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A New Concept about the Static Structure and Alkali Non-Bridging Oxygen Dependence of the Mixed Alkali Effect in Bismuthate Glasses

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Abstract

The x-ray measurements for the glass system of composition $(Bi_2O_3)_{50}(Fe_2O_3)_{10}(Li_2O)_x(K_2O)_{40-x}$ with x between 0 and 40 in steps of 5 has been carried out by means of x-ray powder diffraction using Mo-$K_\alpha$radiation over [scattering vector ,q between 1 and 16A^{-1}] range. X-ray diffraction has been used to calculate the pair distribution function [PDF], g(r), applying the pair potential analytical method. The partial pair distribution function [PPDF], $g_{ij}(r)$, of both the metal non-bridging oxygen M-nboand M-bo (M= K or Li, while M-nboand M-bo refers to the non-bridging and bridging oxygen [nbos] respectively) are also calculated by the same method. Both of g(r) and $g_{ij}(r)$ are studied as a function of the molar fraction $\chi = \frac{Li}{Li+K}$. The PDF, g(r), and the PPDF, $g_{ij}(r)$, of M-nboshows a maximum deviation for these functions around the alkali molar fraction χ of 0.5 while it shows an insignifically deviation in the case of M-bo. These results could be compared with those obtained for the activation energies E_σ and E_D of the conductivity and diffusion respectively which show a maximum deviation around the same alkali molar fraction. They also could be compared with the results of the conductivity which show a minimum deviation at the same ratio. These results lead to the fact that there is a certain relation between the static structure [g(r)] and the mixed alkali effect (MAE).On the other hand the results show a maximum deviation from linearity in the values of PDF's (at first neighbor distance) as function of $\chi = \frac{Li}{Li+K}$ in the case of K-nboand Li-nbo (potassium and lithium non-bridging oxygen). On the other hand no deviation is observed in the case of K-bo and Li-bo (the case of bridging oxygen). The discussion of the results shows that the static structure (distribution of atoms) and the alkali non-bridging oxygen concentration are strongly related to the mixed alkali effect (MAE) phenomenon. The results are discussed in comparison to the different MAE theories.

Introduction

The MAE refers to the non-linear variations properties of glasses. The most celebrated case is the so-called 'mixed alkali' effect in which mixing of two alkali oxide glasses (silicate, borate, phosphate [1-3] and recently bismuthate [4]) of comparable dc conductivities, results in a glass with a dc conductivity orders of magnitude lower than either of the binary end-member glasses [2,3,5]. In recent years MAE was found in mixed crystals (β-alumina) [6], cation and anion (Li^+ and F^-) conducting glass [6-8] and also for glasses containing two glass formers (P_2O_5, B_2O_3) [9]. Although this effect is known for a long time, there is no acceptable theory to explain physical origin of this effect and only limited work has been reported on the frequency dependence of conductivity (ion dynamic) in mixed alkali glasses.

On the other hand MAE was found to be absent in silicate [10], borosilicate [11] and germinate [12] glasses where the total alkali content is less than 10%. Such glasses of course have an equally small quantity of Nbosassociated with these alkali cations, a feature which has not been stressed before. Experiments work on systems where the non-bridging oxygen concentration is independent of that of the alkali ions has been restricted to two published studies of the electrical properties of glasses in the Na_2O – K_2O –Al_2O_3 –SiO_2 system [13]. In both cases the results did not conform to the general pattern which has been established for mixed alkali silicates, borates, etc.

One obvious reason for the difference in the behavior of mixed alkali ions associated with $(AlO_4)^-$ tetrahedral and with non-bridging oxygen ions lies in the bonding affinities of these structural units towards cations. nbos represent highly polar positions in the network with which the alkali ions may be in direct contact , in contrast, the negative charges of units such as $(AlO_4)^-$ and $(BeO_4)^{-2}$ lies at the centers of O_4 tetrahedra ,from which the alkali ions are excluded .

