

Distribution of ionic charge carriers and migration barriers in binary alkali silicate glasses

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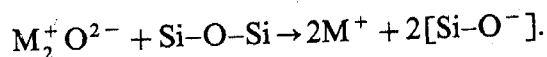
Abstract. Likely spatial distributions of network-modifying (and mobile) cations in (oxide) glasses are discussed here. At very low modifier concentrations, the ions form dipoles with non-bridging oxygen centres while, at higher levels of modification, the cations tend to order as a result of Coulombic interactions. Activation energies for cation migration are calculated, assuming that the ions occupy (face-sharing) octahedral sites. It is found that conductivity activation energy decreases markedly with increasing modifier content, in agreement with experiment.

Keywords. Alkali ions; Silicate glasses; migration energy barriers; Spatial distribution; activation energies; non-bridging oxygen ions.

1. Introduction

Migration barriers of alkali ions in silicate glasses have long been investigated experimentally by electrical conductivity and radioactive tracer self-diffusion measurements (Frischat 1975; Paul 1982). The activation energies are found to decrease rapidly with increasing concentration, x , of modifier oxide (M_2O) in binary silicate glasses, $xM_2O \cdot (1-x)SiO_2$ up to a concentration $x = 0.3$; thereafter, the activation energies tend to level off. This behaviour of the activation energy is found empirically to vary with composition in a similar manner to that of the average number of bridging oxygen (BO) atoms per Si atom, the so-called Stevels parameter (Paul 1982). Evidently, non-bridging oxygen (NBO) ions play an important role in determining the magnitudes of the activation barriers in modified silicate glasses.

Vitreous silica consists of a 3-D network of corner-shared $[SiO_{4/2}]$ units and its structure has been investigated in a number of studies (Elliott 1990). Modification of the network can be visualized as a depolymerization process wherein Si-O-Si bonds associated with BO atoms are broken, with the production in pairs of NBO ($Si-O^-$) centres when alkali oxides are added, viz.



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Evidently there will be Coulombic interactions between the charged M^+ ions and the NBO O^- centres. In addition, M^+ ions polarize the significantly polarizable oxygen atoms (both BO and NBO), inducing strong dipoles on them. The interactions of the induced dipoles with the alkali ions themselves (the polarization self-energy) can be quite substantial at short distances. Furthermore, when the NBO's are present on neighbouring SiO_4 tetrahedra, there is an electrostatic repulsion which tends to force them apart. Since the number of sites on which such NBO's can be located are numerous when the modifier content x is small, it is entropically favourable for the NBO's to be randomly distributed.

Hence, in such materials, there are a number of significant and competing energies of interaction: the Coulombic attraction between M^+ and NBO, the Coulombic repulsion between NBO's and between M^+ ions, the polarization self-energies of the M^+ ions and the entropy associated with the distribution of NBO's ($T\Delta S$ terms). These determine the configuration of the ground state of a modifier cation in silicate melts (and hence in the quenched glasses). Anion polarization self-energies and overlap repulsions can be effectively neglected in this regard. Thus, if these energy terms are known, at least approximately, we can address the question of the variation of the energy barriers.

In this paper we show that, in *dilute* modified glasses, the NBO's tend to be separated from each other, but that the M^+ -NBO pairs tend to remain together. As the modifier content, x , increases, the mutual electrostatic interactions between different pairs of M^+ ions and NBO centres increase, and hence M^+ -NBO separations tend to increase so as preferentially to exploit the Coulombic interactions through a Madelung-type term. For such a situation, we show that the activation barriers for migration decrease with increasing x , by making the assumption that the alkali ions are located at the centres of face-sharing octahedra (comprising oxygen atoms), the faces in common thereby acting as "doorways", or short tunnels, for alkali-ion migration.

2. Glasses with low modifier contents

In modified glasses, several configurations of M^+ with respect to NBO sites can be envisaged. In cases when neighbouring NBO's do not separate, the lowest energy configuration would be as shown in figure 1, comprising a square arrangement of two M^+ and two NBO atoms; the M^+ ions will also be coordinated by other BO atoms not shown in the figure. Evidently there will be a mutual Coulombic interaction between the four charged species but the polarization self-energy will be essentially zero since such close M^+-O^- pairs (effectively acting as dipoles) will polarize neighbouring BO atoms in the opposite directions. Thus, the energy of interaction can be written as:

$$E_1 = -x \left(\frac{4e^2}{r} - \frac{2e^2}{\sqrt{2}r} \right) = -2.6 \frac{xe^2}{r} \quad (1)$$

where r is the M^+-O^- separation and x is the mole fraction of modifier. (It should be noted that a tetrahedral arrangement of the four charged ions results in larger, less negative interaction energy, viz., $E_1 = -2xe^2/r$).

