Mixed alkali effect in polaronic conducting iron borate glasses

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By substituting a second type of alkali into a single alkali glass network, a variety of properties, which are mostly affected by the diffusivities of the alkali species change in a non-linear way. These properties include self-diffusion, electrical conductivity, dielectric loss, and so on. This behaviour is referred to as the mixed alkali effect (MAE). It was pointed out, [1–3] that this effect exists also in glasses in which one of the network modifiers is a non-alkali element such as in the case of Ag_2O-Na_2O-TeO_2 glasses [3].

This effect appears to be common to all ion-conducting glasses. It was observed that [4] the electrical conductivity in mixed Li/K disilicate glasses at 150 °C goes through a minimum value, almost five orders of magnitude, lower than that of either Li_2O-SiO_2 or K_2O-SiO_2 glass.

MAE is of practical importance, as e.g., in the formation of glasses with high electrical resistivity and good chemical durability. Mainly, however, its elucidation is seen as presenting a severe test for all theories of ionic conduction in the vitreous state [5].

Most of the studies of the MAE in glass have been made on glasses free from transition metal ions (TMIs), and there has been little work on mixed-alkali glasses containing TMIs [6]. It was found that no MAE of any significance was observed in Na_2O-K_2O-Fe_2O_3-P_2O_5 glasses, even at a total alkali content of 20 mol%. The absence of MAE has been considered a further evidence of the low mobility of the Na^+ and K^+ ions, and hence they make no detectable contribution to the total conductivity that is electronic in origin [6].

The conduction process in borate glasses containing sufficient amounts of iron oxide, $x Fe_2O_3$-$(50-x)PbO$-$50B_2O_3$ [7], $x Fe_2O_3$-$(100-x)[PbO$-$3B_2O_3]$ [8], and $x Fe_2O_3$-$(60-x)BaO$-$40B_2O_3$ [9], was found to be polaronic in nature. The electrical properties of these glasses showed a semiconducting behaviour due to hopping of small polaron between Fe^{+2} and Fe^{+3} ions.

Recently [10], Doweidar *et al.* reported the results of a study of the structure and properties of Li_2O-Fe_2O_3-B_2O_3 glasses containing up to 10 mol% Fe_2O_3. They found that, the DC conductivity of these glasses is of ionic origin and that the absence of polaronic conduction could mainly be correlated with the presence of a sufficient concentration of Li^+ ions. The predominance of ionic conduction in these glasses is attributed to the high mobility of Li^+ ions [10] compared to that of Ba^{2+} or Pb^{2+} ions in corresponding glasses [7–9].

Li^+ ion has the smallest volume among the alkali ions. The relatively high difference in size between Li^+ and K^+ ions makes glasses containing both of them suitable for studying how MAE is affected by the presence of TMIs in the glass matrix. To do this, transport behavior of Li_2O-K_2O-Fe_2O_3-B_2O_3 has been studied.

Two groups of glass (Table I) were prepared. The glasses have the molar formulae $(25-x)Li_2O$-xK_2O-$10Fe_2O_3$-$65B_2O_3$ (G1) and $(25-x)Li_2O$-xK_2O-$15Fe_2O_3$-$60B_2O_3$ (G2), with $0 \leq x \leq 25$ mol%. Reagent grade H_3BO_3, Fe_2O_3, Li_2CO_3, and K_2CO_3 were mixed together and melted in porcelain crucibles in an electric furnace at a temperature in the range 1050 and 1100 °C, according to the composition. To assure homogeneity, the well-mixed components were added in small portions and the melt was swirled from time to time. The homogenized melt was quenched by pouring it onto a steel plate and quickly pressed by another one to obtain disks having thickness of 1 to 2 mm. The obtained samples are of glassy appearance and free from air bubbles, but X-ray diffraction patterns indicated that there is a tendency for crystallization in G2 glasses.