The aim of the present study is to make a correlation between the arising of the MAE phenomena and the variation of both the total pair distribution function g(r) [static structure] and the partial pair distribution function of the cation –non-bridging and bridging oxygen, $g_{ij}(r)$ of the-M-nbo. and M-bo respectively. The results are discussed on the light of the different MAE theories.

Experimental Work

Glass samples of composition $(Bi_2O_3)_{50}$ $(Fe_2O_3)_{10}$ $(Li_2O)_x$ $(K_2O)_{40-x}$ with x between 0 and 40 in steps of 5 were prepared by molecular weight method using reagent grade Bi_2O_3 , Fe_2O_3 , Li_2CO_3 and K_2CO_3. The mixture was grounded in an agate mortar to achieve good homogeneity and then melted in a porcelain crucible in air at 950^{o}C for15 minute. The liquid was poured and rapidly quenched by pressing between two copper blocks. The glassy state of the sample was examined by x-ray diffraction.

The x-ray measurements have been carried out by means of x-ray powder diffraction using [Shimadzu XD-D1 X-Ray Diffractometer VG-207 II] and Mo-k$_{\alpha}$ radiation over [q between 1 and 16A$^{\circ-1}$] range.

Results and Discussions

Pair Distribution Function, g(r) [Effect Of Static Structure]

All the previous studies [1-4 and 14] were focused on the relation between MAE and the transport properties such as DC conductivity, diffusion coefficient and activation energy in addition to some other properties .In this paper we will try to make a new concept about the relation between both the PDF,g(r), which indicate the static structure and M-non-bridging oxygen, and the MAE arising.

To our knowledge no any studies were conducted concerning the relation between the static structure and MAE. As an example most of the studies were concerned with relation between the density and MAE neglecting any effect for the structure, although the density arises from the distribution of the atoms inside crystal and the non-crystalline solids. All the previous studies [15] proved that g(r) could describes the structure of the non-crystalline in high accuracy. For this reason in this part we will try to give some light on how much g(r) and hence the static structure are affected by the phenomenon of MAE . This study will be divided in to two parts:

Theoretical-background

The structure of non-crystalline materials can only be quantitatively described in terms of the pair distribution function (PDF) g(r), indicating the average probability of finding another atom in a specified volume from an origin atom as a function of radial distance. The (PDF) can be determined from diffraction data of the X-rays or neutrons and the relation between measured diffraction data and the PDF has been described in details [15-17].

The essential equations which are applied to determine the PDF from the experimental x-ray diffraction data are summarized as following:

The total pair distribution function g(r) is given by

$$g(r) = \sum_{i}\sum_{j} W_{ij} g_{ij}(r) \tag{1}$$

where $g_{ij}(r)$ is the partial pair distribution function which is given by

$$g_{ij}(r) = Exp[\tfrac{-V_{ij}(r)}{KT}] \tag{2}$$

$V_{ij}(r)$ is the applied pair potential and the weighting factors W_{ij} are given by

$$W_{ij} = \frac{c_i c_j f_i f_j}{<f>^2} \tag{3}$$

The pair distribution function is related to the reduced PDF by

$$g(r) = \frac{G(r)}{4\pi\rho_0 r} + 1 \tag{4}$$

$$G(r) = \frac{2}{\pi}\int q[S(q)-1]\sin(qr)dq \tag{5}$$

$$S(q) = \frac{[I_a(q)-(<f^2>-<f>^2}{<f>^2} \tag{6}$$

$$I_a(q) = \frac{\alpha I_s}{PA} - Q(q)I_{inc}(q) \tag{7}$$

$$\alpha = \frac{\int[<f^2>-I_{inc}(q)]dq}{\int \frac{I_s}{PA}dq} \tag{8}$$

$$< f^2 >= \sum_{i=1}^{n} c_i f_i^2 \tag{9}$$

$$< f >= \sum_{i=1}^{n} c_i f_i \tag{10}$$

where G(r) reduced pair distribution function (RPDF) , ρ_o average number density, S(q) structure factor, P polarization factor, A absorption factor , Q(q) is the Q factor, I_{inc} (q) incoherent scattering , c_i atomic fraction of i-type ,and f_i atomic scattering factor of atom i .

