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Conduction Modeling in Mixed Alkali Borate Glasses

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Abstract

A theoretical study of mixed alkali glasses in terms of electrical transport processes has been presented. With the use of some assumptions of the previous theories, the activation energy according to our approach is evaluated. The composition dependent of this activation energy in comparison with that estimated from the experimental data is also included. By contrast, no difference has been found in the mixed K-Na borate glasses in all composition regions, while the results for Li-Na containing glasses agree to certain limit of composition ($Li_2O/Na_2O < 1$). Therefore, the proposed approach (which we have attempt) is appropriate to explain the mixed alkali borate glasses in terms of "mixed alkali effect"

Key words: mixed alkali effect, conduction, activation energy and borate glasses.

Introduction

At high temperature most materials liable to show increasing movements of ions. Ion-conducting glasses have several distinct advantages over their crystalline counterparts. These advantages include: continuously variable composition; high value of ionic conductivity; absence of grain boundary and possibility of fabrication of thin film form. A large number of glasses with various mobile ion species, namely Ag^+, Li^+, Cu^+, Na^+, F^-, have been studied [1-3]. These glasses are formed by mixing the glass forming oxides, SiO_2, B_2O_3, P_2O_5, with one or more glass modifiers, Ag_2O, Li_2O,Na_2O. Glasses can also be prepared by using more than glass modifier oxides to produce mixed alkali glasses.

The non-linear behavior of certain properties with respect to alkali content is known as the mixed alkali effect. Various thermodynamic analyses have been given to explain the mixed alkali effect [4,5]. This effect has a significant application [6-8] and makes the mixed alkali glasses of special interest, for instance, low dielectric loss glasses can easily be obtained by incorporating two different alkali.

The dependence of conductivity on ionic radii may be considered the striking feature of the mixed alkali effect. This effect is more pronounced as the difference in size of the two alkali increases as reported by Hakim et al [6,7]. They also observed that the maximum in activation energy is usually seen at approximately equal proportions of alkali content.

Several theoretical models have been proposed to understand the ion transport mechanism in ion conducting glasses. One of these models is the Anderson and stuart model [8]. They assumed that measured activation energy, Ea, which corresponds to the energy barrier for cation migration, is the sum of an electrostatic binding energy, E_b (required to break the ion-oxygen bond and to move the ion halfway between neighbouring sites), and a strain energy, E_s (caused by deformation of the network due to ion movement). They also stated that the ionic mobility, μ, increases with increasing temperature rather than mobile ion concentration, n. Many other models were proposed but Anderson and stuart model still the most acceptable model.

In this study, a modification of this model to explain the mixed alkali effect will be introduced. It is well known that the activation energy for conduction is one of the most sensitive parameters to the changes in the type and concentration of alkali ions. So, the activation energy for conduction as a function of the replacement of one alkali type with another is used to verify the proposed model.

The presented model considers that the transport process is due to cation site-site hopping as:

1. The small radius ions have the opportunity to jump to any adjacent partner sites (back and forth).
2. The small radius ions may also jump to sites belonging to large radius ions.
3. The large radius ions could jump to their partner sites.
4. The jump of large radius ions to small sites is hardly occur.

On application of an electric field, the ions tend to jump more easily in the direction of the field than against it (case 1&3), giving rise to the ionic conduction. This may take place because the nearest neighbour vacancies are large enough to accommodate these cations. While the jump backward (in case 1) consumes energy without profits to the conduction. For the process involving transport of small cation to a large site (case 2), Rouse et al [9] considered that this process causes an increase in the transport conduction. On the contrary, the present model suggested that these ions in such case are trapped and/or need more energy to go in a deep energy wells left by large radius ions and need more energy to take them out again.

The transport of large cation to a small site, however, needs an additional amount of energy (strain energy) to expand the small site so that it can accommodate the large cation.

Generally, all the above interactions can be expressed in terms of the activation energies for cation site-site hopping.

Calculations

The activation energy for conduction can be estimated theoretically as a sum of two terms, the strain energy and the binding energy [8].