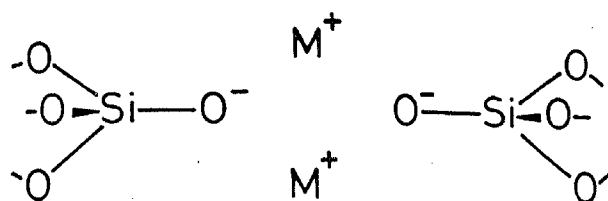
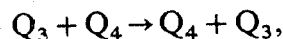


Figure 1. Schematic illustration of the depolymerization caused by the addition of network-modifying cations, M^+ , to glassy silica. At low levels of modification, pairs of dipoles occur, formed from M^+ ions and non-bridging oxygen.

Let us now suppose that (in the melt prior to quenching to form the glass) the M^+ -NBO pairs drift away from each other (but each M^+ ion remains "bound" to an individual NBO site). Since a single NBO in an SiO_4 tetrahedron can be written equivalently as a Q_3 unit, and bonds between tetrahedra can be switched such that



the M^+ ions in such isolated M^+ -NBO pairs can end up occupying energetically favourable sites in which the nearest-neighbour coordination shell comprises the single NBO and a number, n , of BO atoms. For the case of Na^+ , for example, $n = 5-6$, and so the sites are essentially octahedral figure 2. In such a case, the energy of interaction can be written as the sum of two terms, one Coulombic and the other a polarization term, viz.

$$E_2 = -\frac{2xe^2}{r} - \frac{2x \cdot 6\alpha e^2}{r^4} = -\frac{2xe^2}{r} \left[1 + \frac{6\alpha}{r^3} \right]. \quad (2)$$

where the factor of 2 in both terms refers to the two M^+ -NBO configurations under consideration (one of which is shown in figure 2), and where α is the polarizability of the oxygen atoms (assumed to be the same for both BO and NBO configurations).

The configurational entropy associated with the separation of such M^+ -NBO pairs can be estimated as follows: For the composition $xM_2O \cdot (1-x)SiO_2$, there are $N_A(1-x)$ $SiO_{4/2}$ tetrahedra (where N_A is the Avogadro number). Of these, $2xN_A$ tetrahedra are converted to Q_3 units by the incorporation of the modifier, therefore leaving $(1-3x)N_A$ as Q_4 units. An upper limit to the value of the configurational energy can be obtained by simply considering permutations of this number of Q_3 and Q_4 units without any further constraints. (Restricting the number of permutations by precluding some configurations would result in a smaller value of the entropy.) In such a case, the number of complexions arising from such a general permutation would be

$$W = [1-x]! / (1-3x)!(2x)!, \quad (3)$$

and the resulting entropy would be (using Stirling's theorem):

$$\Delta S = k \ln W = R[(1-x)\ln(1-x) - (1-3x)\ln(1-3x) - 2x\ln 2x]. \quad (4)$$

This term is maximal for $x = 0.81$, and ΔS has the value of 0.56 JK^{-1} . The corresponding term, $T\Delta S$, will tend to stabilize the separated arrangement of the M^+ -NBO pairs in the melt. Taking the glass-transition temperature, T_g , as the last temperature

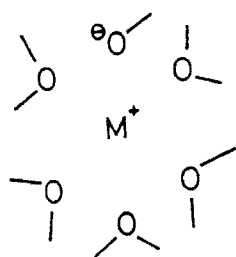


Figure 2. Schematic (two-dimensional) representation of an octahedral interstice containing a network-modifying cation, M^+ , formed from bridging oxygens and a non-bridging oxygen.

at which thermal equilibrium existed in the melt, and assuming, as usual, that this value also characterises the glassy phase, the largest value of $T\Delta S$ is $T_g\Delta S \approx 4.2$ kJ/mol or 0.04 eV, where $T = T_g \approx 900$ K for alkali silicate glasses.