Experimental Results and Discussions

The x-ray diffraction (XRD) for all the glass samples studied were carried out and **Fig.(1)** is selected as an example to show the XRD for the sample (x=0). The other samples showed the same behavior.

Using the equations from (1) to (10) the structure factor s(q) was calculated and represented in **Fig.(2). Figs.(1,2)** indicate the glassy state properties of the sample.

The reduced pair distribution function (PRDF), G(r),could be calculated from equation (5) by applying Fourier transformations and substituting in equation (4) ,g(r) was obtained .The experimental g(r) for the studied glasses is represented in **Fig.(3-a)** and it is compared with the calculated one as shown in **Fig.(3-b).**

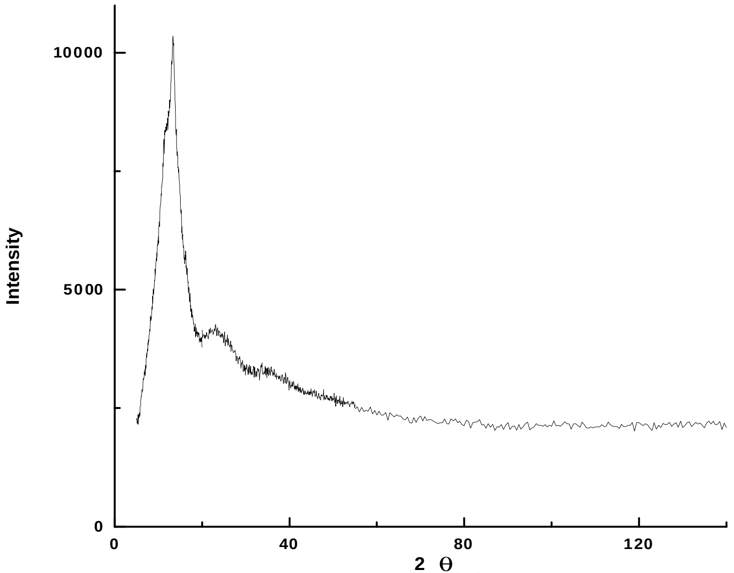

Fig.(1)

Figure 1: X-Ray diffraction pattern for the glass sample $(Bi_2O_3)_{50}(Fe_2O_3)_{10}(K_2O)_{40}$

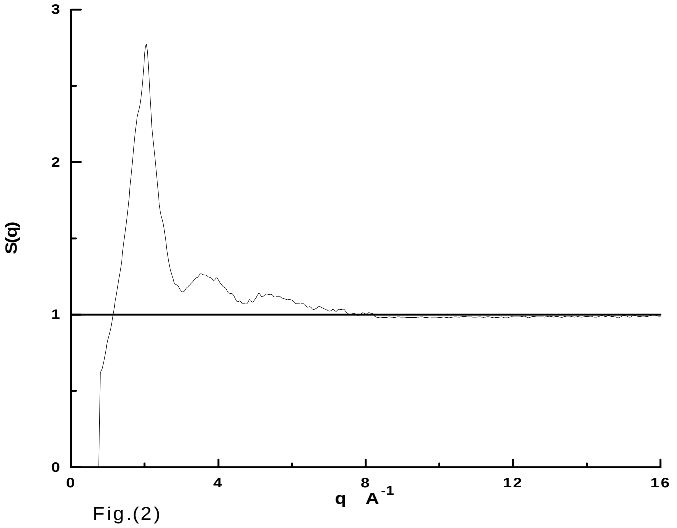

Fig.(2)

Figure 2: Structure factor of $(Bi_2O_3)_{50}(Fe_2O_3)_{10}(K_2O)_{40}$ oxide glass

The well agreement between the experimental and the calculated g(r) as shown in **Fig. (3-b)** prove the high accuracy of the proposed model of pair potential analytical method [18] which is applied in our calculations. It is noted that the first neighbor distance (r=3.75 $\overset{0}{A}$) {first peak}which corresponding the Bi-O-Bi bond length remains unchanged in all glass compositions. **Fig.(3-a)** shows that at the first neighbor distance ,there is an increase in the values of g(r) with the increase of x (Li concentration) and reach maximum at x=20.