The strain energy

The motion of alkali ions in the structure causes elastic deformation. If the pathway has a radius, r_m ,which is smaller than the ionic radius , r, then it is required an energy to enlarge this pathway and make it suitable for ion migration. This additional energy is denoted by the strain energy. An expression is given [13] to calculate this energy as

$$E = 4\pi G r_d (r - r_d)^2, \qquad (1)$$

where G is the shear modulus, r is the radius of the mobile ion and r_d is the increase in the radius of the pathway (cylindrical cavity) which required for ion migration. The value of r_d together with r_m should be > r. It was assumed [10] that r_d is constant. An attempt is performed to calculate the strain energy assuming that r_d is variable depends on the time. This assumption is in the light of the relaxation of r_d after the passage of the ions. During the time of this relaxation, another ion may try to cross the same cavity. An equation is proposed to calculate r_d at any time is given by:

$$r_d = (r-r_m) + B \exp(-\alpha t) \sin(2\pi t/\tau) \qquad (2)$$

Where B and α are constants and τ is the periodic time for the oscillation of r_d. The estimation of the average strain energy for all the moving ions using formula (2) gives a value identical to that estimated assuming a specific constant r_d .

The binding Energy

The binding energy, E_b , is the sum of different types of energies as: Coulombic, E_c, repulsive,E_r , polarization, Ep, and Van der Waal, E_v. Many authors [7,8] suggested that the contribution of the polarization and Van der Waal's energies are two small compared with the other two terms and can be neglected. For glasses with two types of alkali ions, the polarization energy has considerable effect and can't be ignored.

$$E_b = E_c + E_r + E_p \qquad (3)$$

where E_c, E_r, and E_p are inversely proportional with $(r+r_o)$, $(r+r_o)^9$ and $(r+r_o)^3$ respectively [11], and r_o is the radius of oxygen ion. So, the binding energy is given as;

$$E_b = -[AZZ_o e^2/(r+r_o)] \qquad (4)$$

where A is the Madelung constant and its value will considered to be equal 1.2 which is less than its value for the crystal structure (A=1.6) [8].

The binding energy , E_b, is the energy required to separate the alkali ions from its partner oxygen from the radius sum to infinity, while the activation energy is the change in the electrostatic energy as the ion moves from one equilibrium position to another.

This amount of energy is much less than the binding energy and is denoted by ΔE_b,

$$\Delta E_b = E_{b2}-E_{b1}= -(\beta E_b/\varepsilon), \tag{5}$$

where β is called the displacement factor and can be calculated from: $\beta = (2.1-r)/3.5$ and ε is the dielectric constant of glass. Accordingly, the activation energy , E_a, can be given as:

$$E_a = [(\beta AZZ_o e^2)/ \varepsilon (r+r_o)]+ 4 \pi G r_d(r+r_d)^2 \tag{6}$$

The total activation energy of mixed alkali glasses is the sum of the activation energies for each type of ions. Since the concentration of mobile ions is proportional to the alkali oxide content, thus, for ion 1 with molar ratio x and ion 2 with molar ratio y;

$$E_a = x (E_a)_1 +y (E_a)_2 \tag{7}$$

Results and Discussion

It is known that certain properties as the transport process are strongly influenced by the "mixed alkali effect". An increase in the electrical resistivity by several orders of magnitude was observed [13]. On the other hand, our approach attempts to discuss the changes of activation energy with the changes in the molar ratio of modifiers. This model assumes that ion transport is considered to be "site preferred" which takes place by hopping from one site to another rather than the migration through specific pathways. The mobility of the ions is considered to be dependent essentially on the mechanism of hopping process and overall glass composition [13].

