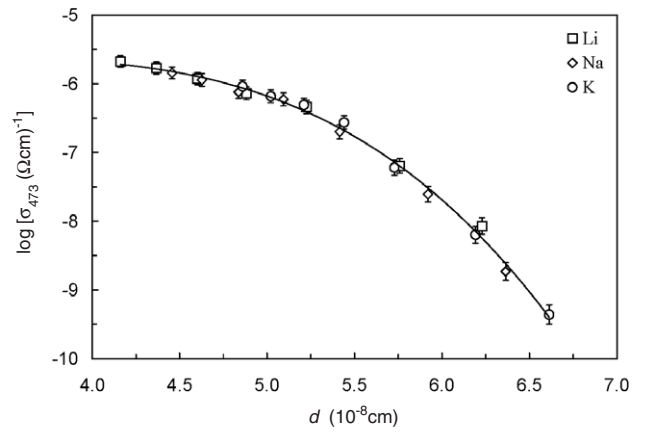


Figure 4. Logarithm of conductivity at 473 K as a function of the average inter-ionic separation distance d between alkali ions in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ (\square), $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ (\diamond) and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ (\circ) glasses. The solid line is a fitting plot.

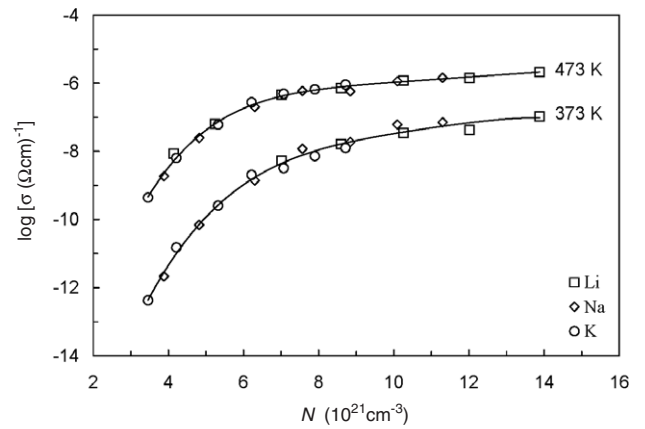


Figure 5. Logarithm of conductivity at various temperatures as a function of the concentration N of alkali ions in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The lines are fitting plots.

with this assumption. It shows a significant increase in E when the separation distance d increases. The latter can be taken as $N^{-1/3}$, where N is the concentration (number per cm^3) of alkali ions in glass. N can be obtained from the composition and the molar volume of glass [19] (table 1). For a glass with the molar formula $x\text{R}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$, N would be $(2xN_A/V_m)$, where N_A is Avogadro’s number and V_m is the molar volume of glass.

In light of the above conclusion that E might be the main factor affecting the change in conductivity of the glasses that are studied, a correlation may exist between the conductivity and the inter-ionic separation distance. Figure 4 shows a unique dependence of $\log \sigma_{473}$ on d for $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses, despite of the different volumes of the alkali ions and then E_b and E_g . This result leads to a significant conclusion that both E_b and E_g have minor effects on E . Taking into account that d depends on N , then a unique dependence of $\log \sigma$ on N may be observed. Figure 5 clearly reveals that the conductivity of the glasses that are studied can be correlated with the concentration of alkali ions. A linear dependence between $N^{-3/2}$ and $\log \sigma$ is shown

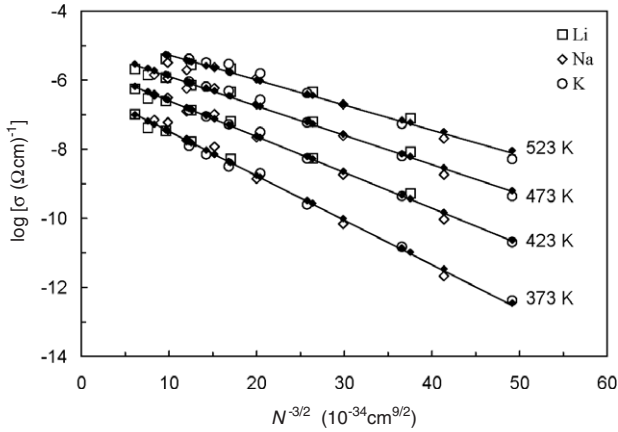


Figure 6. Correlation between the logarithm of conductivity at various temperatures and $N^{-3/2}$. N is the concentration of alkali ions in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The open symbols are experimental results and the \blacklozenge symbol represents calculated data obtained from equation (8). The lines are fitting plots for the experimental results.