By contrast, we can compare this entropy term with the (Coulombic and polarization) energy terms, E^1 and E^2 [equations (1) and (2)] which are each of the order 3–6 eV; hence, the entropy term is completely negligible in determining whether or not M^+ –NBO pairs separate. The condition for separation of the pairs to be energetically favourable is when $E_2 < E_1$, i.e. when $12\alpha/r^3 > 0.6$. This condition is satisfied for the case, of sodium silicate glasses, if $\alpha(\text{oxygen}) = 0.5 \text{ \AA}^3$ since $r \approx 2.3 \text{ \AA}$. The value of α for O^{2-} ion has been reported to vary widely and it depends on the metal ion to which oxygen is covalently bonded. The value of α for an NBO should be lower than that of O^{2-} ion and close to that of a BO. In view of the fact that O^{2-} has a polarizability of about 1.3 \AA^3 we adopt a value of 1.0 \AA^3 for polarizabilities of both BO and NBO in the present problem.

The condition determining the low-modifier-content limit is that the Q_3 units should be isolated, i.e. not in contact. A percolation path of contacting Q_3 species begins to be established at $x = 0.16$ (Elliott 1993), and so this marks the low-modifier-content limit. Thus, for $x \leq 0.16$, we expect that M^+ –NBO ion pairs always remain separated (but each pair remains bound together).

We have assumed that the only type of modified $[\text{SiO}_{4/2}]$ units present in the glass are Q_3 configurations. Hence, equilibria of the type $2Q_3 \rightleftharpoons Q_4 + Q_2$ have been neglected. We note in passing that such general equilibria between Q_n species have been considered in detail by Gurman (1990), who postulates that the equilibrium (in the melt) is governed by the term $\exp[-\Delta E/kT]$ where the ‘‘bond-ordering energy’’ $\Delta E = E_{bb} + E_{nn} - 2E_{nb}$ and where b and n denote BO and NBO sites respectively present in the same $[\text{SiO}_4]$ tetrahedron. If the BO sites are assumed, for simplicity, to be uncharged, and the NBO sites carry a single negative charge, then $\Delta E \approx E_{nn} \sim 14.4/r_{nn}$ eV, where $r_{nn}(\text{\AA})$ is the intratetrahedral separation between NBO sites (in a Q_2 configuration). Typically, $r_{nn} \approx 2.7 \text{ \AA}$, and so $\Delta E \approx 5.4$ eV, very much higher than the value for ΔE inferred by Gurman (1990) from a mass-action treatment of the relative proportion of Q_n species derived from Raman and NMR data, viz $\Delta E \approx 2kT_g \approx 0.2$ eV, casting doubt on this approach. Gurman (1990) also made an estimate for ΔE based on electrostatic arguments similar to ours but the value he obtained (≈ 0.25 eV) was arrived at by including the dielectric constant (a value corresponding to the bulk value, $\epsilon \approx 10$). We regard this procedure as very dubious, since the charges on NBO sites in a Q_2 unit cannot be screened by the bulk dielectric constant at such

short distances. Only by reducing the charge on an NBO to $0.2e$ can the magnitude of the electrostatic interaction be reduced to a value comparable to that deduced from mass-action considerations of bond-ordering energies.

3. Glasses with higher modifier contents

In the low modification regime ($x \rightarrow 0$), there are several equivalent positions for an M^+ ion around an NBO site for which the energy of the system is effectively the same. However, at high modifier contents, each M^+ ion interacts (Coulombically) with several other ions and its equilibrium position therefore corresponds to a position of minimum Coulombic energy. Thus, when it moves (adiabatically) out of such a position, the interaction energies are expected to be altered drastically. The vacated position is quite similar to that of a Schottky defect in crystalline solids. Indeed, the imbalance of charge (virtual charge of opposite sign) at the "vacancy" when an ion is not at the equilibrium position causes polarization and, hence, results in a polarization energy if the surrounding ions do not readjust their positions correspondingly.

4. Migration energies in the low- and high-modification regimes

Recent EXAFS analyses of the structure of alkali silicates suggest that, except for Li^+ ions, the alkali ions occupy sites in which they are coordinated by 5–6 oxygen atoms (Greaves *et al* 1991); six-fold coordination of Na^+ ions in glasses is perhaps the most frequently observed. We further assume that the local geometry of the sites is octahedral. The triangular faces of such octahedra could be connected to similar octahedra and/or to tetrahedra. Although a space-filling arrangement of all-face-sharing octahedra is not possible, it is possible to envisage an arrangement where an octahedron shares faces with *two* other octahedra, thereby forming a (zig-zag) chain of connected octahedra. When the modifier content is large ($x > 0.16$), there is, on average, one NBO per octahedron. As a result, the path involving face-sharing octahedra becomes decorated with NBO sites forming a percolation path of connected NBO sites (Elliott 1993). This picture is somewhat reminiscent of the "channels" in the modified random network (MRN) picture of Greaves (1985), except that here we are more specific about the coordination polyhedra, and their connections, to the network modifier sites.