This result is confirmed from the relation of g(r) as a function of χ shown in **Fig.(4)**.The increase in the values of g(r) (maximum value at χ =0.5) may be due to the movement of the alkali modifiers (Li ions in this case) to occupy the spaces between the network formers Bi-O-Bi (which remains unchanged) and hence an arising of MAE. On the other hand the replacement of K atoms by those of Li atoms leads to change in the distribution of atoms in the glass matrix and hence change in the values of g(r). As a result of the change in the structure of the studied glass samples, all its related properties such as density, conductivity and metal non-bridging oxygen (M-nbo) are also change.

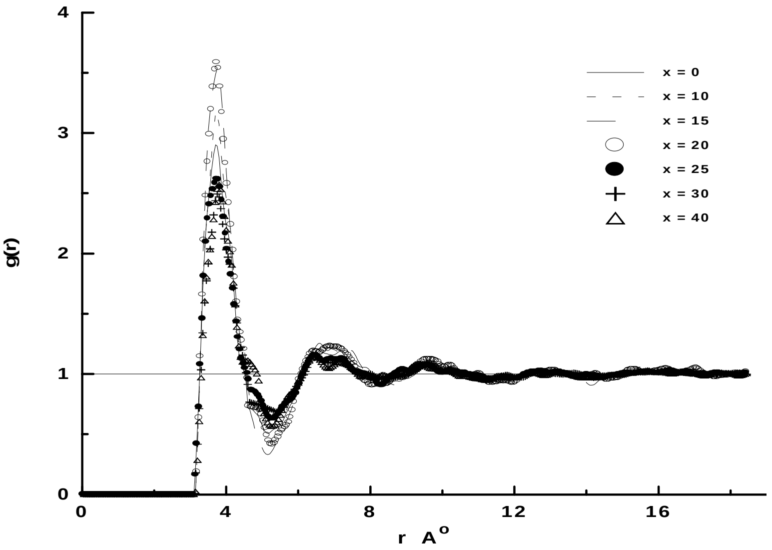

Figure 3a: Experimental pair distribution function (PDF) of $(Bi_2O_3)_{50}$ $(Fe_2O_3)_{10}$ (Li2O)x(k2O)$_{40-x}$

To give more version about the relation between the structure and MAE we suppose the shell of radius $(r+\Delta r)$ shown in **Fig. (5)**. At the χ =0.5 almost all the Li atoms (due to its small ionic radius) will locate on the shell$(r+\Delta r)$.This will lead to a maximum distribution of atoms around the distance r and hence maximum value of g(r).Also, a more less chance to the alkali atoms to move at this ratio (due to the high concentration of atoms) and a minimum deviation of both the diffusion coefficient and conductivity is observed.

The above discussion could be compared with Stevel's model [18] who visualizes the glass network as containing interstices of varying diameters such that alkali ions of different sizes are more easily accommodated in these sites (mixed alkali glasses) than when all the alkali ions have the same size (single alkali glasses).The alkali ions in mixed alkali glasses thus locate in the more energetically favorable sites, thereby increasing the energy required for alkali ion movement.

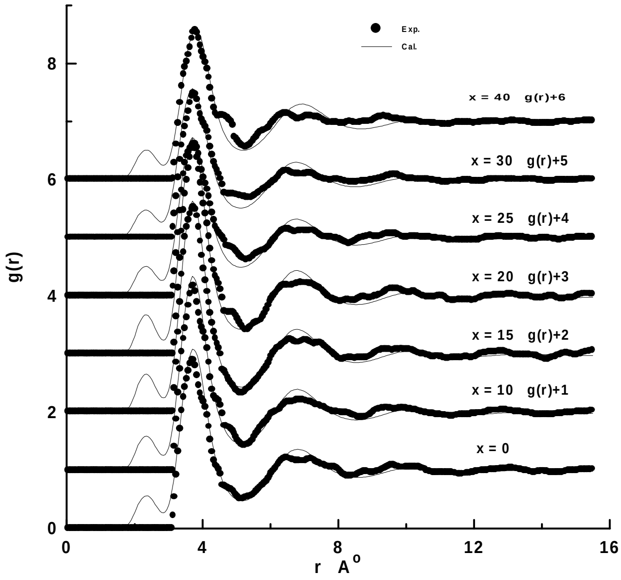

Figure 3b: Experiment and calculated pair distribution functions of $(Bi_2O_3)_{50}$ $(Fe_2O_3)_{10}$(Li2O)x(k2O)$_{40-x}$