The plates were used to measure the DC conductivity. A silver paste coating was applied to the flat surfaces to serve as electrodes. The radius of the coated area was 5 mm. The resistance was measured using an insulation tester type TM14 (Levell Electronics Ltd.) with 10^3 to 10^{13} ohm range. Three samples of each glass were used to measure the resistance. The experimental error in determining the high temperature activation energy for conduction is estimated to be less than 0.02 eV, whereas the relative error in conductivities is expected to be ±5%.

Density measurements were carried out using Archimedes method with xylene as an immersion liquid at room temperature. Four samples of each glass were used to determine the density (D). The density values were reproducible to ± 0.02 g/cm^3. The molar volume (V_m) was calculated using the formula

$$V_m = \sum x_i M_i / D \quad (1)$$

where x_i is the molar fraction of the oxide (i) and M_i is its molecular weight.

Figs 1 and 2 show the temperature dependence of the DC electrical conductivity of the studied glasses

TABLE I Compositions, density, and the activation energy for electric conduction of the studied glasses

Group	B_2O_3 (mol%)	Fe_2O_3 (mol%)	Li_2O (mol%)	K_2O (mol%)	D (g/cm^3)	W (eV)
G1	65	10	25	0	2.497	0.77
	65	10	20	5	2.478	0.86
	65	10	15	10	2.457	0.95
	65	10	12.5	12.5	2.449	1.03
	65	10	10	15	2.439	1.05
	65	10	5	20	2.416	1.01
	65	10	0	25	2.396	0.83
G2	60	15	25	0	2.650	0.78
	60	15	20	5	2.623	0.93
	60	15	15	10	2.585	1.02
	60	15	12.5	12.5	2.568	1.03
	60	15	10	15	2.560	1.02
	60	15	5	20	2.533	0.99
	60	15	0	25	2.497	0.88

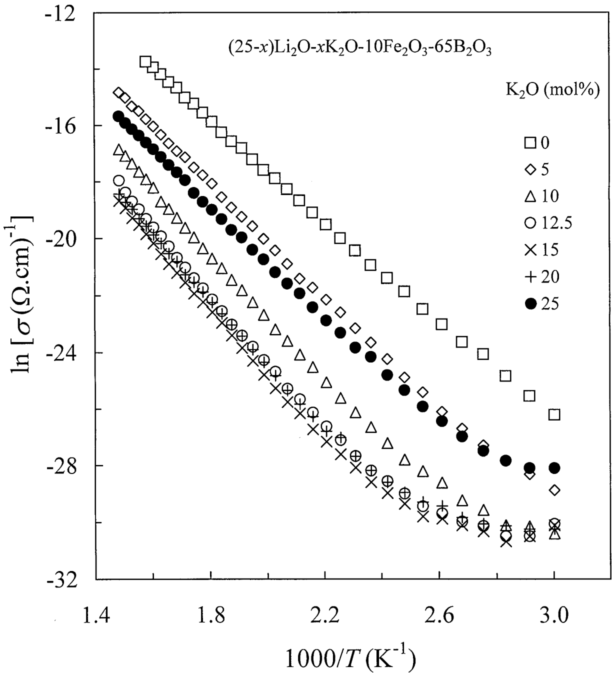

Figure 1 Temperature dependence of the DC electrical conductivity of $(25-x)Li_2O$-xK_2O-$10Fe_2O_3$-$65B_2O_3$ glasses.

for groups 1 and 2, respectively. In both series, there is some deviation from linearity at certain temperatures, especially for glasses characterized by low conductivity values. The deviation from linearity is more obvious for glasses of G2 containing higher content of Fe_2O_3. The temperature at which the deviation from linearity takes place (T_d) depends on the glass composition. The high-temperature activation energy (W) was calculated by applying Arrhenius equation to the linear part of the plots. For this part, the dependence can be represented as

$$\sigma = \sigma_0 \exp(-W/KT) \qquad (2)$$

where σ is the conductivity at temperature T (in K), σ_0 is the pre-exponential factor and K is the Boltzmann constant. Values of W are given in Table I.