The principal motif is a pair of face-sharing octahedra, which we may consider first to contain an NBO site and an Na^+ ion. This arrangement is a generalization of the model involving dioctahedra containing *only* non-bridging sites considered for the case of highly modified lithium thioborate glasses by Rao *et al* (1993). The simplest representation of two-face-sharing octahedra is as three equilateral triangles in parallel ABAB stacks, with their centres aligned to form an axis (see figure 3). Viewed along the axis, this arrangement has cylindrical symmetry which permits easy evaluation of all relevant distances. Let us suppose that one of the oxygen atoms in the dioctahedron is an NBO and consequently the remaining eight oxygen atoms are BO configurations. If this situation represents the overall average composition, then the ratio of NBO sites to BO sites is $1/8 = 2x/(2 - 3x)$, corresponding to the modifier content $x = 0.11$ which is within the low-modification regime.

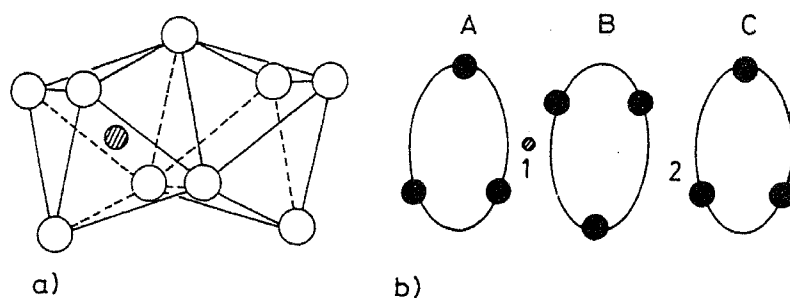


Figure 3. Two face-sharing octahedral interstices (a) and an equivalent representation of the dioctahedron (b) emphasizing the local cylindrical symmetry of such a unit. In (b) the oxygen ligands lie on circles A, B, C and the stable positions of the cation M^+ are between such rings.

The NBO can be present on any of the three rings shown in figure 3. Let us first suppose that the NBO is on ring A (or C) and that the ion M^+ is at position 1 (or 2). We consider that the primary event of migration is the motion of the M^+ ion from position 1 (or 2) to 2 (or 1). When the ion moves through the migration doorway which is the middle ring comprising three BO atoms, it displaces these atoms radially outwards. These displaced atoms, in turn, exert an outward compression on the rest of the structure through the covalent bonds connecting into the network. This is the source of the so-called strain energy (Chan and Elliott 1991). For the purpose of this calculation, we assume that all the octahedra are regular, and consequently, from the geometry of octahedra, when the M^+ ion is at the centre of the central ring (the activated saddle-point position), the BO atoms on the ring are displaced by a distance of $0.18r$ (where r is the normal M^+-BO or M^+-NBO distance) so that the M^+-BO distance in the saddle-point position is also r .

Let the energy of the M^+ ion in the ground state (position 1 or 2) be E_G and in the activated saddle-point state be E_S . The activation barrier is therefore $\Delta E = E_S - E_G$. If we consider Coulombic, polarization and overlap repulsion terms only, neglecting the strain-energy term which is very small, ≤ 0.1 eV (Rao *et al* 1993; Elliott 1993), and if we use an exponential form of the repulsion energy (Rao *et al* 1993), then

$$E_G = -\frac{e^2}{r} - \frac{6\alpha e^2}{r^4} - \frac{3\alpha e^2}{((11/3r)^{1/2})^4} + 6b \exp(-r/\rho) \quad (5)$$

and

$$E_S = -\frac{e^2}{\sqrt{2}r} - \frac{3\alpha e^2}{r^4} - \frac{6\alpha e^2}{(\sqrt{2}r)^4} + 3b \exp(-r/\rho), \quad (6)$$

where again we have assumed that the polarizabilities α of both BO and NBO species are the same. Thus, the migration activation energy is:

$$\Delta E \approx 0.29e^2/r + 1.72\alpha e^2/r^4 - 3b \exp(-r/\rho). \quad (7)$$

Hence the activation energy consists of positive Coulombic and polarization terms and a negative repulsive contribution. In the situation pictured in figure 3, the motion of the ion is in a direction opposite to that of the Coulombic attraction.