Fig. (4) Shows also a lower values of g(r) in the side of high concentration of K (χ is between 0 and 0.5) than that of Li side. This could be interpreted as due to two reasons:

(a) In the side of high concentration of K and due to its higher ionic radius (r_K=1.33 A^0) which is almost equal to that of Bi, it can not occupy the possible spaces between Bi-O-Bi bonds. This leads to a gradual decrease in the maximum peak in this side, see fig. (4).

(b) On the other hand, in the side of high concentration of Li (χ is higher than 0.5), there is a more chance for Li to occupy the spaces between Bi-O-Bi bonds due to its smaller radius (r_{Li}=0.68A^0) .In the same time a shift in the maximum peak will occur in this side, and hence the number of ions on the shell(r+Δr), see **Fig. (5)** will decrease leading to a pronounced decrease in the maximum peak.

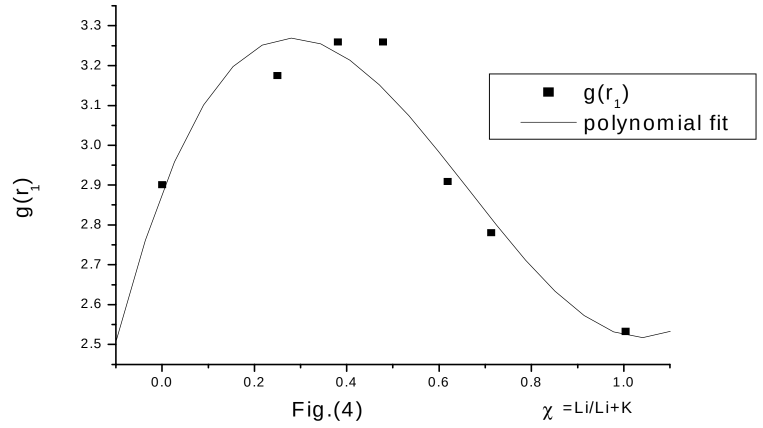

Figure 4: The values of (PDF) at the first neighbor distance as a function of mole fraction χ.

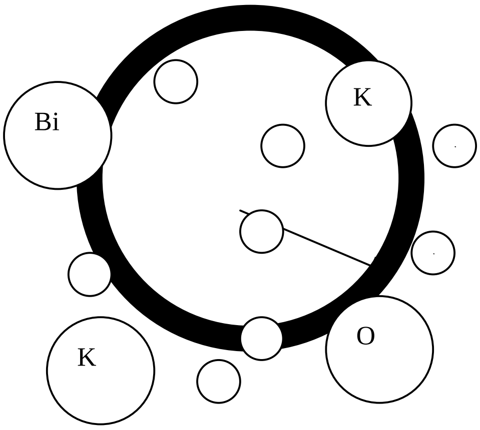

Figure 5: A schematic representation for the distribution of the Li and K ions around the other ions (in studied glass) lies a certain shell .

Effect of Non-Bridging Oxygen Content

About half of the proposed models postulate non-bridging ions in the alkali oxides as necessary centers to produce MAE especially in DC conductivity. However, experimentally very little is known about how non-bridging oxygen can affect the mobility of different alkali ions. The present study has established, for the range of compositions studied here, that the concentration of non-bridging oxygen in a glass is an important contributory factor in the development of such effects. Appling the pair potential analytical method [19] we could calculate PDF for lithium and potassium-bridging oxygen [Li-bo and K-bo] as well as lithium and potassium non-bridging oxygen [Li-nboand K-nbo].The results of the calculations are represented in **Figs (6) and (7). Fig.(8-a,b)** shows the values of PPDF in the case of M-nbo and M-bo as a function of alkali mole fraction χ.