in figure 6. For any specific temperature, the straight line can be represented by

$$\log \sigma = SN^{-3/2} + A \quad (5)$$

where S and A are respectively the slope and intercept of the straight line. Both S and A vary with the temperature T . In figure 7 there is a linear dependence between these parameters and $1/T$. The slope S can be given as a function of T as

$$S = -10^{34}(207.7/T - 0.2). \quad (6)$$

Likewise, the intercept is given as

$$A = -2132/T - 0.5. \quad (7)$$

By inserting these relations into equation (5), one obtains

$$\log \sigma = -10^{34}(207.7/T - 0.2)N^{-3/2} - (2132/T + 0.5). \quad (8)$$

From this semi-empirical relation, it is possible to calculate the electric conductivity of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses as a function of N and T . The filled symbol in figure 6 represents $\log \sigma$ values calculated from (8). It is to be noticed that, since N equals $(2xN_A/V_m)$, then equation (8) can be rewritten as

$$\log \sigma = -10^{34}(207.7/T - 0.2)(V_m/2xN_A)^{3/2} - (2132/T + 0.5). \quad (8a)$$

The quantity $(V_m/2xN_A)$ is the mean volume per alkali ion. A plot like that in figure 4 can be observed when representing $\log \sigma$ versus $(V_m/2xN_A)$ for $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. It can then be said that the unique dependence observed in figure 6, for a specific temperature, is indeed a function of the volume per alkali ion in the glass matrix.

Sidebottom *et al* [20, 21] analyzed the ionic conductivity of various glasses to get information on the ‘length scales’ of the transport process. They found a linear relation between ‘the

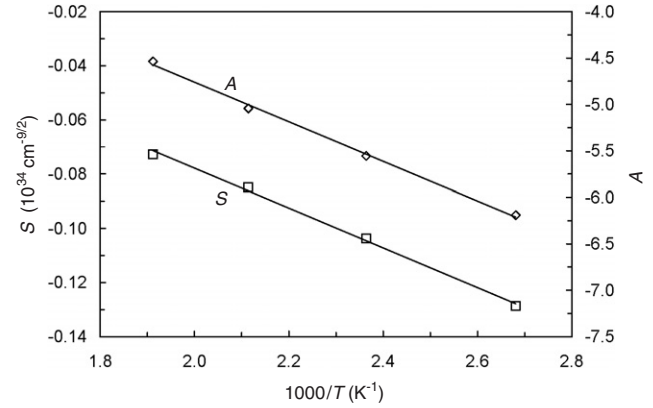


Figure 7. The slope S and intercept A of the lines in figure 6 as a function of the reciprocal of the absolute temperature.

average diffusional displacement of an ion per activated jump’ and the average inter-ionic separation distance. This result may lead to an assumption that the average inter-ionic separation distance is a summation of a definite number of the average diffusional displacements.

Roling *et al* [22] indicated that, for alkali borate, alkali silicate and alkali germinate glasses, the proportionality between the diffusion displacement and the inter-ionic separation is restricted only for low modifier oxide concentration (<10 mol%). Deviation from proportionality is observed in highly modified glasses.

The dependence of the transport length on the inter-ionic distance d shown by Roling *et al* [22] can be looked at, from another point of view, as a nonlinear dependence like that presented in figure 4. This suggests that the behavior in figures 4 and 5 can be correlated with the transport length, which might be concentration and temperature dependent. Unfortunately, the glasses investigated by Roling *et al* [22] have alkali oxide contents that are lower than in the present study.

Voss *et al* [23] investigated the ionic conduction of single- and mixed-modifier sodium and rubidium alumino-germanate and borate glasses. They indicated that the activation enthalpy of the electrical conductivity increases linearly with an increasing ratio $\langle d_R \rangle / \langle d_{\text{network}} \rangle$, where $\langle d_R \rangle$ is the average inter-ionic distance of the modifier ions and $\langle d_{\text{network}} \rangle$ is the average distance between network former atoms.

In this respect, it can be said that the inter-ionic distance d plays an important role in the dynamics of electrical conduction. However, these aspects, together with the present study, reveal that more efforts are needed for a full understanding of the mechanisms of electrical conduction and the parameters controlling it in ionic conducting glasses.