The individual terms in (7) can be evaluated as follows. The Coulombic term is

equal to 1.82 eV if the $\text{Na}^+ - \text{O}^-$ distance is taken to be $r = 2.3 \text{ \AA}$. If the polarizability of oxygen atoms (BO and NBO) is 1.0 \AA^3 , the polarization term contributes 0.88 eV. The repulsive contribution can be estimated, as is commonly done for ionic systems, by assuming that the net repulsive energy in the ground state is approximately 20% of the total ionic cohesive energy (Rao *et al* 1993), viz

$$6b \exp(-r/\rho) = 0.2\alpha_M e^2/r, \quad (8)$$

where α_M is an appropriate Madelung constant. If α_M is taken to have the value = 1.7 (Rao *et al* 1993), then the net repulsive term in (7) is $\Delta E^R = 0.17e^2/r = 1.06 \text{ eV}$ for the case of $\text{Na}^+ - \text{O}^-$ interactions. Thus, the total (conductivity) activation energy is estimated from (7) to be $\Delta E = 1.66 \text{ eV}$. This estimate compares well with experimental values of the ionic d.c. conductivity activation energy for low-modifier-content oxide glasses, for which $E_a \leq 1.7 \text{ eV}$ (Frischat 1975; Martin 1988). However, there are uncertainties related to the polarization term because of the corresponding uncertainty in the value of the polarizability, α , of the oxygen species. Uncertainties are also present in the repulsive and Coulombic terms due to the nature of assumptions made about their relation and also due to the assumption of the value of the Madelung constant.

At the beginning of the high-modification regime, we would expect more NBO centres to be present and possibly also a more extended structure consisting of face-sharing octahedra. We consider one such configuration in figure 4, where three dioctahedra share mutual faces. The three M^+ ions associated with this unit are located at the positions marked \oplus and the three NBO sites at the positions denoted by \ominus . The dotted lines indicate the resemblance to a "unit cell" in this representation, although we should remember that such face-sharing octahedra actually form contorted chains with no unique axis of propagation. The dots in figure 4 without associated labels are BO atoms. The composition of the cluster thus comprises 3 NBO and 15 BO atoms or $2x/(2 - 3x) = 3/15$, corresponding to a modifier content $x = 0.15$ which marks the beginning of the high-modification regime.

When the central M^+ ion moves to the position between rings 4 and 5, it is in a similar site to where it was before the migration step because it is still in the vicinity of an NBO atom at a distance r . However, the energy would be slightly different

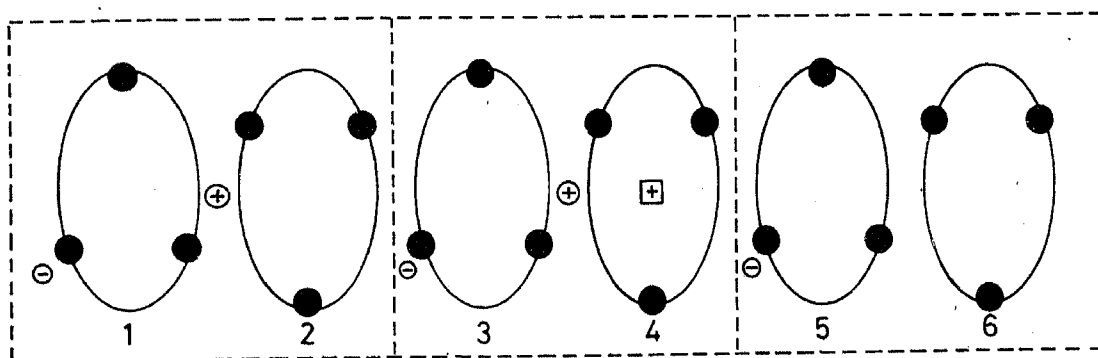


Figure 4. A schematic representation of three face-sharing dioctahedra. Filled circles on the rings represent oxygen atoms; those denoted by \ominus are non-bridging sites. Stable positions for the cations M^+ are denoted by \oplus and a metastable, saddle-point position at the centre of a common face is denoted by \boxplus . Although this representation implies that such linked dioctahedra form straight chains, in practice such chains are contorted.