Both the high-temperature activation energy and the natural logarithm of conductivity at 403 K ($\ln\sigma_{403}$)

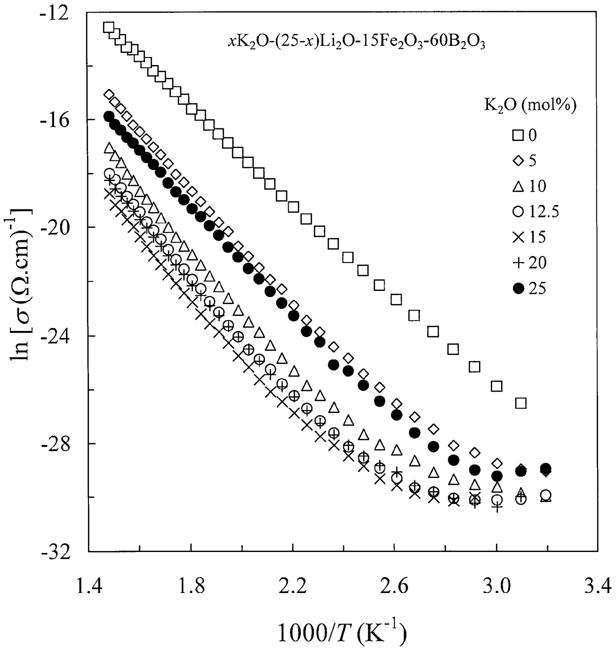

Figure 2 Temperature dependence of the DC electrical conductivity of $(25-x)Li_2O$-xK_2O-$15Fe_2O_3$-$60B_2O_3$ glasses.

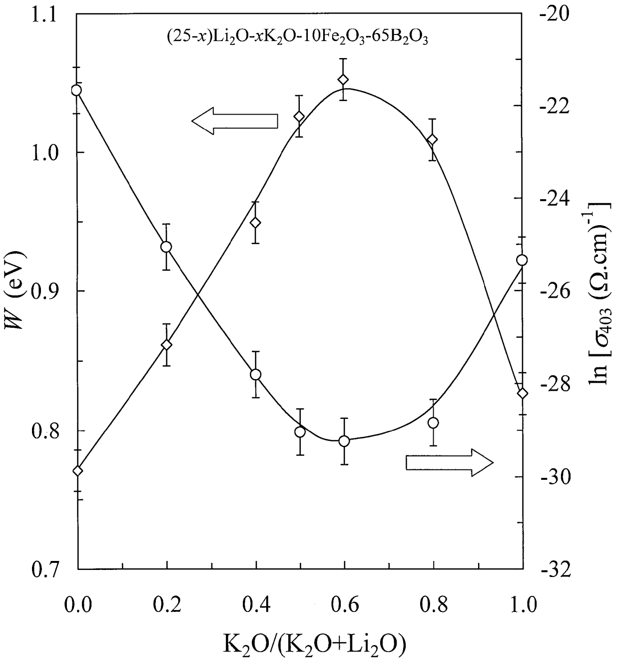

Figure 3 Change in the activation energy, W, and the natural logarithm of conductivity at 403 K, $\ln\sigma_{403}$, with X [$K_2O/K_2O + Li_2O$] for $(25-x)Li_2O$-xK_2O-$10Fe_2O_3$-$65B_2O_3$ glasses. The lines are drawn as guides for the eyes.

are plotted in Fig. 3 (G1) and Fig. 4 (G2) versus the ratio $X = K_2O/(K_2O + Li_2O)$. Along the composition range studied, the conductivities show a minimum at $X \approx 0.6$. The change in $\ln\sigma_{403}$ is more than three orders of magnitude in both groups, while the activation energy increases more than 0.3 eV at that composition. The plots of W and $\ln\sigma_{403}$ become broader for glasses of G2 that contains higher content of Fe_2O_3.