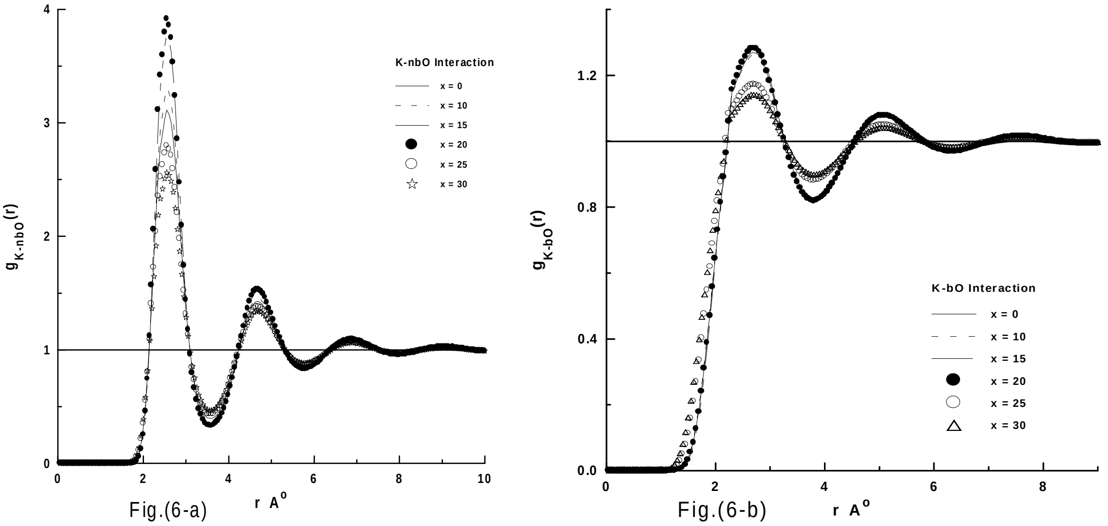

Fig.(6-a) Fig.(6-b)

Figure 6-a,b: Values of PDF's at first neighbor distance for K-nboand K-bo interactions respectively.

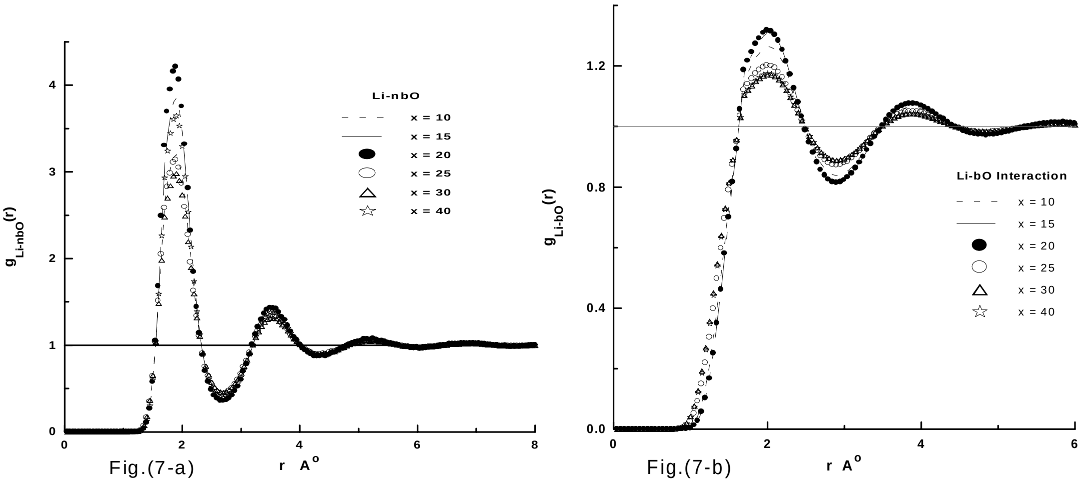

Fig.(7-a) Fig.(7-b)

Figure 7-a,b: Values of PDF's at first neighbor distance for Li-nboand Li-bo interactions respectively.