because of the influence of the other cation. With the same notations as used before, we will calculate E_G and E_S (the superscripts C, P and R refer to Coulombic, polarization and repulsion terms, respectively). Thus,

$$E_G^C = -\frac{e^2}{r} - \frac{e^2}{r(11/3)^{1/2}} - \frac{e^2}{r(27/3)^{1/2}} + \frac{2e^2}{4r/3^{1/2}} = -\frac{0.99e^2}{r}, \quad (9)$$

and

$$E_G^S = -\frac{e^2}{r\sqrt{2}} - \frac{e^2}{r\sqrt{2}} - \frac{e^2}{r(38/3)^{1/2}} + \frac{e^2}{r(3/3)^{1/2}} + \frac{e^2}{r(5/3)^{1/2}} = -\frac{0.77e^2}{r}, \quad (10)$$

Similarly

$$E_G^P = -\frac{6\alpha e^2}{r^4} - \frac{6\alpha e^2}{[r(11/3)^{1/2}]^4} - \frac{6\alpha e^2}{[r(27/3)^{1/2}]^4} = -\frac{0.54e^2}{r}, \quad (11)$$

and

$$E_S^P = -\frac{3\alpha e^2}{r^4} - \frac{6\alpha e^2}{(r\sqrt{2})^4} - \frac{6\alpha e^2}{[r6^{1/2}]^4} - \frac{3\alpha e^2}{[r(38/3)^{1/2}]^4} = -\frac{0.38e^2}{r}, \quad (12)$$

where again a value of $\alpha = 1.0 \text{ \AA}^3$ has been used. As before

$$E_G^R = 6b \exp(-r/\rho), \quad (13)$$

and

$$E_S^R = 3b \exp(-r/\rho), \quad (14)$$

and we take the relative value of the repulsive energy as given in (8). Thus, $E = \Delta E^C + \Delta E^P + \Delta E^R = 0.21e^2/r = 1.26 \text{ eV}$. Thus, a marked decrease is predicted in the value of the ionic migration energy from the value characteristic of low concentrations of network modifiers. The ionic d.c. conductivity activation energy decreases to plateau values in the range 0.6–0.8 eV in oxide glasses when modifier content increases to values $x = 0.2$ – 0.3 (Frischat 1975; Martin 1988). However, in addition to the uncertainties in the theoretical estimate, there are uncertainties in values of the numerical constants like the polarizability. Equations (11) and (12), may also be erroneous, since the last term in E_G^P , (11), and the last two terms in E_S^P , (12), are affected by the polarization of other cations.

We expect the Coulombic and polarization energy contributions to vary rather nonlinearly as the modifier ion content x increases. However, in the absence of detailed structural models in which the positions of cations and non-bridging anion sites are known (as a function of x), it would be inappropriate to speculate on the likely behaviour of E_r as a function of composition between the two representative values estimated above. It is interesting to note here that in the low alkali regime the ratio of Coulombic to polarization energy was $1.8/0.88 \approx 2.0$ and it decreased to $22/16 \approx 1.4$, thereby suggesting that the polarization energy term becomes increasingly more important at higher levels of modification. A somewhat similar conclusion was arrived at by Elliott (1993) independently; activation energy at low modifier contents depends primarily on the Coulombic term, whereas at higher levels of modification, the smaller polarization term becomes dominant.

5. Conclusions

It has been shown that the structural environment of network-modifying cations, M^+ , in glasses could be markedly different in two composition regimes: (1) in the low-modifier-content regime, ion pairs (M^+ -non-bridging anion) are formed and occur at well-separated distances; (2) at higher modifier contents, the ion pairs are further separated and tend to order for taking advantage of Madelung-type Coulombic energy terms. It has also been demonstrated that modifier-ion clustering does not occur until very high levels of modification are reached.

Activation barriers for Na^+ ion migration in oxide glasses have been calculated for two representative values of modifier content ($x = 0.11$ and 0.15), corresponding respectively to the low-modification regime and the beginning of the high modification regime. Assuming that the alkali ions occupy (face-sharing) octahedral sites, coordinated by bridging and non-bridging oxygen species. These calculations show that the (ionic conductivity) activation energy decreases markedly with increasing modifier content, in conformity with experimental observation.

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