Figure (1) represents the calculated activation energy for mixed K-Na borate glasses. At low K-content ($K_2O/Na_2O < 1$), K^+ ions have low mobility compared with Na^+ ions, then it may act to block Na^+ ions be least mobile since they are surrounded by high concentration of Na^+ sites; the diffusion in such case required defect formation in addition to migration energy. However, Na^+ ions surrounding the K^+ sites will also be less mobile since a fraction of their jumps requires movement into the K^+ sites which is equivalent to the defect formation [14]. Increasing K_2O content in sodium borate glasses decreases the mobility of Na^+ ions through more blocking mechanism. The overall result appears as a decreasing in the mobility of Na^+ ions due to the exchange of Na_2O by K_2O. This has a dramatic effect on the conduction and consequently on the associated activation energy. As seen in fig.(1) for sodium borate glass , all the number of Na^+ ions are mobile and the activation energy has a value of 13.8 kcal./mole. The effect of the addition of K^+ ions can be observed as an increase in the activation energy to reach a maximum value of 32.5 kcal./mole for $K_2O/Na_2O =1$. Tomandl et al [15] suggested that the mobility of Na^+ ions decreases through blocking effect of K^+ ions. They found that each added K^+ ion can immobilize more than 20 Na^+ ions. Our approach confirms the above suggestion, since the activation energy increases by about 18 orders of magnitude upon exchange of 16.67 mole K_2O by the same molar fraction of Na_2O.

A decreasing trend in the activation energy can be monitored in fig.(1) when the ratio of $K_2O/Na_2O > 1$. In such case, the conduction will be due to the majority of K^+ ions and minority of Na^+ ions. It seems that Na^+ ions are not capable to block the motion of K^+ ions and glasses behave much like single K-borate. It is also observed that the values of the activation energy caculated according to our model, with the polarization term, agree quite well with that obtained experimentally [16]. On the other hand, the values of the activation energy calculated without the polarization term, according to ref.[8], give values slightly differ from the experimental.