In Fig. 5 is shown the composition dependence of the temperature T_d at which the deviation from linearity takes place for the studied glasses. A maximum value of T_d is observed at about $X \approx 0.6$ and 0.5 for G1 and G2 glasses, respectively.

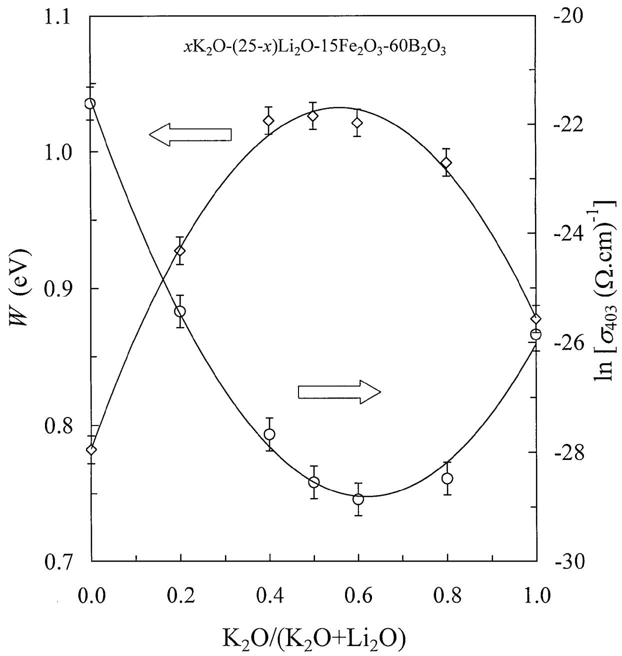

Figure 4 Change in the activation energy, W, and the natural logarithm of conductivity at 403 K, $\ln\sigma_{403}$, with X molar ratio for $(25-x)Li_2O$-xK_2O-$15Fe_2O_3$-$60B_2O_3$ glasses. The lines are drawn as guides for the eyes.

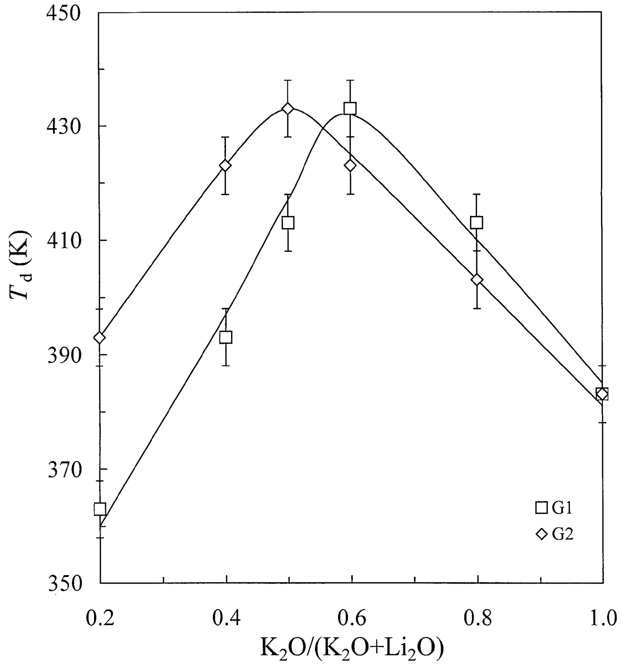

Figure 5 Relation between the temperature at which the deviation from linearity takes place, T_d, in $\ln\sigma - 1/T$ plots and X molar ratio for the studied glasses. The lines are drawn as a guide for the eye.

Figs 6 and 7 show the composition dependence of both density and molar volume for G1 and G2, respectively. It is observed that the density of both groups decreases linearly with increasing K_2O content at the expense of Li_2O content. An opposite behavior is observed for the molar volume of both groups.