One may consider the basic relation

$$\sigma = \sum n_i \mu_i q_i. \quad (9)$$

This defines the conductivity σ in terms of the concentration (n_i), the mobility (μ_i) and the charge (q_i) of a mobile ion of type i in the glass. By n_i we mean the number of mobile ions per cm^3 . In alkali borate glasses, alkali ions are assumed to be the charge carriers. Therefore, in a binary

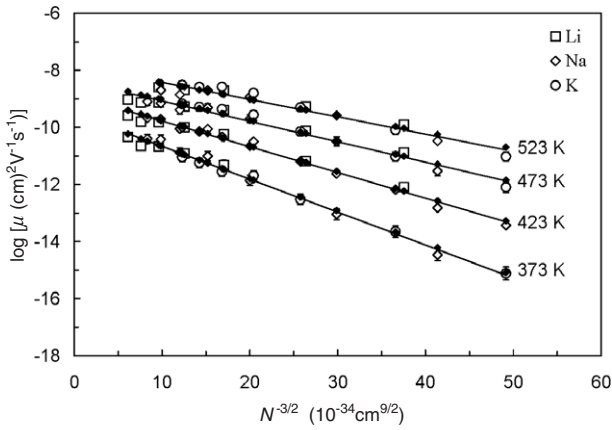


Figure 8. Correlation between the logarithm of average mobility $\log \bar{\mu}$ at various temperatures and $N^{-3/2}$ for $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses. The open symbols are experimental results and the \blacklozenge symbol represents calculated data obtained from equation (11). The lines are fitting plots of the experimental results.

alkali borate glass there would be one type of charge carrier. It is worth stating that, under the effect of an applied potential difference, only a fraction of the alkali ions would be mobile at any specific moment. For this reason, it is mainly not possible to determine μ_i from a simple conductivity measurement. As an approximation, it can be assumed that all the alkali ions present in glass contribute to the conduction process. Thus one can use the total concentration N_i of alkali ions in glass rather than n_i . By using this approximation it would be possible (from equation (9)) to calculate the average mobility ($\bar{\mu}$) of the alkali ions in glass. For a single type of alkali ion (binary alkali borate glasses) equation (9) can be rewritten as

$$\sigma = N\bar{\mu}q \quad (10)$$

with $q = 1.602 \times 10^{-19}$ C.

This relation shows that, at a specific temperature, the conductivity is a function of both N and $\bar{\mu}$. On the other hand, equation (8) indicates that the conductivity at a certain temperature is determined only by the concentration of the alkali ions in glass. A comparison between equations (8) and (10) reveals that $\bar{\mu}$ might also be a function of N . Figure 8 shows a linear change in $\log \bar{\mu}$ with $N^{-3/2}$. Like the behavior in figure 6, the slope and the intercept change linearly with $1/T$. The correlation between $\log \bar{\mu}$ and $N^{-3/2}$ can be expressed as

$$\log \bar{\mu} = -10^{34}(203.6/T - 0.22)N^{-3/2} - (2180/T + 4). \quad (11)$$

This relation, together with equation (10), indicates that only N determines the conductivity of the glasses studied at a certain temperature. This conclusion can be attained by equating the right-hand sides of equations (1) and (10). This produces

$$N\bar{\mu}q = \sigma_0 \exp(-E/kT). \quad (12)$$

The factor σ_0 is given as [24]

$$\sigma_0 = 6kT/nq^2d^2fs \quad (13)$$

or [25]

$$\sigma_0 = 2kT/nq^2d^2f. \quad (14)$$

In these relations, n is the concentration of mobile ions, d is the separation distance between adjacent potential wells (inter-ionic distance), f is the frequency of the mobile ion vibration, and s is the number of holes directly surrounding the mobile ion. The parameters n , d , f and s are all dependent on N . Then we may conclude, from equation (12), that E also depends on N . It appears therefore that N is the main factor that determines the electrical conduction in the glasses that are studied.

5. Conclusion

The electrical conduction of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$, $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ and $\text{K}_2\text{O}-\text{B}_2\text{O}_3$ glasses is dominated by the inter-ionic distance which, in turn, depends on the concentration of alkali ions (number per cm^3) in the glass. It has been shown that the pre-exponential factor and the activation energy for conduction are dependent on the concentration of alkali ions. The conductivity can be expressed by an equation whose variables are only the concentration of alkali ions and the temperature, regardless of the type of alkali ion.

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