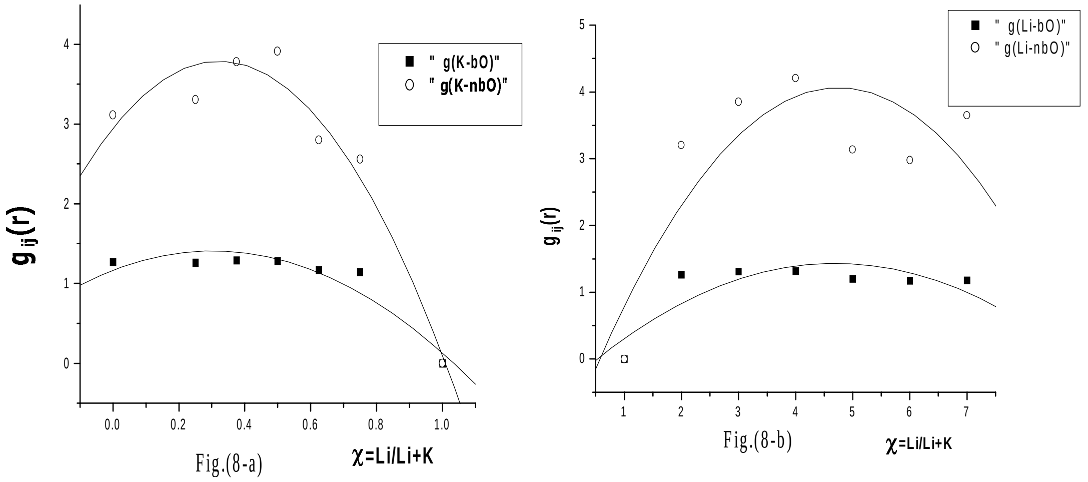

Fig.(8-a) Fig.(8-b)

Figure 8-a,b: Values of PDF's at first neighbor for the interactions in figs.(6and 7) as a function of alkali mol fraction χ.

The results show a clear maximum deviation from linearity in the case of ion-non-bridging oxygen (k and Li-non-bridging oxygen) while an insignificantly deviation is observed in the case of ion bridging oxygen at χ =0.5. Figure (8-a,b) show also that the g_{ij}(r)-nbo goes through a strong maximum when potassium ions are gradually replaced by lithium ions .This maximum deviation is slightly higher in the case of Li-nbo. As noted earlier, Hayward [13] concluded that a minimum concentration of nbos was necessary in sodium-potassium glasses to produce MAE .It had not possible for him, to determine whether the O^- ions exert their influence by acting merely as relatively stable sites within the glass network for the closer concentration of dissimilar alkali ions or whether they take a more participatory role in the mixed alkali interaction. Weyl and Marboe [20] consider the interaction between dissimilar alkalis to result from the anharmonic thermal vibration of alkali ions about the non-bridging oxygen ions. They suggested that when the alkali ions bonded to the non-bridging oxygen ions are identical, their thermal vibrations are symmetrical (harmonic) and in phase. When the alkali ions have different masses, however, the thermal vibrations are said to become asymmetrical (anharmonic) thereby reducing the repulsive forces between dissimilar alkali ions, which results in a stronger alkali –oxygen bond The important feature of this theory is that the MAE is attributed to differences in atomic mass, with no special structural differences between single and mixed alkali glasses. According to Mazurin theory [21] of the field strength the substitution of a cation of low field strength (e.g. K^+) for one of higher field strength (e.g. Li^+) causes a reduction in the degree of O^- polarization and a resulting increase in the ability of O^- ions to form bonds with nearly mobile (Li^+) cations and hence more pronounced in MAE. Lam et al. [22] have studied the structural of sodium –aluminosilicate glasses using x-ray photoemission spectroscopy (XPS) They were able to identify changes in the concentration of non-bridging oxygen when replacing a silicon by an aluminum by measuring the strength of (XPS) peak corresponding to the 1s level of the oxygen atom .Contrary to the generally accepted picture, they found that the introducing of an aluminum ion in place of a Si ion does not eliminate a non-bridging oxygen. The aluminum enters into tetrahedral bonding with oxygen's, but the charge is compensated by the uniform transfer of electron charge density from the non-bridging oxygen to aluminosilicate network. In this process the identity of non-bridging oxygen is maintained (at least for small aluminum additions), but its effectiveness as a high electron density center is reduced in favor of the glass network at large. As a consequence the attraction of an alkali ion to non-bridging oxygen is reduced. If this attraction in some way helps to produce the MAE, the reduction in the MAE observed by Hayward [13] may then be related to this reduction in attraction.