The temperature dependence of the DC conductivity for the studied glasses is linear in the high-temperature region (Figs 1 and 2). The linearity indicates that the activation energy for the same composition is constant over this range of temperature. For lower temperatures, the activation energy changes with temperature as can be predicted from the curvature in $\ln\sigma - 1/T$ plots. The linear dependence of the plots for Li_2O-Fe_2O_3-B_2O_3 glasses in Figs 1 and 2 reveals that the conduction is ionic. In these glasses the contribution to the conductivity from polaronic hopping is masked by the highly mobile Li^+ ions. On the other hand, in K_2O-Fe_2O_3-B_2O_3 glasses the dependence of $\ln\sigma$ on $1/T$ is

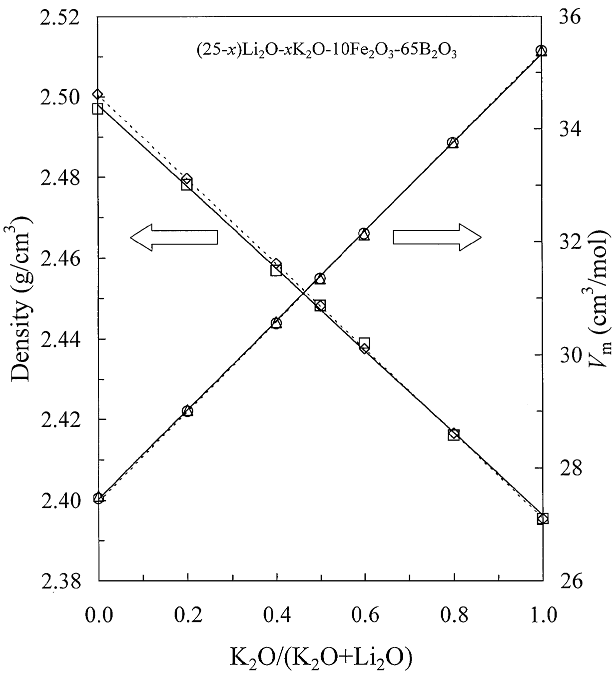

Figure 6 Variation in density, D, and molar volume, V_m, with X content for $(25-x)Li_2O$-xK_2O-$10Fe_2O_3$-$65B_2O_3$ glasses. The symbols (□) and (△) represent experimental data for D and V_m while (◇) and (○) represent calculated values of D from Equation 3 and the corresponding values of the molar volume, respectively. Solid line is the fitting plot of the experimental data. Dashed line is the fitting plot of the calculated values.

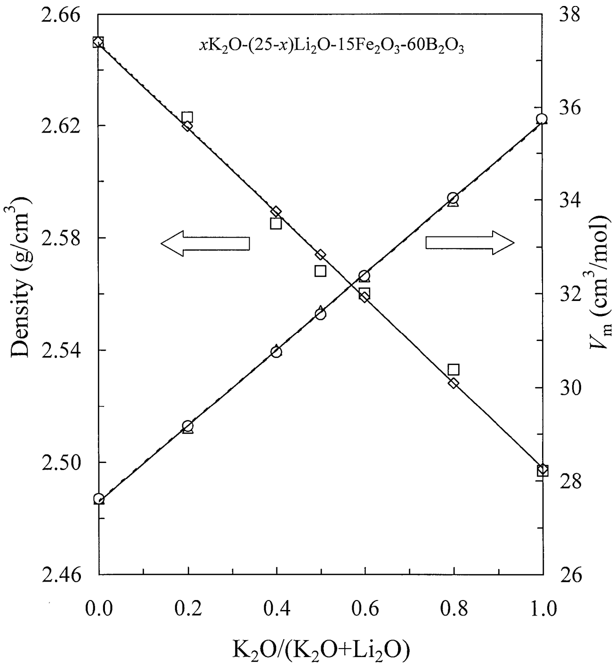

Figure 7 Variation in density, D, and molar volume, V_m, with X content for $(25-x)Li_2O$-xK_2O-$15Fe_2O_3$-$60B_2O_3$ glasses. The symbols (□) and (△) represent experimental data for D and V_m while (◇) and (○) represent calculated values of D from Equation 3 and the corresponding values of the molar volume respectively. Solid line is the fitting plot of the experimental data. Dashed line is the fitting plot of the calculated values.

non-linear over a certain temperature region. This reveals that the polaronic conduction is not suppressed by the conduction through K^+ ions. Such an effect can be attributed to the relatively lower mobility of the K^+ ions because of their greater size.