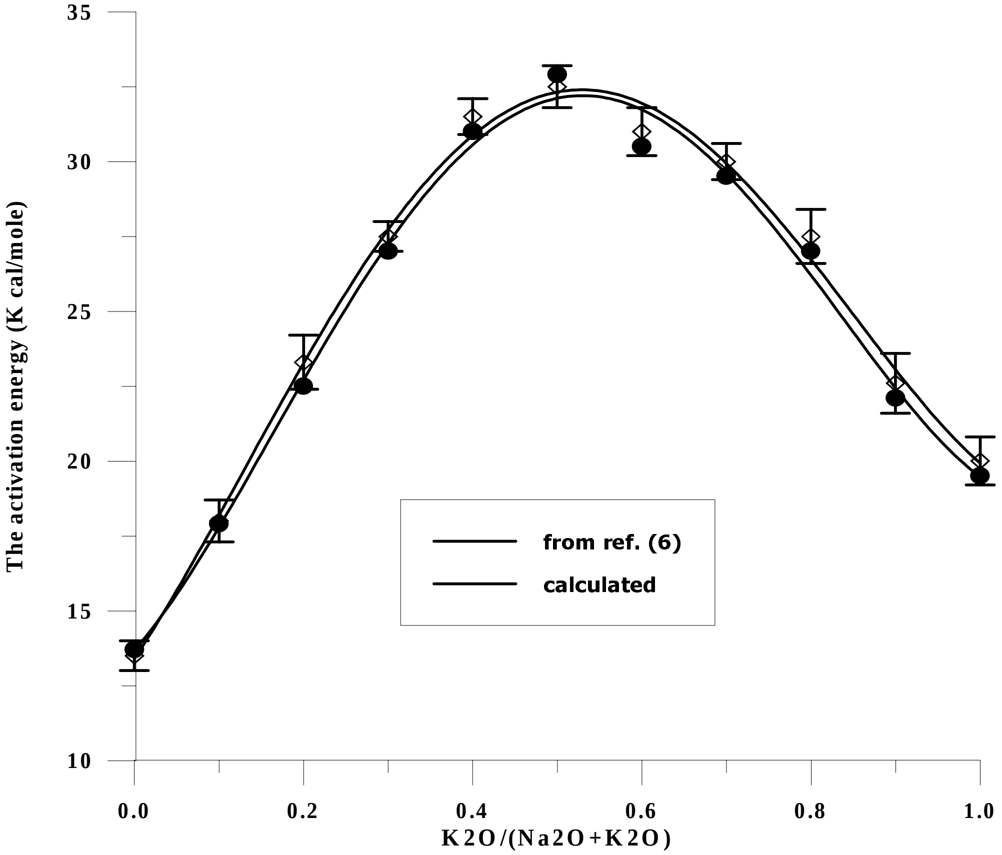

Figure 1: Dependence of the activation energy (calculated and from ref. 6) on the molar ratio of mixed sodium and potassium oxides glasses.

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The dependence of the activation energy on the mixed Li- Na content in borate glasses is also introduced in fig.(2).

The general feature of this figure does not differ much from that observed for K-Na containing glasses. Both the calculated and the estimated activation energy from the experimental data [17,18], continue their monotonic decline to reach a maximum value at $Li_2O/Na_2O = 1$. The increase in the activation energy in this region may attributed to the decrease of Na^+ ions and their partner sites. Li^+ ions can also occupy some Na^+- sites which requires more energy. The mobility of these ions in the defect sites is negligible. On the other hand, the jump of Na^+ ions to Li^+ sites requires more strain energy to enlarge the cavity of these sites. While for $Li_2O/Na_2O > 1$, the lithium ions are considered the major charge carriers. It is observed a faster decrease in the calculated activation energy than that noticed experimentally. This leads us to think about the role of Li^+ ions on the conduction process and open the field for more studies involving different mixed alkali borate glasses containing lithium oxide.

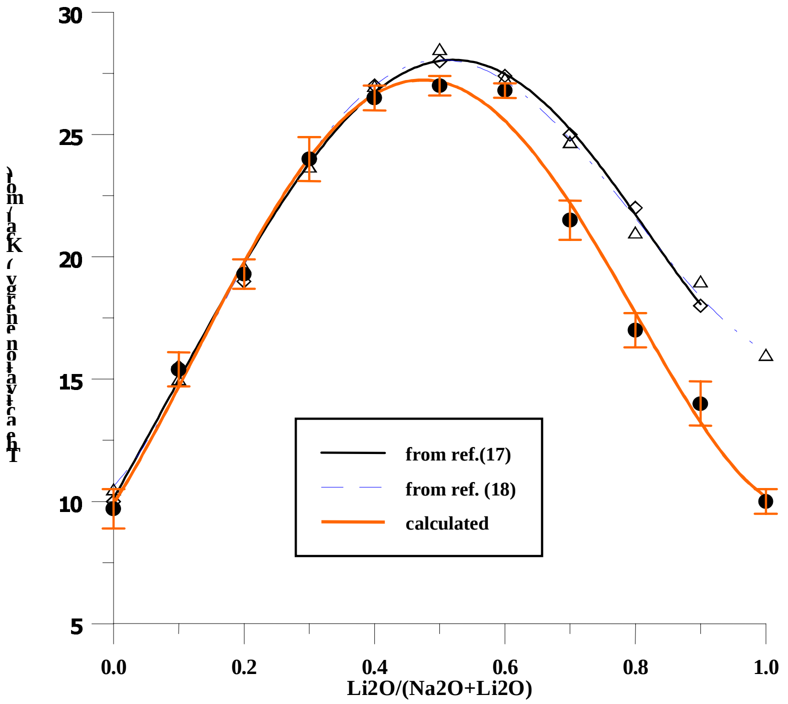

Figure 2: Dependence of the activation energies (calculated, from ref.17 and ref.18 on the molar ratio of the mixed sodium potasium oxide glasses.

Conclusions

The following remarks can be given in the light of the present study:

1. The polarization energy is introduced as one of the factors affecting the binding energy.

2. The strain energy was calculated assuming that the shear modulus is variable depends on the glass composition.
3. The validity of our approach is tested by comparing the calculated activation energy with that obtained experimentally [16,18].

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