Jain et.al. [23] studied some halogen doped lithium- sodium borate glasses to further investigate the role of nbos ions in producing the MAE. The behavior of electrical conductivity is observed as a fraction (~ 1%) of the total oxygen's replaced by a halogen molecule, keeping the total alkali concentration fixed. At these small doping levels, the bulk of the glass structure should remain nearly unchanged, and the changes in the MAE, will be primarily due to differences in the properties of non-bridging oxygen and a halogen ion.

The mechanisms for configurationally changes in the network structures which have described by Lacy [24] include several in which bridging and non-bridging oxygen ions exchange roles. These procedures are all reversible and will be thermally activated.

Although large imbalances of local electrostatic charge could not be tolerated in a glass forming network, it is doubtful whether M^+ ions can all be considered as being in direct contact with O^- ions. In many cases the situation will arise whereby an M^+ ion is partially occluded from its O^- site by bridging oxygen. In such circumstances, the charge of the bridging oxygen to non-bridging role would obviously be energetically favorable. Similarly, for an alkali ion in close proximity to an O^- ion, the assumption by the latter of a bridging function would be equally unfavorable.Viewing the glass structure as a whole, the enhanced probability of energetically favorable non-bridging / bridging oxygen configuration change with rise in temperature should serve to reduce the overall mean M^+-O^- separation distance within the network. The corresponding slight increase in the mean bond strength of M^+-O^- associations would then exhibit itself as a progressive rise in activation energy. This trend is found for the maximum deviation of M^+-nboat an equally alkali mole fraction which is attributed to the arising of MAE phenomenon.

On the other hand on the basis of NMR studies of single alkali borate and silicate glasses [25, 26], Raman studies on ($MO_{1/2}$)-TeO_2 glasses (M=Li, Na, K, Rb or Cs) [27], neutron diffraction radial distribution function analysis on alkali germinate glasses [28] and DC conductivity and DSC measurements [29], the correlation between the MAE and the non-bridging oxygen concentration has been discussed and it was reported that generally beyond a certain limit of the alkali content an increasing amount of nbos would be contained in the glass matrix. Some modeling studies suggested that the alkali ions would be located in the vicinity of the nbos and the alkali ions movement accompany the motion of the nbos in the same direction [30] and it has been reported that no MAE can occur without the presence of nbos [31]. Mobile alkali ions migrate along pathways or conduction channels which become more established as the alkali ions content increases where the glass structure would be modified to be like islands separating the pathways through which the “1-D transport process” migration occurs and the transport path of the the mobile is defined by the location of the nbos [30,32,33]. However some studies suggested that nbos is not necessary for the MAE to occur [23, 34]. On the other hand, it has been suggested that migration of the alkali ions in a mixed alkali glass occurs by “the interchange transport process” where on type of the alkali ions preferentially jumps to a vacant site previously occupied by the same kind of the alkali and not to a site previously occupied by an unlike alkali ion [29, 35] and this mechanism also requires the presence of nbos in glass matrix. The preferential “interchange transport process “would be minimized or inhibited when the content of the two unlike ions become comparable and the MAE occurs.

Conclusion

The present work proved that the static structure [g(r)] and the alkali non-bridging oxygen are strongly related to the MAE phenomenon. The results obtained in the present work with those conducted in the previous studies [18-24] proved the importance of the non-bridging oxygen ions existence in glass for arising the MAE phenomenon.

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