The appearance of both linearity and non-linearity in the plots of Li_2O-K_2O-Fe_2O_3-B_2O_3 glasses indicates that the nature of conduction may be mixed ionic-polaronic. Ionic conduction in glasses obeys Arrhenius equation (Equation 2), while the change in W with temperature is a characteristic feature for the small polaron hopping conduction [9, 11–15]. It is then assumed that a greater linear part of $\ln\sigma$-$1/T$ plot means a greater contribution of the ionic conduction and a lower contribution of the polaronic conduction. The temperature (T_d), at which the deviation from linearity takes place, changes from one composition to another. This temperature can be taken as an indicator for the transition from ionic to polaronic one. Below T_d polaronic conduction is predominant, whereas ionic conduction predominates for $T > T_d$.

However, both of $\ln\sigma$ and W show non-linear trends upon replacing Li_2O by K_2O (Figs 3 and 4). In Fig. 3, is shown that $\ln\sigma_{403}$ reaches a minimum and W a maximum at $X \approx 0.6$. This result is in contrast to the results of Mogus-Milankovic *et al.* [6]. They reported that no mixed alkali effect was observed in Na_2O-K_2O-Fe_2O_3-P_2O_5 glasses, even at a total alkali content of 20 mol%. They referred the absence of MAE in these glasses to the low mobility of Na and K ions, so they make no detectable contribution to the total conductivity that is electronic in origin.

In a recent work [16] it is suggested that the MAE might be due to changes in mobility of the alkali ions in glass. With increasing the concentration of one type of alkali ions, its mobility increases. In turn the mobility of the other type of charge carriers decreases due to the decreasing concentration. The resultant is that the overall mobility of the charge carriers undergoes a minimum at nearly equal concentrations of the modifier oxides. In Li_2O-Fe_2O_3-B_2O_3 glasses containing up to 10 mol% Fe_2O_3 [10], the ionic conduction was found to suppress the polaronic one due to the high mobility of lithium ions, and the conduction is mainly carried out by Li^+ ions. In the studied glasses, Li^+ ions are replaced by the less mobile K^+ ions. This lowers the overall mobility of the charge carriers and allows the features of polaronic conduction to be observed.

A behavior like that of W is obtained for T_d for the two groups of the studied glasses. Fig. 5 shows a maximum in T_d at $X \approx 0.6$ and 0.5 for G1 and G2 glasses, respectively. The change in T_d with increasing X reflects the transformation from more ionic conduction to more polaronic one. An increase in T_d means that the polaronic conduction becomes effective over a wider range of temperature. Therefore, the temperature region in which the ionic conduction dominates would be smaller. Thus, the dependence T_d on X may also characterize the MAE in these glasses.

In Figs 6 and 7 both the density and molar volume are presented versus X. There is a linear decrease in the density and a linear increase in the molar volume for both groups. In general, the density of mixed alkali glasses shows only slight deviations from linearity [4].

In Li_2O-B_2O_3 glasses the increase in Li_2O content up to 30 mol% results in an increase in density [17, 18], although the relative molecular mass of Li_2O is much lower than that for B_2O_3. The increase in density in such cases is attributed to the conversion of BO_3 units into BO_4 ones. The density of the latter is markedly higher than that of the prior. In the studied glasses Fe_2O_3 content is fixed for each series, while Li_2O is replaced by K_2O. Thus the oxygen/boron ratio does not change in replacing one alkali oxide by another. Therefore, there would be no significant change in the relative number of BO_3 units that convert into BO_4 ones. This result reveals that the decrease in density may be due to an expansion in the glass matrix when replacing the smaller Li^+ ions by the larger and heavier K^+ ions. Considering the volumes of Li^+ and K^+ ions, it can be concluded that the linear increase in V_m (Figs 6 and 7) is due to an increase in the free volume of glass.

The linear change in density reveals that each oxide in glass would contribute a specific factor. This means that the density of the studied glasses can be given as

$$D = \sum f_i C_i \qquad (3)$$

where f_i is a factor having the unit of density for the oxide (i) in glass, and C_i is the mole fraction of that oxide. The factor due to B_2O_3 (f_B) can be taken as the density of the vitreous B_2O_3 (1.8245 g/cm^3) [17], while the factor of Fe_2O_3 (f_{Fe}) is 5.03 g/cm^3 [10]. In Table I the densities of the single-alkali glasses are 2.497 g/cm^3 for ($25Li_2O$-$10Fe_2O_3$-$65B_2O_3$) and 2.396 g/cm^3 for (25 K_2O-$10Fe_2O_3$-$65B_2O_3$). From these values and the factors of B_2O_3 and Fe_2O_3 one can calculate the factors f_{Li} and f_K for both Li_2O and K_2O, respectively. By using the fitting equations of the density data in Fig. 6, it is found that $f_{Li} = 3.247$ g/cm^3 and $f_K = 2.827$ g/cm^3. Similar calculations were performed for G2. Table II presents the obtained factors for the studied glasses and also those for lithium-iron borate glasses [10]. It is concluded that f_i increases

TABLE II Factors of density for the studied glasses and Li_2O-Fe_2O_3-B_2O_3 [10]

Group	Molar formula	f_B	f_{Fe}	f_{Li}	f_K
G1	$(25-x)Li_2O$-xK_2O-$10Fe_2O_3$-$65B_2O_3$	1.8245	5.03	3.247	2.827
G2	$(25-x)Li_2O$-xK_2O-$15Fe_2O_3$-$60B_2O_3$	1.8245	5.03	3.204	2.594
G3	$^a(25-x)Li_2O$-xFe_2O_3-$75B_2O_3$[10]	1.8245	5.03	3.247	–
G4	$^a25Li_2O$-xFe_2O_3-$(75-x)B_2O_3$[10]	1.8245	5.03	3.247	–

$^a0 \leq x \leq 10$ mol%.

in succession $f_{Fe} > f_{Li} > f_K > f_B$. From the data in Table II it is noticed that both f_{Li} and f_K decrease when increasing the Fe_2O_3 content in glass.

B_2O_3 represents the glass network, which contains cavities that can be occupied by another modifier ions. So the contribution of B_2O_3 to the density of the studied glasses is lower than the other oxides. As a heavy oxide Fe_2O_3 contributes to the density with the greatest fraction. On the other hand, although the molecular weight of Li_2O is smaller than that of K_2O, lithium oxide contributes to the density with a factor greater than that for K_2O. This may be the reason for the decrease in the density when substituting Li_2O by K_2O. The ◇-symbols in Figs 6 and 7 represent calculated densities obtained from Equation 3 and the f_i factors given in Table II. The agreement between the calculated and experimental densities indicates that the role of Fe_2O_3 would be similar in both series of glasses. This result is consistent with the results of Doweidar *et al.* for $(25-x)Li_2O$-xFe_2O_3-$75B_2O_3$ and $25Li_2O$-xFe_2O_3-$(75-x)B_2O_3$ glasses [10].

In summary, the results of DC electrical conductivity of Li_2O-K_2O-Fe_2O_3-B_2O_3 glasses as reported in this paper are in line with the behavior of the MAE, although polaronic conduction was observed in these glasses. This behaviour is dissimilar to that of Na_2O-K_2O-Fe_2O_3-P_2O_5 glasses. For the studied glasses T_d changes with composition through a maximum and can be taken as a characteristic feature of the MAE in these glasses. Both the density and molar volume change linearly with composition. Each oxide in the studied glasses was found to make a specific contribution to the density.

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